The Chemistry of Dienes and Polyenes. Volume 2
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CHAPTER **3**

Photopericyclic reactions of conjugated dienes and trienes

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I. INTRODUCTION

The photochemistry of conjugated polyenes has played a central role in the development of modern molecular photochemistry, due in no small part to its ultimate relevance to the electronic excited state properties of vitamins A and D and the visual pigments, as well as to pericyclic reaction theory. The field is enormous, tremendously diverse, and still very active from both experimental and theoretical perspectives. It is also remarkably complex, primarily because the absorption spectra and excited state behavior of polyene systems are strongly dependent on conformation about the formal single bonds in the polyene chain, which has the main effect of turning on or off various pericyclic reactions whose efficiencies are most strongly affected by conformational factors.

The present review focuses on the excited singlet state photochemistry of non-phenylated conjugated dienes and trienes, emphasizing pericyclic reactions. Conjugated tetraenes and arylated polyenes will receive only brief, occasional mention, in spite of their obvious relevance and the huge amount of work that has been done on their photochemistry and photophysics. Triplet state photochemistry has also been omitted. This approach has been taken in order to provide a practical limit to the already overwhelming amount of literature which needs to be covered, and for 'chemical' reasons as well. Arylated polyenes tend to exhibit the same high reactivity toward photoinduced E,Z-isomerization as their non-arylated counterparts, but behave differently in most other respects: they fluoresce efficiently in fluid solution at room temperature and, in general, do not display the same rich reactivity toward pericyclic photoprocesses as non-arylated systems. The reader is directed to several excellent reviews[1–5] and particularly recent articles[6–10] on aryl-polyene photochemistry and polyene triplet state photochemistry for further information on these topics. The photochemistry of octatetraene has also been reviewed in detail recently[11].

Theoretical treatments of organic photochemical reactions have evolved enormously over the past ten years. Polyene photochemistry has been at the very center of this revolution, which would appear to be taking us away from the classic model of van der Lugt–Oosterhoff, who first detailed the critical role of the doubly-excited 2^1A_g state in directing the ring closure of 1,3-butadiene to cyclobutene along the favored disrotatory reaction pathway which is predicted by the Woodward–Hoffmann rules[12]. These and later calculations throughout the 1970s and 1980s treated the electrocyclization to cyclobutene [13–16], E,Z-isomerization[16–18] and *cis*,*trans*-conformer interconversion[16] of acyclic dienes (for example) in more-or-less separate fashion; that is to say, in terms of a model in which each of these reactions follow their own distinct reaction pathways on the excited state surface(s), to a series of minima which correspond to avoided crossings with the ground state surface at the same molecular geometries. Internal conversion to the ground state at the pericyclic minimum then results in branching between starting material and a single product. This model (as do the conceptually even simpler Woodward–Hoffmann rules) assumes a given, usually symmetrical excited state reaction coordinate which mirrors that for the identical process on the ground state surface. On a qualitative level, they generally conform to the essential features of most photochemical pericyclic reactions of conjugated polyenes, the most general exception being the photochemical ring opening of cyclobutene[19,20]. They clearly remain quite powerful from a predictive point of view.

However, more recent, much higher level calculations on a wide variety of systems suggest that the reaction funnel[21] where decay to the ground state surface occurs is more frequently a conical intersection (at which the ground and excited surfaces touch) than an avoided crossing (where they do not)[22–26], a concept which was first recognized by photochemists over thirty years ago[27,28] and then largely ignored. Perhaps the most important ramifications of this model result from the fact that decay to the ground state at a conical intersection must occur with unit efficiency; product selection occurs partly as a result of the structure of the excited molecule at the conical intersection and partly because it connects the excited reactant to two or more ground state products. The unit efficiency of internal conversion to the ground state at a conical intersection dictates that this process must occur on the vibrational timescale, which means that if there exists an essentially barrierless path linking the Franck–Condon region to the conical intersection, then product formation can be essentially complete within a hundred femtoseconds or so. Recent ultrafast time-resolved experiments indicate that, in fact, the photochemistry of a number of simple polyenes follows exactly these characteristics. More concise descriptions of these concepts and their relationship to earlier theoretical models are given in several recent reviews[21–25,29].

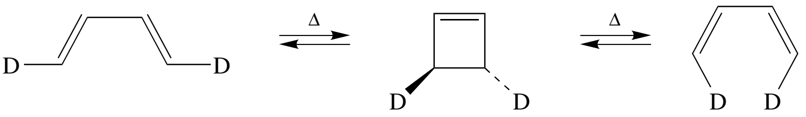
II. GROUND STATE CONFORMATIONAL EQUILIBRIA AND *E,Z*-ISOMERIZATION

Throughout this chapter, the *E*/*Z* nomenclature will be employed to denote geometric isomerism about the double bonds of the polyene chain, while the *cis*/*trans* (‘*c*/*t*’) nomenclature will be used only to denote conformational isomerism about the formal single bonds.

In the absence of substituents, the most stable conformer of linear polyenes is the all-*trans* conformer, with the energies of mono-*cis* conformers being higher by 0.8–2.7 kcal mol^{-1} and the barriers to single-bond rotation being on the order of 3–5 kcal mol^{-1}[30–32]. This means that at room temperature, the various single-bond conformers undergo essentially unrestricted interconversion, with the all-*trans* conformer comprising >95% of the mixture. Of course, the equilibrium composition can be displaced in favor of the less stable conformers at higher temperatures, a fact which frequently results in temperature-dependent photochemistry because polyene photochemistry tends to be highly dependent on ground state conformational factors (*vide infra*). As well, it has often been exploited for the preparation of samples enriched in the less stable conformers for study by matrix isolation techniques at very low temperatures, where conformational interconversion (‘conformerization’) is slow.

The barriers to rotation about the formal double bonds in aliphatic dienes and trienes are in the range 40–55 kcal mol^{-1}, depending on the degree of conjugation, substitution, and ring strain if the polyene moiety is incorporated in a ring. For example, aliphatic dienes such as *Z*-1,3-pentadiene (*Z*-**1**) and *E*,*Z*-1,4-dideuterio-1,3-butadiene undergo thermal *E*,*Z*- isomerization with E_a *ca* 53 kcal mol^{-1} and $\log A$ *ca* 14 in the gas phase[33]. This should be compared to the corresponding values for thermal isomerization of *Z*-2-butene, $E_a = 66.2$ kcal mol^{-1} and $\log A = 14.6$[34,35]. Thermal isomerization of *E*-1,3,5-hexatriene (*E*-HT), on the other hand, proceeds with $E_a = 44.3$ kcal mol^{-1} and $\log A = 12.9$[36]. Similar values have been determined for the Arrhenius parameters for thermal isomerization about the central bonds of other aliphatic trienes[37]. The trend toward decreasing E_a with increasing conjugation is consistent with the long-accepted view that thermal *E*,*Z*-isomerization of non-polarized alkene systems proceeds via rotation about the double bond, through a *ca* 90° twisted transition state with 1,2-biradical character at the isomerizing bond[35,37].

Interpretation of the rate constants and Arrhenius parameters for thermal *E*,*Z*-isomerization is not always straightforward mechanistically, however, since sequential electrocyclic ring closure/ring opening reactions can often provide a lower energy route to the same products as formal rotation about a single C=C bond. This can be illustrated by Brauman and coworkers' classic study of the thermal isomerization of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-1,4-dideuterio-1,3-butadiene (*E*,*E*-**BD**-d_2)[33]. At 637 °C, the *E*,*E*- and *Z*,*Z*-isomers interconvert, but neither yield the *E*,*Z*-isomer. The rate constant for this interconversion is about twenty times larger than that for isomerization of the *E*,*Z*-isomer to *E*,*E* and *E*,*Z*, which can only proceed by the 'conventional' double-bond isomerization pathway (equation 1). The results are consistent with the $E,E \rightleftharpoons Z,Z$ isomerization proceeding via the intermediacy of *trans*-3,4-dideuteriocyclobutene (*trans*-**CB**-d_2), whose formation is expected to proceed with E_a *ca* 45 kcal mol^{-1}.



(1)

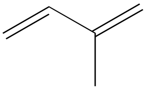
E,*E*-**BD**-d_2 *trans*-**CB**-d_2 *Z*,*Z*-**BD**-d_2

III. THE EXCITED SINGLET STATES OF CONJUGATED POLYENES: UV ABSORPTION AND EMISSION SPECTRA

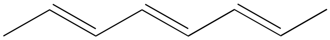
The electronic spectroscopy of polyene systems has been so extensively investigated and is so thoroughly covered in numerous books and reviews[1,3,11,21,38] that only a brief general summary need be presented here.

Two excited singlet states are relevant to the direct photochemistry of conjugated polyenes: the one-photon-allowed 1^1B state (S_2) and the two-photon-allowed 2^1A state (S_1). Excitation to the 1^1B state involves promotion of one electron from the highest occupied π-MO in the ground (1^1A) state to the lowest unoccupied π^*-MO, and is responsible for the prominent, often-structured band in the UV absorption spectra of conjugated polyenes. The 1^1B state of polyenes is well-accepted to be ionic in character, with the formal C−C single bonds enjoying increased double bond character and hence restricted rotation compared to the ground state[1,16,39]. The opposite is true of the formal C=C bonds. At the Franck–Condon geometry, the 2^1A state is the lower energy state in all conjugated polyenes from 1,3,5,7-octatetraene up[3,11,40]. Its placement in relation to the 1^1B state in 1,3-butadiene and 1,3,5-hexatriene has been the subject of some debate (see References 38, 41 and 42 and references cited there), but it is clear that the two states are at least very close in energy and in any event fairly minor geometric distortions cause them to cross; internal conversion from the spectroscopic (1^1B_u) state to the 2^1A state is almost always very efficient. The 2^1A state is thus the true 'photoactive state' in polyene photochemistry. This excited state is covalent in character with little π-bonding; thus, the electronic structures of the 2^1A states of shorter-chain polyenes are best described as polyradicaloid and, as a result, the barriers to twisting about any of the C−C bonds in the 2^1A state are very low[11].

Recent theoretical and spectroscopic studies indicate that in aliphatic dienes and trienes, excitation to the spectroscopic 1^1B state usually results in facile twisting about the termini in the stereochemical sense dictated by orbital symmetry selection rules for the appropriate electrocyclic ring closure, motions which are often accompanied by some degree of planarization of the carbon framework. In general, relatively minor distortions along this reaction coordinate take the excited molecule via a barrierless route (and hence commonly within femtoseconds after excitation) to a geometry where the 1^1B and 2^1A states cross, and internal conversion to the latter state takes place. Further twisting, now involving several or all of the C−C bonds in the polyene framework, leads the molecule in the 2^1A state to a conical intersection with the ground state surface, from which partitioning between starting materials and one or more photoproducts occurs. As a result of the essentially barrierless decay to the ground state which such results imply, quantum yields for fluorescence of non-phenylated conjugated dienes and trienes are usually extremely low in the gas phase and in solution. For example, extremely weak fluorescence has been observed for isoprene **(2)** in cyclohexane solution at ambient temperatures ($\Phi_F < 10^{-6}$)[43], and for 1,3,5-hexatriene and 2,4,6-octatriene **(3)** as mixtures of isomers in the gas phase under isolated molecule conditions[44]. Experimental indications of the various distortions which take place in the first few hundred femtoseconds after excitation to the 1^1B state have been obtained using resonance Raman, fluorescence and other spectroscopic techniques[1,11,40,41,43,45–48]. Time-resolved resonance Raman and other spectroscopic techniques have been used to show that excited state deactivation (including product formation) in dienes and trienes is usually complete within a few picoseconds or less after excitation[49–52].

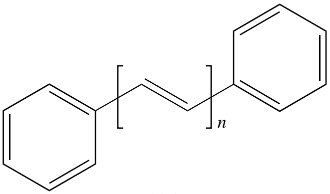


(2)



(3)

1,3,5,7-Octatetraene and higher unsubstituted polyenes, on the other hand, are well-known to exhibit (2^1A−1^1A) fluorescence at low temperatures, implying the presence of ever-deepening minima on the 2^1A surface as the degree of conjugation increases[1,11]. A recent theoretical paper describes the common structural features of the $2^1A/1^1A$ conical intersections of the series of all-*trans* linear polyenes and radicals [$H_2C(CH)_nCH_2$] from $n = 1-6$[53]. Fluorescence is readily observable at room temperature from the all-*E*-α,ω-diphenylpolyenes **(4_n)** irrespective of chain length, a property which has made possible very detailed measurements of the excited state dynamics of these systems[1–3]. The photochemistry of these more extensively conjugated systems tends to be dominated by *E*,*Z*-isomerization to a much greater extent than is the case with aliphatic dienes and trienes, and pericyclic reactivity is relatively rare[11,3]. This is almost certainly the direct result of the differences in the morphology of the 2^1A potential energy surfaces which are invoked by increasing conjugation.



(4_n)

Conformation about the formal single bond(s) has well-known effects on the position of the lowest energy ($1^1A \rightarrow 1^1B$) absorption band in dienes and the higher polyenes, which is primarily due to π-overlap effects on the energy of the highest occupied π molecular orbital[54–57]. It is also the single most important factor in determining the type of product(s) formed upon direct irradiation. Much of the complexity associated with the photochemistry of acyclic (or, more specifically, conformationally-mobile) polyenes is due to the fact that more than one conformer is present under the conditions of irradiation, and their photochemistries differ. Thus in general, the overall product distribution will depend on the equilibrium distribution of conformers present under the particular reaction conditions, their relative extinction coefficients at the excitation wavelength and the specific product distribution that each conformer yields upon excitation. This usually results in wavelength-dependent photochemistry.

IV. SINGLET STATE PHOTOCHEMISTRY OF CONJUGATED DIENES AND TRIENES

The direct irradiation of conjugated polyenes results in a rich and varied photochemistry, the course of which depends mainly on the degree of conjugation and the ground state conformational properties of the polyene system. In the absence of heavy atoms or substituents which specifically promote spin–orbit coupling, intersystem crossing is slow compared to reactive excited singlet state decay processes[58–60]. With systems in which more than one double bond geometric isomer exists, *E*,*Z*-isomerization almost invariably dominates the excited singlet state photochemistry, even when it results in the formation of a relatively unstable, transient ground state species. This is even more true of the excited triplet states of conjugated polyenes. The process is not subject to the same sort of conformational constraints as other polyene photoprocesses are, so in view of this and its overall importance to the photochemistry of all polyene systems, it will be treated separately.

Acyclic systems (particularly conjugated dienes) also undergo efficient conformational isomerization about one of the formal C−C single bonds upon direct excitation, although this can only be detected under conditions where the individual conformers do not interconvert in the ground state (such as in rigid matrices at very low temperatures). However, a large body of evidence indicates that individual conformers generally do not interconvert within the lifetime of the excited state, which forms the basis of the well-known 'NEER (Non-Equilibration of Excited-state Rotamers) Principle'[61].

Pericyclic isomerization reactions (electrocyclic reactions, sigmatropic rearrangements and formal intramolecular cycloadditions) constitute the most interesting aspect of polyene photochemistry (from our perspective), since the efficiencies of these reactions are critically dependent on the ground state conformational properties of the system, and the extent to which excited state decay by double- or single-bond twisting is impeded due to structural constraints. Although the quantum yields may be low, the chemical yields of these products can often be quite high, particularly when excited state decay by torsion about the formal double bonds is non-productive. When geometric isomerism about one or more of the double bonds is possible, then the observed product distributions from irradiation of individual geometric isomers are usually conversion-dependent, because *E*,*Z*-isomerization is generally much more efficient than other processes. The observed product distribution reflects that of the starting isomer only at very low conversions, and changes continuously as the system converges to a pseudo-photostationary state of geometric isomers, which generally have very similar absorption spectra and hence cannot be selectively excited.

Direct *E*,*Z*-photoisomerization is sufficiently ubiquitous in the photochemistry of all polyene systems that it will be considered first in its own separate section, although the coverage will be brief. Next will be considered photochemical *cis–trans* conformational interconversion, a non-productive process which often dominates in the assortment of excited state decay pathways available to the excited singlet states of conjugated polyenes. The bulk of the review of polyene excited singlet state photochemistry is directed at rearrangement reactions, which include pericyclic and biradical-derived processes and is divided into specific reaction types.

A. Direct *E,Z*-Isomerization

Torsion about one of the formal double bonds is invariably the most efficient excited singlet state decay process of acyclic polyenes, and also often occurs efficiently in cyclic systems of moderate-to-large ring size[2,3,11,60,62]. *E*,*Z*-isomerization in the excited singlet state manifold takes place about only one of the double bonds per photon, as was initially demonstrated for 2,4-hexadiene **(5)** by Saltiel and coworkers[59] and has since been shown to be quite general. Table 1 contains a summary of quantum yields for the direct *E*,*Z*-photoisomerization, in solution, of acyclic and cyclic polyenes **1**, $\mathbf{4}_2$, $\mathbf{4}_3$, **5–18** bearing various substituents. For the most part, quantum yields for direct *E*,*Z*-photoisomerization of aliphatic dienes are not highly dependent on the structure of the system (i.e. acyclic, cyclic or exocyclic).

Because *E*,*Z*-isomerization is reversible and proceeds with quantum yields which are generally much higher than those for other productive decay processes, direct irradiation of polyenes in solution leads to the formation of a pseudo-equilibrium mixture of geometric isomers, whose composition is dependent on the quantum yields for isomer-interconversion, the extinction coefficients at the excitation wavelength (λ_{ex}) of the interconverting isomers and the quantum yields for formation of other products which do not revert to any of the geometric isomers of the original polyene[60,62].

The *E*,*Z*-photoisomerization of alkenes is accurately viewed in terms of the Mulliken model for ethene[74], in which the excited alkene relaxes to a discrete twisted excited state intermediate (${}^1p^*$), from which internal conversion to the ground state occurs (for reviews see References 2, 3, 60, 62, 75 and 76). The geometry of ${}^1p^*$ is common to both alkene geometric isomers and corresponds roughly to that of the transition state for ground state *E*,*Z*-isomerization. The intermediate is then considered to partition itself between the *E*- and *Z*-isomers in a ratio $\alpha/(1-\alpha)$, which is often assumed (but not required) to be about 0.5[65]. This model and its extension to the direct *E*,*Z*-photoisomerization of conjugated dienes is shown in Scheme 1, where the twisted intermediates are represented as 1,2-biradicals[18,59,63,77,78]. Thus, the quantum yields for direct *E*,*Z*-photoisomerization of alkenes and conjugated dienes are given by equations 2, 3a and 3b, respectively, where the ϕ_{p^*} terms are the state efficiencies for formation of the twisted intermediates from the spectroscopic excited states of the starting compounds. We (gently) suggest that this model is inappropriate for aliphatic dienes and trienes, given the ultrafast timescale on which the ground state is populated in these systems, but it certainly remains valid (or at least very useful) for higher polyenes and arylated systems, whose photochemistry tends to be confined to *E*,*Z*-isomerization[3].

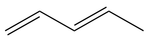
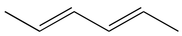
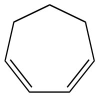
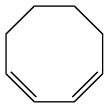
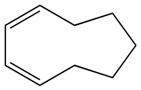
$$\Phi_{E\to Z} = (1-\alpha)\phi_{E\to p^*}; \qquad \Phi_{Z\to E} = \alpha\phi_{Z\to p^*} \tag{2}$$

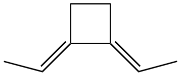
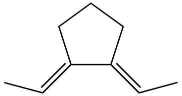
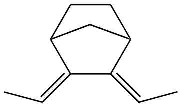
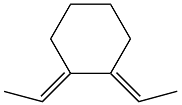
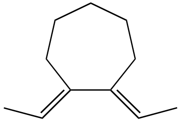
$$\Phi_{EE\to EZ} = (1-\alpha_{Ep^*})\phi_{EE\to Ep^*}; \quad \Phi_{EZ\to EE} = \alpha_{Ep^*}\phi_{EZ\to Ep^*} \tag{3a}$$

$$\Phi_{EZ\to ZZ} = (1-\alpha_{Zp^*})\phi_{EZ\to Zp^*}; \quad \Phi_{ZZ\to EZ} = \alpha_{Zp^*}\phi_{ZZ\to Zp^*} \tag{3b}$$

There has been considerable debate over whether the *E*,*Z*-photoisomerization (as well as other photoprocesses) of conjugated polyenes proceeds via neutral (2^1A) or zwitterionic

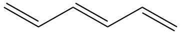
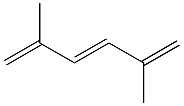
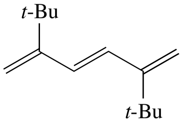
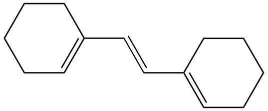
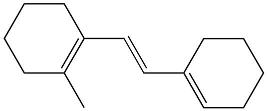
TABLE 1. Quantum yields for direct E,Z-photoisomerization of conjugated polyenes

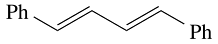
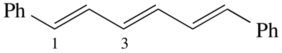
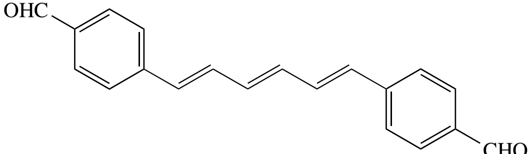
Compound	Solvent	λ_{ex} (nm)	$E \rightarrow Z$	$Z \rightarrow E$	Reference
 **(1)**	c-C_6H_{12}	254 228	0.08 0.022	0.10 0.025	63 64
 **(5)**	C_5H_{12}	254	0.37 (EE) 0.29 (EZ)	0.17 (EZ) 0.41 (ZZ)	59
 **(6)**	CH_3OH	254		~0.26	66
 **(7)**	C_6H_{14}	248		0.28	67
 **(8)**	C_5H_{12}	254		0.26	68

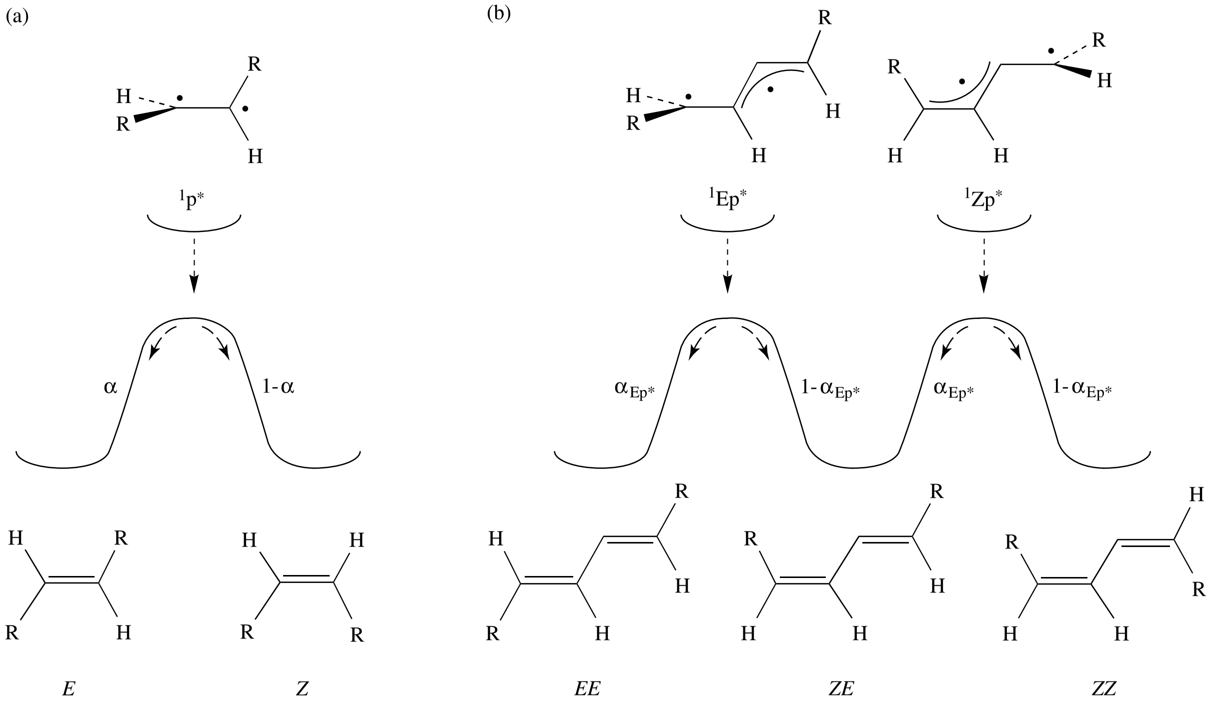
 **(9)**	C_5H_{12}	254	0.12 (*EE*) 0.011 (*EZ*)	0.11 (*EZ*)	69
 **(10)**	C_5H_{12}	254	0.24 (*EE*) 0.09 (*EZ*)	0.39 (*EZ*)	69
 **(11)**	C_5H_{12}	254	0.30 (*EE*) 0.06 (*EZ*)	0.28 (*EZ*)	69
 **(12)**	C_5H_{12}	254	0.20 (*EE*)	0.27 (*EZ*)	70
 **(13)**	C_5H_{12}	254	0.21 (*EE*)	0.14 (*EZ*)	70

(*continued overleaf*)

TABLE 1. *(continued)*

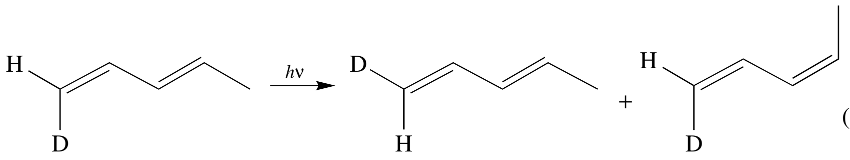
Compound	Solvent	λ_{ex} (nm)	$E \rightarrow Z$	$Z \rightarrow E$	Reference
 **(HT)**	C_5H_{12}	265	0.016	0.034	71
 **(14)**	C_5H_{12}	254	0.004	0.37	72
 **(15)**	C_5H_{12}	254	0.046	0.052	72
 **(16)**	Et_2O	296–312	~0.46	n.d.	73
 **(17)**	Et_2O	296–312	~0.40	n.d.	73

 **(4_2)**	c-C_6H_{12}	325	0.11 (*EE*)	0.04 (*EZ*) 0.20 (*ZZ*)	65
 **(4_3)**	c-C_7H_{14}	366	0.011 (*EEE*-1) 0.048 (*EEE*-3)	0.139 (*ZEE*-1) 0.221 (*EZE*-3)	4
	MeCN		0.075 (*EEE*-1) 0.049 (*EEE*-3)	0.171 (*ZEE*-1) 0.138 (*EZE*-3)	
 **(18)**	Toluene $CHCl_3$ MeCN	*ca* 365	<0.003 (*EEE*-1) 0.13 (*EEE*-1) 0.33 (*EEE*-1)	0.68 (*ZEE*-1) 0.39 (*ZEE*-1) 0.29 (*ZEE*-1)	6



SCHEME 1. The biradical model for the direct *E*,*Z*-photoisomerization of (a) alkenes and (b) conjugated dienes

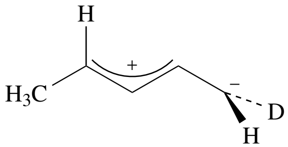
(1^1B) twisted excited state intermediates. The latter was first proposed by Dauben and Ritscher[79] and subsequently received considerable theoretical support[17,39,80–82] (however, see Reference 83). Experimental support for zwitterionic twisted intermediates in diene[79,84–86] and triene[4,86] photoisomerizations has come from studies of unsymmetrically substituted systems, albeit mostly aryl-substituted ones. For example, Squillacote and Semple showed that the direct irradiation of *E*-1,3-pentadiene-*Z1d* (*E*-$\mathbf{1}_{Z1d}$) with 229 nm light results in the formation of *E*-1,3-pentadiene-*E1d* (*E*-$\mathbf{3}_{E1d}$) and *Z*-1,3-pentadiene-*Z1d* (*Z*-$\mathbf{1}_{Z1d}$) in a ratio of about 25 : 1 (equation 4)[85]. They explained the result in terms of the intermediacy of a polarized allyl (cation)–methylene (anion) intermediate **(19a)**, rather than the oppositely-polarized structure **(19b)** proposed by Dauben and Ritscher to explain the regio- and stereoselective photoisomerizations of *E*- and *Z*-ethylidenecyclooctene (**20**; *vide infra*)[79]. Soon after, Muthuramu and Liu reported that the *E*,*Z*-photoisomerization of the fluorinated 1-phenyl-4-carboalkoxybutadienes **21** proceeds regioselectively about the phenyl-substituted double bond, consistent with the Dauben intermediate[86]. Saltiel and coworkers have reported a particularly interesting example of solvent- and substituent-dependent regioselectivity in the *E*,*Z*-photoisomerization of *E*,*E*,*E*-1,6-diaryl-1,3,5-hexatrienes **(22)**; the quantum yields for isomerization about the central double bond in the parent molecule (**22**; X = H) are insensitive to solvent polarity, while those for isomerization about a terminal bond are enhanced seven-fold in acetonitrile compared with hydrocarbon solvents[4]. Isomerization of the substituted derivatives proceeds regioselectively to yield the 1-*Z* and 3-*Z* isomers, and in both cases the quantum yield for terminal bond isomerization is enhanced dramatically in polar solvents. The results were explained in terms of competing torsional relaxation about the central and terminal bonds via biradicaloid and zwitterionic twisted intermediates, respectively. For the parent and cyano derivatives, the latter is polarized in the same sense proposed by Dauben and Ritscher. Interestingly, the polarization appears to be reversed in the case of the methoxy derivative.



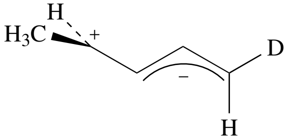
(*E*-$\mathbf{3}_{Z1d}$) (*E*-$\mathbf{3}_{E1d}$) (*Z*-$\mathbf{3}_{Z1d}$)

25 : 1

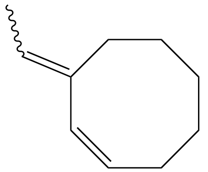
(4)



(19a)

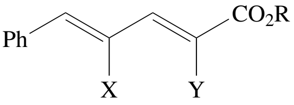


(19b)

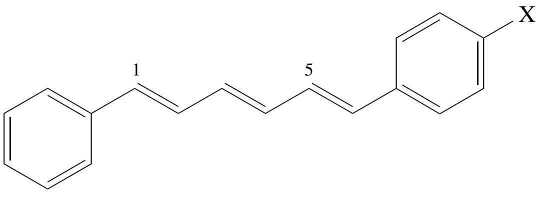


(20)

More recent high level *ab initio* calculations on 1,3-butadiene confirm that zwitterionic allylmethylene twisted species correspond to energy minima on the 1^1B potential

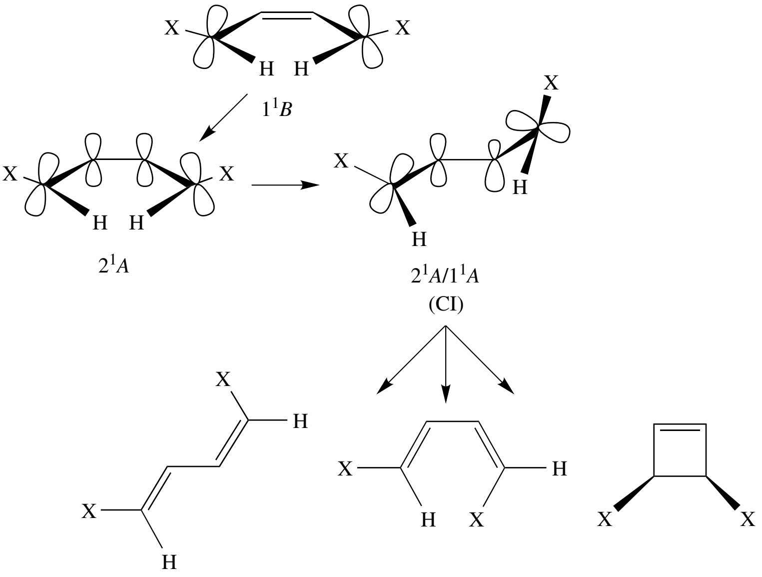


(21) X, Y = H and/or F



(22) X = H, CN, OMe

energy surfaces of both the s-*cis* and s-*trans* conformers, but suggest them to lie some 30 kcal mol^{-1} above the ground state surface at the same geometry[16,87]. The more recent calculations indicate the presence of a barrierless pathway linking the spectroscopic (1^1B_u) state to a $2^1A_g/1^1A$ conical intersection, which provides a far more efficient pathway to one-bond *E*,*Z*-isomerization and the formation of other products[88,89]. These calculations suggest that the funnels to the ground state surfaces for both s-*cis* and s-*trans* 1,3-butadiene are tetraradicaloid structures in which there is substantial twisting about all three C−C bonds. The favored pathways to the ground state surface proceed through conical intersections at which there is significant disrotatory twisting of the termini, hence providing a pathway for both cyclobutene formation (*vide infra*), *E*,*Z*-isomerization and s-*cis*/s-*trans* conformer interconversion via the same funnel geometry (Scheme 2). Calculations by the same group on a few substituted butadiene systems indicate that while their photochemistries should be dictated by similar pathways for excited state decay, both the structure at the conical intersection and the torsional dynamics of the molecule in the excited state are affected significantly by steric and polar factors associated with the substituents[87,90]. Calculations on the *E*,*Z*-photoisomerization of *Z*- and



SCHEME 2. Excited state reaction path for butadiene

E-1,3,5-hexatriene[91,92], *E*,*E*-1,3,5,7-octatriene[93] and longer polyenes related to the visual pigments[94–97] have been reported as well.

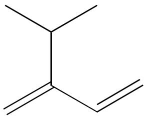
Clearly, substituents can be expected to have significant effects on the energy of the zwitterionic 1^1B minimum in butadiene, perhaps even to the point where it assumes the role of the funnel to the ground state surface. At the very least, they can be expected to affect the morphology of the 1^1B surface in the Franck–Condon region. Thus, even in cases where theory predicts that torsional decay to the ground state occurs at a (covalent, tetraradicaloid) $2^1A/1^1A$ conical intersection, polar factors could very well dictate the regiochemistry of *E*,*Z*-isomerization through their effects on the dynamics of the 1^1B-2^1A-1^1A internal conversion sequence.

So far, experimental tests of the $2^1A/1^1A$ conical intersection mechanism for acyclic diene and triene excited singlet state decay have largely been confined to ultrafast time-resolved spectroscopic studies, which have recently been reviewed[98,99]. Leigh and Postigo addressed the ramifications of the model on the quantum yields for *E*,*Z*-photoisomerization of aliphatic s-*cis*-dienes, specifically to probe the possible effects of constraining the torsional mobility about the 'central' formal single bond (C2–C3 in 1,3-butadiene)[69]. Indeed $\Phi_{EE \rightarrow EZ}$ decreases regularly with decreasing central bond torsional mobility throughout the series of compounds **9–11** (Table 1), a trend which seems difficult (but not impossible) to explain in terms of the allylmethylene mechanism for diene *E*,*Z*-isomerization. Olivucci and coworkers have explained the trend as due to structurally-induced constraints on bending of the C1–C2–C3 bond angle, which approaches 90° at the $2^1A/1^1A$ conical intersection of s-*cis*-butadiene, rather than on torsional freedom about the central C–C bond[87]. The quantum yields for electrocyclic ring-closure to the isomeric cyclobutene derivatives (both in these and the 1,2-bismethylene analogs of **9–11**[100]) vary in the same way as those for *E*,*Z*-photoisomerization, which is consistent with the idea that the two processes proceed via decay through the same conical intersection.

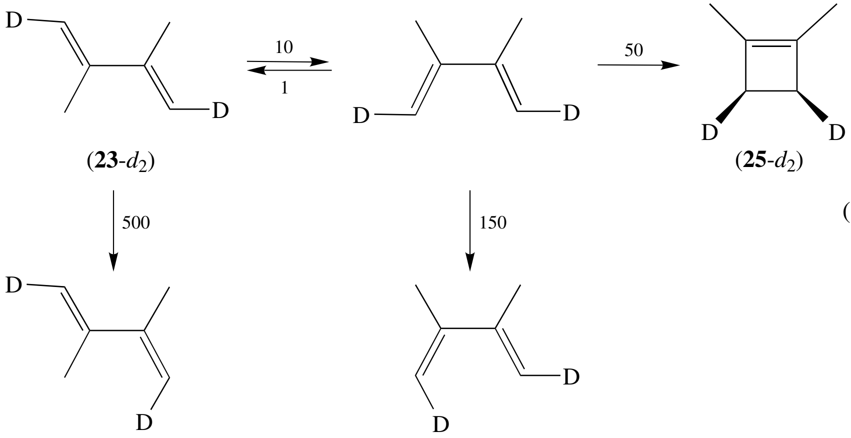
Intriguingly, the conical intersection model also suggests that *E*,*Z*-isomerization of acyclic dienes might be accompanied by conformational interconversion about the central bond, reminiscent of the so-called 'Hula-Twist' mechanism for the efficient *E*,*Z*-photoisomerization of the visual pigment rhodopsin in its rigid, natural protein environment[101]. A study of the photochemistry of deuterium-labelled 2,3-dimethyl-1,3-butadiene (**23**-d_2) in low temperature matrices (*vide infra*) found no evidence for such a mechanism in aliphatic diene *E*,*Z*-photoisomerizations[102]. On the other hand, Fuss and coworkers have recently reported results consistent with the operation of this mechanism in the *E*,*Z*-photoisomerization of previtamin D_3 (*vide infra*)[103].

B. *cis*,*trans*-Conformational Interconversion

As mentioned earlier, conformational isomerization about the formal single bonds of polyene systems is facile in the ground state, where it occurs with activation barriers on the order of 2–4 kcal mol^{-1} in acyclic systems[104]. The process also occurs in acyclic dienes upon direct excitation, as was shown by Squillacote and coworkers using low temperature matrix isolation techniques, at temperatures where thermal conformational re-equilibration is suppressed (10–20 K)[105]. Thus, direct irradiation of *trans*-1,3-butadiene in an argon matrix at 15 K results in the efficient formation of the *cis*-conformer, distinguishable from the *trans*-conformer by its distinct UV absorption and infrared spectra[105,106]. The process is quite general, at least for aliphatic dienes such as isoprene (**2**), 2-isopropyl-1,3-butadiene (**24**), 2,4-hexadiene (**5**) and 2,3-dimethylbutadiene (**23**)[102,107]. Its efficiency is unusually low in the latter case, as has been established by irradiation of the 1,4-d_2 isotopomer (**23**-d_2) in matrices at 15 K. These experiments allowed the relative efficiencies of *cis*,*trans*-conformer interconversion, *E*,*Z*-isomerization and electrocyclic ring-closure to **25**-d_2 to be determined quantitatively as shown on the arrows in equation 5[102].



(24)



(**23**-d_2) (**25**-d_2)

(5)

Photochemical *cis*,*trans*-conformational interconversion is also known to occur in larger polyenes. Brouwer and Jacobs have reported the results of irradiation of *E*- and *Z*-2,5-dimethyl-1,3,5-hexatriene **(14)** in argon matrices at 10 K[108]. Irradiation of the *E*-isomer gives rise to various rotamers, while irradiation of the *Z*-isomer results only in *E*,*Z*-isomerization. Photochemical *trans*/*cis* conformer interconversion has also been observed for *E*,*E*-1,3,5,7-octatriene in matrices at temperatures below 10 K[32].

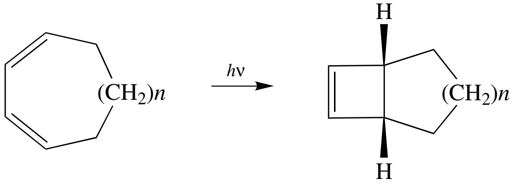
C. Photopericyclic Reactions of Conjugated Dienes

1. Cyclic and acyclic conjugated dienes

Aliphatic dienes undergo three main photochemical pericyclic processes, whose individual efficiencies depend largely on the torsional angle about the central bond in the specific diene conformer which is excited. These are (a) cyclobutene formation, (b) bicyclo[1.1.0] butane formation and (c) [1,5]-hydrogen migration. A fourth process, methylcyclopropene formation, has also been observed in minor amounts in several cases.

a. Cyclobutene formation. Electrocyclic ring closure to yield cyclobutenes is the best known photopericyclic reaction of 1,3-dienes, and occurs as well in higher polyenes which contain an s-*cis* butadienyl moiety. The process is highly stereospecific, proceeding with the disrotatory stereochemistry predicted by orbital symmetry selection rules[109], and occurs with quantum yields approaching *ca* 0.1 in conformationally-constrained s-*cis* dienes, so long as the C1−C2−C3−C4 dihedral angle is on the order of *ca* 40°

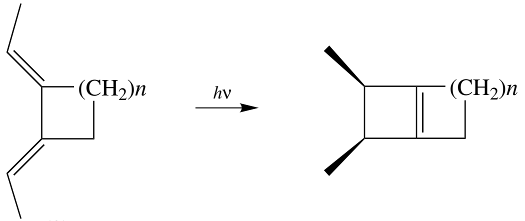
or less. This conclusion is derived from consideration of the quantum yields for cyclobutene (**26**–**32**) formation in the various cyclic and exocyclic 1,3-diene systems shown in equations 6 and 7. Thus, the quantum yields for cyclobutene formation decrease systematically throughout the series of cyclic and exocyclic dienes **6**–**8**[66–68] and **9**–**13**, respectively (the norbornyl analogue (**11**) closes with $\Phi = 0.03$)[69]. A similar trend was reported for the *E*,*Z*-isomers of **9**–**13**,[69] and for the bis-methylene homologues of these compounds[100].



(6)

(**6**) $n = 1$
(**7**) $n = 2$
(**8**) $n = 3$

(**26**) $n = 1 : \Phi = 0.09$
(**27**) $n = 2 : \Phi = 0.01$
(**28**) $n = 3 : \Phi = 0.002$

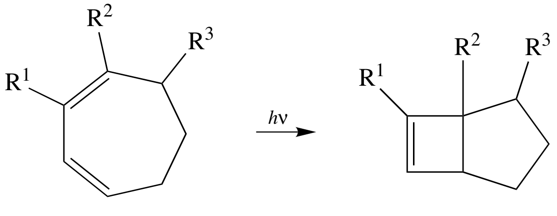


(7)

(**9**) $n = 1$
(**10**) $n = 2$
(**12**) $n = 3$
(**13**) $n = 4$

(**29**) $n = 1 : \Phi < 0.005$
(**30**) $n = 2 : \Phi = 0.10$
(**31**) $n = 3 : \Phi = 0.05$
(**32**) $n = 4 : \Phi = 0.15$

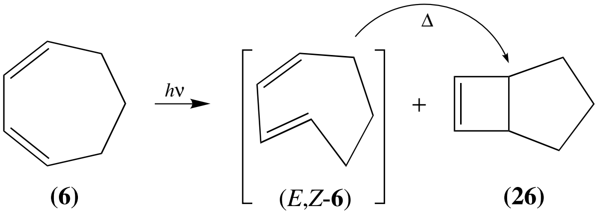
The direct irradiation of 1,3-cycloheptadiene (**6**)[110–113] and various substituted derivatives (**33**)[110,113–115] in hydrocarbon solvents provides a very clean, high yield route to the corresponding bicyclo[3.2.0]hept-6-ene derivatives (**34**; equation 8)[116]. The reaction also proceeds cleanly with a variety of heterocyclic analogues[117–121]. It should be noted that the value of Φ listed in equation 6 for the parent compound is that estimated for the direct, excited state ring closure pathway. In fact, **26** is formed with a quantum yield of 0.35 when the diene is irradiated in solution at room temperature[66,110,122]. The difference has been shown to be due to a second route for formation of this product which competes with the direct pathway: *E*,*Z*-photoisomerization to yield the highly strained (transient) *E*,*Z*-1,3-cycloheptadiene (*EZ*-**6**; Φ *ca* 0.26), which undergoes rapid ground state (conrotatory) ring closure at ambient temperatures (equation 9). This was demonstrated by acid-catalyzed trapping of *E*,*Z*-**6** as the methanol addition product, from which it was concluded that *ca* 75% of **26** is formed by the two-step pathway.[66,122] The analogous process does not occur upon direct irradiation of 1,3-cyclooctadiene (**7**) in solution at room temperature[123] since the *E*,*Z*-diene isomer (the major product) is thermally stable under these conditions; the ring closure product (**27**) is formed as a true primary photochemical product, with a quantum yield on the order of *ca* 0.01[67]. The lower quantum yield for ring closure of **7** compared to that of 1,3-cycloheptadiene is a reflection of the larger central bond angle in the 8-membered ring diene; even lower quantum yields for ring closure are observed in *Z*,*Z*- and *E*,*Z*-1,3-cyclononadiene **(8)**[124].



(33) **(34)**

(8)

R^1–R^3 = Me, Et, *i*-Pr, *t*-Bu, $CH_2CH_2OCH_3$
CH_2COCH_3, CO_2Me



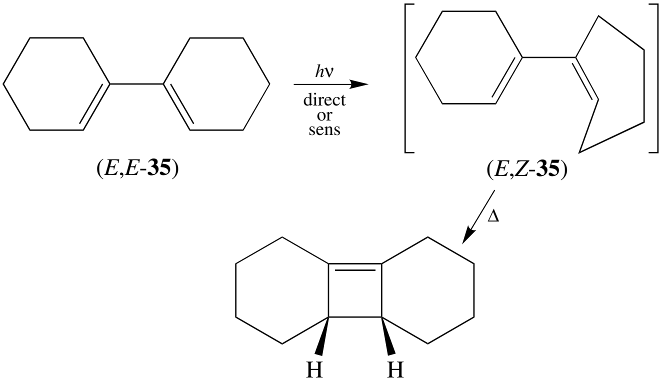
(6) (*E*,*Z*-**6**) **(26)**

Φ_{EZ} *ca* 0.26 Φ_{CB} *ca* 0.09

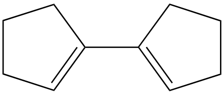
(9)

A related example is that of 1,1′-bicyclohexenyl **(35)**, which photocyclizes to yield *cis*-tricyclo[6.4.0.0^{2,7}]dodec-1-ene (*cis*-**36**) upon either direct[112] or triplet-sensitized[58] excitation. The triplet-sensitized reaction proceeds via initial *E*,*Z*-isomerization to yield the strained *E*,*Z*-1,1′-bicyclohexenyl (*E*,*Z*-**35**), which undergoes rapid (conrotatory) thermal ring closure to the tricyclic cyclobutene derivative (equation 10). This mechanism was first suggested by Liu[123], and subsequently verified by Saltiel and coworkers on the basis of laser flash photolysis experiments, which allowed the direct detection of the strained diene[125]. In the direct irradiation, methanol trapping experiments demonstrated that *cis*-**36** is formed by two competing pathways: direct disrotatory ring closure and a two-step pathway involving thermal ring closure of *E*,*Z*-**35**[125]. Interestingly, direct irradiation of 1,1′-bicyclopentenyl **(37)** does not lead to ring closure[112,126], but instead results in the formation of a non-conjugated diene isomer in low efficiency[127].

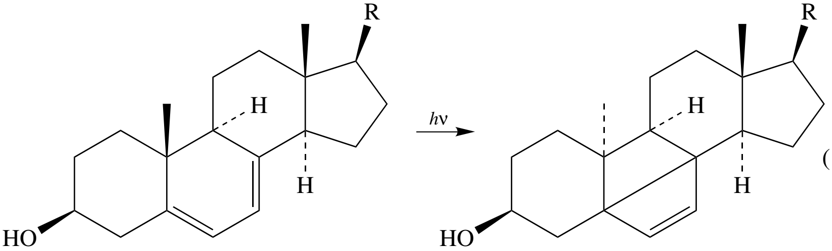
Photoelectrocyclic ring closure also occurs in some 1,3-cyclohexadiene systems, although, in general, the efficiency of the process is quite low unless the diene moiety is held in a planar conformation[128] or photoelectrocyclic (conrotatory) ring opening to the corresponding 1,3,5-hexatriene isomer (which is intrinsically more efficient than ring closure; *vide infra*) is structurally blocked[129]. The latter is aptly illustrated by the photochemistry of the pro-vitamin D isomers pyrocalciferol **(38)**, which leads to **39** (equation 11), and isopyrocalciferol **(40)**, which gives **41** (equation 12). In fact, this represents the first examples of this reaction to be reported[61,130,131]. Additional examples which illustrate the conformational requirements of the two possible electrocyclic pathways available to 1,3-cyclohexadienes will be discussed in a later section of this review.



(*E*,*E*-**35**) (*E*,*Z*-**35**) (*cis*-**36**) (10)

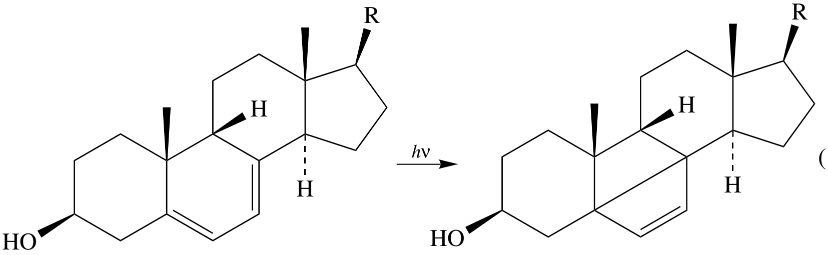


(37)



(38) **(39)** (11)

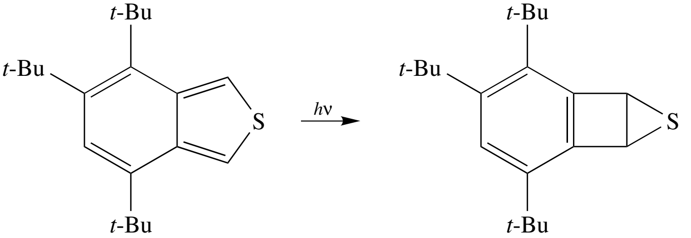
Φ = 0.011



(40) **(41)** (12)

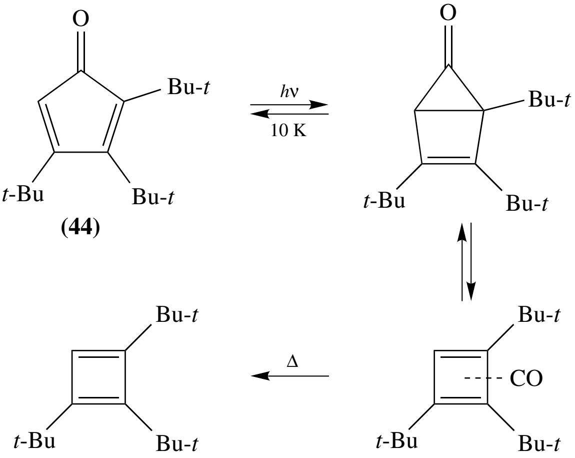
Φ = 0.068

Because of the substantial strain involved in the formation of fused 3- and 4-membered rings, cyclopentadiene itself does not undergo ring closure upon irradiation[132]. The reaction is common, however, in heterocyclic cyclopentadiene analogues[133,134], a recent example of which is shown in the formation of **43** from **42** (equation 13)[135]. It also occurs in certain substituted cyclopentadienones (e.g. **44**), as exemplified by Maier and coworkers' classic low-temperature synthesis of tri(*tert*-butyl)cyclobutadiene (**45**; equation 14)[136].



(42) **(43)**

(13)

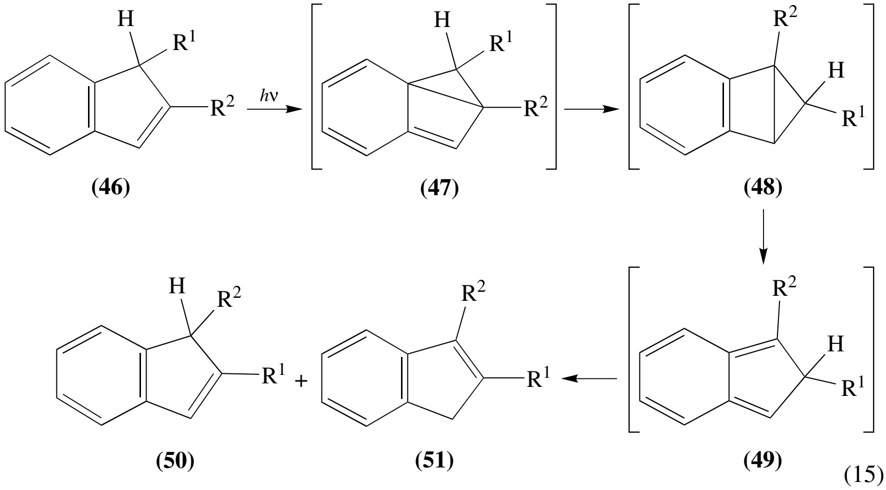


(45)

(14)

Indene derivatives **(46)** undergo phototransposition reactions which have been attributed to a multistep mechanism involving initial ring closure to the isomeric bicyclo[2.1.0]pent-2-ene (**47**), followed by [1,3]-migration of the cyclopropyl ring to give **48**, ring opening to the isoindene structure **(49)**, and finally [1,5]-H migration to re-aromatize the system and yield **50/51** (equation 15)[137–139].

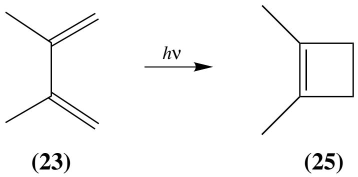
With acyclic dienes, the quantum yield for cyclobutene formation (Φ_{CB}) rarely exceeds *ca* 0.1, the expected result of the fact that the planar s-*trans* conformer normally comprises the bulk (96–99%) of the conformer distribution at room temperature. However, Φ_{CB} is often significantly larger than the mole fraction of s-*cis* form estimated to be present in solution. For example, 1,3-butadiene, whose near-planar (dihedral angle 10–15°[105,106]) s-*cis* conformer comprises *ca* 1% of the mixture at 25 °C, yields cyclobutene with $\Phi_{CB} = 0.04$[140], along with very small amounts of bicyclo[1.1.0]butane[141]. A second well-known example is that of 2,3-dimethyl-1,3-butadiene (**23**; *ca* 4% *gauche* s-*cis* at 25 °C[107]), which yields 1,2-dimethylcyclobutene **(25)** with $\Phi_{CB} = 0.12$ (equation 16)[111]. Most likely, these apparent anomalies can be explained as due to selective excitation of the s-*cis* conformers under the experimental conditions employed, since it is well established that s-*trans* dienes do not lead to cyclobutene directly[102]. A clearer example of this is provided by the reported wavelength dependence of the photochemistry of *E*- and *Z*-1,3-pentadiene (**1**; equation 17)[64]. Irradiation of the two diene isomers at 229 nm, near the absorption maximum of the s-*trans* conformers, results only in *E*,*Z*-isomerization. Longer wavelength irradiation (254 nm) of the *E*-isomer leads to *E*,*Z*-isomerization (with different quantum yields than at shorter wavelengths), and formation of 3-methylcyclobutene **(52)** and 1,3-dimethylcyclopropene **(53)**. Cyclopropene formation is a relatively minor reaction of s-*cis* diene conformers and has been reported in relatively few instances[64,77,142].



(46) **(47)** **(48)**

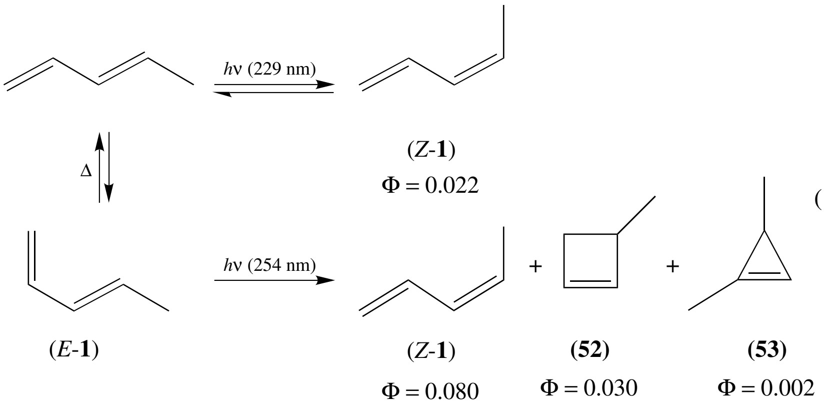
(50) **(51)** **(49)**

(15)



(23) **(25)**

(16)



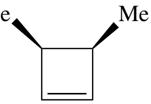
(*Z*-**1**)
$\Phi = 0.022$

(*E*-**1**) (*Z*-**1**) **(52)** **(53)**

$\Phi = 0.080$ $\Phi = 0.030$ $\Phi = 0.002$

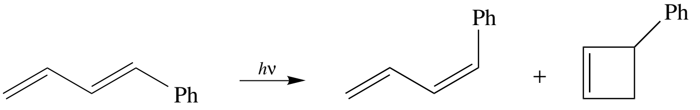
(17)

Other aliphatic acyclic dienes such as isoprene **(2)**[102,111], 2-isopropyl-1,3-butadiene **(24)**[102], and *E*,*E*-2,4-hexadiene **(5)**[78] also yield the corresponding cyclobutene, all via excitation of the s-*cis* conformer. The latter yields the disrotatory ring closure product, *cis*-3,4-dimethylcyclobutene **(54)**, stereospecifically[78].

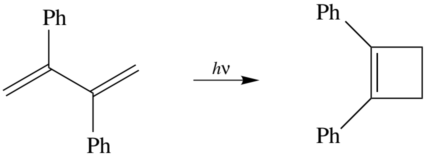


(54)

Phenylated systems generally close to cyclobutenes with extremely low efficiency or not at all. For example, *E*-1-phenylbutadiene **(55)** undergoes efficient *E*,*Z*-isomerization to *Z*-**55** upon direct irradiation[143] and affords 3-phenylcyclobutene **(56)** only after extended periods of time (equation 18)[144]. Various aryl-substituted derivatives of **55** undergo ring closure as well[145]. The quantum yield for cyclobutene formation is also extremely small for 2,3-diphenyl-1,3-butadiene (**57**, equation 19)[146], but because *E*,*Z*-isomerization is degenerate, the direct irradiation of this compound affords 1,2-diphenylcyclobutene **(58)** in useful chemical yields. 1,4-Diphenyl-1,3-butadiene (**4**$_2$) evidently does not undergo photochemical ring closure[147].



(*E*-**55**) (*Z*-**55**) **(56)** (18)



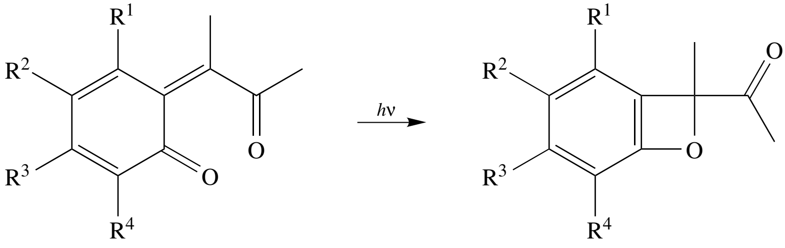
(57) **(58)** (19)

Systems in which one of the C-atoms in the diene unit is replaced by a heteroatom also undergo photoelectrocyclic ring closure in selected cases. For example, Adam and coworkers have recently reported the synthesis of an extended series of benzoxete derivatives **(60)** via photocyclization of the cyclohexadienones **59** (equation 20)[148].

A final example that is so remarkable to deserve mention is the photoisomerization of alkenyne **61** to its isomer **63** (equation 21)[149]. In a recent reinvestigation of the reaction, Johnson and coworkers have provided computational evidence for the intermediacy of the 1,2-cyclobutadiene isomer **62** in the phototransposition reaction[150].

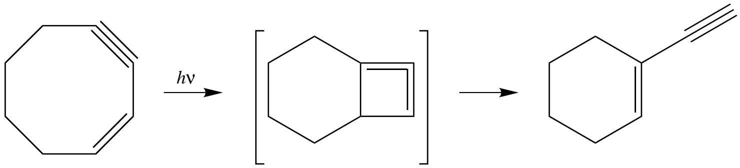
As mentioned in the Introduction, the ring closure of s-*cis* butadiene to cyclobutene has been at the very center of the evolution of theoretical understanding of polyene photochemistry to its current state[25,87–89,151]. Early *ab initio* calculations recognized the crucial role of the 2^1A_g state in the isomerization, and successfully accounted for the disrotatory stereospecificity of the reaction in terms of a 'two-dimensional' model in which the planarity of the carbon framework is more or less maintained throughout[12,13,15].

Within the confines of these geometric restrictions, internal conversion to the ground state surface is considered to occur at minima on the 2^1A_g surface, whose structures correspond roughly to those of the transition states for the ground state con- and disrotatory interconversion of 1,3-butadiene and cyclobutene. Disrotatory ring closure is preferred because internal conversion at the disrotatory 2^1A minimum is faster than that on the conrotatory side, basically because the energy gap to the ground state is smaller owing to the higher activation energy for thermally-forbidden disrotatory interconversion.



(20)

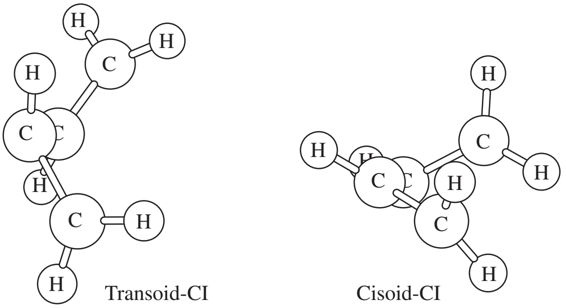
(59) **(60)**



(21)

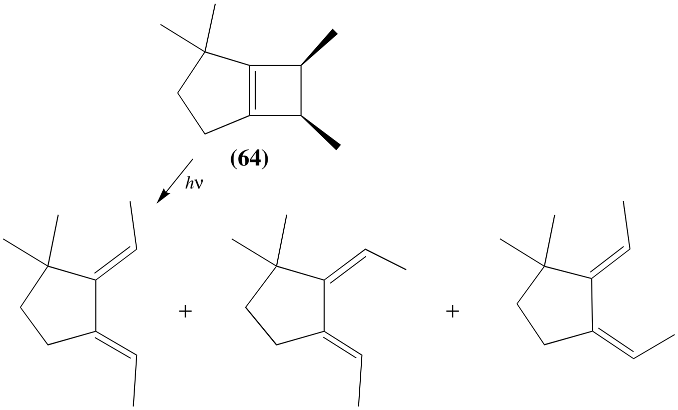
(61) **(62)** **(63)**

The more recent calculations of Bernardi, Robb and Olivucci and their groups suggest that the reaction involves much more profound skeletal distortions than are allowed for in the older models[151]. According to these calculations, the ground state surface is accessed at a conical intersection (CI) with the 2^1A surface, the most readily apparent structural feature of which is twisting about all three C−C bonds. $2^1A/1^1A$ conical intersections have been located at various angles of twist about the central bond, and with various angles of both conrotatory and disrotatory twisting about the termini[88]. The two conical intersection geometries which are thought to be most important in the photochemistry of s-*trans* and s-*cis* 1,3-butadiene are depicted in Scheme 3. In addition to being substantially twisted about the central bond, the termini in both structures are twisted in disrotatory fashion. Evolution along the disrotatory 2^1A pathway from an s-*cis* starting geometry to the disrotatory s-cisoid CI (Scheme 3) was found to encounter a lower barrier than that to the conrotatory s-cisoid CI, explaining the preferred stereochemistry which has been found experimentally. Later calculations at a higher level provided details on the ionic 1^1B surface of s-*cis* butadiene, and conclude that the complete evolution of the excited molecule from the Franck–Condon region to the ground state surface via disrotatory twisting should occur in less than *ca* 1 ps[89]. The calculations are consistent with the *ca* 10 fs lifetime estimated by Trulson and Mathies for the spectroscopic 1^1B state of isoprene[43]. Similar calculations have been carried out for 2,3-dimethylbutadiene **(23)** and 2-cyanobutadiene (*vide infra*)[87] and for dienes with bulky substituents at C2/C3[90], and successfully explain many of the features of diene photochemistry which result from conformational factors and the steric and electronic effects of substituents.



SCHEME 3. Calculated transoid and cisoid CIs for butadiene

We note that the reverse reaction, the photochemical ring opening of cyclobutene, is one of the few photoelectrocyclic reactions which consistently does not proceed stereospecifically[19,20,152]. In fact, we believe that the reaction does proceed with the disrotatory stereospecificity predicted by the Woodward–Hoffmann rules[109], at least when the reaction is initiated by irradiation of the cyclobutene in its π,π^* (1^1B) absorption band. The loss of stereospecificity most likely occurs because ring opening proceeds entirely on the 1^1B surface, and the 2^1A state is not accessed until the diene is nearly fully formed. This would lead one to predict that the distribution of isomeric dienes obtained from the reaction should be that characteristic of the direct *E*,*Z*-photoisomerization of the allowed diene isomer[70]. Indeed, direct irradiation of the unsymmetrically substituted bicyclic cyclobutene derivative **64** yields the same mixture of forbidden diene isomers (*E*,*Z*- and *Z*,*E*-**65**) as are produced when the allowed isomer (*E*,*E*-**65**) is itself irradiated in solution (equation 22)[153]. The jury is still out, however, as more recent results indicate that the $\pi,R(3s)$ excited state also contributes to the photochemical ring opening of alkylcyclobutenes, with the same stereochemistry as that associated with the thermal ring opening process[154]. Unlike the 1^1B-initiated process, the Rydberg-derived one appears to proceed with 100% (conrotatory) stereospecificity.



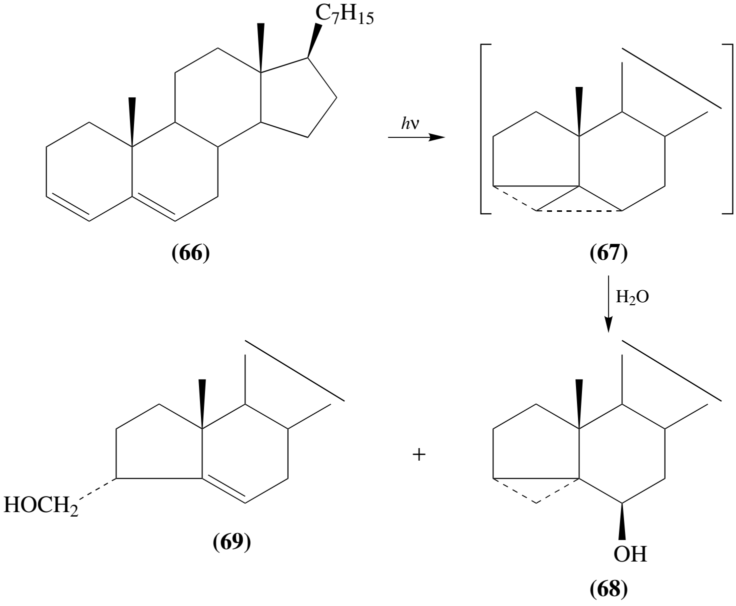
(64)

(22)

(*E*,*E*-**65**) (allowed)

(*E*,*Z*-**65**) (*Z*,*E*-**65**) (forbidden) *b. Bicyclo[1.1.0]butane formation.* Bicyclobutane formation is usually a relatively minor process in diene photochemistry, but has been reasonably well studied nonetheless. Early reports of the reaction centered around steroidal, s-*trans* dienes such as $\Delta^{3,5}$-cholestadiene **(66)**, whose irradiation in the presence of water leads to the formation of alcohols (**68**, **69**) resulting from rapid hydrolysis of the isomeric bicyclo[1.1.0]butane derivative **67** (equation 23)[155]. As mentioned above, bicyclobutane formation occurs with very low efficiency from irradiation of 1,3-butadiene itself in solution (roughly one-sixth of the yield of cyclobutene or less, depending on the solvent)[141,156], in spite of the fact that the conformer distribution in the parent molecule is *ca* 99% s-*trans* under ambient conditions. While this might suggest that the reaction proceeds with highest efficiency from s-*trans* dienes only when there is built in some restriction to rotation about the central bond of the diene system, the fact that irradiation of 2-cyano-1,3-butadiene **(70)** in ether solution yields the corresponding cyclobutene **71** and bicyclobutane **72** in relative yields of 1 : 3.2 (equation 24)[157] indicates that electronic factors also play a role in discriminating between the two modes of reaction.

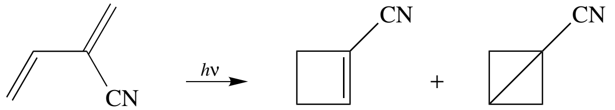
The reaction is highly stereospecific, as was shown by Dauben and Ritscher in their study of the photochemistry of the isomeric 3-ethylidenecyclooctenes **20** (equation 25 and 26)[79]. The fact that two isomeric bicyclobutanes (**73** and **74**) which are both epimeric at a single stereocenter are produced from *E*,*Z*-**20** is incompatible with an intramolecular $[\pi 2s + \pi 2s]$-cycloaddition mechanism for the process. This and other considerations led Dauben and Ritscher to propose that the reaction is initiated by twisting about one of the double bonds (the endocyclic one, in this case) to a relaxed allylmethylene geometry with zwitterionic (allyl anion/methylene cation) character, which proceeds to product by conrotatory 1,3-closure of the allyl moiety in concert with 2,4-bonding. In the present examples, the two conrotatory ring closure pathways available to the zwitterionic allymethylene species lead to different products (**73** and **74**) in the case of *E*,*Z*-**20**, and to the same product **(75)** in the case of *Z*,*Z*-**20** (equation 27)[79].



(66) **(67)**

(69) **(68)**

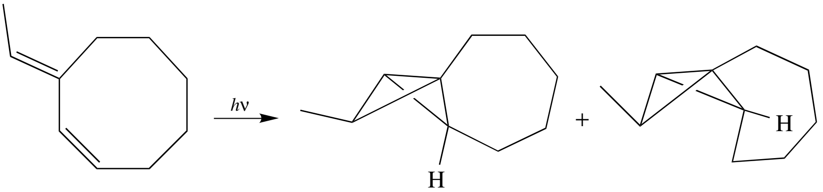
(23)



(70) **(71)** **(72)**

1 : 3.2

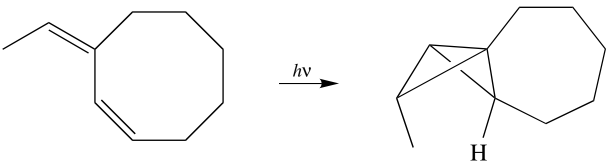
(24)



(*E*,*Z*-**20**) **(73)** **(74)**

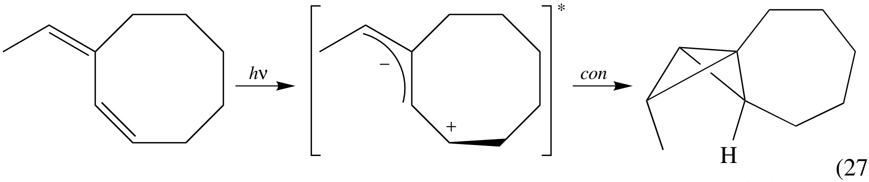
75% 25%

(25)



(*Z*,*Z*-**20**) **(75)**

(26)



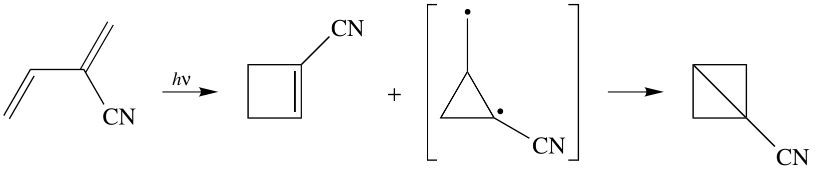
(*Z*,*Z*-**20**) **(75)**

(27)

This suggests that the unusually high yields of bicyclo[1.1.0]butane **72** from irradiation of 2-cyano-1,3-butadiene (**70**; equation 24) might be due to a change in the preferred dynamics of the excited molecule, as a result of an effect on the 1^1B surface due to polar factors (*vide supra*); i.e., in Dauben's terminology, through stabilization of a zwitterionic (allyl anion/methylene cation) excited state intermediate by the 2-cyano substituent. CAS-SCF calculations on the covalent 2^1A surface of this molecule suggest that the cyano group has only slight effects on both the structures of the transoid and cisoid conical intersections of 1,3-butadiene and the favored pathways to them on the 2^1A surface; rather, the main factor is proposed to result from the radical-stabilizing effects of the cyano group, and the reaction is tentatively predicted to involve the formation of the ground state 1,3-biradical intermediate **76** (equation 28)[87].

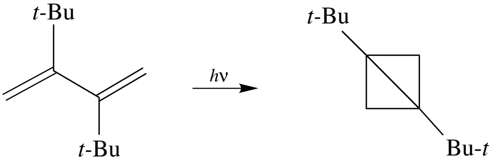
More recent results have provided additional detail on the conformational requirements for bicyclo[1.1.0]butane formation from conjugated dienes[158]. Hopf and coworkers have shown that high yields of the isomeric bicyclobutane **78** are obtained from irradiation of

2,3-di-*tert*-butyl-1,3-butadiene (**77**; equation 29)[158], whose X-ray crystal structure shows it to exist in a twisted s-*trans* conformation with a C1−C2−C3−C4 dihedral angle of 84°[159]. Irradiation of the permethylated derivative of this compound **(79)** also leads primarily to bicyclobutane **(80)** formation, along with minor amounts of cyclobutene **(81)** and [1,5]-H migration **(82)** products (equation 30)[158]. A recent computational study indicates that the bulky substituents at C2/C3 in **77** change the preferred excited state decay route from the disrotatory, cyclobutene-producing pathway favored by the parent s-*cis* 1,3-butadiene to a pathway involving concerted conrotatory rotation of the terminal methylenes which favors bicyclo[1.1.0]butane formation[90], in essential agreement with Dauben's simple model for the process.



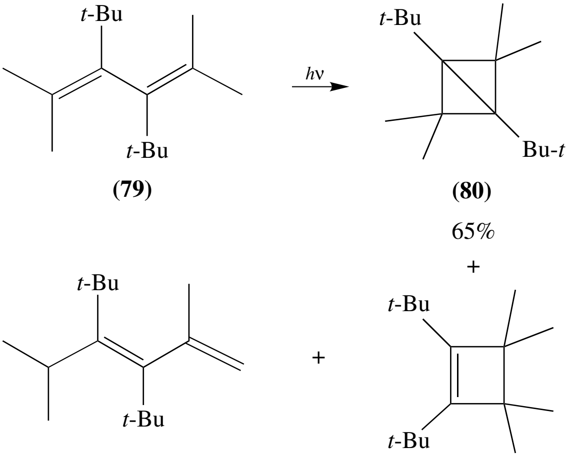
(70) **(71)** **(76)** **(72)**

(28)



(77) **(78)**

(29)

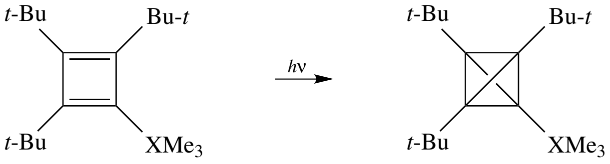


(79) **(80)** 65%

(30)

(82) 10% **(81)** 25%

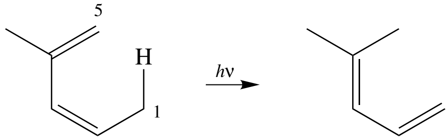
A final, related example is the formation of tetrahedranes **(84)**, from irradiation of *tert*-butyl substituted cyclobutadienes such as **83** (equation 31), a reaction which has been extensively exploited by Maier and coworkers[160–163].



(83) X = C, Si, or Ge **(84)**

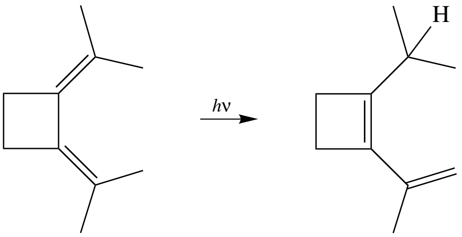
(31)

c. [1,5]-Hydrogen migration. Photochemical [1,5]-hydrogen migration competes with other reactive processes in s-cisoid dienes which bear a **Z**-alkyl group (most commonly, methyl) at either C1 or C4 of the butadienyl system. Orbital symmetry considerations predict that the reaction should proceed in supra-antarafacial fashion[109], although as far as we know this has never been explicitly proven. As with the other pericyclic photoreactions of conjugated dienes, [1,5]-hydrogen migration occurs in significant yields only when other reactive decay pathways lead to degenerate rearrangement or are structurally blocked[112,164,165]. A few examples of systems which undergo this reaction in reasonably high chemical yields involve the formation of **86** from **Z**–**85** (equation 32), and of **88** and **90** from **87** and **89**, respectively (equations 33 and 34)[112,165,166]. Many other examples are known as well[158,167,168].



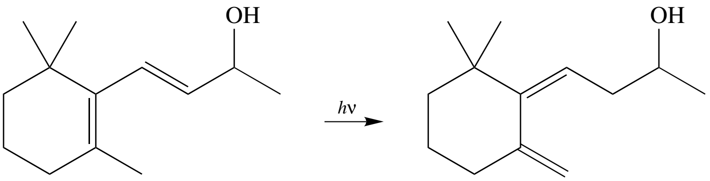
(*Z*-**85**) **(86)**

(32)



(87) **(88)**

(33)

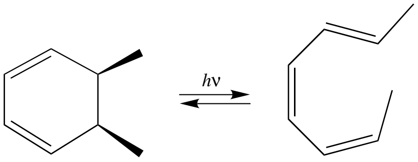


(89) **(90)**

(34)

2. Electrocyclic ring opening of 1,3-cyclohexadienes

a. Experimental studies. By far the most common photochemical reaction of 1,3-cyclohexadienes is electrocyclic ring opening to the corresponding *Z*-1,3,5-hexatriene derivative, as illustrated by the formation of **92** from *cis*-5,6-dimethyl-1,3-cyclohexadiene **(91)** (equation 35)[169]. The reaction is well-known to proceed with nearly 100% conrotatory stereospecificity[129], as predicted by orbital symmetry selection rules[109]. This is also true of the reverse reaction, the photochemical electrocyclic ring closure of *Z*-1,3,5-hexatrienes[170]. This reversibility, as well as the fact that 1,3,5-hexatrienes undergo a number of other conformation-dependent photoprocesses in addition to ring closure (*vide infra*), makes both systems exceedingly challenging to study experimentally.



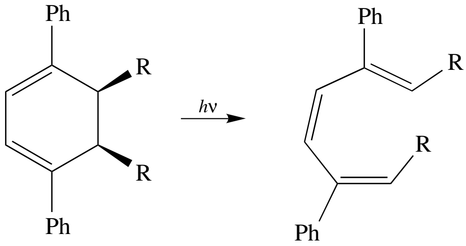
(91) **(92)**

(35)

Nevertheless, a great deal is known about the process, largely through the early pioneering work of the groups of Havinga and Jacobs[129,171] and of Dauben[172] on the photochemistry of Vitamin D, its various isomers and related systems. A large number of reviews have been published over the years on the photochemistry of 1,3-cyclohexadiene/1,3,5-hexatriene systems[116,128,129,170,173–175] and the reader is directed to these for more comprehensive treatments of the subject than can be provided here.

1,3-Cyclohexadiene itself undergoes smooth photochemical ring opening to *Z*-1,3,5-hexatriene in both the gas phase ($\Phi = 0.13$)[176] and in solution ($\Phi = 0.41$)[71,177]. As is almost always the case, extended irradiation in solution leads to the formation of a variety of isomeric products due to secondary irradiation of the *Z*-triene and its *E*-isomer (*vide infra*)[71].

Unlike other diene photopericyclic reactions, cyclohexadiene ring opening proceeds with reasonable efficiency in phenyl-substituted derivatives, although the quantum yields are generally significantly lower than those of non-arylated systems. Two examples of the conversion of **93** to **94** are shown in equation 36[178,179]



(93) **(94)**

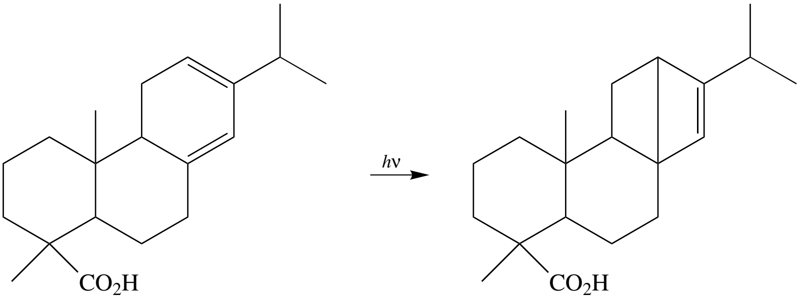
(36)

(**a**) R = Me

(**b**) R = CO_2Me

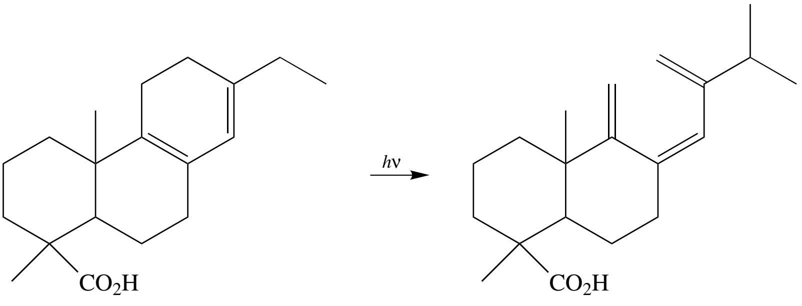
R = CO_2Me: $\Phi = 0.08$

Through study of the photochemistry of a large number of polycyclic cyclohexadienyl systems coupled with conformational analyses, Dauben and his group established that the electrocyclic ring opening of 1,3-cyclohexadienes proceeds most efficiently from a half-chair conformation, in which the diene moiety is twisted about the C2−C3 bond at an angle of *ca* 20°, while (disrotatory) ring closure to the isomeric bicyclo[2.2.0]hex-2-ene is favored by planar or near-planar conformations. For example, laevopimaric acid **(95)**, which possesses a central bond dihedral angle on the order of *ca* 10°[180], undergoes predominant electrocyclic ring closure to yield **96** (equation 37)[181], while irradiation of its more highly twisted isomer, palustric acid **(97)**, leads only to ring opening giving **98** (equation 38)[182]. The competition between the two modes of reaction is also affected by steric effects of remote substituents on the cyclohexadienyl or an ancillary ring, most likely through their effects on the central bond dihedral angle[128]. Illustrative examples of fluorinated 1,3-cyclohexadienes which undergo highly selective ring closure are shown by the formation of **100** and **101** from **99** (equation 39)[183,184] and of **103** from **102** (equation 40)[185]; many more are cited in the review by Laarhoven[116].



(95) **(96)**

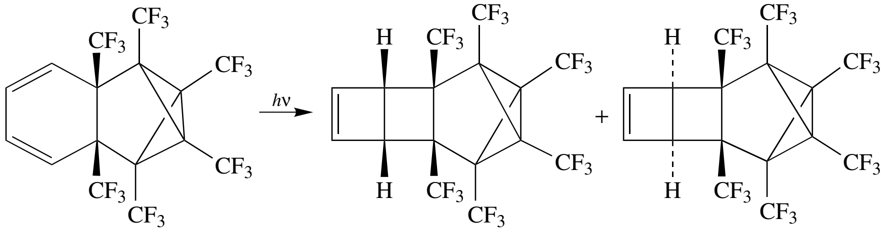
(37)



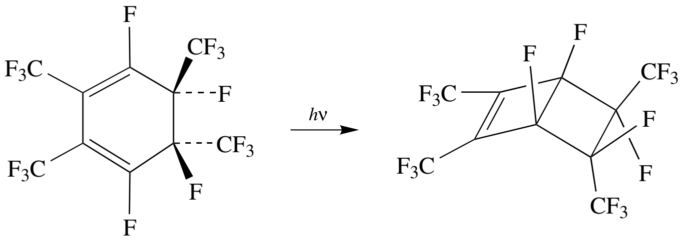
(97) **(98)**

(38)

The photochemistry of cyclohexadienyl systems is quite commonly wavelength-dependent, an effect which can be caused either by differences in the absorption spectra of various conformers of the substrate or by photostationary state effects which arise because the ring opening to the isomeric *Z*-triene is photochemically reversible. For example, *syn*-bicyclo[4.3.0]nona-1,4-diene **(104)** undergoes predominant ring opening to **107** upon irradiation in its main absorption band (254 nm), but yields the ring closure products **105** and **106** upon irradiation at 300 nm, at the extreme red edge of its absorption spectrum

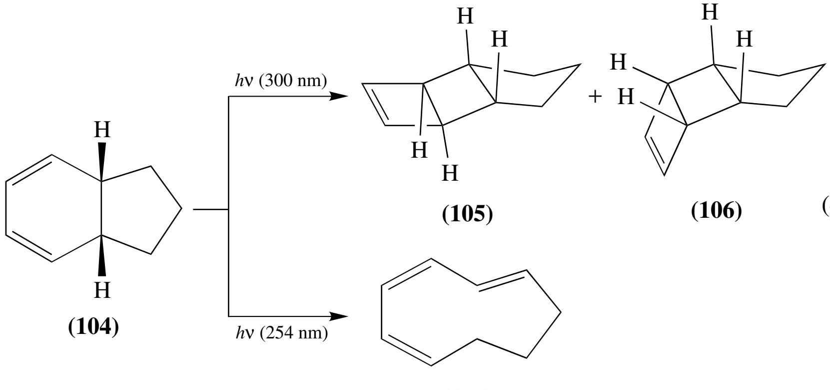


(99) **(100)** **(101)** (39)



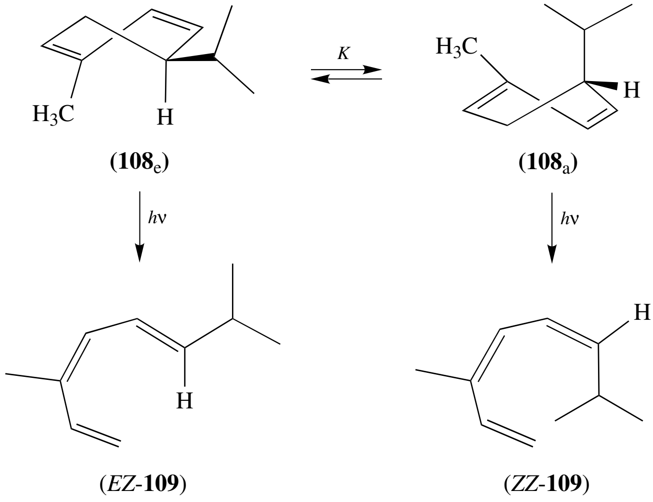
(102) **(103)** (40)

(equation 41). This could be due to specific excitation of a planar diene conformer, which is present in exceedingly low concentrations and absorbs at longer wavelengths relative to the most stable, twisted s-*cis* conformer of the diene. An alternative explanation for the long-wavelength result is that the **104** : **107** photostationary state at 300 nm lies so strongly in favor of the cyclohexadiene isomer (because of the much stronger absorption spectrum of the triene at this wavelength) that the triene is never present in detectable amounts in spite of the fact that the quantum yield for its formation may be high; the ring closure product builds up, even though it may be formed with a substantially lower quantum yield than the triene, simply because it is not photochemically active at this wavelength[128].



(104) **(105)** **(106)** **(107)** (41)

When substituents are present at C5 and/or C6 of the cyclohexadienyl system, two possible stereoisomers can be formed via conrotatory ring opening. In general, however, the reaction exhibits a high degree of torquoselectivity — another manifestation of the ground state conformational control of photoreactivity which is a common feature of polyene photochemistry. This was first demonstrated by Baldwin and Krueger with an investigation of the photochemistry of α-phellandrene **(108)**[186]. The photochemistry of this molecule had been delineated earlier by Havinga and coworkers[187], who reported it to yield a 3 : 1 mixture of two geometric isomers of 3,7-dimethyl-1,3,5-octatriene **(109)** which reacted further on prolonged irradiation. Through comparison of the temperature dependences of the primary photoproduct ratios and the ORD and CD spectra of the starting material, Baldwin and Krueger provided strong evidence that the two primary products *EZ*- and ***ZZ*-109** are each formed selectively from different ground state conformers of the diene, as shown in equation 42. The major product of the photolysis is *E*,*Z*-**109**, the diene isomer derived from ring opening of the pseudoequatorial conformer ($\mathbf{108}_e$), which was calculated to be 0.46 kcal mol^{-1} more stable than the pseudoaxial conformer ($\mathbf{108}_a$)[186].

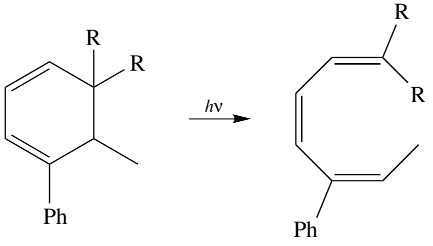


(42)

This feature of 1,3-cyclohexadiene ring opening is quite general, and is explained in terms of the Principle of Least Motion: the most favored conrotatory ring opening mode is generally that in which a pseudoaxial substituent at C5 or C6 is rotated inward (i.e., yielding *Z*-stereochemistry in the product) while a pseudoequatorial substituent is rotated outward, since these rotations require the least motion for the developing sp^2 centers to overlap with the existing π-system[188]. The distributions of *E*- and *Z*-triene isomers obtained from irradiation of a series of 5-alkyl-1,3-cyclohexadienes[189] and from several 6-methyl-1-phenylcyclohexadienes **(110)** also illustrate the principle. In the latter cases, direct irradiation produces only a single diene isomer **111** (equation 43)[179,188,190–192]. This has been termed 'accordant' ring opening, because it is in accord with the chirality of the diene[186].

The ring opening of 1,3-cyclohexadienes is normally well-behaved from a stereochemical point of view: the reaction proceeds to yield only the 3-*Z* triene isomer(s) corresponding to conrotatory ring opening. This indicates that the ring opening process is accompanied by diabatic funnelling to the ground state surface in the normal manner. Scattered reports exist, however, of examples in which the 3-*E* triene isomer has been observed in the very early stages of the reaction and concluded to be a primary ring opening product[193–195]. If this is correct, then it suggests that ring opening of cyclohexadienes can in certain cases occur adiabatically to generate the 3-*Z* triene in an excited state[194], as is known to be the general case for the photochemical ring opening of alkylcyclobutenes (*vide supra*)[70]. In our experience, however, such observations are fraught with pitfalls due to secondary photolysis effects[154] and must be interpreted with a great deal of caution. The possibility deserves closer scrutiny, however.

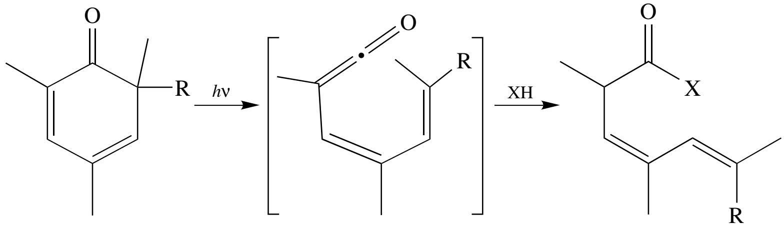
6,6-Disubstituted 2,4-cyclohexadienones **(112)** undergo photoinduced electrocyclic ring opening to the transient ketene derivatives **113**, which can be trapped by nucleophiles to prepare the corresponding carboxylic acid derivatives (**114**; equation 44)[196,197]. The reaction has been employed successfully for the synthesis of various carboxylic acids, esters and amides.



(43)

(110) **(111)**

R = H, Me, or Ph

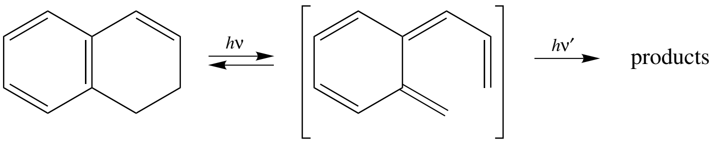


(44)

(112) **(113)** **(114)**

X = OH, OR′, NHR″, NR_2'''

1,2-Dihydronaphthalenes — benzannelated cyclohexadiene derivatives — e.g. **115**, undergo a rich photochemistry which is initiated by electrocyclic ring opening to yield the corresponding *ω*-vinyl-*ortho*-quinodimethane (equation 45)[170]. Depending on substitution, the *ortho*-quinodimethanes **116** can undergo a variety of fairly rapid thermal isomerizations (including ring closure to regenerate the dihydronaphthalene), but evidently build up in sufficiently high concentrations that secondary photochemical reactions typical of 1,3,5-hexatrienes can result (*vide infra*). A more complete account of 1,2-dihydronaphthalene photochemistry appears later in this review.

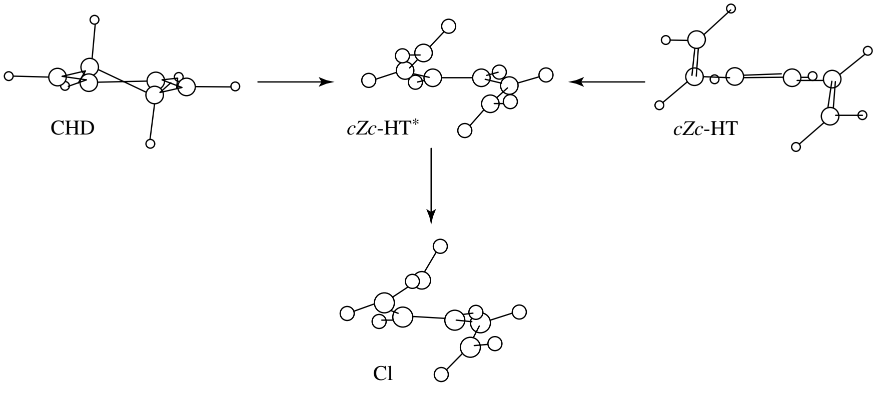


(45)

(115) **(116)**

b. Theoretical and time-resolved spectroscopic studies. The ring opening of 1,3-cyclohexadiene (CHD) has recently been studied by ultrafast time-resolved spectroscopic techniques, which afford information on the evolution of the excited molecule during the first few hundred femtoseconds after excitation. Using resonance Raman spectroscopic techniques, Mathies and coworkers concluded that relaxation of the spectroscopic 1^1B state occurs with a lifetime of *ca* 10 fs in cyclohexane solution and is accompanied by conrotatory motions of the sp^3 hydrogens; ground state *Z*-1,3,5-hexatriene (*Z*-HT) is formed with a time constant of *ca* 6 ps, probably via the intermediacy of the 2^1A state[51,198]. Similarly, an appearance time of τ *ca* 11 ps was determined for the formation of ground state **108** from photolysis of α-phellandrene (**108**)[51]. Transient absorption measurements, on the other hand, suggest a sub-picosecond time constant for product formation from CHD[199]. Using time-delayed photoionization or intense field ionization in conjunction with time-of-flight mass spectrometry[200], Fuss and coworkers have assigned gas-phase lifetimes of 43 and *ca* 80 fs for the 1^1B and 2^1A states, respectively, and have presented results consistent with the formation of *cZc*-HT within 200 fs of the initial excitation event[201,202]. The sub-picosecond appearance time of the ground state product provides strong evidence that the reaction proceeds via an essentially barrierless pathway from the spectroscopic 1^1B state to the ground state through a $2^1A/1^1A$ conical intersection.

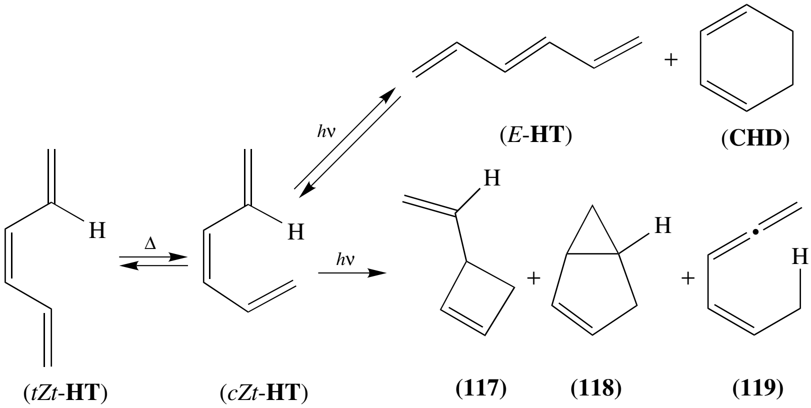
The photochemical interconversion of 1,3-cyclohexadiene (CHD) and *cZc*-1,3,5-hexatriene (*cZc*-HT) (*vide infra*) is a more demanding computational problem than butadiene ring closure, and, as a result, relatively few theoretical studies have been reported[203–206]. Again, however, the results which have been reported are consistent with the results of product and fast time-resolved spectroscopic studies of the process. For example, computation of the minimum energy pathway on the 1^1B state of cyclohexadiene starting from the Franck–Condon geometry indicates that conrotatory twisting and accompanying stretching of the 5,6 bond take the molecule by a barrierless pathway to a $1^1B/2^1A$ state crossing; thus, the stereochemistry of the process is defined and the 5,6 bond essentially broken by the time (*ca* 30 fs) the molecule enters the 2^1A state surface[205]. The molecule relaxes from there to a shallow biradicaloid minimum on the 2^1A surface (*cZc*-HT*; Scheme 4) which is common to both the ring opening and ring-closure processes. This intermediate then decays to the ground state surface via a $2^1A/1^1A$ conical intersection (CI) located *ca* 1 kcal mol^{-1} higher in energy[204,205]



SCHEME 4. Calculated excited state intermediates in the interconversions of CHD and *cZc*-HT[204,205]

D. Photopericyclic Reactions of Conjugated Trienes

The photochemistry of conjugated trienes has received a great deal more attention over the past 40 years than is the case with dienes, and has been reviewed in detail by many of the experts in the field[116,129,170–172,175,207]. As with dienes, *E*,*Z*-photoisomerization usually dominates the photochemistry, and most of the accompanying photorearrangement processes are strongly conformation-dependent. However, as the degree of conjugation increases, so too does the number of possible pericyclic and other photorearrangement processes. Most of these require the central C=C bond to have the *Z*-stereochemistry, and that at least one of the two single bonds be in an s-*cis* conformation. In addition to *E*,*Z*-isomerization and *cis*,*trans* interconversion of conformers, the processes characteristic of the *Z*-1,3,5-hexatrienyl moiety are (conrotatory) electrocyclic ring closure to the corresponding 1,3-cyclohexadiene, (disrotatory) electrocyclic ring closure to the corresponding 3-vinylcyclobutene, bicyclo[3.1.0]hex-2-ene formation, and antara-supra [1,5]-H migration to yield an isomeric vinylallene derivative (equation 46). In general, trienes with the *E*-stereochemistry at the central C=C bond tend to be relatively unreactive except toward isomerization to the *Z*-isomer, because the ground state conformational distribution normally favors the fully extended *tEt* form. As might be expected, however, 3-vinylcyclobutene formation has been found to occur in systems bearing substituents (such as 2-alkyl groups) which stabilize *cEt* relative to *tEt*-conformers[208]. Alkyl substitution also introduces several other common processes in 3-*E*- and 3-*Z*-hexatrienes as well, though they are usually minor and will not be discussed explicitly here. Examples include the formation of methylenecyclopropane and/or allylcyclopropene derivatives in systems bearing alkyl substituents at C2(5) (see References 72 and 209 for discussions of the mechanisms of these processes), and antarafacial [1,5]-hydrogen migrations in those containing alkyl substituents at C3(4) of the trienyl moiety[210]. As in the photochemistry of conjugated dienes, the observed product distributions are usually wavelength-dependent, which largely reflects the different absorption properties of the various triene conformers present at equilibrium.



(46)

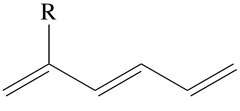
1. The photochemistry of Z-1,3,5-hexatriene

The simplest member of the family, *Z*-1,3,5-hexatriene (Z-HT), has been studied in detail in both the gas phase[176,211–213] and in solution[177,188,214] and illustrates all five of the productive photoreactions which are characteristic of the *Z*-1,3,5-hexatrienyl moiety.

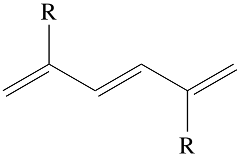
In solution, an initial photoequilibrium is established between the Z- and E-isomers, while the rearrangement products **117** and **118** are formed along with traces of cyclohexadiene (CHD) over much longer irradiation times (equation 46). In solution, the major products are 3-vinylcyclobutene **(117)** and bicyclo[3.1.0]hex-2-ene **(118)**; Z-1,2,4-hexatriene **(119)**, which is a major product in the gas phase[176,211], is formed in relatively low yields. The quantum yields for E,Z-photoisomerization of Z- and E-1,3,5-hexatriene in pentane solution (265 nm excitation) are $\Phi_{Z\rightarrow E} = 0.034$ and $\Phi_{E\rightarrow Z} = 0.016$, respectively[188].

2. The NEER Principle

One reason for the rather low quantum yields for product formation from Z-1,3,5-hexatriene is thought to be that the ground state conformer distribution is heavily weighted in favor of the relatively unreactive *tZt*-conformer[129]. Substituents and structural constraints have quite substantial effects on the conformer distribution, and hence on the quantum yields and distribution of products observed. These effects are well understood, having been worked out independently by Havinga and coworkers, who examined the photochemistry of various 2-alkyl- and 2,5-dialkyl-1,3,5-hexatrienes (**120** and **121**, respectively)[129,207,215,216], and by Dauben and coworkers with their studies of the photochemistry of substituted 6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalins **(122)**[217]. Both bodies of work were predicated on the effects of substituents at the 2- and/or 5-positions of the 1,3,5-hexatrienyl moiety on the ground state conformational distribution, and provided the first systematic verification of the 'NEER' Principle, which was first proposed to explain some of the early results in the vitamin D field[61]. The NEER Principle states that each conformer of a given polyene affords its own specific assortment of photoproducts, and the individual excited conformers do not interconvert within their lifetimes. Such behavior is now known to govern both the singlet and triplet state photochemistry of almost all polyene systems.

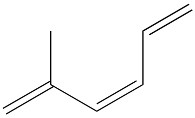


(120)

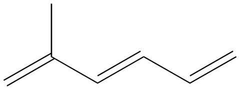


(121)

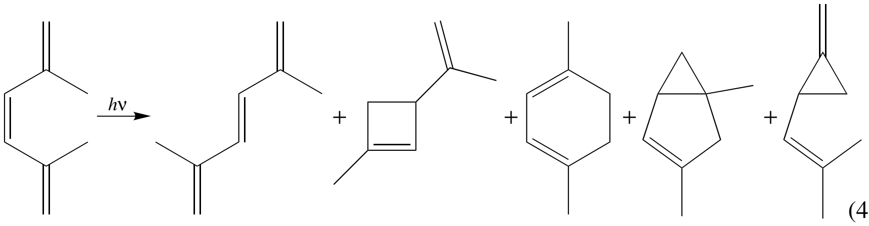
The validity of the principle can be demonstrated by comparing the product distributions obtained from irradiation of Z-1,3,5-hexatriene (Z-**HT**) with those of Z-2-methyl- and Z-2,5-dimethyl-1,3,5-hexatriene at 254 nm (Z-**123** and Z-**14**, respectively)[215]. The ^{1}H NMR and UV absorption spectra of these three compounds suggest that their ground state conformational equilibria differ significantly. The parent compound ($\lambda_{\max} = 254$ nm; ε 41,000) exists predominantly as the *tZt* conformer and yields only small amounts of cyclization products (*vide supra* and equation 46); Z-**123** ($\lambda_{\max} = 259$ nm; ε 22,400) exists predominantly in the *cZt* form and affords significantly higher yields of its bicyclo[3.1.0]hex-2-ene, 3-vinylcyclobutene and vinylallene isomers (along with E-**123**); Z-**14** ($\lambda_{\max} = 237$ nm; ε 12,300) is rich in the *cZc* form and affords mainly the cyclohexadiene **125**, and the vinylcyclobutene **124**, in addition to E-**14** and small amounts of **126** and **127**. Much higher yields of cyclohexadiene **125** are obtained with longer-wavelength irradiation, where the *cZc* conformer absorbs more strongly than the other conformers (equation 47)[216]. Other Z-2,5-dialkyl-1,3,5-hexatrienes exhibit similar behavior[72,218].



(Z-**123**)



(E-**123**)

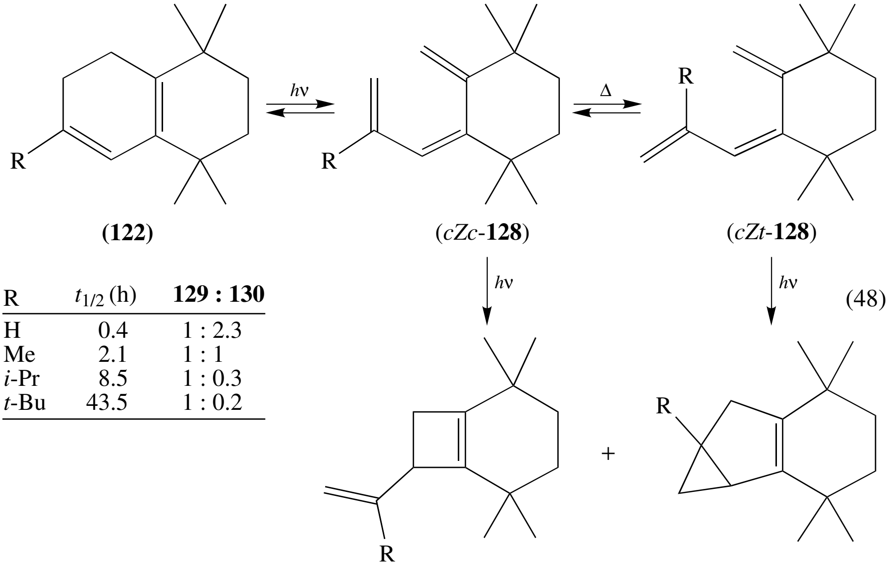


(47)

(Z-**14**) (E-**14**) **(124)** **(125)** **(126)** **(127)**

	(E-**14**)	**(124)**	**(125)**	**(126)**	**(127)**
254 nm :	8.05	0.93	0.75	0.05	0.27
313 nm :	1.13	0.01	8.85	0.05	0.01

Dauben and coworkers reached similar conclusions on the basis of their extensive investigations of the photochemistry of 3-alkyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalins **(122)**[217]. Direct irradiation of these compounds leads to the formation of **129** and **130** due to secondary irradiation of the initially formed triene **128**, which exists as an equilibrium mixture of conformers cZc-**128** and cZt-**128** (equation 48). Their results showed that as the steric bulk of the 3-substituent increases, the rate of disappearance of starting material decreases and the cyclobutene **(129)**: bicyclo[3.1.0]hex-2-ene **(130)** product ratio



(122) (cZc-**128**) (cZt-**128**)

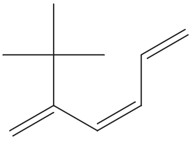
R	$t_{1/2}$ (h)	**129 : 130**
H	0.4	1 : 2.3
Me	2.1	1 : 1
i-Pr	8.5	1 : 0.3
t-Bu	43.5	1 : 0.2

(48)

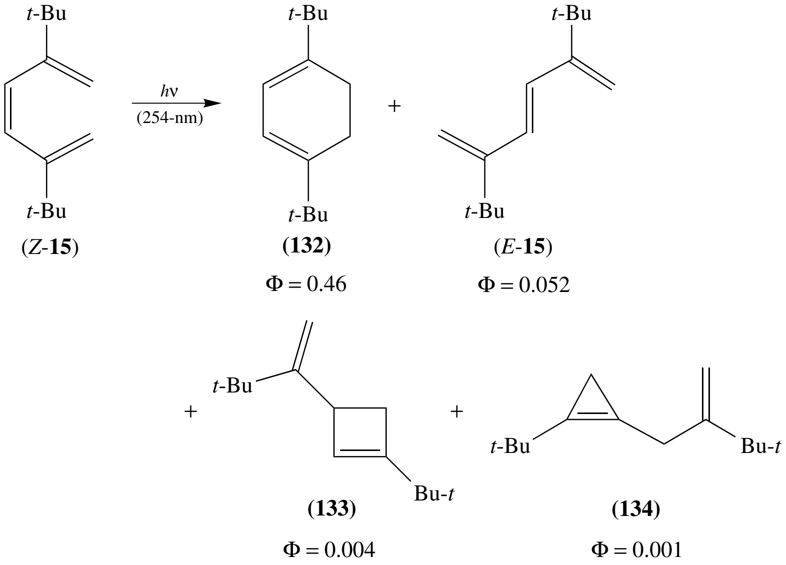
(129) **(130)**

increases. This behavior is consistent with a steady increase in the proportion of *cZc*-**128** present at equilibrium, with increasing steric bulk of the 3-substituent. It also suggests that the cyclobutene product arises predominantly from excitation of the *cZc* conformer, while the bicyclo[3.1.0]hexene derivative is formed from the *cZt* form (*cZt*-**128**).

The proposal that the wavelength dependence of the product yields from irradiation of *Z*-**14** is due largely to selective excitation of specific conformers is supported by the observation that the UV spectrum of the compound can be simulated accurately by a 9 : 1 combination of the spectra of *Z*-2-*tert*-butyl- (*Z*-**131**) and *Z*-2,5-di-*tert*-butyl-1,3,5-hexatriene (*Z*-**15**), which serve as model compounds for the *cZt* and *cZc* conformers of *Z*-**14**, respectively[219]. Both *Z*-**15** and the perfluorinated *E*,*Z*,*E*-4,5-dimethyl-2,4,6-octatriene derivative **(135)** are thought to adopt preferred helical *cZc* conformations, and undergo highly selective electrocyclic ring closure to the corresponding cyclohexadienes **132** and **136**, respectively upon irradiation (equations 49[72] and 50[185]). In the reaction of *Z*-**15** the cyclobutene **133** and the cyclopropene **134** are also formed, but in low quantum yields (equation 49).



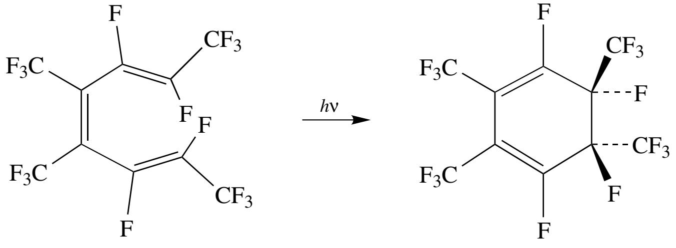
(*Z*-**131**)



(49)

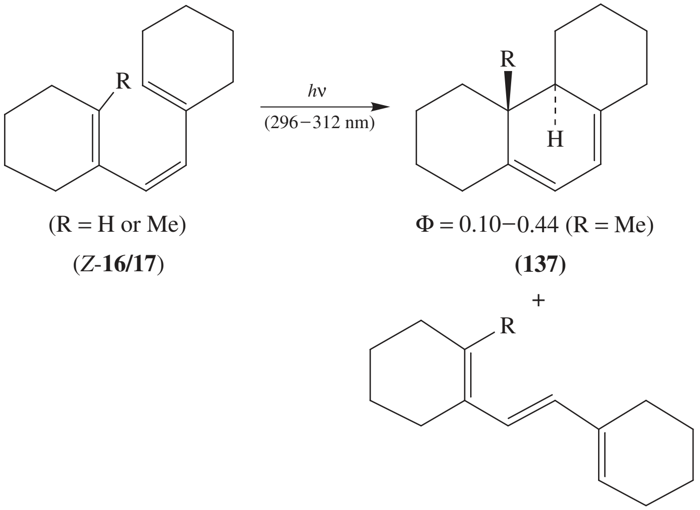
Very dramatic wavelength effects on the quantum yields for *E*,*Z*-isomerization to *E*-**16/17** and (especially) electrocyclic ring closure to **137** of the previtamin D_3 analogues *Z*-**16/17** (equation 51) have recently been reported[73], following an earlier report of similar behavior for previtamin D_3 itself (*vide infra*)[220]. The analogues exhibit an almost twofold increase in the quantum yields for ring closure over only a 3 nm range in excitation wavelength (306–309 nm). For example, the quantum yield for ring closure of

Z-**17** (R = Me) to **137** increases from 0.23 at 306 nm to 0.42 at 309 nm. It is suggested that at wavelengths below 306 nm, excitation populates the 1^1B state which can isomerize or decay to the 2^1A state, from which cyclization ensues. Excitation wavelengths above 306 nm result in direct promotion to the 2^1A state, accounting for the increased quantum yields for cyclization. To what extent this mechanism might contribute to the wavelength dependence observed with other triene systems is not yet clear.



(135) **(136)**

(50)



(R = H or Me)

(*Z*-**16/17**)

$\Phi = 0.10-0.44$ (R = Me)

(137)

+

(51)

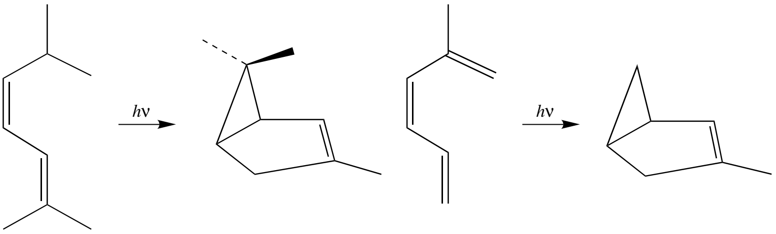
$\Phi = 0.35-0.46$ (R = Me)

(*E*-**16/17**)

3. Formation of bicyclo[3.1.0]hex-2-enes: The 'photochemical Diels–Alder reaction'

The formation of bicyclo[3.1.0]hex-2-enes is a common reaction of cyclic and acyclic *cZt*-1,3,5-trienes. While it has been frequently depicted as a $[\pi 4 + \pi 2]$-cycloaddition and it often exhibits the stereochemistry expected of a concerted $[\pi 4s + \pi 2a]$ process[109], it is well known that it just as often does not. The stereochemistry, conformational requirements and scope of the reaction have been thoroughly studied by a number of workers, and have been extensively reviewed[116,128,170–172].

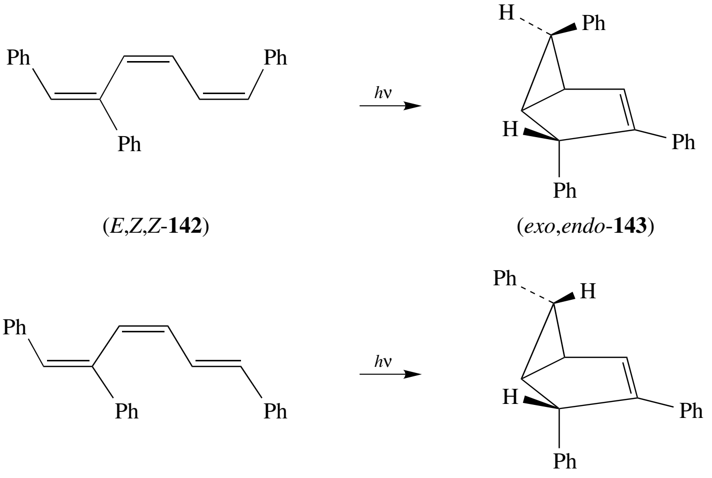
In general, the regiochemistry of the reaction is such that the more highly substituted terminal carbon of the 1,3,5-hexatrienyl moiety (e.g. of **138**) ends up as C6 of the bicyclo[3.1.0]hex-2-ene structure **(139)** while with 2-substituted trienes having identically substituted terminal carbons, such as **140**, the cyclopropyl group is formed at the opposite end of the system (cf **141**, equation 52)[188,210]. This is mainly due to steric factors which stabilize one *cZt* conformer relative to the other.



(52)

(138) **(139)** **(140)** **(141)**

The stereochemistry of the reaction varies. For example, irradiation of *E*,*Z*,*Z*- and *E*,*Z*,*E*-1,2,6-triphenylhexatriene (*E*,*Z*,*Z*- and *E*,*Z*,*E*-**142**, respectively) proceeds with formal [π4s + π2a] stereochemistry to yield the *exo*,*endo*- and *exo*,*exo*-bicyclo[3.2.0]hex-2-ene derivatives (**143**; equation 53), in chemical yields in excess of 75%[221]. Irradiation of the *Z*,*Z*,*E*- and *Z*,*Z*,*Z*-isomers leads to the same two products in nearly the same yields, via 2-photon processes of which the first is selective *E*,*Z*-isomerization to the *E*,*Z*,*E*- and *E*,*Z*,*Z*-isomers, respectively. In contrast, irradiation of *E*,*Z*,*Z*- and *E*,*Z*,*E*-**144** affords the *endo*,*endo*- and *endo*,*exo*-isomer **145**, the products corresponding to formal [π4a + π2a] cycloaddition (equation 54)[191,192].

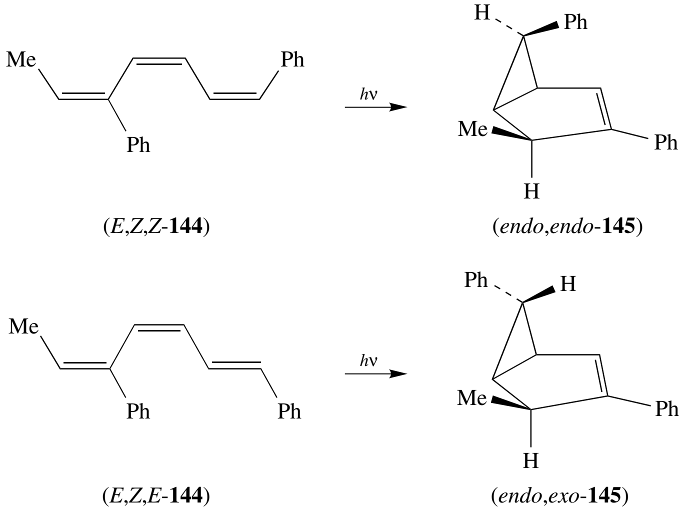


(*E*,*Z*,*Z*-**142**) (*exo*,*endo*-**143**)

(53)

(*E*,*Z*,*E*-**142**) (*exo*,*exo*-**143**)

Dauben and coworkers produced a number of lovely examples of the reaction in the course of their studies of the photochemistry of large-ring (C_8–C_{11}) cyclic trienes, many of which were produced by photochemical electrocycloreversion of the isomeric annulated cyclohexadiene derivatives (cf Reference 172 and references cited therein). Two examples of the photochemistry of the *Z*,*Z*,*E*-cyclic trienes **147** and **152**, formed by accordant ring opening of the corresponding *cis*-fused annulated cyclohexadienes **146** and **151**, respectively, are shown in equations 55 and 56[222]. The products are **148**–**150** in equation 55 and **153** and **154** in equation 56.



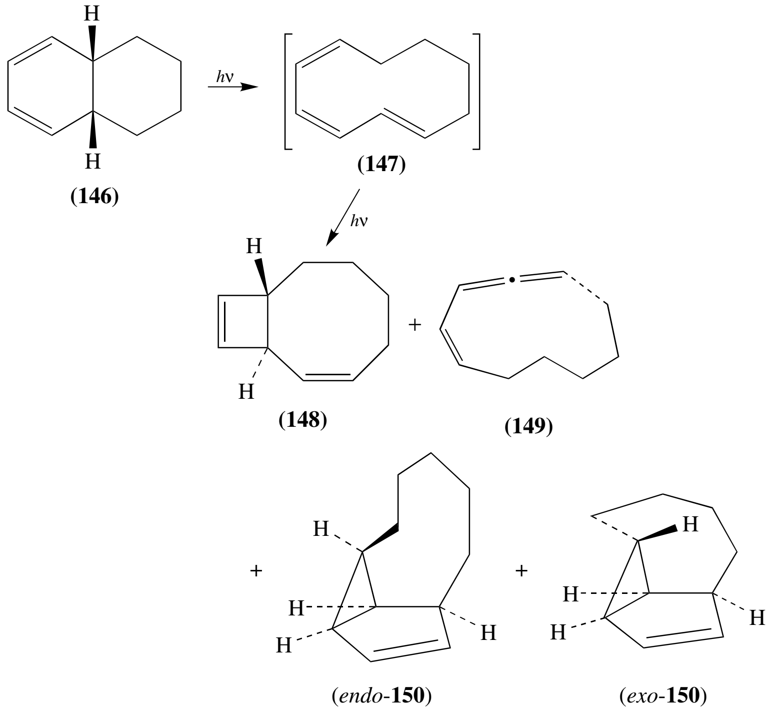
(*E*,*Z*,*Z*-**144**)

(*endo*,*endo*-**145**)

(*E*,*Z*,*E*-**144**)

(*endo*,*exo*-**145**)

(54)



(146)

(147)

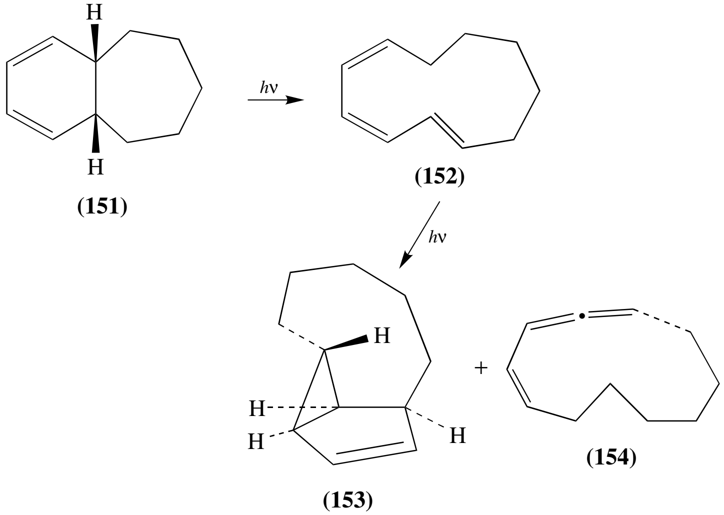
(148)

(149)

(*endo*-**150**)

(*exo*-**150**)

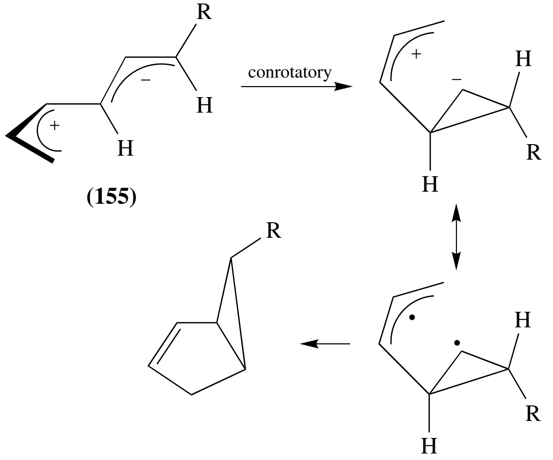
(55)



(151) **(152)** **(153)** **(154)**

(56)

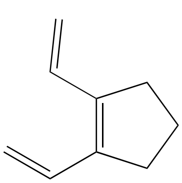
Dauben and coworkers proposed a stepwise mechanism for the reaction involving initial twisting about the central C=C bond, conrotatory ring closure of the s-*trans* half of the molecule, and then non-stereospecific ring closure to form the cyclopentene ring (equation 57)[172,170]. Both experimental evidence[128] and theoretical calculations[39,80,83] support a zwitterionic structure for the twisted intermediate **(155)**. This mechanism is analogous to that proposed by Dauben and Ritscher for the formation of bicyclobutanes from irradiation of s-*trans* dienes[79]. Tanaka and Fukui have discussed an alternative mechanistic treatment based on FMO theory[223]. Garavelli and coworkers have recently suggested that the formation of bicyclo[3.1.0]hexenes from *cZc*-1,3,5-hexatriene proceeds via the intermediacy of a ground state methylenecyclopentenyl biradical[206].



(155)

(57)

Jacobs and coworkers have recently reported an investigation of the photochemistry of the structurally locked *Z*-triene 1,2-divinylcyclopentene **(156)**, which suggests that constraining the torsional mobility about the central C=C bond of the Z-hexatrienyl moiety has important ramifications on the excited state decay pathways leading to product formation[224]. The compound was found to be astonishingly stable to irradiation. Even more remarkable is the fact that it fluoresces at room temperature in methanol solution ($\Phi = 0.01$; $\tau = 8.5$ ns), providing the first reported example of fluorescence from a simple aliphatic triene in fluid solution. The emission was attributed to the 2^1A state, stabilized by the torsional rigidity about the central C=C bond of the 5-membered ring. Fluorescence can also be observed from trienes bearing large alkyl groups at the terminal carbons, such as previtamin D_3 (*vide infra*)[220] and the carotene analogue **157**[225], though only at low temperatures in viscous or rigid media. The quantum yield of fluorescence from the latter compound is $\Phi_F = 0.61$ in 3-methylpentane at 77 K, and it decreases to a value of 0.04 as the temperature is increased to 110 K. The viscosity of 3-methylpentane decreases by roughly 13 orders of magnitude over this temperature range[225].



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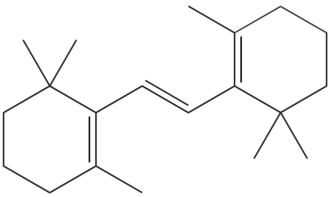


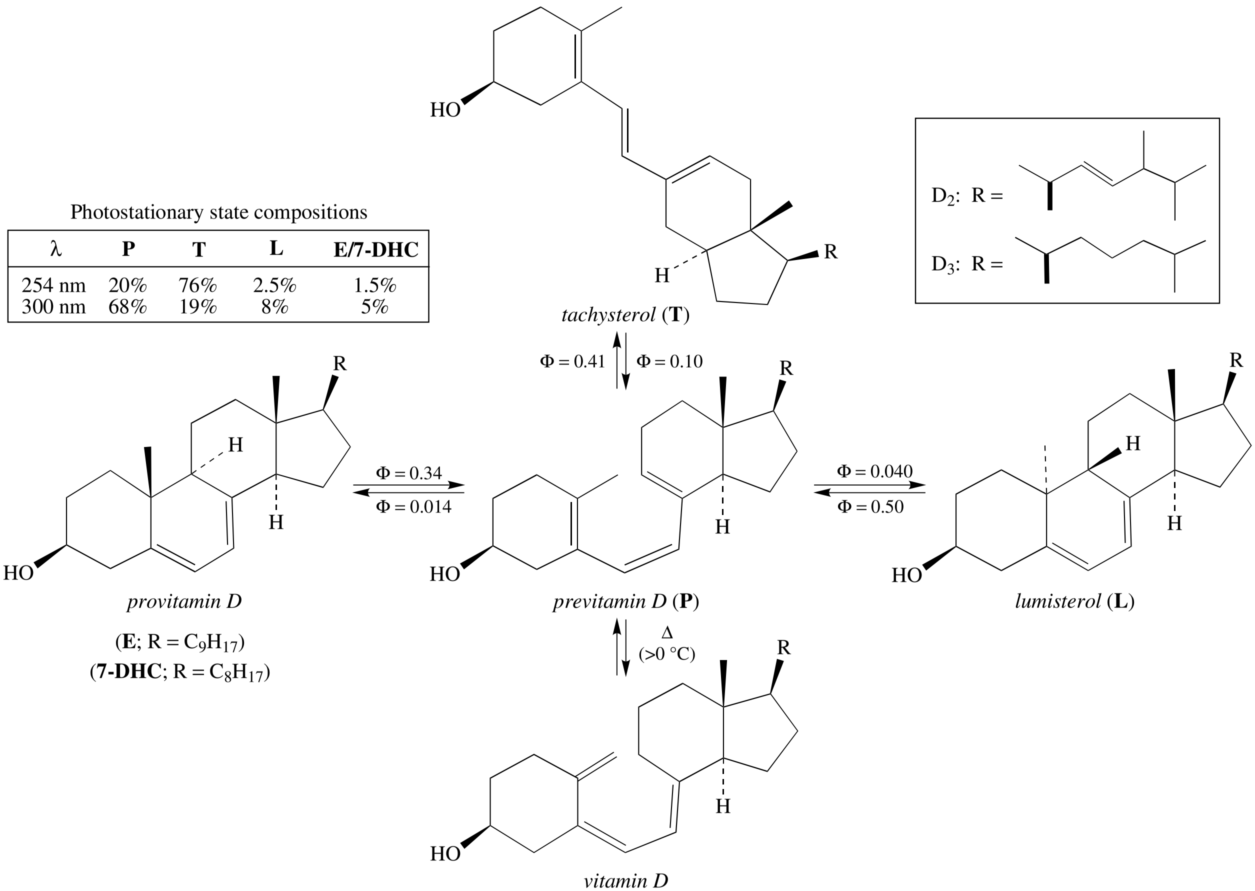
(157)

4. The photochemistry of vitamin D and its isomers

The photochemistry of vitamin D and its various isomers has been reviewed comprehensively many times[129,171,172,207,226], but as it lies at the very heart of hexatriene/cyclohexadiene photochemistry, it seems fitting to provide a very brief overview of the salient features here.

Vitamin D **(D)** is the generic name of two triene natural products which differ only in the structure of the side chain on the steroidal backbone. It is synthesized photochemically from the steroid natural product provitamin D: ergosterol (**E**; R = C_9H_{17}) in the D_2 series and 7-dehydrocholesterol (7-DHC); R = C_8H_{17} in the D_3 series. UV irradiation of provitamin D results in efficient conrotatory ring opening to yield previtamin D, which then yields vitamin D via a reversible antarafacial [1,7]-H shift which is rapid at room temperature and above. The irradiation actually leads to the rapid establishment of a pseudophotostationary state of four isomers which are linked via reversible photoreactions of previtamin D **(P)**: the double bond isomer tachysterol **(T)** and the steroids provitamin D and lumisterol **(L)**, which are interconverted with P via conrotatory electrocyclization and electrocycloreversion. Scheme 5 illustrates this photoequilibrium along with the quantum yields of the various interconversions[227] and the photostationary state compositions obtained with 254 nm irradiation[207]. The photostationary state compositions with 300 nm[228] irradiation are also included.

Prolonged irradiation of the mixture leads to the formation of a huge variety of secondary products due to competing photoreactions of the triene members of the series **P**, **T** and **D**. Many of these are formed as a result of the more common triene photoprocesses which have already been discussed. Many more are formed via less generic processes which involve the cyclic moieties at the two ends of the triene or intervention of the solvent in either catalytic or direct fashion. The so-called ‘toxisterols’ arise from irradiation



Photostationary state compositions

λ	**P**	**T**	**L**	**E/7-DHC**
254 nm	20%	76%	2.5%	1.5%
300 nm	68%	19%	8%	5%

SCHEME 5. Photochemical interconversions of vitamin D isomers

of **P** and **T** under various conditions, while 'suprasterols' are the products of irradiation of **D**: cyclobutene, bicyclo[3.1.0]hexene, vinylallene and 1,5-H shift isomers. The exact structures and mechanisms of formation of these compounds are covered comprehensively in the aforementioned reviews[129,171,172,207,226] and hence will not be discussed here.

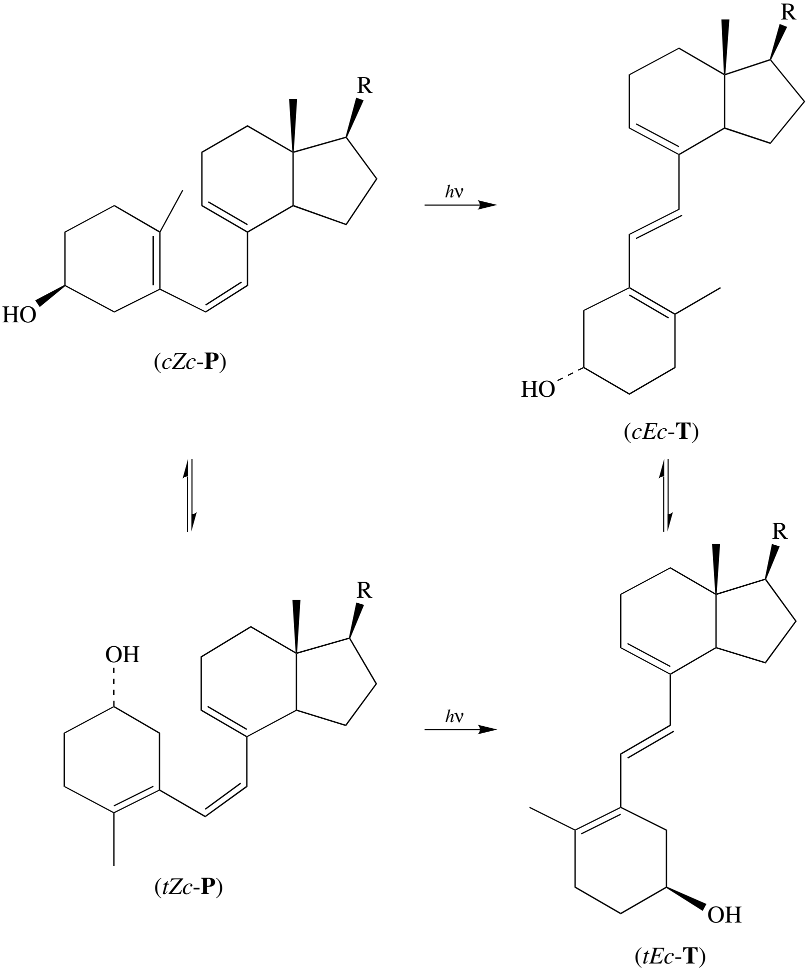
The wavelength dependence of the photochemistry of the system has been extensively investigated[129,220,227–229]. The quantum yields for the ring-opening reactions of **E**/7-DHC and **L** are wavelength dependent, but those of ring closure and *E*,*Z*-isomerization of **P** change markedly with excitation wavelength. This is now thought to be due to some combination of both ground state conformational effects (the 'NEER' principle)[227,230] and excited state effects associated with the excited state properties of previtamin D[220,228]. Dauben and Phillips found that the major change in quantum yields occurs over a very narrow wavelength range (302.5–305 nm), which is too abrupt to be accounted for by the relative extinction coefficients of the various single-bond conformers[228]. A thorough investigation of the fluorescence of previtamin D (lifetime, wavelength dependence of the quantum yield and temperature dependence) led Dauben, Kohler and their coworkers to the conclusion that excitation wavelengths above 305 nm results in selective excitation of the 2^1A state, which leads to preferential ring closure[220]. This pattern was shown to apply as well to the related trienes **137**, in a more recent paper from Dauben's group (*vide supra*)[73]. Recently, Fuss and Lochbrunner have suggested an alternative mechanism based on a direct competition on the excited state surface between ring closure and isomerization[231]. They suggested that the partitioning between the two reaction modes is dependent on sufficient photon energy to overcome an excited state barrier to *E*/*Z*-isomerization.

The *E*,*Z*-photoisomerization of previtamin D to tachysterol has also received recent attention. Jacobs and coworkers examined the process in various solvents at 92 K and found evidence for the formation of a triene intermediate which converts thermally (E_a *ca* 6.5 kcal mol^{-1}) to the more stable *tEc* rotamer of tachysterol (*tEc*-**T**; equation 58)[230]. The rate of this conversion is viscosity dependent. They identified this intermediate as the *cEc* rotamer, produced by selective excitation of the *cZc* rotamer of previtamin D. In a re-examination of the low temperature *E*,*Z*-photoisomerization of previtamin D as a function of excitation wavelength, Fuss and coworkers have suggested an alternative mechanism, in which *tEc*-**T** is produced directly from *cZc*-**P** and *cEc*-**T** directly from *tZc*-**P** (equation 59)[103]. This mechanism involves isomerization about both the central double bond and one of its associated single bonds — the 'hula-twist' mechanism of Liu and Browne[101] — and involves a smaller volume change than the conventional mechanism for *E*,*Z*-isomerization. The vitamin D system has also been the subject of recent theoretical study by Bernardi, Robb and Olivucci and their coworkers[232].

Other recent studies have examined the effects of substituents on the photochemistry of vitamin D analogues[233,234].

5. Theoretical and time-resolved spectroscopic studies of triene photochemistry

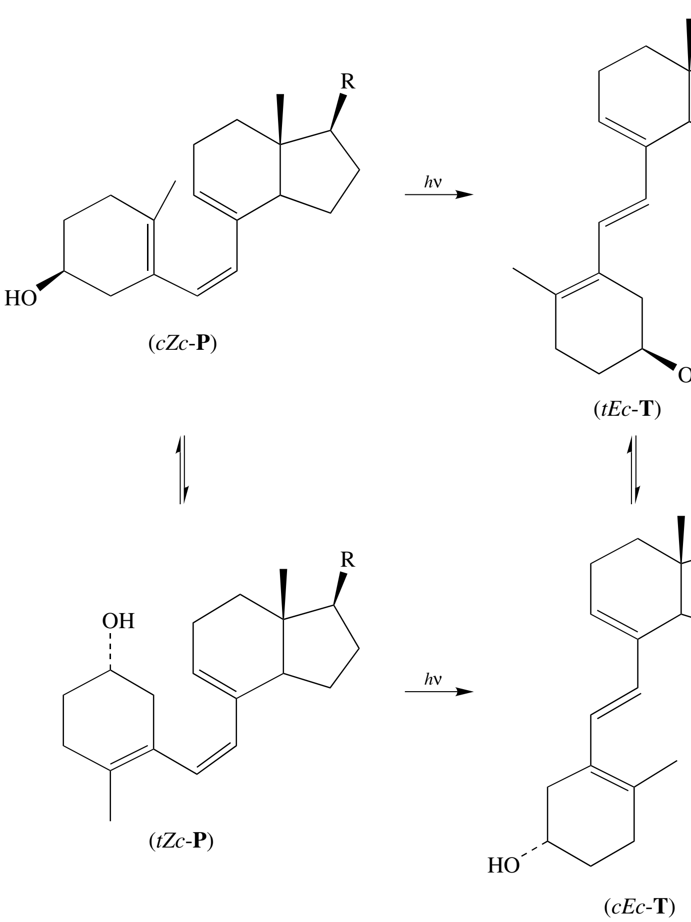
The dynamics of relaxation of the excited singlet states of *E*- and *Z*-1,3,5-hexatriene (HT) have recently been studied in the gas phase and in solution. In the gas phase, population of the 2^1A state of the *Z*-isomer by internal conversion from the spectroscopic 1^1B state has been estimated to occur with a lifetime τ_{1B} of about 20 fs, while the lifetime of the 2^1A state has been determined to be $\tau_{2A} = 730$ fs[47]. The lifetime of the latter in ethanol solution has been determined by Fuss and coworkers to be $\tau_{2A} = 470$ fs[52]. A similar 2^1A lifetime has been reported for *E*-1,3,5-hexatriene in cyclohexane and acetonitrile solution by Ohta and coworkers[48].



(*cZc*-**P**) (*cEc*-**T**) (*tZc*-**P**) (*tEc*-**T**)

(58)

As mentioned earlier, computational studies of the photochemical ring closure of *cZc*-1,3,5-hexatriene (*cZc*-**HT**) have been reported only relatively recently. Pichko and coworkers studied the reaction using semi-empirical methods, along with those of a few heteroatomic analogs[235], while *ab initio* CAS-SCF calculations have been reported by Robb and Olivucci and their coworkers[205,206]. The latter find evidence for evolution of the initially excited (1^1B) molecule on the femtosecond timescale to an acyclic biradicaloid intermediate on the 2^1A surface, in which there is little bonding character between C5 and C6 (Scheme 4). Bond formation and partitioning between overall *E*,*Z*-isomerization, *cis*/*trans* conformer interconversion, electrocyclic ring closure and bicyclo[3.1.0]hexene formation is proposed to occur mainly on the ground state surface, after it is entered at a $2^1A/1^1A$ conical intersection about 1 kcal mol^{-1} higher in energy[204,206]. In the case of *tZt*-**HT**, which was discussed in Section IV.D.1, this partitioning is thought to occur on both the 2^1A and ground state potential energy surfaces[91].

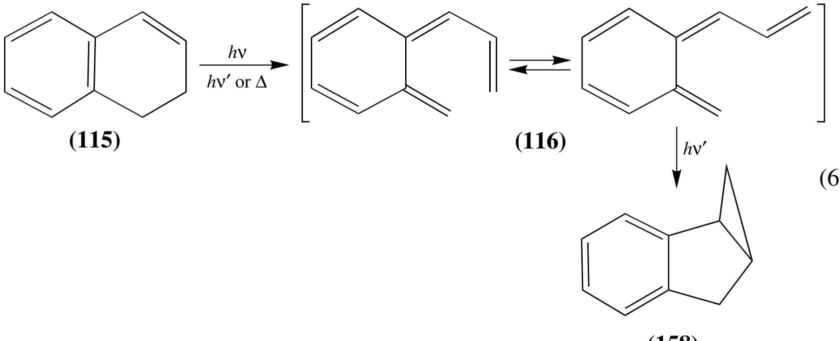


(59)

6. Benzannelated dienes and trienes[116,170,175]

As mentioned earlier, direct irradiation of 1,2-dihydronaphthalenes leads to a variety of photoisomerization reactions which can be attributed to the initial formation of the ω-vinyl-*ortho*-quinodimethane isomer by electrocyclic ring opening. For example, irradiation of the parent compound **115** with an intense, broad-band light source yields the isomeric benzobicyclo[3.1.0]hexene derivative **(158)** as the main photoproduct, via secondary photolysis of the initially-produced ω-vinyl-*ortho*-quinodimethane isomer **116** (equation 60)[236,237]. Such compounds are short-lived due to rapid thermal ring closure to regenerate the starting material, but have been detected by low temperature spectroscopic techniques ($\lambda_{max} > 400$ nm) in derivatives bearing 1- or 4-phenyl substituents[238–240].

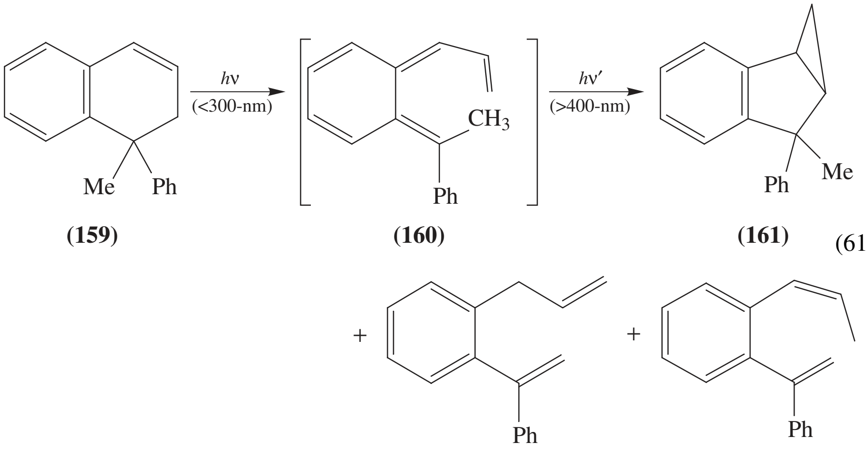
The photochemistry of ω-vinyl-*ortho*-quinodimethanes is typical of trienes in which at least one of the two C−C bonds is frozen in the s-*cis* conformation: competing electrocyclic ring closure to regenerate the precursor, formation of benzobicyclo[3.1.0]hex-2-enes and [1,5]-H shifts to arylallenes. The only triene photoproduct which is not generally



(115) **(116)** **(158)**

(60)

formed is the isomeric 3-vinylbenzocyclobutene. The presence of alkyl substituents at C1 and/or C2 leads to the formation of other, additional products due to rapid thermal and/or photochemical hydrogen migrations in the *ortho*-quinodimethane intermediate, as exemplified by the photochemistry of 1-methyl-1-phenyl-1,2-dihydronaphthalene **(159)** which gives products **161**–**163** via the *ω*-vinyl-*ortho*-quinodimethane **160** (equation 61)[238].



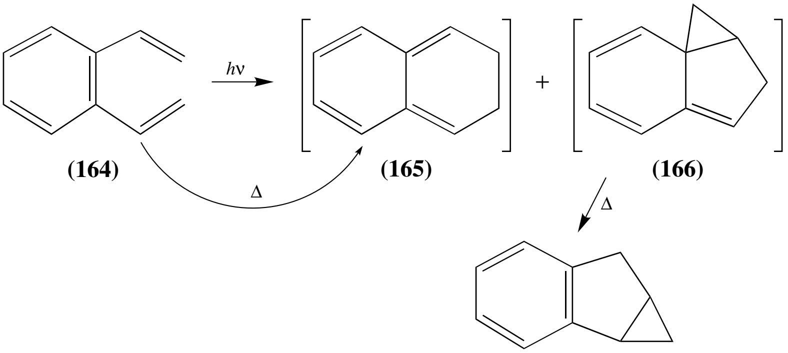
(159) **(160)** **(161)** (61)

(162) **(163)**

Direct irradiation of *ortho*-divinylbenzene **(164)** leads to the formation of the benzobicyclo[3.1.0]hex-2-ene isomer **167** as the major product. Deuterium labelling and methanol trapping experiments suggested the intermediacy of both **165** and **166**, the expected products of irradiation of a benzannelated 1,3,5-hexatriene (equation 62)[144].

7. Photochromic materials based on cyclohexadiene/hexatriene interconversions

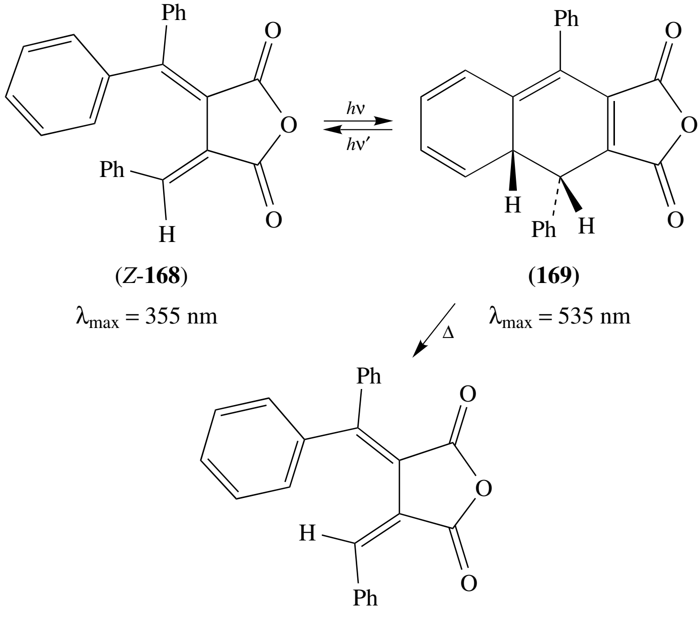
Aryl-substituted fulgides are the products of condensation of aromatic ketones with succinic anhydride, and form one of the oldest and most important groups of organic photochromic materials[241]. First discovered in the early part of the last century by Stobbe[242], they are now well known to owe their photochromic behavior to reversible (conrotatory) electrocyclic interconversion with the dihydronaphthalene isomer. For example, *Z*-**168** interconverts photochemically with **169** via conrotatory electrocyclization/electrocycloreversion (equation 63)[243]. As is often typical with fulgide-derived dihydronaphthalenes, **169** is thermally labile with respect to disrotatory electrocyclic ring opening to yield *E*-**168**.



(164) **(165)** **(166)**

(167)

(62)



(*Z*-**168**)

$\lambda_{max} = 355$ nm

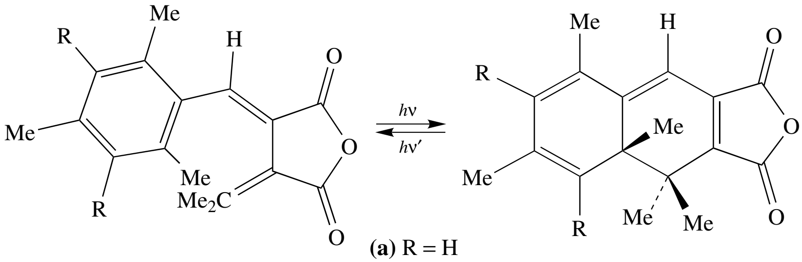
(169)

$\lambda_{max} = 535$ nm

(63)

(*E*-**168**)

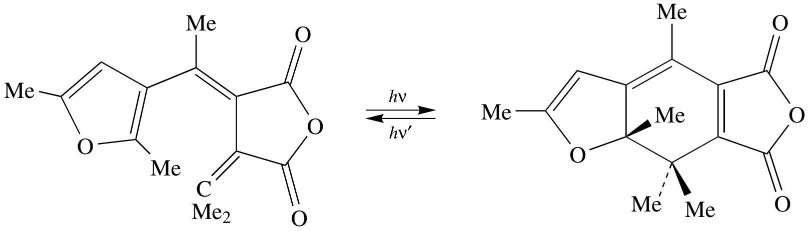
E,*Z*-isomerization is the main competing singlet state photoreaction of aryl fulgides. The effects of substituents on the UV absorption spectra of both the open and closed forms, and on the quantum yields for *E*,*Z*-isomerization and electrocyclic ring closure, are quite dramatic, and an impressively large number of compounds in this class have been studied in detail, mostly by Heller and his group. The most useful class of materials are those containing only one aryl ring, substituted in the 2- and 2′-positions so as to block the occurrence of irreversible thermal, photochemical or oxidative reactions of the colored (closed) form, which lead to 'fatigue'. For example, the pale yellow materials **170** undergo photochemical ring closure to the highly colored 1,8-dihydronaphthalenes **171**, which are thermally stable up to 160°C, but undergo efficient electrocycloreversion on exposure to white light (equation 64)[244].



(64)

(170) (**a**) R = H (**b**) R = OMe **(171)**

The furyl fulgide **172** has found use as a stable, recyclable actinometer for conventional photochemical experiments in the 313–366 nm wavelength range, where $\Phi_{173} = 0.20$ and is independent of temperature and concentration[245]. It has also been developed as an actinometer in one- and two-laser flash photolysis experiments[246]. The colored form **173** can be converted back to **172** by simple exposure to visible light (equation 65).

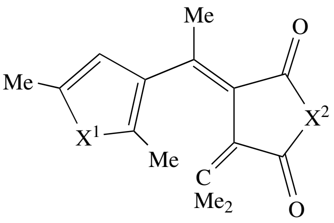


(65)

(172) **(173)**

$\lambda_{max} = 346$ nm (log ε 3.81) $\lambda_{max} = 494$ nm (log ε 3.89)

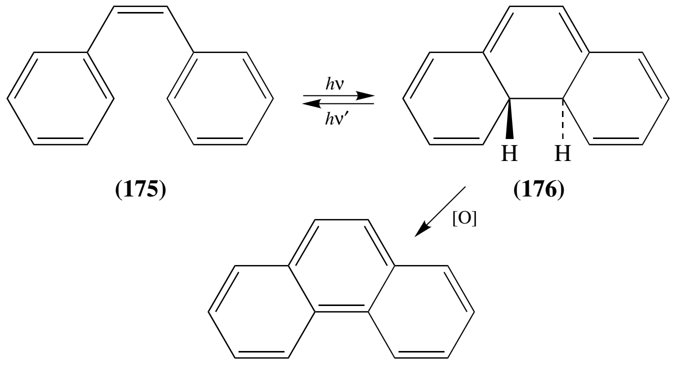
A number of related systems (e.g. **174**) have also been examined for their potential as photochromic materials, and the field continues to be an active one[247–250].



(174)

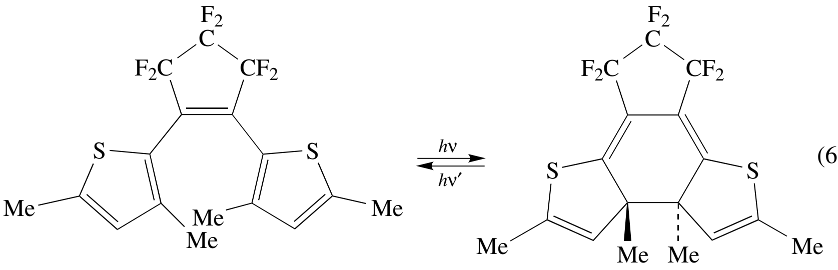
X^1 = O, S, NR
X^2 = O, NR

Another important class of photochromic materials based on reversible triene photocyclization are 1,2-diarylalkenes, of which the Z-stilbene **(175)**/9,10-dihydrophenanthrene **(176)** system is the prototype (equation 66)[251,252]. As with the fulgide systems, it is necessary to replace the *ortho*-hydrogens on the aryl rings with alkyl groups, in order to prevent irreversible thermal and photochemical oxidative processes (e.g. to **177**) involving the ring-closed forms. Accordingly, materials such as **178/179** (equation 67)[253,254] show excellent absorption properties and fatigue resistance, and continue to be of great interest[255–258]. Irie and Uchida have recently reviewed this field in detail[259].



(175) **(176)** **(177)**

(66)



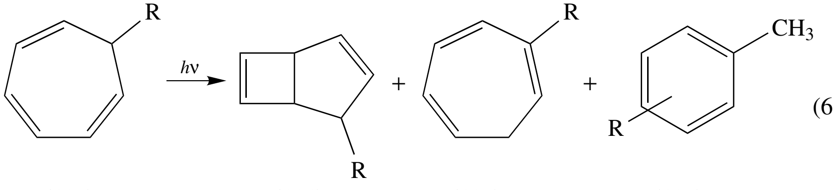
(178) **(179)**

(67)

8. Cyclic trienes

Substituted 1,3,5-cycloheptatrienes **(180)** exhibit three photochemical reactions: 4π-electrocyclic ring closure to yield the isomeric bicyclo[3.2.0]hepta-2,6-dienes **181**, suprafacial [1,7]-hydrogen migration to give **182**, and rearrangement to toluenes **183** (equation 68)[110,116,122,260–266]. The major photoproduct in solution is frequently that of electrocyclic ring closure, which occurs via a true excited state process with no detectable competition from the E,Z-photoisomerization/thermal ring closure pathway that is known for 1,3-cycloheptadiene[122]. In most cases, however, [1,7]-hydrogen migration is known to be significantly more efficient than ring closure[267,268]; for example, the process occurs *ca* 500 times more rapidly than ring closure in the parent molecule[262,263]. In substituted systems, the high efficiency of [1,7]-H shifts compared to ring closure frequently leads to the formation of a variety of isomeric photocyclization products.

The quantum yield for toluene formation is very low in solution but approaches unity in the gas phase at low pressures[269]. The toluene was suggested to be formed from vibrationally excited ground state molecules, following rapid internal conversion from the excited singlet state manifold, perhaps involving the intermediacy of norcaradiene (bicyclo[4.1.0]hepta-2,4-diene)[269,270]. The hot ground state mechanism for toluene formation has received considerable support from time-resolved and steady-state experiments on cycloheptatriene and several of its derivatives[180,271–274].

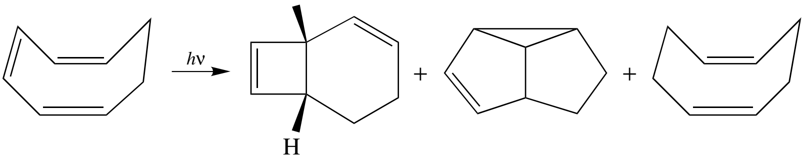


(68)

(180) **(181)** **(182)** **(183)**

The photochemistry of the parent molecule (R = H) has recently been studied using ultrafast time-resolved spectroscopic techniques[49,98,99,198,275–277]. Within *ca* 20 fs of excitation to the spectroscopic $1^1A''$ state (the 1^1B_u state of 1,3,5-hexatriene) the molecule flattens, a process which has been associated with internal conversion to the lower lying $2^1A'$ state (the 2^1A_g state of 1,3,5-hexatriene)[50,277]. Deactivation of the $2^1A'$ state then takes place within the next 60–80 fs, followed by competing [1,7]-H migration, ring closure and internal conversion on the ground state surface[98,99,275]. The fact that these processes occur so quickly suggests that at least part of the photoreaction is coupled with internal conversion, which is a characteristic of a reaction which proceeds through a conical intersection between the ground and excited states[23,278].

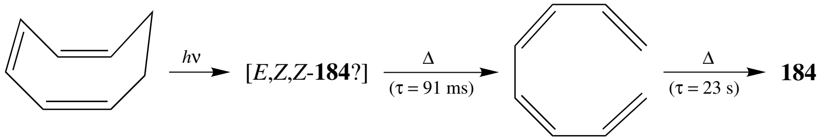
The direct irradiation of 1,3,5-cyclooctatriene **(184)** in ether or hydrocarbon solvents leads to the slow formation of two stable isomers corresponding to disrotatory 4π-electrocyclization **(185)** and bicyclo[3.1.0]pentene **(186)** formation along with small amounts of the reduced product **187** (equation 69)[279–281]. Conventional flash photolysis experiments later showed that, in fact, the main primary photochemical process is the formation of a short-lived stereoisomer ($\tau = 91$ ms)[282], most likely identifiable as *E*,*Z*,*Z*-**184**. The transient decays to yield a second transient species ($\tau = 23$ s) identified as *Z*,*Z*-1,3,5,7-octatetraene **(188)**, which in turn decays by electrocyclic ring closure to regenerate **184**[282] (equation 70). The photochemistry of **184** has been studied on the picosecond timescale using time-resolved resonance Raman spectroscopy[49].



(69)

(184) **(185)** **(186)** **(187)**

Several examples of the photochemistry of larger-ring (C_9–C_{12}) cyclic trienes have already been cited (*vide supra*), and a great many more have been studied, particularly by Dauben and coworkers. These have been reviewed thoroughly elsewhere; in general, they tend to be well-defined conformationally and exhibit much of the photochemistry discussed earlier for acyclic systems[116,172,175].



(70)

(184) **(188)**

V. CONCLUSION

The field of polyene photochemistry certainly cannot be given proper justice in a single chapter and so we have limited our coverage rather severely, focussing on pericyclic reactions originating from the excited singlet state manifolds of conjugated dienes and trienes. Even this rather small part of the field is incredibly large, and we have been admittedly terse in our coverage of it. Our main goal was to summarize the salient features of this aspect of polyene photochemistry, emphasizing the interplay between classical product studies, time-resolved spectroscopy and theoretical chemistry. We hope that we have been successful in conveying a reasonably accurate picture of the impressive breadth of the work that has been done in this area and that more will be stimulated as a result.

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CHAPTER **4**

Photochemistry of non-conjugated dienes

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I. INTRODUCTION

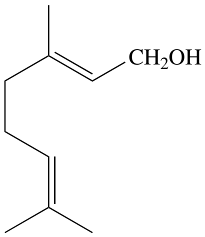
Photochemistry in the area of non-conjugated dienes has burgeoned over the past decade or so and many topics of interest appear under this general heading. Obviously, such a chapter cannot be encyclopaedic and therefore some selection of areas to be covered has been made. In addition, a choice has been made in the time covered. The general area of diene photochemistry under review here has been of interest practically since the re-awakening of interest in organic photochemistry. Thus there is at least forty years of modern study. An excellent compendium was published more than thirty years ago by Schönberg[1]. This dealt with photochemical reactions in general but includes many examples related to the non-conjugated dienes. The subject matter is also covered to some extent in most of the standard texts dealing with organic photochemistry[2] and also in specialized texts[3]. In the last thirty years there have also been useful annual compendia of photochemical results and advances and these have provided an extensive source of references[4]. In addition, there are some general reviews from the earlier periods which are also of value[5,6].

II. ELECTRON TRANSFER REACTIONS

A. Acyclic and Cyclic Dienes

There are a variety of photochemical reactions that non-conjugated dienes can undergo. One of these that is currently of considerable interest is the reactivity brought about by electron-accepting sensitizers such as the cyanoarenes. The photoreactivity of these systems involves the photochemical excitation of the sensitizer to an excited state[7]. Thereafter, the reactivity is dependent on the ease of oxidation of the alkene or diene. With the transfer of an electron from the diene to the photoexcited sensitizer a radical cation is formed. It is this intermediate that brings about the various processes which occur within the diene systems under investigation.

There are many examples of such reactivity and some of these have been reviewed by Roth and coworkers[8], a research group that is extremely active in this area. An example that is typical of the processes encountered involves the cyclization of the diene geraniol (**1**). In this case the sensitizer is 9,10-dicyanoanthracene (DCA) and the reactions are carried out in methylene chloride. The authors[9] state that a contact radical-ion pair is involved, i.e. the radical cation of the diene is in close proximity to the radical anion of the DCA. Reaction within this yields the cyclopentane derivatives **2** and **3** in the yields shown. The ring formation is the result of a five centre CC cyclization within the radical cation of **1**. When a more powerful oxidant such as *p*-dicyanobenzene is used as the sensitizer in acetonitrile as solvent, separated radical-ion pairs are involved. This leads to intramolecular trapping and the formation of the bicyclic ethers **4** and **5**[9]. The bicyclic ether incorporates an aryl group by reaction of the radical cation of the diene with the radical anion of the sensitizer (DCB). This type of reactivity is referred to later. Other naturally occurring compounds such as (*R*)-(+)-α-terpineol **(6)** and (*R*)-(+)-limonene **(7)** can also be converted into the corresponding radical cations using *p*-dicyanobenzene (DCB) as the electron-accepting sensitizer[10]. Cyclizations can also be brought about with tetraenes such as **8** under SET conditions in aqueous acetonitrile solution. A variety of electron-accepting sensitizers was used but 1,4-dicyano-2,3,5,6-tetramethylbenzene was found to be especially effective. The radical cation formed from **8** undergoes a cascade cyclization to yield the product **9**[11].



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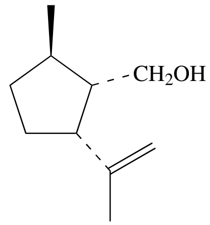

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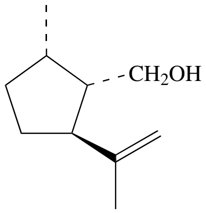

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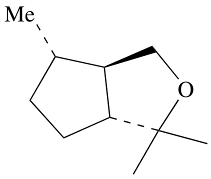

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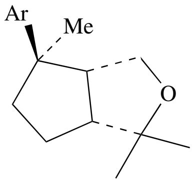

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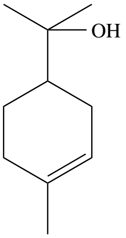
Ar = p-NCC_6H_4



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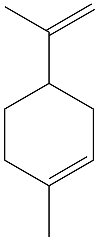

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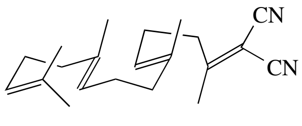

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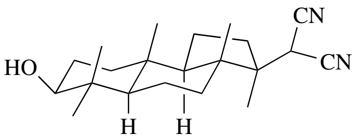
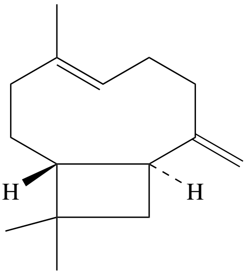


(9)

The radical cations of diene systems in cyclic molecules are also capable of reaction as demonstrated by Demuth, Roth and their coworkers[12]. They have studied the influence of phase on the photochemical reactivity of some naturally occurring dienes. Thus the irradiation of the diene **10** in homogeneous solution (acetonitrile/water) in the presence of an electron-accepting sensitizer such as cyanonaphthalene (CN) or DCB brings about *trans*,*cis*-isomerization only. However, when the electron transfer reaction is carried out in the presence of sodium dodecyl sulphate, transannular hydrogen abstraction reactions yield the two products **11** and **12**. Similar reactivity is observed with *trans*-geranyl acetate **13** and all-*trans*-farnesyl acetate **14**. The authors[12] report that these cyclizations are the first examples of biomimetic processes brought about under SET conditions.



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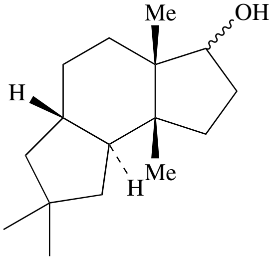

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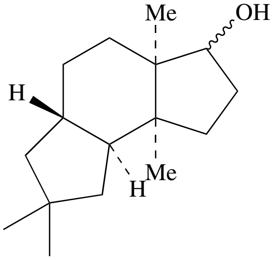

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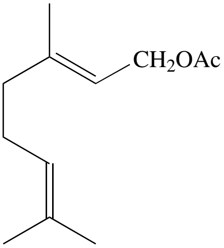

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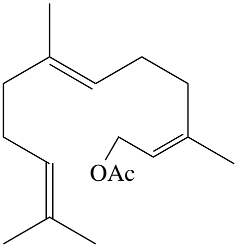
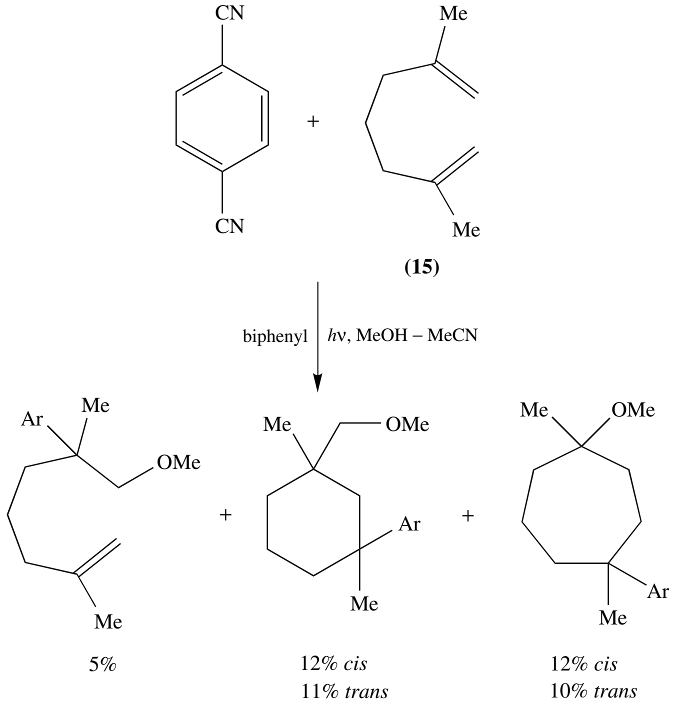


(14)

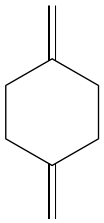
In some instances the intermediate radical cations formed from non-conjugated dienes undergo addition to the cyanoarene sensitizer. Such reactions involve the replacement of a cyano group on the arene by the diene moiety. These reactions have been termed photo-NOCAS (photochemical Nucleophile–olefin combination, Aromatic substitution) processes. Such behaviour is observed with the 2,6-dimethylhepta-1,6-diene **15**. When this is irradiated in methanol solution under electron-transfer conditions with DCB as the electron-accepting sensitizer and biphenyl as the co-sensitizer, the products (obtained in low yields) formed from this treatment are shown in Scheme 1. In this there are three distinct reaction types, each involving combination between the diene, MeOH and the sensitizer. These reaction types are addition of MeOH to the open chain system, cyclization to a cyclohexane product and cyclization to a cycloheptane[13]. Considerable effort has been expended on the study of the photo-NOCAS processes and Arnold and his coworkers have supplied details of the factors that control the regiochemistry[14]. As can be seen, reaction with an alkene moiety is quite common and is also illustrated for the diene **16**. In this molecule cyclization of the radical cation is unlikely and all the reactions



Ar = 4–cyanophenyl

SCHEME 1

encountered involve addition to an alkene group. The reaction is again carried out in methanol with DCB as the sensitizer and biphenyl as the co-sensitizer. This treatment gives low yields of **17** and **18** by trapping of the radical cation of the diene **16** by methanol[15]. In acetonitrile as solvent, many products are formed such as **19** and **20** by reaction with the solvent acetonitrile or the sensitizer, respectively.



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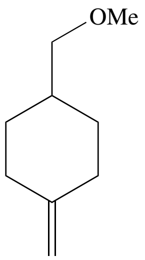

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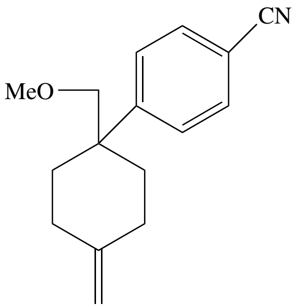
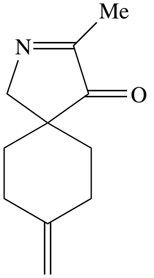
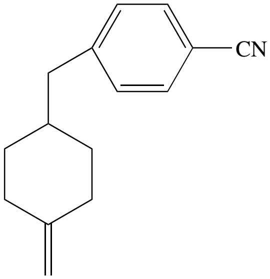


(18) 20%

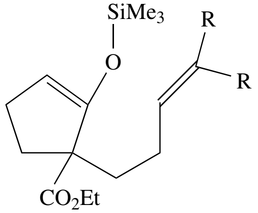


(**19**) 2%

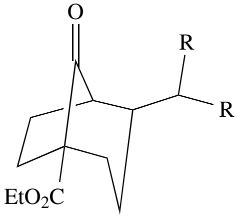


(**20**) 2%

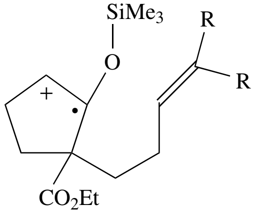
The synthetic application of SET processes is also of considerable interest since viable synthetic routes to a variety of molecules can be devised. For example, Heidbreder and Mattay[16] have shown that silyl derivatives of enols can undergo cyclization following radical cation formation. Irradiation at 450 nm of **21** in acetonitrile using DCA as the electron-accepting sensitizer ultimately brings about the formation of bicyclic compounds **22**. The process involves cyclization within the radical cation **23**. Several other examples of this type of cyclization have been reported, again using the same reaction conditions. This has helped to demonstrate the scope of the process. Thus the parent system **24**, R = H, affords the cyclic ketone **25** in 25% yield. The effect of chain length and substituents on the reaction has also been evaluated. Thus **24**, R = Me, is converted into the mixture of isomers **26** while **27** affords **28**. Tricyclic products such as **29** can also be obtained in moderate yields from the cyclization of **30**. The basic reaction of **24** is solvent-sensitive. This is demonstrated by the formation of three products when the reaction is carried out in acetonitrile/propan-2-ol. These were identified as the original product (**25**, 30%) and two minor products **31** formed in 11% and **32** formed in 9%[17].



(21) (**a**) R = H
(**b**) R = Me

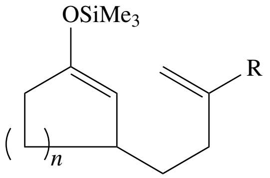


(22) (**a**) 24%
(**b**) 59%



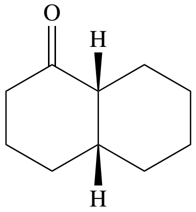
(23)

The presence of hetero-atoms within the system, remote from the alkene double bonds, does not have an adverse influence on the SET processes that occur. Thus irradiation of the diene **33** in benzene solution with 1,4-dicyanonaphthalene as the electron-transfer sensitizer affords the cyclobutane **34** in 78% yield. Various examples of the reaction were described giving cyclobutane derivatives in 54–69% yield. Benzene, or an arene solvent, is vital for the success of the reaction. When acetonitrile is used, allylation of the sensitizer (akin to the photo-NOCAS reaction) results in the formation of the three products **35**–**37**[18]. (2 + 2)-Cyclization of this type described for **33** is also seen with the dialkenyl ether **38**. When **38** is irradiated using $\lambda > 350$ nm or $\lambda > 450$ nm in acetonitrile



(24) $n = 2$

(27) $n = 1$, R = H



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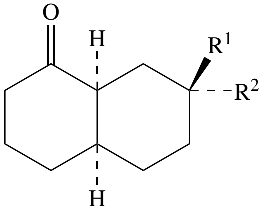
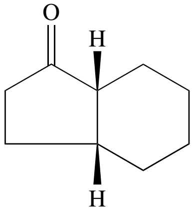


(26)

R^1	R^2	
Me	H	9%
H	Me	11%



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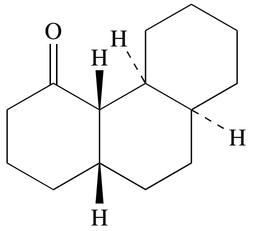

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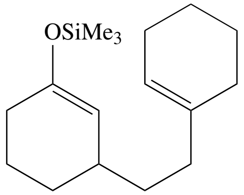

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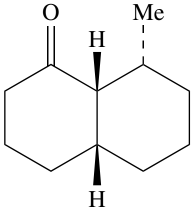

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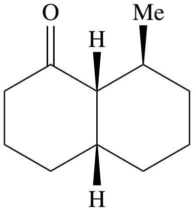

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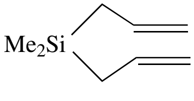

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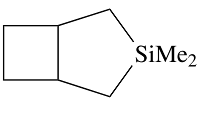

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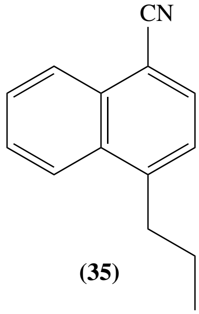

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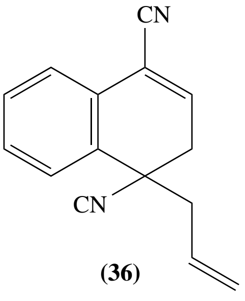
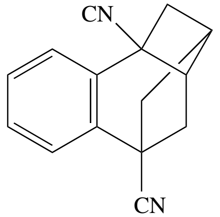


(36)

solution with tetracyanoethylene as the electron-accepting sensitizer, the product **39** is obtained. Again a radical cation cyclization is proposed to account for this[19].



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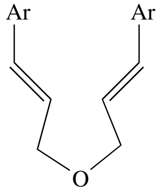

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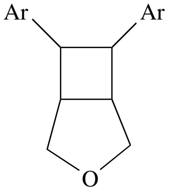
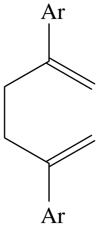


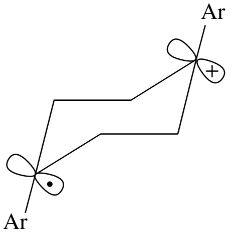
(39)

Ar = 4-MeOC_6H_4

A study of the photochemical Cope reaction of the hexadienes **40** has been carried out under photoinduced electron-transfer conditions. Evidence was gathered for the formation of a chair cyclohexane-1,4-radical cation **41**[20]. In such systems, where the radical cation is formed using DCA as the sensitizer, a degenerate Cope process is operative. Thus when the tetradeuterio derivative **42** is used, rearrangement affords a (52 : 48) mixture of the two dienes **42** and **43**[21]. Related to this general problem, DCA-sensitized reactions of the isomeric dienes **44** and *E*,*E*-**45** and the cyclization product, the bicyclohexane **46**, have been studied in considerable detail[22]. At low conversions, the irradiation of **46** affords a mixture of the dienes **44** and *E*,*E*-**45** in ratios that are independent of temperature. The influence of the position of the aryl groups on the diene skeleton has also been studied. This does not appear to affect the conversion to a cyclic radical cation. Thus the SET-induced reaction of the diene **47** has shown that the open chain radical cation of the diene **48** cyclizes preferentially to the radical cation **49**[23].

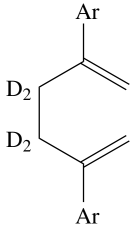


(**40**)

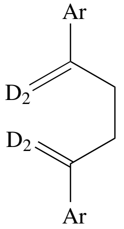


(**41**)

Ar = *p*-MeOC_6H_4

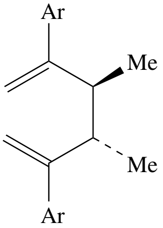


(**42**)

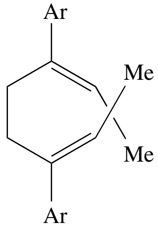


(**43**)

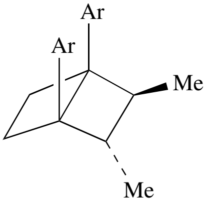
Ar = 4-XC_6H_4
X = OMe, Me, Cl



(**44**)

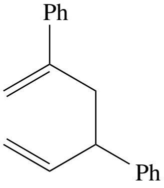


(**45**)



(**46**)

Ar = 4-MeOC_6H_4



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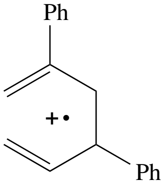

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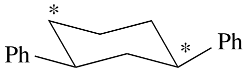
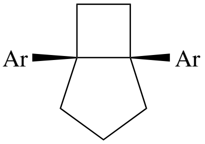
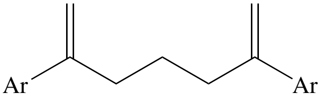


(49) * = + or •

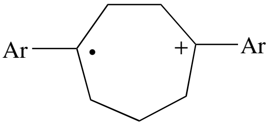
Cyclization of the type that leads to the formation of **46** from **44** and **45** is also observed with a longer insulator between the two alkene components of the non-conjugated diene. Thus the cyclobutane derivatives **50** can be formed from the dienes **51**. Again a radical cation **52** is formed from **51** using SET to DCA. This provides an efficient path to the bicyclic compounds **50**[24]. Griesbeck and coworkers[25] have also reported on the cyclization of **51**. In addition, they have examined the reactions encountered with the dienes **53** where cyclization to the bicyclo[4.2.0]octane system **54** takes place via the radical cation. The cyclization in these molecules is not quite as efficient as in the previous examples. The head:head product, i.e. the cyclooctenes **55**, are formed in competition with the other process. A further study of these cyclizations has examined the influence of solvent on the conversion of **56** into the two products **57** and **58**. The mechanism proposed again utilizes a cyclic radical cation as intermediate and this has been substantiated by trapping experiments with oxygen[26]. Further study has examined the influence of an alkyl substituent on one of the double bonds of the dienes **59** and **60**. Stereoselective intramolecular $(2 + 2)$-cycloadditions occurred on DCA sensitization, yielding the *endo* and *exo* bicycloheptanes **61** and **62**, respectively. Although the reactions with the E-isomer **59** appeared not to be stereoselective, this effect was found to be time-dependent and shorter irradiation times gave better selectivity[27].



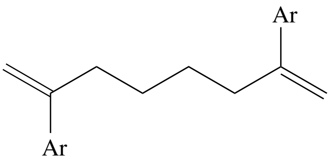
(50) yield (%)
53
80
76



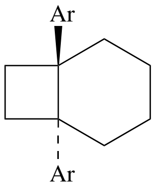
(51) Ar = 4-$MeOC_6H_4$
Ar = 4-MeC_6H_4
Ar = Ph



(52)



(53)
Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$



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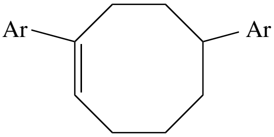

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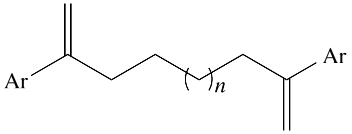
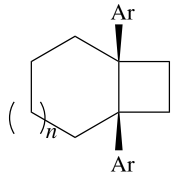


(56)

$n = 1$ or 2, Ar = 4-MeOC$_6$H$_4$ or Ph



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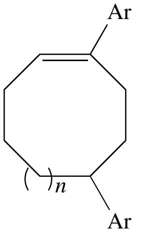
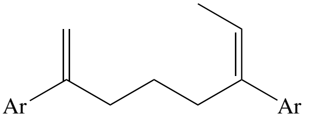


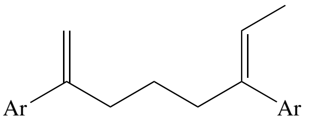
(58)

		yield (%)	Solvent
$n = 1$ a	0	86	MeCN
a	65	31	C_6H_6
b	58	24	MeCN
$n = 2$ a	0	9	MeCN
b	10	21	MeCN



(59)

(a) R = 4-MeOC$_6$H$_4$
(b) Ar = Ph



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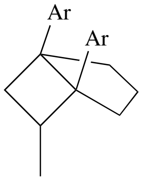

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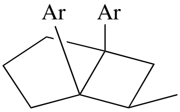
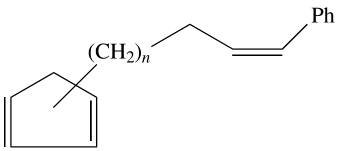


(62)

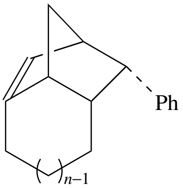
	61	**62**	ratio *endo*: *exo*
$E_{a'}$	65	0	0
$E_{b'}$	70	0	0
$Z_{a'}$	27	45	1 : 1.7
$Z_{b'}$	32	34	1 : 1.7

Yoon and Chae[28] have described the DCA-induced photochemical conversion of the cyclopentadiene derivatives **63** into several products. However, only the *anti*-Bredt adduct **64** is different from those obtained by thermal activation. The experimental data collected have implicated a triplex intermediate **65** in the formation of **64**. This triplex is the result of interaction between the diene, the non-conjugated alkene component and the sensitizer. While a mixture of cyclopentadienes was used, it is likely that the products **64** are formed exclusively from the 2-isomer **66**.



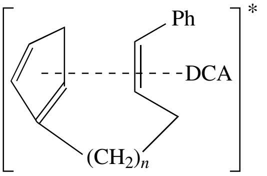
(63)

$n = 2$ or 3

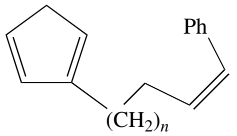


(64)

$n = 2$	12%
$n = 3$	13%

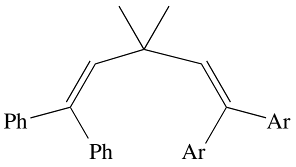


(65)



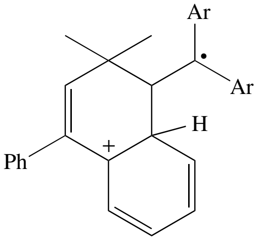
(66)

Zimmerman and Hofacker[29] have studied the photochemically induced SET reactivity (using DCA or DCN) of the heavily arylated 1,4-dienes **67**. The radical cations formed by this treatment undergo regioselective cyclization to the cyclic radical cation **68** that ultimately affords the final products **69**. Other dienes with 1,1-diphenyl substituents are also reactive. Thus 1,1-diphenylhepta-1,6-diene **(70)** can be converted into its radical cation **(71)**. This cyclizes under attack from the solvent acetonitrile (or propionitrile) via the six-membered transition state shown in **72**. This affords the adduct **73**. Cyclization of the radical cation is not exclusive and trapping by adventitious water, affording the alcohol **74**, takes pace in competition. The length of the chain linking the two alkene moieties is fairly critical for the success of the reaction. When this is shortened to two methylene groups, only the alcohol **75** is formed on irradiation of the diene **76**[30]. Multiple phenyl substituents on the diene as in **77** influence the eventual outcome of the reaction. Cyclization still involves a radical cation **(78)** that is formed on irradiation (through Pyrex at $\lambda > 280$ nm) in acetonitrile/benzene in the presence of DCB as the electron-accepting sensitizer. However, attack on a phenyl group is the principal reaction mode and this yields **79** in 87%[31].



(67)

Ar = p–XC_6H_4
X = H, MeO, Me, Cl, CN



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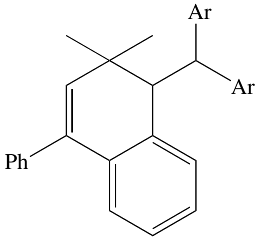

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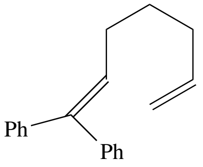

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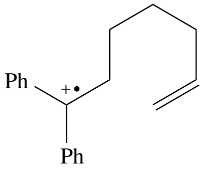

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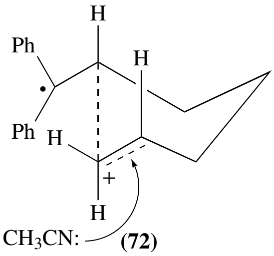

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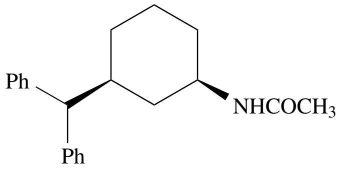

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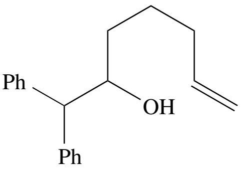

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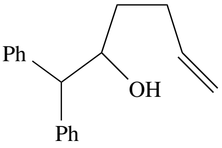

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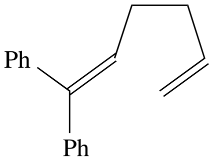

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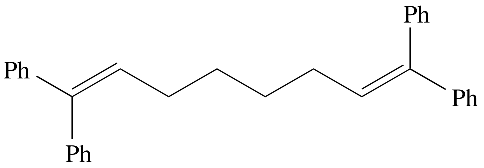

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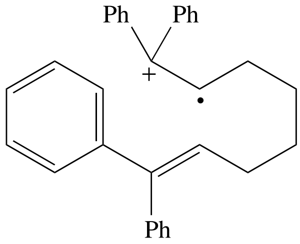

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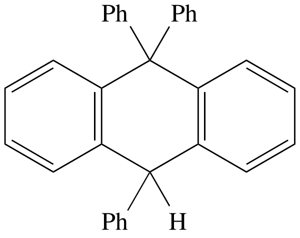
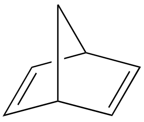


(79)

B. Norbornadienes and Related Systems

One of the interesting molecules that has been studied in considerable detail is norbornadiene **(80)**. Much of this interest has been associated with the interactions between the double bonds of the system. Thus irradiation affords quadricyclane **(81)**. This area of study will be discussed later in this chapter. The radical cation **82** can also be formed from both norbornadiene and quadricyclane by irradiation in acetonitrile/methanol solution with the DCB/phenanthrene sensitizer system. Several products (Scheme 2) are formed in low yield and it should be noted that there is little difference in the yields of products obtained from either starting material. However, it is evident that attack by methanol occurs from the *exo* face[32].



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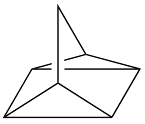

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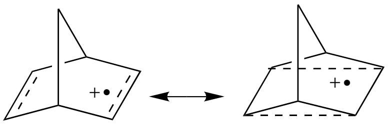

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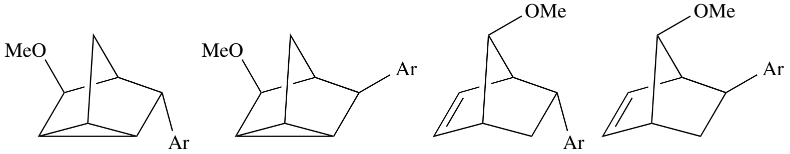
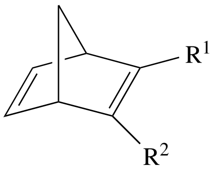


norbornadiene	6	5	6	3
quadricyclane	5	4	4	2

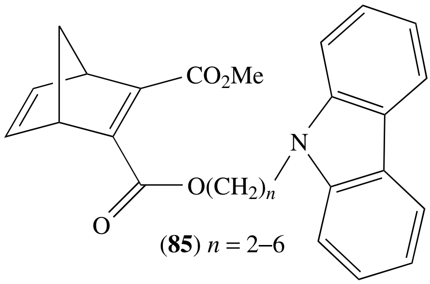
Ar = p-NCC_6H_4

SCHEME 2

The cyclization of norbornadienes into quadricyclanes can also be achieved by electron-transfer sensitization by donation. Such a process obviously will form the radical anion of the norbornadiene. For the formation of the radical anion, suitable electron-accepting substituents must be attached to the norbornadiene skeleton as in the derivatives **83** and **84**. The results using these derivatives have shown that a variety of sensitizers such as phenanthrene, anthracene, pyrene and *N*-methylcarbazole are effective although the most efficient was phenanthrene[33]. Other sensitizers such as acridine yellow and acridine orange are also effective. The photo-isomerization is accompanied by quenching of the fluorescence of the dye[34]. The mechanism by which the cyclization takes place using electron-donating sensitizers is thought to involve an exciplex of the radical-ion pair. The excited triplet state of the diene is produced by back electron transfer in the radical-ion pair within a solvent cage[35]. Intramolecular SET within a norbornadiene system is also a possibility and has been investigated using the norbornadienes **85**. Here the influence of both chain length and conformation was assessed[36,37].

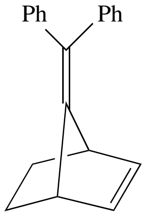


(**83**) $R^1 = R^2 = CN$
(**84**) $R^1 = R^2 = COOH$ or CO_2Me



(**85**) $n = 2$–6

Dienes closely related to the norbornadiene system have also proved of interest in SET-induced reactions. Thus, the diene **86** can be transformed into the corresponding radical cation **87** on irradiation in the presence of an electron-accepting sensitizer. This radical cation reacts with methanol to yield the ether **88**. Such reactivity is reminiscent of the behaviour of the radical cation of norbornadiene under similar conditions. Intramolecular trapping of these non-classical radical cations has also been studied using the diene **89**. The resultant radical cation formed by irradiation in the presence of a suitable electron-accepting sensitizer gives the two products **90** and **91**[38]. Irradiation of the radical cation **92** with visible light brings about cyclization to the radical cation **93**[39].



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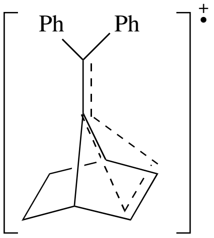

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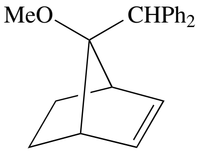

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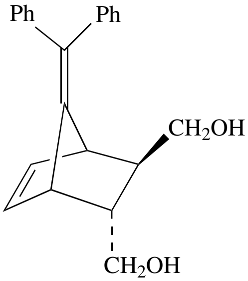

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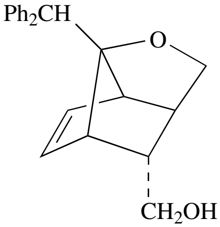

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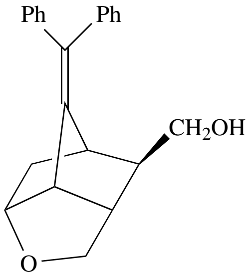

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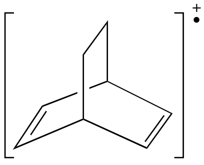

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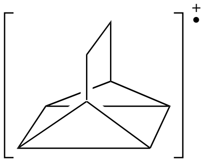
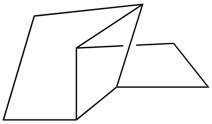


(93)

III. CYCLOBUTANE FORMATION

A. Copper(I) Triflate Controlled Reactions

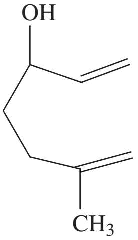
One of the exciting areas that has gained importance over the recent decade is the photochemical cyclization of non-conjugated dienes in the presence of species that can act as templates. One such species that has been used is copper(I) salts. The earliest example of the use of copper salts in the intramolecular photocycloaddition of non-conjugated dienes is that described for cycloocta-1,5-diene. When this is irradiated in the presence



(94)

of copper(I) chloride, the tricyclic compound **94** is formed in 30% yield. The authors[40] suggested that the cyclization to this product involved free radicals.

More modern studies have made use of copper(I) triflate (CuOTf) as the reagent. This compound is well known to form complexes with dienes and it provides a template on which cycloadditions can be effected[41]. Several examples of this type of cyclization have been reported and cycloadditions based on this approach provide a useful route to cyclobutane derivatives. Thus, a new stereochemical synthesis of grandisol has been developed using the copper(I)-catalysed cycloaddition of the dienol **95** to afford the isomeric bicycloheptenols **96**[42]. The *exo*/*endo* ratio in this cyclization is solvent-dependent. The racemic grandisol **(97)** can be synthesized starting from the heptenol **(96)** in eight steps. A more detailed study by Langer and Mattay[43] has reported on the use of the copper triflate controlled (2 + 2)-cycloaddition of 1,6-dienes such as the (*S*)-diene **98**. This affords the two enantiomerically pure cyclobutane derivatives **99** and **100**. These can be converted into enantiomerically pure (+)-grandisol **(97)** and the corresponding (−)-grandisol. The use of chiral copper catalysts was also examined. This only gave products with low enantiomeric excesses (ee) <5%. The authors[43] reason that low ee values are due to the low reactivity of the chiral copper complexes.



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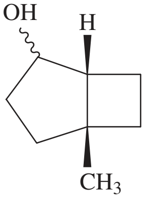

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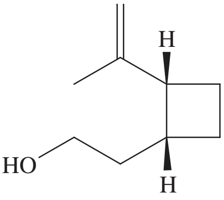

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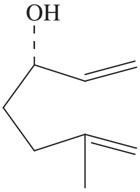

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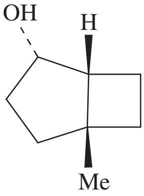

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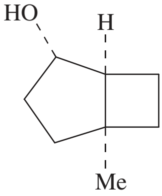
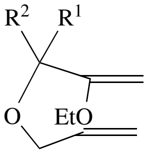


(100)

The presence of an oxygen atom in the chain linking the two alkene moieties does not appear to affect the efficiency of the cyclizations encountered. Thus, the (2 + 2)-intramolecular cycloaddition of the divinyl ether **101a** in ether solution with CuOTf affords a reasonable yield of 67% of the tetrahydrofuran derivative **102a**. The influence of substituents was studied using **101b,c** and stereoselectivity in the cycloaddition was observed[44]. Copper triflate controlled cyclizations of this type can be used to construct suitable key molecules for the synthesis of naturally occurring compounds. To this end the dienes **103** and **104** have been cyclized intramolecularly to yield the cyclobutanes **105** and **106**, respectively, in moderate to good yields. The products from these reactions are key intermediates in the synthesis of natural products such as cedrene **(107)**[45]. Other examples of this type of cyclization have been used as a route to cyclopentanone derivatives. This involves the copper triflate influenced (2 + 2)-photocycloaddition of the dienes **108** to afford the cyclobutane derivatives **109**. The stereochemistry of the cycloaddition was studied and it can be seen that the dienes **108a**, **108c** and **108d** afford mixtures of *exo* and *endo* isomers while diene **108b** yields only a single isomer. The conversion to the cyclopentanones that were the main target of the work is carried out by rearrangement of the products **109**[46,47]. These adducts are key components in an approach to the synthesis of $\Delta^{9(12)}$-capnellene. Approaches to other systems involve the cyclization of the dienes **110** under the copper(I) controlled conditions. This affords the adducts **111** that can be transformed by thermal reactions into variously substituted derivatives of cyclopentane[48].



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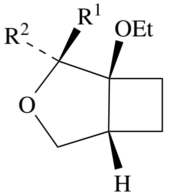

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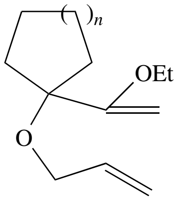
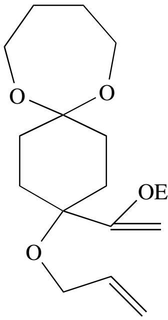


(103)

(a) $R^1 = R^2 = Et$
(b) $R^1 = CH_2CH_2Ph, R^2 = Me$
(c) $R^1 = Et, R^2 = Me$



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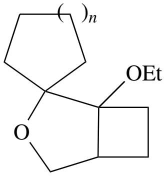
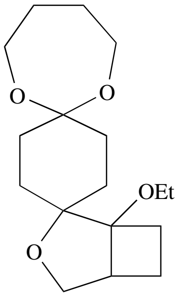


(105)

n = 2,3 or 1



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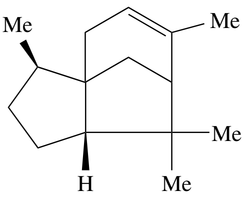

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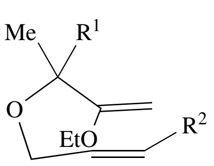

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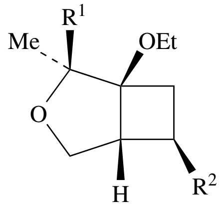
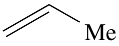
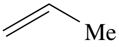
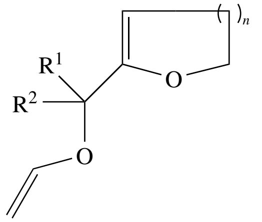
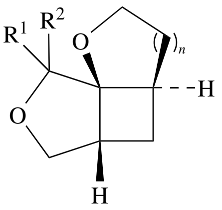


(109)

R^1	R^2	yield (%)	*exo* : *endo*
(a) Me	Me	41	2.5:1
(b) Me	Ph	53	0:100
(c) Me		52	2.2:1
(d) $PhCH_2$		52	3:1



(110)

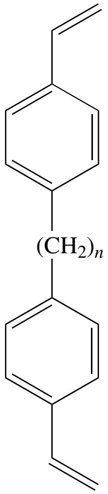


(111)

R^1	R^2	yield (%)	
		$n = 1$	$n = 2$
(a) Me	Me	50	46
(b) Me	CH_2CH_2Ph	59	45
(c) Me	CH_2Ph	70	40
(d) $-(CH_2)_4-$		45	58
(e) $-(CH_2)_5-$		60	57

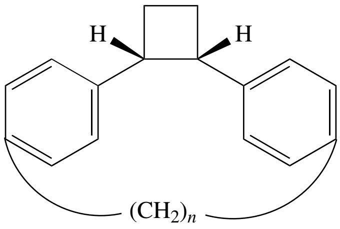
B. Cyclophane Syntheses

An interesting reaction that has been developed over the past decade is the application of (2 + 2)-cycloaddition reactions to the synthesis of cyclophanes[49]. One of the earliest examples of this is the selective conversion of the bis(arylalkenes) **112** into the adducts **113**. The yield of product is dependent to some extent on the chain length separating the aryl groups and the best yield of 41% is obtained when the separation includes four methylene units ($n = 4$). Lower yields are recorded with the other derivatives. Mixtures of products are formed when the *m*-isomers **114** are used. This affords **115** and **116**. The yields of these are better than those obtained from the *p*-isomers **112**[50,51]. Nishimura and coworkers[52] have examined the ease with which such cyclobutanes, e.g. **115**, $n = 2$, undergo thermal reversal to starting material **114**. Other more constrained systems have been synthesized by chemical modification of **115**, $n = 3$. This yielded the derivative **117** as a mixture of *exo*- and *endo*-isomers[53]. Naphthalenophane analogues can also be obtained in moderate yield by the photochemical cyclization of the corresponding alkenes **118**, **119**[54] and **120**[55]. Phenanthrene-based cyclophanes can also be prepared in moderate yields by the intramolecular photocycloaddition of the vinylphenanthrene derivatives **121**. The *syn*-cyclophanes **122** are formed exclusively[56].

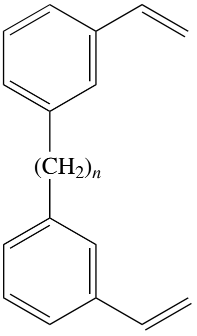


(**112**)

$n = 3, 4, 5$ or 6

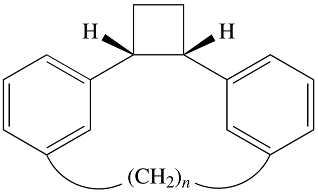


(113)

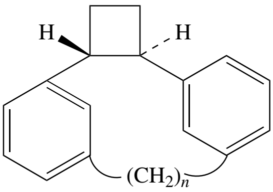


(114)

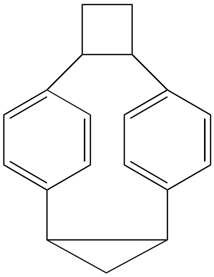
$n = 2, 3, 4, 5$ or 6



(115)

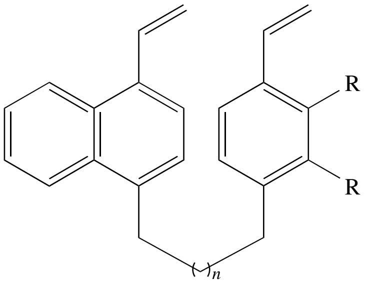


(116)

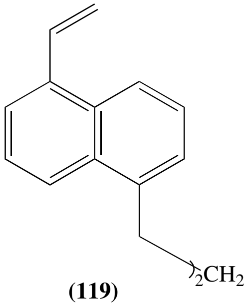


(**117**)

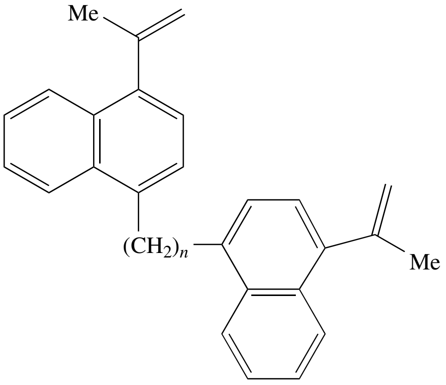
Similar intramolecular cycloadditions are encountered where an ether linkage has been incorporated into the *meta* or *para* linking groups **123**. In these cyclizations the better yields were obtained from the *para*-attached systems. The yields obtained are again dependent on the chain length of the separator and are indicated below the appropriate structures **(124)**[57]. Other hetero-atom-substituted cyclophanes **(125)** can be obtained by irradiation of the divinyl compounds **(126)**[58,59]. The use of tin and germanium derivatives



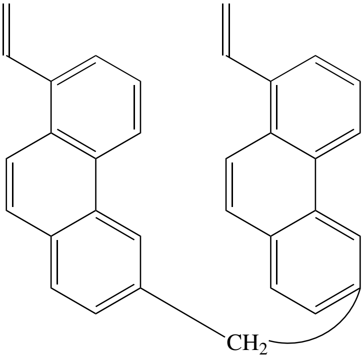
(118) **(a)** $n = 1$, R = H
(b) $n = 1$, 2, or 3
RR = $(CH{=}CH)_2$



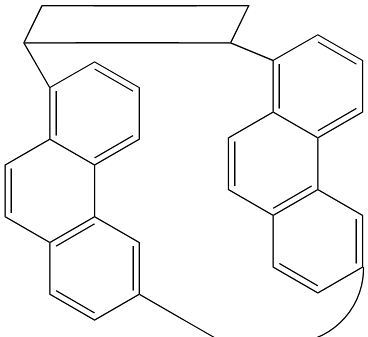
(119)



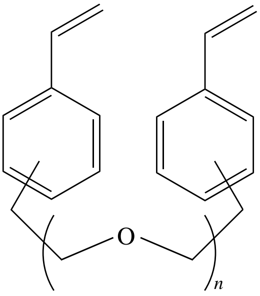
(120) $n = 3$ or 4

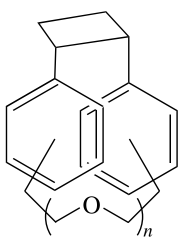


(121)



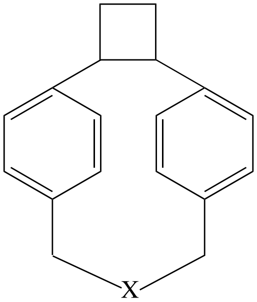
(122) $n = 3$ 49%
$n = 4$ 38%



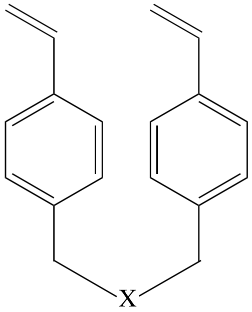


(123) **(124)**

$n = 1$ *para* - attachment	85%
$n = 1$ *meta* - attachment	40%
$n = 2$ *para* - attachment	63%
$n = 2$ *meta* - attachment	mixture of *cis* 26% and *trans* 6%

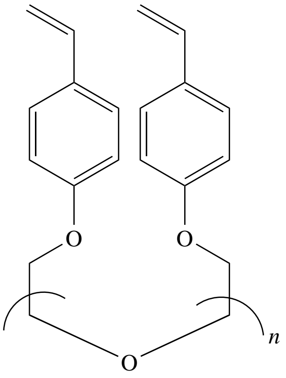


(**125**) X = S or Se, $SiMe_2$



(**126**)

has also been examined[59]. A natural extension of the study has been the development of synthetic approaches to crown-ether based systems. These **(128)** can be formed in high yield (up to 90%) by the irradiation $\lambda > 280$ nm of the derivatives **(127)**. Some evidence for the involvement of biradicals within the cycloaddition process was found from the fact that a low yield of **129** was obtained. This is presumed to be the result of trapping of the biradical by oxygen[60,61]. The high yield of adducts obtained from these irradiations is thought to be due to the flexibility of the ether linkages that permits facile face-to-face approach of the two alkenyl groups. The use of the (2 + 2)-photocycloaddition reactions in the synthesis of so-called paddlanes **(130)** has been studied. Irradiations of the starting materials **(131)** are carried out through Pyrex and yields are best when cyclohexane is used as the solvent. The yields of the adducts formed by the double (2 + 2)-cycloaddition which forms two cyclobutane moieties is excellent. These products are accompanied by small amounts of the cycloaddition product **132** formed by a single (2 + 2)-cycloaddition process[62]. Other cyclophanes with two cyclobutane moieties have also been isolated following the irradiation of the derivative **133**. In this instance, however, the yields are not good and the three isomers **134**, **135** and **136** are obtained in a total yield of 20%[63]. Further examples of compounds of this type have been synthesized by cyclization of **137**[64].



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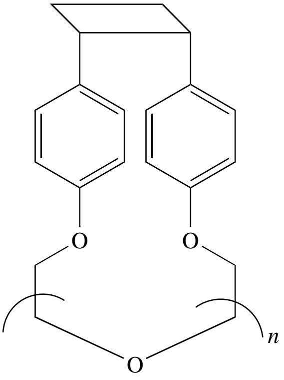
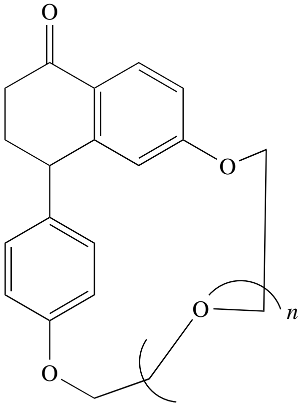
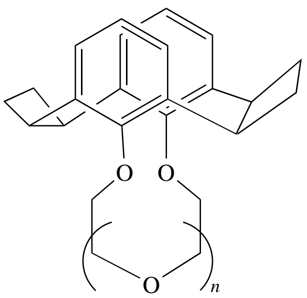


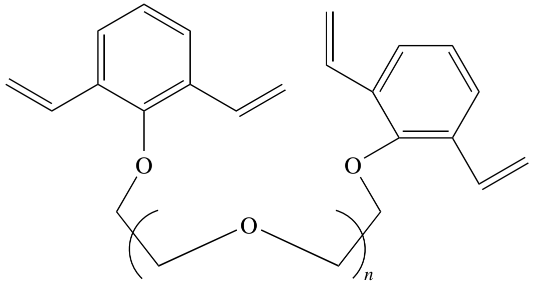
(128) *n* = 3 or 4



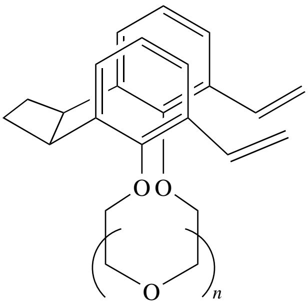
(129)



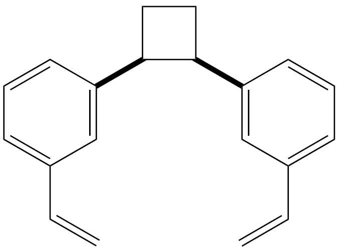
(130) *n* = 2 84%
n = 3 92%



(131) *n* = 2
n = 3



(**132**) *n* = 2 or 3 6%



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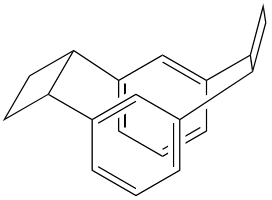

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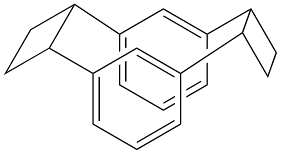

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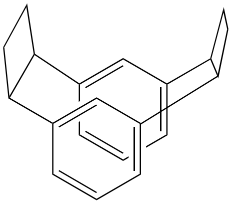

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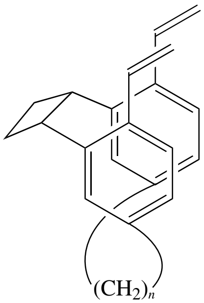
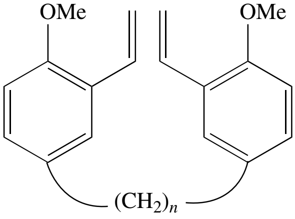


(137)

The aryl groups of the styryl systems need not be unsubstituted, as has been illustrated before for the cyclizations encountered in the synthesis of naphthalenophanes from **120**. Indeed cyclization to afford a cyclobutane derivative where methoxy groups are on the adjacent ring position to the vinyl moieties has also been studied. The irradiation of **138** affords the *m*-cyclophanes **139** and **140**[65]. Further study has sought to evaluate the steric effect of *o*-methoxy groups in such molecules[66].



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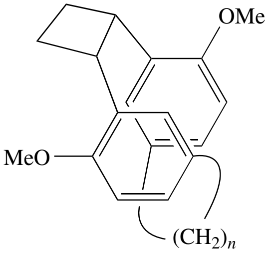
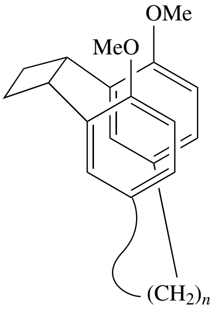


(139)

$n = 2–6$

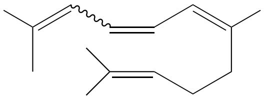


(140)

C. Other Cycloadditions

1. Open-chain Systems

Before illustrating the scope of this method for the synthesis of complex structures, there are examples in the literature where non-conjugated dienes are in open-chain systems but also undergo such (2 + 2)-cycloaddition reactions. Typical of this is the irradiation of the tetraene **141** that yields the bicyclooctene **142**[67]. This cycloaddition probably involves excitation of the diene component and it is the excited state of this that adds to the terminal alkene. In the more complex system **143** the conjugated triene component is the most likely chromophore of the heptaene that will be excited. Addition within this molecule also occurs to an isolated double bond to yield the product **144**. Cycloaddition to form a cyclobutane derivative is also observed as a result of mercury-sensitized vapour-phase photolysis at 254 nm of the fluorinated diene **145**. This yields the two cyclobutane derivatives **146** and **147** as well as the cross-addition product **148** in ratios of 5.7 : 1.0 : 2.8. When the reaction system was diluted with nitrogen the formation of the (2 + 2)-cycloadducts became dominant. Similar additions were observed for the diene **149**. The straight (2 + 2)-adduct **150** and the cross-addition product **151** are formed in a ratio of 1 : 4[68]. One of the double bonds can be contained within a ring as in the cycloaddition encountered in the study of cyclopropene **(152)**. Sensitized irradiation affords the tricyclic compounds **153** by a head-to-head (2 + 2)-cycloaddition[69].



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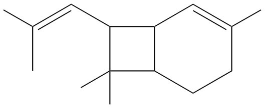
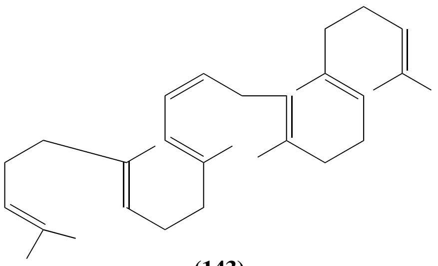


(142)



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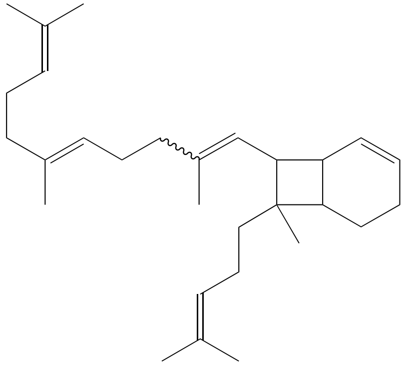

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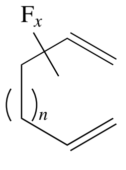
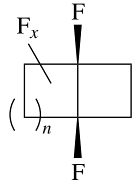


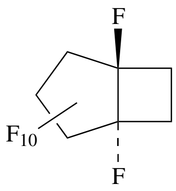
(145) $n = 2$, $x = 12$

(149) $n = 1$, $x = 10$



(146) $n = 2$, $x = 10$

(150) $n = 1$, $x = 8$



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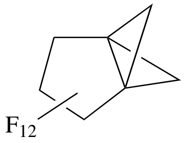

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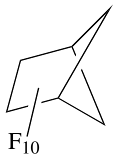

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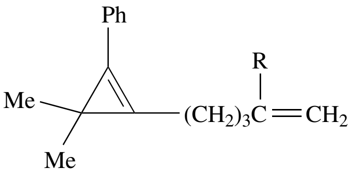
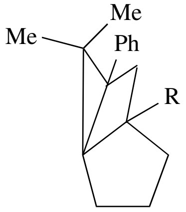
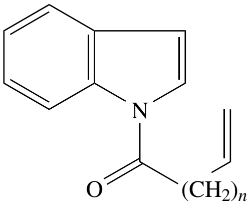


(152) (**a**) R = H
(**b**) R = Me



(153)

(2 + 2)-Cycloadditions have also been reported for the indole derivatives **154** as an effective method for the synthesis of the polycyclic adducts **155**. The yields, as can be seen from those quoted, range from moderate to good. The quantum efficiencies for the cyclizations are also reasonable. Interestingly, the ester derivatives **156** are photo-unreactive[70,71]. Head-to-head (2 + 2)-cycloaddition is also observed on irradiation of the diallylic amines **157**. This yields the cyclobutanes **158**. The reaction is diastereoselective and detailed semi-empirical calculations supported the proposed mechanism for the formation of these products[72,73]. The silyl ethers **159**–**161** are reactive by a (2 + 2)-cycloaddition in the singlet state while sensitization only brings about *trans–cis* isomerization. Irradiation of **159** brings about cyclization to cyclobutane derivatives. Thereafter the silyl ethers groups can be cleaved to afford cyclobutane diastereoisomers such as **162**. It is interesting to note that in the cycloaddition of **159**, R = cyclopropyl leading to **162**, R = cyclopropyl, the cyclopropane ring remains intact. This presumably gives information about the intermediates involved in the cycloaddition and any cyclopropyl methyl radical species that could be formed is not sufficiently long-lived to undergo ring-opening. Cycloaddition can also occur to the furan double bond of **160** and to the alkyne moiety in **161** to yield, in this instance, cyclobutene derivatives[74,75]. In other dienes where the alkene moieties are held more rigidly within the tethered system, as with **163**, irradiation readily affords the cyclobutane derivative **164**[76].



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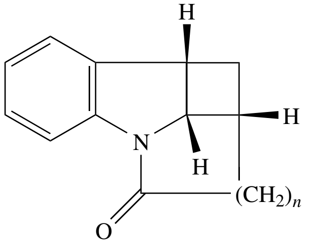
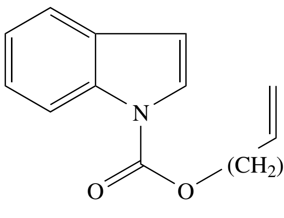


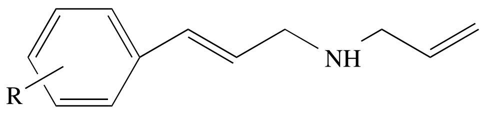
(155)

$n = 1$ 29% $\phi = 0.0078$
$n = 2$ 92% $\phi = 0.017$
$n = 3$ 25% $\phi = 0.0032$



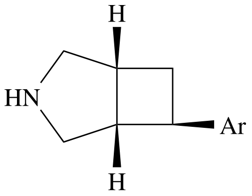
(156)

Intramolecular (2 + 2)-photocycloaddition has proved to be an excellent route to the synthesis of the so-called cage compounds. Ideally, this route utilizes substrates where the two alkene moieties are held face-to-face within a pre-formed structure. The irradiation brings about excitation and coupling of the two groups to afford a cyclobutane ring.



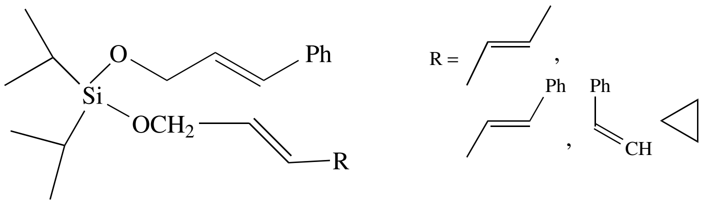
(157)

R = H, 4-F, 4-Cl, 4-NO_2, 3-Cl, 2-F

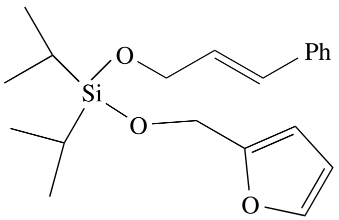


(158)

Ar = RC_6H_4



(159)



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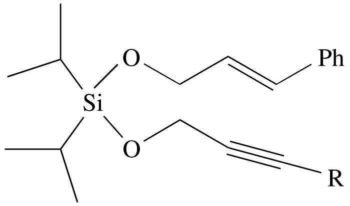
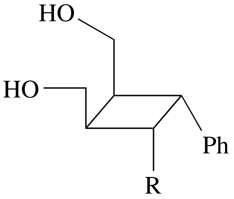
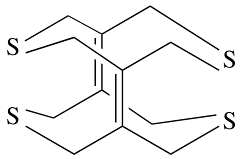


(161)

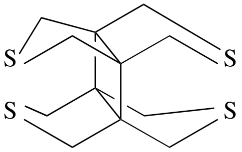
R = Ph, CO_2Me



(162)



(163)

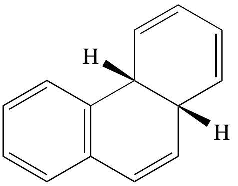


(164)

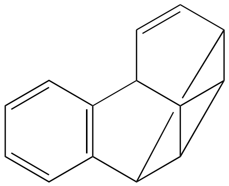
Such compounds are of use in the study of ring strain and also in synthetic approaches to starting materials for more complex systems. Several review articles have highlighted this[77]. The ring systems formed by these reactions are generally quite complex. In order to classify the reactions, a simple approach has been adopted. Not all the complexity is described in this nomenclature and only the atoms involved in the ring system formed are included.

2. Bicyclo[2.1.0]pentane systems

An example of this type of ring system is given by the photochemical cyclization observed within the hydrocarbon **165**. Irradiation converts it into the tetracyclic isomer **166**[78].



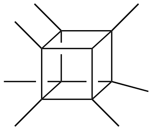
(165)



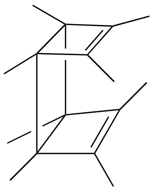
(166)

3. Cubanes and related compounds

Only a trace of the corresponding cubane **167** is formed on irradiation of the tricyclooctadiene **168** in pentane at ambient temperatures using a 125-watt mercury arc lamp. The principal product **169** is the result of rearrangement within a biradical intermediate[79]. A review of the synthetic approaches to cubane and to its reactions has been published[77]. The diene **170** photochemically converts on irradiation in pentane solution at 254 nm to yield a photostationary mixture of the cubane **171**, the starting material **170** and the isomeric diene **172**[80]. Other additions of this type have been used for synthesis of the propellaprismane **173**, essentially a heavily substituted cubane, by the intramolecular $(2 + 2)$-photocycloaddition of the diene **174**[81].



(167)



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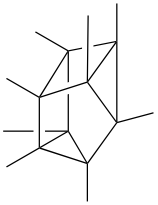

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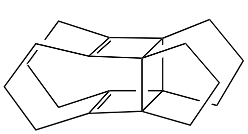

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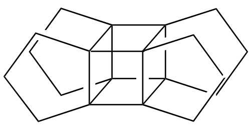
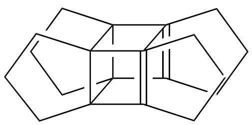
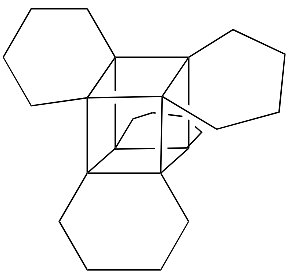


(171)

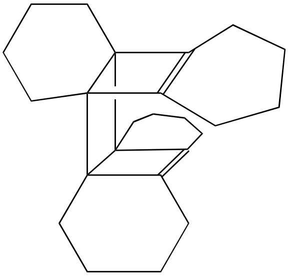


(172)

Less complex non-conjugated diene systems also lead to cubane-like derivatives as in the diene **175**. Here the outcome of the reaction is dependent upon the excited state. Thus, direct irradiation brings about fragmentation with the formation of 1,4-difluorobenzene and excited-state naphthalene while triplet-sensitized irradiation follows a different path with the formation of the cage compound **176**[82].



(173)



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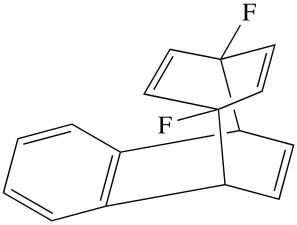

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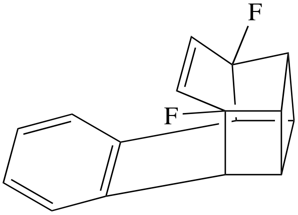
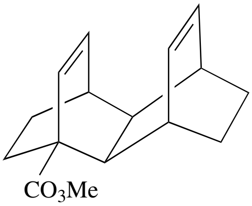


(176)

4. Hexacyclotetradecane systems

Normal (2 + 2)-photocycloaddition takes place on the acetone-sensitized irradiation of the per-ester **177** to yield the cage compound **178** in 76%. This product can be transformed chemically into the hexacyclotetradecane **179**[83]. Analogously, the tetraene **180** undergoes photochemical cage formation yielding **181**[84]. These cyclizations are typical of the type where the π-moieties are held rigidly face-to-face within the framework. There are many examples of cycloaddition within such systems. A further example is the irradiation of the triene **182** through quartz in a mixture of acetone and benzene. The reaction is chemically efficient and the cycloaddition product **183** is formed in 80% yield[85]. Other cyclizations such as the formation of the cage compound **184** in 90% from direct irradiation of a benzene solution of the diene **185** and **186** from **187** have been reported[86]. The presence of hetero-atoms does not seem to effect the cyclization adversely and the irradiation of **188** results in a quantitative (2 + 2)-cycloaddition yielding **189**[87]. The irradiation of **190** in acetone is also efficient. This irradiation presumably involves the triplet state and gives an almost quantitative yield of the cycloadduct **191**[88].



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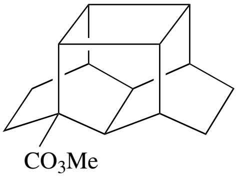

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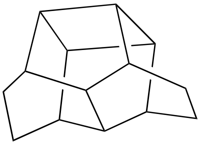

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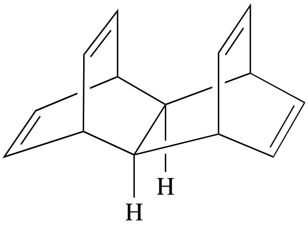

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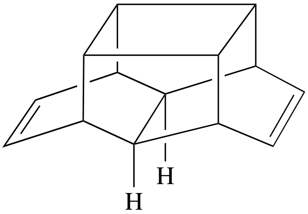

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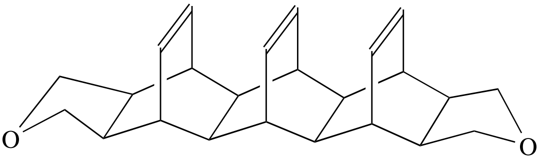

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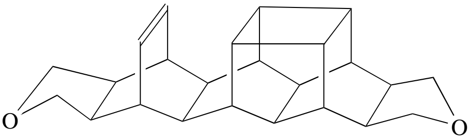

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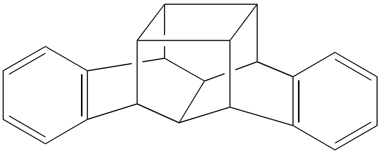

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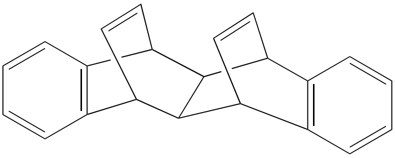

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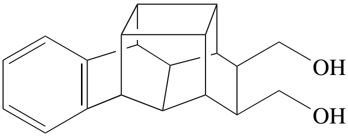

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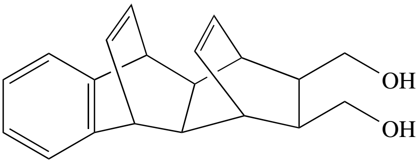

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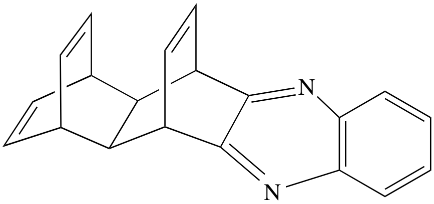

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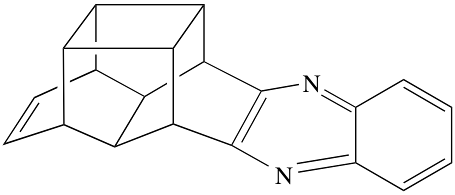

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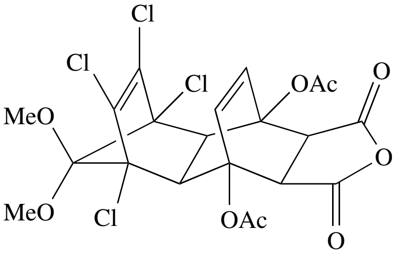

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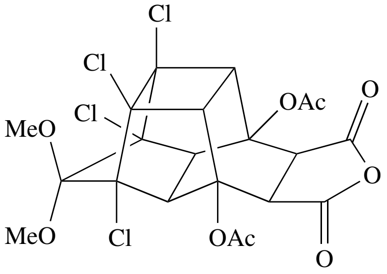
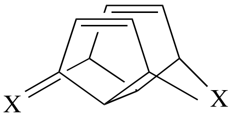


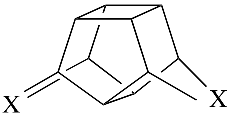
(191)

5. Pagodanes and related molecules

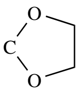
It seems from the examples cited above that, provided the alkene moieties are held in a rigid framework, addition is often highly efficient. This is again demonstrated by the conversion of **192** into **193** or **194** into the pagodanes **195** by either direct irradiation in ether with a quartz filter or by acetone-sensitization through Pyrex[89]. Prinzbach and Weber[77d] have reviewed the synthesis of such compounds. A benzene ring can also be one of the components of the reaction system as demonstrated by the photo-ring closure of **196a** into **197a**. In the case of the resultant diene **197a**, the remaining double bonds of the aromatic ring were trapped by Diels–Alder addition[90]. The bis arene **196b** is also reactive and gives the cycloaddition product **197b**[91]. Melder and coworkers[92] have made use of such cycloadditions, using the slightly more substituted derivative **198**, as a path to [1.1.1.1]pagodanes. Irradiation at 254 nm of **198** affords the (2 + 2)-cycloaddition product **199**.

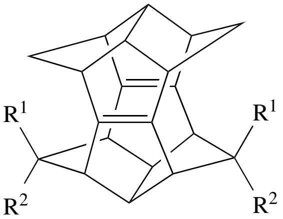


(192)



(193)

X = CH$_2$,  , CO or C=C(CN)$_2$



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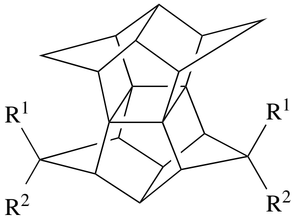
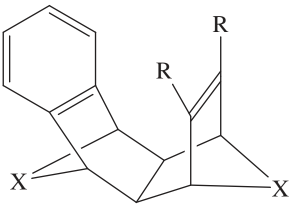
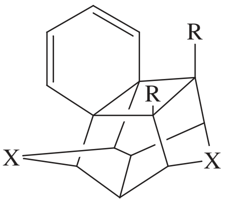
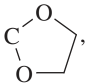


(195)

$R^1 = R^2 = H$
$R^1 = CO_2Me$, $R^2 = H$
$R^1R^2 = O$

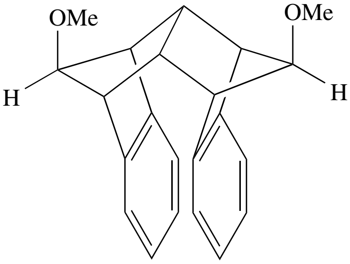




(196) (**a**) $X = CH_2$ or  , $R = H$

(196) (**b**) $X = CH_2$, $RR = (CH{=}CH)_2$

(197a)
(197b)



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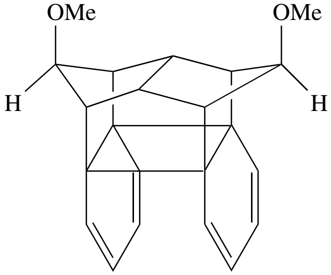
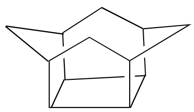


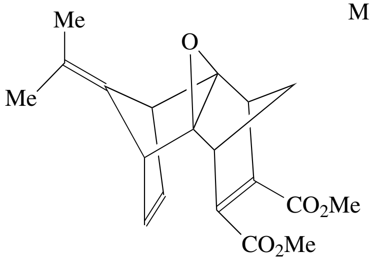
(199)

6. Peristylane and related molecules

Syntheses of the complicated structures such as the peristylane system **200**, a 4[peristylane], can also be approached by (2 + 2)-photocycloadditions. Thus, irradiation of the adduct **201**, formed by epoxidation of the air-sensitive adduct **202**, affords the cage compound **203** when acetone-sensitization is employed[93]. Triplet-sensitized irradiation (350 nm) in acetone of the triene **204a** and the tetraene **204b** affords the cage compounds **205** in 32% yield[94,95].



(200)



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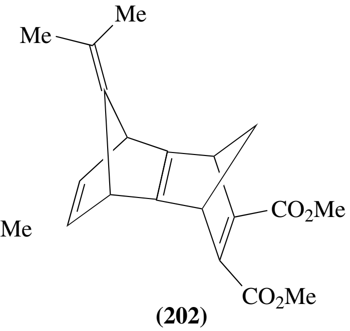

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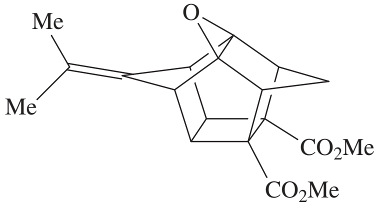

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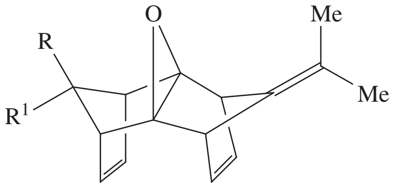
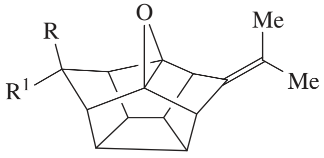


(204) (a) R = R^1 = H

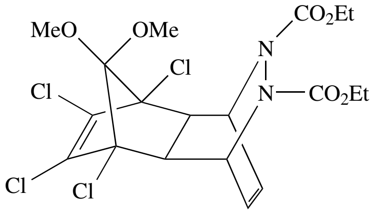
(204) (b) $\mathrm{R\,R} = {=}{<}^{\mathrm{Me}}_{\mathrm{Me}}$



(205) (a) R = R^1 = H

(205) (b) $\mathrm{RR} = {=}\mathrm{C}{<}^{\mathrm{Me}}_{\mathrm{Me}}$

Cycloaddition is also observed on irradiation of the diene **206** to yield the adduct **207**. This product can be hydrolysed and decarboxylated to afford the corresponding azo compound[96]. The adduct **208** is photochemically converted into the cage compound **209** in 38% yield on irradiation at 254 nm[97].



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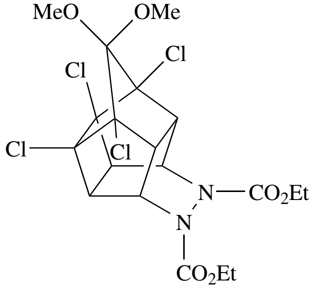

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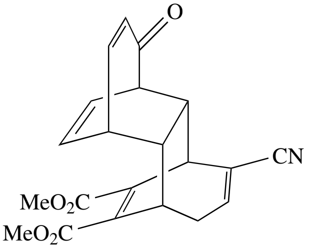

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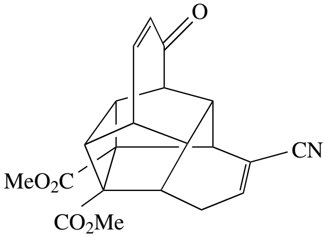
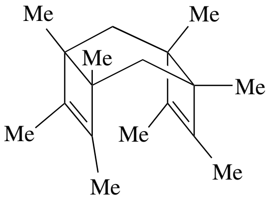


(209)

7. Miscellaneous cycloadditions

Irradiation of the bis-alkene **210** brings about the formation of the bishomocubane **211** in good yield[98]. The triene **212** is of interest and has been shown to be photochemically reactive, yielding the adduct **213** on irradiation. Several approaches to **212** have been reported over the years. One such approach follows the path of photocyclization of **214** to yield **215** that can be converted to the desired product **212**[99]. A variety of sensitizers can be used for the excitation of alkenes to bring about the (2 + 2)-cycloaddition. Commonly, acetone has been used but, in at least one case, the formation of the cage compound **216** from the diene **217**, tetraphenylporphine has been found to be of use[100].



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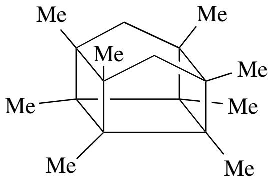

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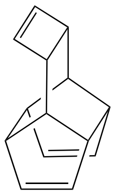

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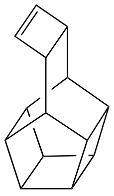

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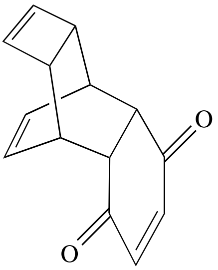

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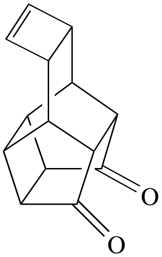

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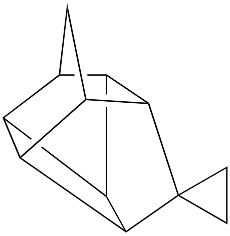

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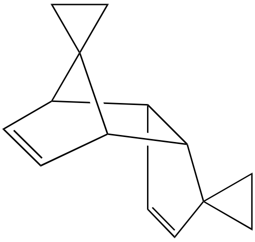
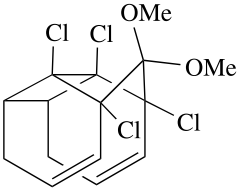


(217)

The approach to highly complex cage systems is not always straightforward. Thus while (2 + 2)-cycloaddition within **218** readily affords **219**, the more highly strained diene **220** fails to cyclize upon irradiation[101]. Previously, it has been mentioned that Prinzbach and his coworkers[77] have synthesized a variety of complex structures using a photochemical (2 + 2)-cycloaddition as a key step in the approach. Another complex structure, the isopagodane, has also been synthesized. One of the approaches leading to these compounds involves a double (2 + 2)-photocycloaddition. Thus irradiation in benzene solution brings about the formation of **221** from **222**. Cycloaddition is also possible in **221** and this yields **223**[102]. Cycloaddition by acetone-sensitized irradiation also brings about the ring closure of the diene **224**. This yields the heptacyclic product **225** that is a key intermediate in the synthesis of bishomohexaprismane molecule **226**[103,104].



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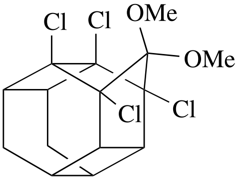

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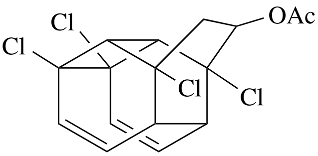

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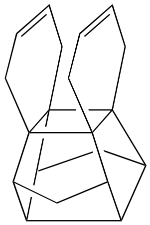

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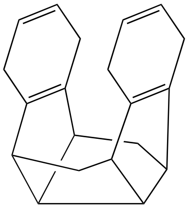

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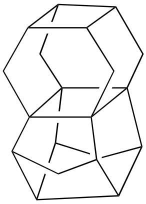
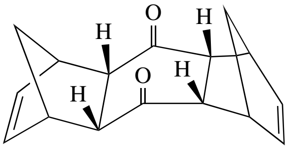


(223)



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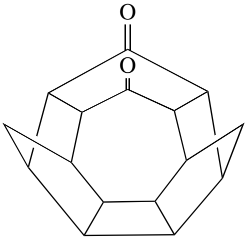

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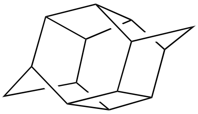


(226)

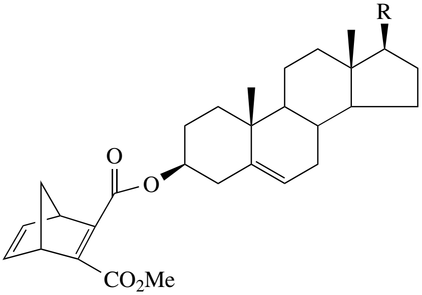
IV. CYCLIZATION OF NORBORNADIENES AND RELATED COMPOUNDS

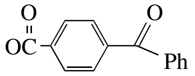
A. All Carbon Systems

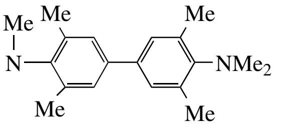
One of the areas that has been studied in considerable detail is that of the cyclization reaction of norbornadiene to quadricyclane that can be brought about either by direct or by sensitized irradiation. This was first reported by Cristol and Snell[105] and soon became an area of interest to others[106,107]. Since these early investigations where much of the work focused on the homoconjugation of the system, a great deal of research has been carried out and a good understanding of the processes involved has now been acquired. Much of this earlier work has appeared in most textbooks devoted to photochemistry and, in addition, most of the standard textbooks and monographs on the subject now have details of these reactions. Since this is the case the present section will highlight what has been achieved in the last decade or so.

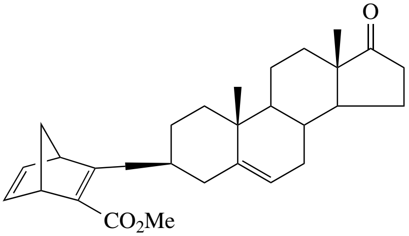
As mentioned above, the ring closure of norbornadiene to quadricyclane can be brought about by sensitization. Interest in this area has shown that tetraphenylporphine can be a useful sensitizer for the conversion of norbornadiene into quadricyclane[108]. Part of this research is associated with energy storage systems and several copper(I)-based photosensitizers have been synthesized in an attempt to improve the norbornadiene/quadricyclane solar energy storage system [109]. In this respect, also, Yang and coworkers[110] have reported that the conversion of quadricyclane back into norbornadiene can be sensitized by dibenzoylmethanatoboron difluoride.

Interest in intramolecular energy transfer has also been reported and bichromophoric norbornadiene derivatives have been synthesized for this study[111]. Cao and coworkers[112] report that intramolecular triplet energy transfer from the benzophenone moiety to the norbornadiene unit in **227** takes place with a rate constant of $6.1 \times 10^4\,s^{-1}$. The bichromophoric system **228** undergoes intramolecular electron transfer by a through-bond mechanism on irradiation. The transfer is from the benzidine moiety to the norbornadiene moiety and occurs with 12% efficiency. The ultimate intermediate is the triplet radical ion pair[113]. Irradiation ($\lambda > 300$ nm) of the norbornadiene derivative **229** results in excitation of the androstene carbonyl group. Apparently, this affords the triplet excited state that transfers triplet energy by a through-bond mechanism to the norbornadiene. This undergoes cyclization to the corresponding quadricyclane. The energy transfer occurs with 18.6% efficiency[114]. Calculations have dealt with the energetics of the photoisomerization within the norbornadiene/quadricyclane system[115]. Constrained environments have also been of interest in a number of areas and norbornadiene cyclization has not been excluded. Thus, a study of the photoisomerization of some norbornadienes has been carried out within the constrained environment of β-cyclodextrin[116].



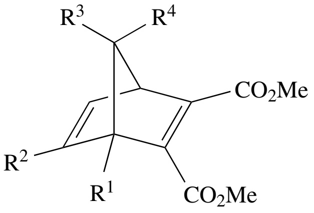
(227) R =


(228) R =


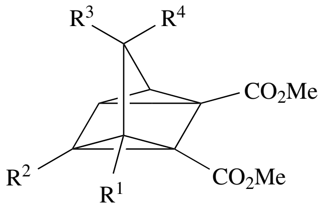


(229)

The simple systems such as **230** are also of interest. These readily undergo cyclization to the quadricyclanes **231** in good yield. The principal reason for the study of these systems was an attempt to obtain energy storage molecules. Thus the reverse reaction is important and the quadricyclanes **231** can undergo ring-opening when treated with silver ion[117]. If the use of the norbornadiene/quadricyclane as energy storage systems is to be exploited, systems have to be devised that can be cyclized using sunlight. This is the case with the water-soluble norbornadiene **232** which is efficiently converted into the corresponding quadricyclane on irradiation with sunlight[118]. Other norbornadienes with carboxylic acid functional groups, e.g. **233**, also undergo efficient cyclization to **234**[119] as does **235** into **236** in a yield of 75%[120]. The photochemical formation of the quadricyclanes **237** by acetophenone-sensitized irradiation of **238** has been reported. The quadricyclanes were used as substrates in an approach to the synthesis of 1,5-dehydroquadricyclane[121].

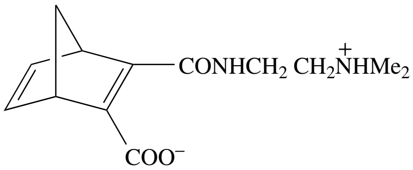


(230)

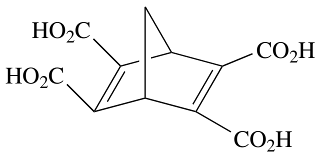


(231)

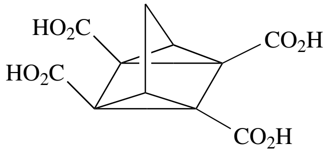
$R^1 = R^2 = R^3 = R^4 = H$
$R^1 = Me, \quad R^2 = R^3 = R^4 = H$
$R^2 = Me, \quad R^1 = R^3 = R^4 = H$
$R^3 = Me, \quad R^1 = R^2 = R^4 = H$
$R^4 = Me, \quad R^1 = R^2 = R^3 = H$
$R^1 = R^2 = H, R^3 = R^4 = Me.$



(232)



(233)



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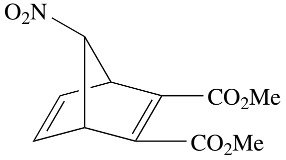

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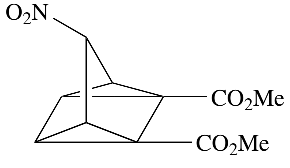

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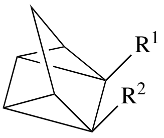
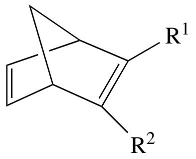


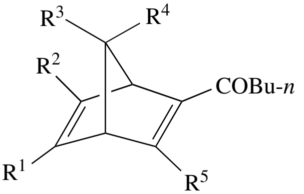
(237)



(238)

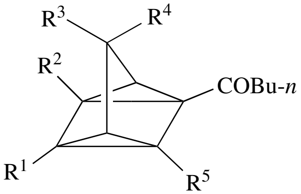
$R^1 = Br, R^2 = Br$ or Cl

The variety of derivatives that undergoes cyclization is almost limitless, as shown by the conversion of **239** into **240**. Here, one of the functional groups on the norbornadiene is ketonic[122]. The isomerization of other keto or aldehydo derivatives of norbornadiene into

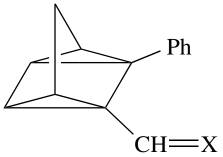


(239)

R^1—R^4 = H or Me
R^5 = CHFEt, CF_2Et or CF_3

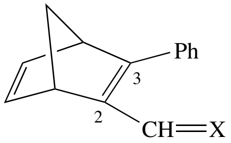


(240)

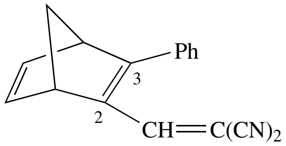


(241)

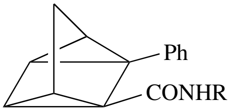
(**a**) X = O
(**b**) X = NPh
(**c**) X = NC_6H_4OMe-*p*



(242) (**a**) X = O
(**b**) X = NPh
(**c**) X = NC_6H_4OMe-*p*



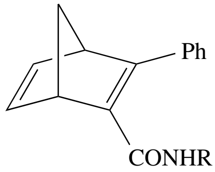
(243)



(244)

R = Ph, 1-Naphthyl, 2-Naphthyl

the corresponding quadricyclanes has also been reported[123]. Thus, the formation of the quadricyclane **241a** occurs on irradiation of the phenyl-substituted norbornadiene **242a**. The imines **241b** and **241c** are photoreactive under the same conditions. Again interest in these was centred on quadricyclanes as energy storage systems and copper(II) porphyrins rapidly brought about reformation of the photoreactive norbornadiene[124]. The imines **242b** and **242c** are also photoreactive[124] as is **243**[125], and the corresponding quadricyclanes are formed on irradiation. The conversion of the norbornadienes **243** and **242b**, has sought to examine structural effects. These derivatives showed a substantial lengthening of the C2−C3 double bond in comparison with unsubstituted derivatives. The authors[125] observe that the quantum yield for the conversion of norbornadienes to quadricyclanes increases with shortening of the C2−C3 double bond. Efficiency of cyclization is also affected by changes in substitution as in the formation of the quadricyclanes **244** that can be obtained by irradiation of the norbornadienes **245** at 313 nm. The quantum yield for the cyclization, which can be as high as 0.71, can be enhanced by the change in substitution on the amide group[126,127]. Other studies have focused on the kinetics of the photochemical isomerization of the norbornadienes **246** into the corresponding quadricyclanes. The quantum yields for the processes were found to be in the range of 0.18 to 0.36. In these examples the authors[128] suggest that the results are in agreement with the involvement of a radical cation mechanism (see earlier for examples of electron transfer processes applied to the norbornadiene system) in the cyclization. Others have studied the changes in efficiency of cyclization brought about by substituents on the aryl group in the conversion of the norbornadienes **247** into the quadricyclanes **248**[129]. The yields shown under the products illustrate the qualitative effect on the overall yields of product. This is also the case in measurements of the quantum yields of the processes.



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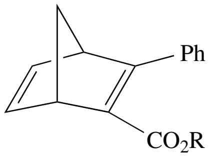
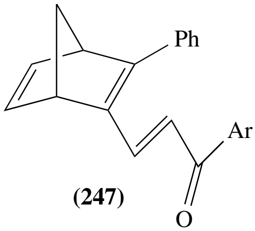


(246)

R = H, $PhCH_2$, p-$MeOC_6H_4(CH_2)_n$ (n = 1, 6)



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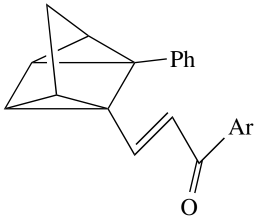
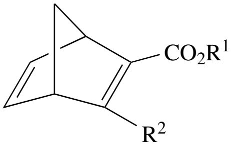


(248)

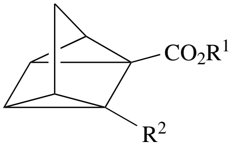
	yield (%)
Ar = p-MeC_6H_4	40
Ar = p-ClC_6H_4	96–100
Ar = p-BrC_6H_4	
Ar = m-$O_2NC_6H_4$	

Investigations have also examined the photochemical outcome of the inclusion of other aromatic substituents onto the norbornadienes. Examples of this are the direct and sensitized irradiation of the naphthyl-substituted derivatives **249** that brings about cyclization to **250**. Sensitization of the cyclization with ketones such as benzophenone leads to a much cleaner reaction. Biacetyl has also been used as the sensitizer[130,131]. Cyclization also occurs with the norbornadiene **251**[132].



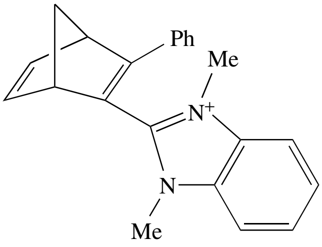
(249)

R^1 = 1- or 2-naphthyl
R^2 = H or CO_2R^1



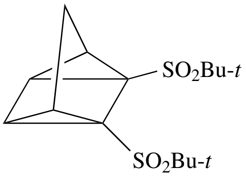
(250)

R^1 = 1- or 2-naphthyl
R^2 = H or CO_2R^1



(251)

The incorporation of sulphonyl groups does not inhibit the cyclization process as demonstrated by Gleiter and Ohlbach[133], who have reported the efficient synthesis of the quadricyclane **252** by irradiation of the norbornadiene derivatives **253**. A study has also been made of the sulphonyl-substituted norbornadiene derivatives **254**[134,135].



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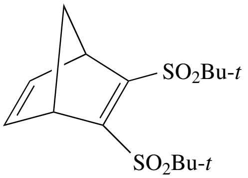

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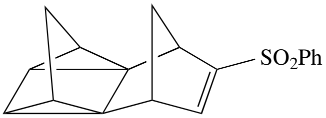
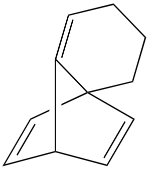
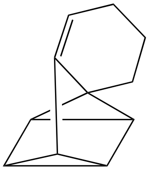


(254)

Cyclizations have also been reported within strained systems such as the conversion of **255** to **256**[136] or the formation of **258** from **257**[137].



(255)



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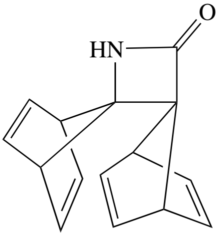

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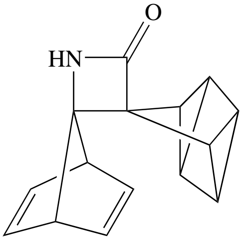
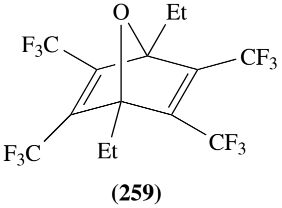


(258)

B. Hetero Norbornadiene Systems

Like the cyclization of the parent system, the photocyclization of hetero analogues of norbornadiene was reported many years ago. Recent interest in this area will serve to illustrate the potential of the conversions. Thus the irradiation of the oxanorbornadiene system **259** brings about conversion to the oxepine **260**[138]. The formation of **260** presumably arises by quadricyclane **261** formation, followed by secondary photolytic ring-opening. Other research has shown that irradiation of the oxanorbornadiene **262** follows the same reaction mode and it undergoes (2 + 2)-cycloaddition to the quadricyclane derivative **263**. Apparently, in this instance, cycloreversion affords the ylide **264** that can be trapped by suitable addends, giving the adducts illustrated in Scheme 3[139].



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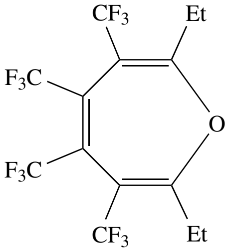

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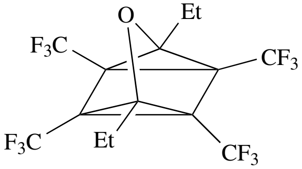
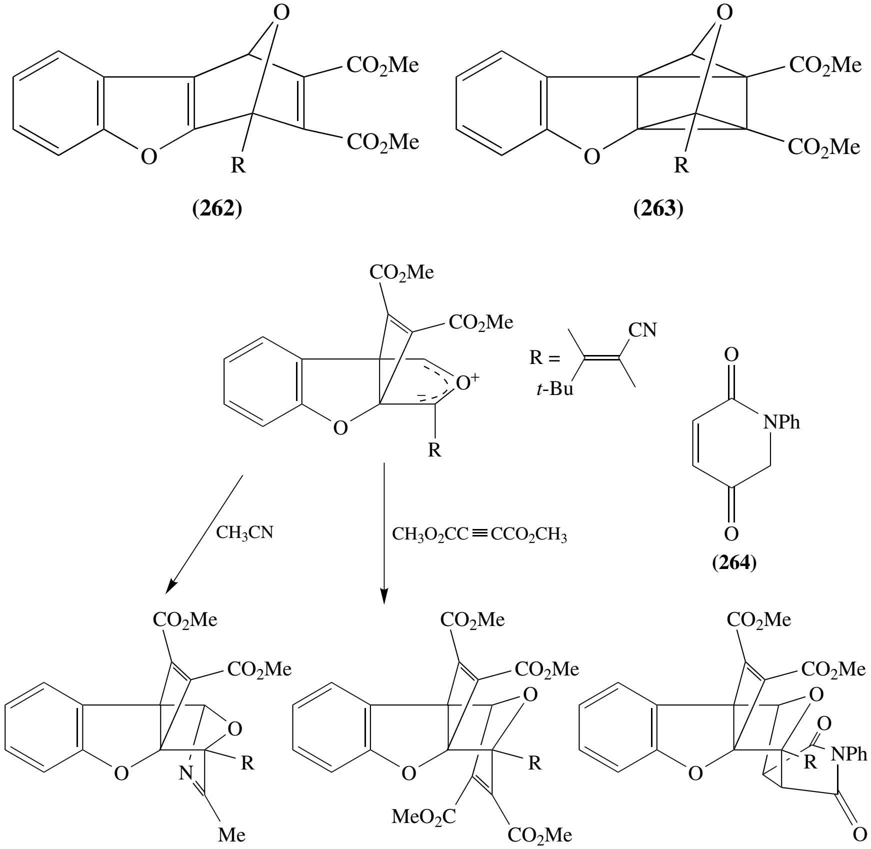


(261)



(262)

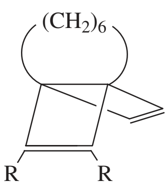
(263)

(264)

SCHEME 3

C. Prismanes

Benzenoid compounds on irradiation can be converted into the corresponding 'Dewar' benzene amongst other derivatives[140]. These Dewar derivatives, exemplified by **265**, are also photochemically reactive and can undergo conversion into the corresponding prismane structure. This is probably the path followed on irradiation of the *para*-cyclophanes **266** at wavelengths greater than 270 nm. This yields the prismanes **267**[141]. Gleiter and coworkers[142,143] have also reported the photochemical behaviour of a number of benzene derivatives such as **268**. Irradiation of this compound leads to the formation of the Dewar benzene **269** and the prismane **270**. Isomers of **270** can also be formed by cyclization of the Dewar benzene derivatives **271a**. Other examples, such as **271b**, also cyclize efficiently, giving high yields of product. The irradiation of these derivatives uses a variety of wavelengths to achieve the cyclization. Structural proof for the prismanes formed by cyclization of **271c**[144] has been obtained by X-ray crystallography[145]. With the bis-system **272**, the photo (2 + 2)-cycloaddition also occurs on irradiation at $\lambda > 320$ nm in ether. However, the initial prismane product undergoes a 1,5-hydrogen migration to yield **273** in 90% yield[146].



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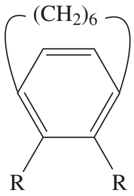

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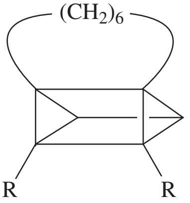
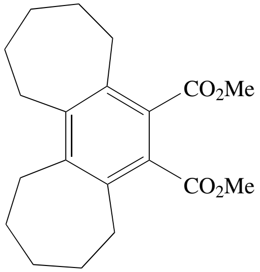


(267)

R = CH_2OH, $CH_2OCONHC_6H_{11}$, $CH_2OCONHC_6H_5$, CO_2Et or CH_2OAc



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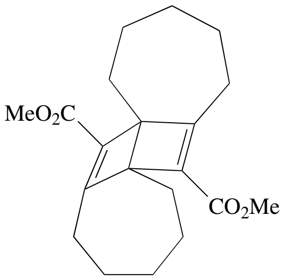

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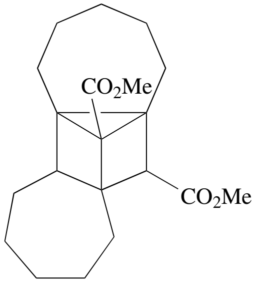

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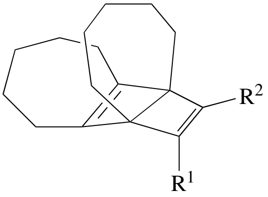
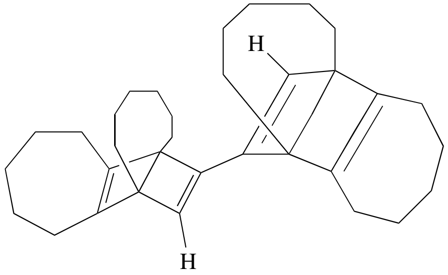


(271) **(a)** $R^1 = H$ or $(CH_2)_2$ OH, $R^2 = H$
(b) $R^1 = SO_2Bu$-*t*, $R^2 = H$, Me, Ph
(c) $R^1 = R^2 = CO_2Me$



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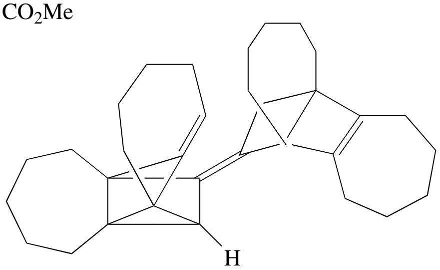


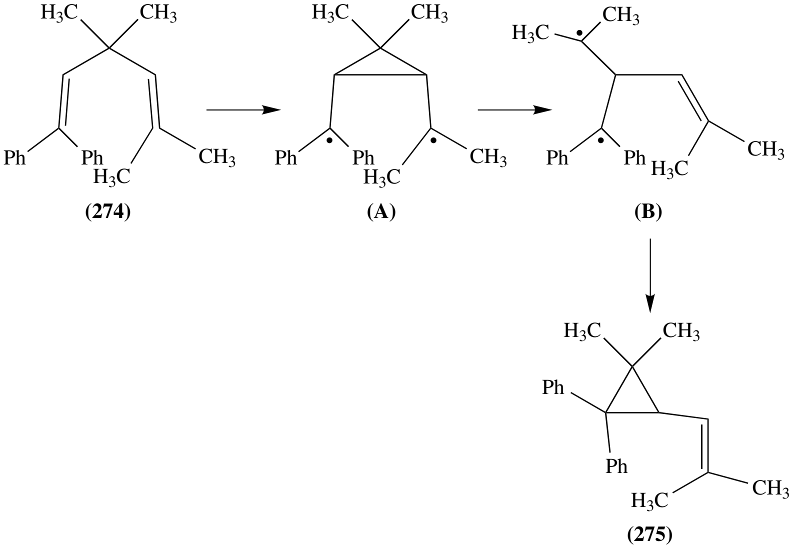
(273)

V. DI-π-METHANE PROCESSES

A. Open-chain Systems

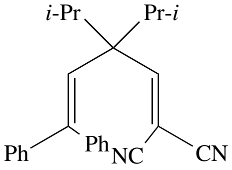
Perhaps one of the most ubiquitous photochemical reactions undergone by non-conjugated dienes is that encountered in the 1,4-diene system. This is referred to as the all-carbon di-π-methane reaction. This system is one in which a central tetrahedral carbon atom is flanked by two vinyl groups. The fundamental reaction was discovered and reported in 1967 by Zimmerman and his coworkers[147]. A detailed account of this reaction and the closely related oxa-di-π- and the aza-di-π-methane rearrangements has been published recently[148]. This review gives the history of how and when the reaction was discovered and its developments in all its guises up to the present time. Others have reviewed other aspects of the reaction[149]. This section of this review will be devoted to the last decade of results.

The basic skeletal transformation exhibited by this system is shown in Scheme 4. Regardless of whether or not the reaction involves a singlet or a triplet, this scheme is a reasonable interpretation of the rearrangement. This shows the fundamentals of the reaction with the two alkene moieties separated from each other by the saturated carbon atom. The usual outcome of the irradiation is conversion to a vinyl cyclopropane, a 1,2-migration. Thus the two steps shown in Scheme 4, the formation of the 1,4-biradical **A** and then its transformation into the 1,3-biradical **B**, fundamentally brings about a 1,2-migration of a vinyl group. Calculations dealing with the outcome of the di-π-methane rearrangement of 1,4-dienes have been reported[150].

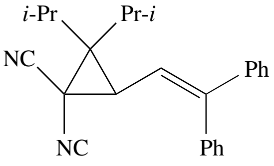


SCHEME 4

The reaction in its basic form is illustrated by the conversion of **274** into **275**. This transformation shows the control exercised within the two biradicals **A** and **B** on the final outcome of the reaction[151]. Another typical di-π-methane process, this time with electron-withdrawing substituents on one of the vinyl moieties, arises on acetophenone-sensitized irradiation of the diene **276**. This yields the cyclopropane **277** in 35% yield. The

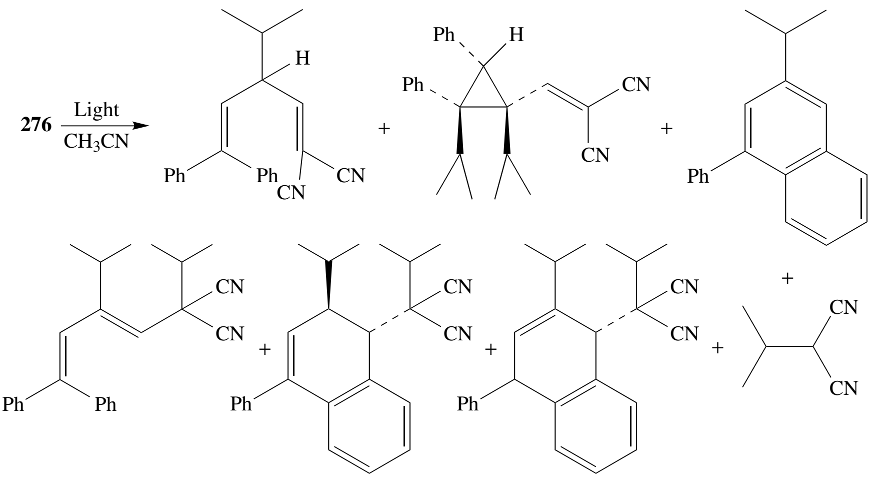


(276)

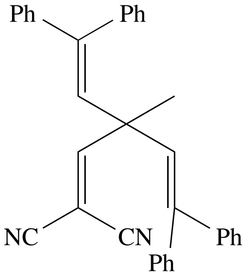


(277)

reaction is reasonably efficient with a quantum yield of 0.041[152]. The outcome of direct irradiation in acetonitrile shows how a change in the excited state provides other reaction paths. Certainly in this instance with **276** the reaction is much more complex and, even though the di-π-methane rearrangement is still operative, six other products are formed as a result of rearrangement, cyclization or fragmentation. These products are shown in Scheme 5. Environment has also been shown to change the outcome of reactions and this is demonstrated by the photochemistry of the dienes **278** and **279** in the crystalline phase. The dicyanodiene **278** yields only the cyclopentene **280**. This is formed via the 1,4-biradical intermediate **281**. Normally one would expect this to transform by the di-π-methane path, but in the crystalline phase the cyclopentene is the principal product. The tetraphenyl diene **279** also shows different behaviour under the same reaction conditions as above and reacts only by vinyl–vinyl bridging to afford the 1,4-biradical **282** and ultimately product **283**. The authors[153,154] suggest that 'confinement control' is responsible for the selectivity observed. The quantum yield for product formation in the crystalline phase is much lower than the quantum efficiency in solution phase. Other studies[155] have shown the influence on the outcome of irradiation when the diene **284** is entrapped in poly(methyl methacrylate). The products from the reactions are shown in Scheme 6 and illustrate that the least motion path is involved in the photochemical reactions. Note that the di-π-methane product is analogous to that formed from the irradiation of **276** with the cyano groups on the cyclopropane ring. The solution phase reactivity of **284** has been studied previously[156].



SCHEME 5



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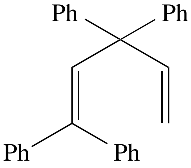

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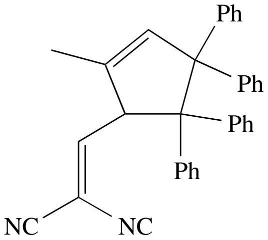

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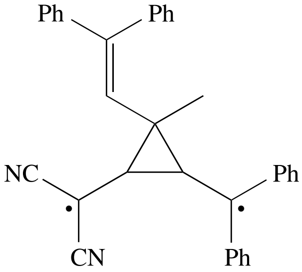

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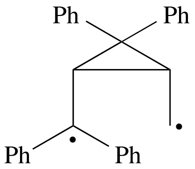

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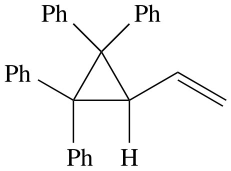

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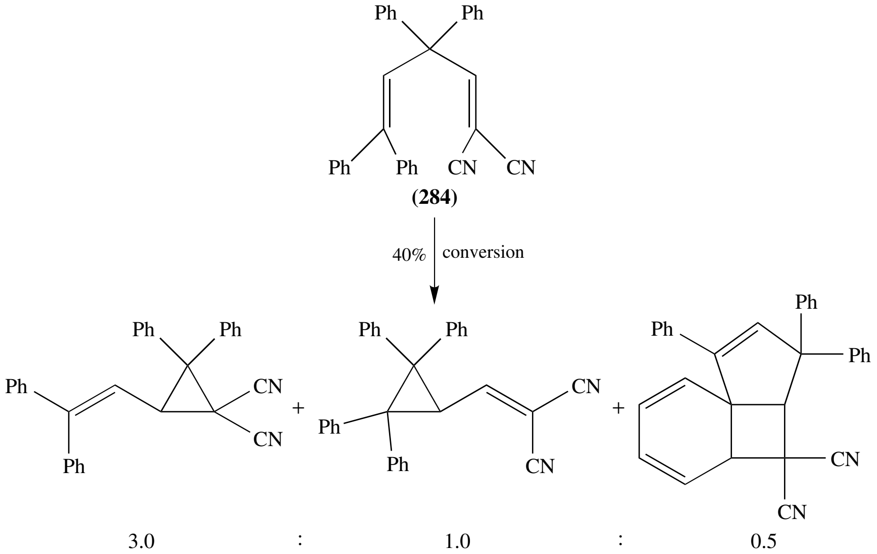
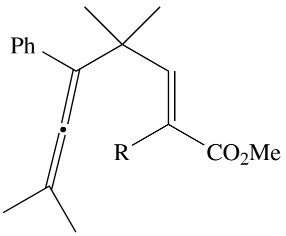
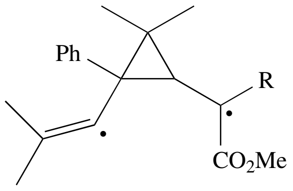


SCHEME 6

Not every 1,4-diene undergoes the di-π-methane rearrangement. In the case of the allenyl alkenes **285** direct irradiation at 254 nm in hexane excites the molecule to its triplet state. Bridging within this affords the intermediate 1,4-biradical **286**. Bond formation then yields the major products **287**, a housane and **288**. The latter compound is formed by trapping within the biradical, using an ester function. Minor products are also formed. Irradiation at $\lambda > 280$ nm fails to yield products. However, acetophenone sensitization is effective[157]. A housane derivative **289** is also formed in 53% yield on irradiation of **290** using acetone sensitization. Interestingly, in this example there is competition from a di-π-methane process that gives a low yield of the cyclopropane **291**[158]. The ring-opening of the bridging 1,4-biradical in this example follows the normal path to yield the more heavily substituted 1,3-biradical prior to the formation of **291**.



(285) **(a)** R = CO$_2$Me
(b) R = H



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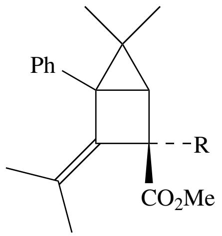
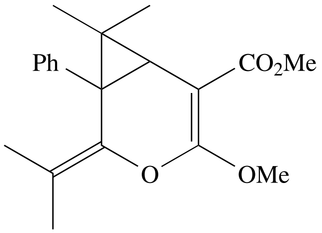
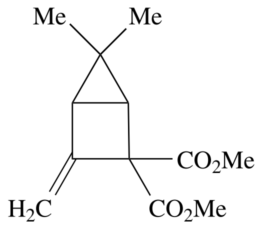


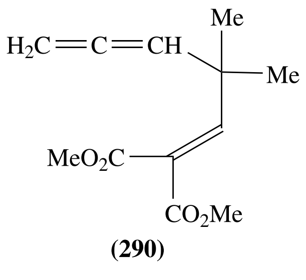
(287) **(a)** 15%
(b) 25%



(288) **(a)** 18%
(b) 15%



(289)



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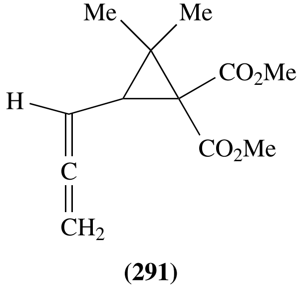
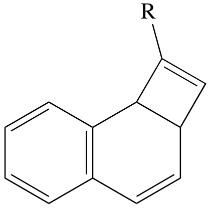


(291)

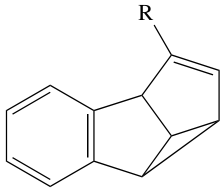
B. Cyclic Systems

1. Benzotrienes

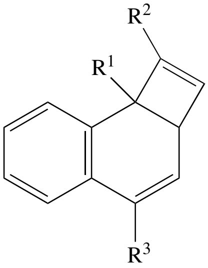
The benzotrienes **292** and **293**, which have the di-π-methane 1,4-diene system, are both photochemically and thermally reactive. Irradiation of **292** under either direct or sensitized conditions results in the formation of the semibullvalene **294** in 46% and 45% yield, respectively. This product arises by a di-π-methane process in either the singlet or triplet excited states. The involvement of such a reaction has been proven by the use of suitable labelled compounds. Other products, isomeric benzocyclooctatetraenes and naphthalene, are also formed[159]. Like the methyl analogue the parent **293** is also photochemically reactive on both direct (wavelengths >280 nm) or sensitized (p-dimethylaminobenzophenone using wavelengths >345 nm) irradiation. The quantum yields for the formation of the semibullvalene **295** are 0.069 on direct irradiation and 0.082 for the sensitized approach. In this instance the authors[160] have shown that the semibullvalene formed on direct irradiation is obtained by two reaction paths, a 1,2-shift process in competition with a di-π-methane rearrangement, in a ratio of 17 : 83. The triplet process leading to **295** occurs exclusively by the di-π-methane reaction path. Semibullvalene products are also formed on irradiation of the cyano-substituted dienes **296**. Direct irradiation of **296a** gives the semibullvalene **297** in 55%. Sensitized irradiation is also effective and yields a mixture of the same semibullvalene **297** in 78% and the isomer **298** in 7%[161]. Direct or sensitized



(292) R = Me
(293) R = H

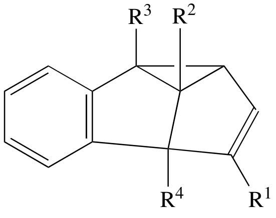


(294) R = Me
(295) R = H



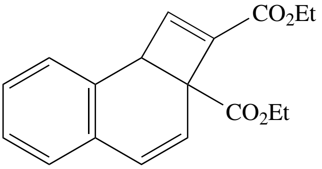
(296)

	R^1	R^2	R^3
(a)	H	CN	CN
(b)	CH	H	CN
(c)	CN	H	H

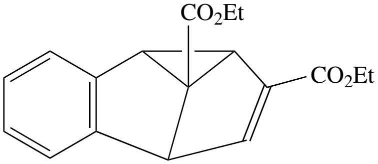


	R^1	R^2	R^3	R^4
(297)	CN	H	H	H
(298)	H	CN	H	H
(299)	H	H	CN	H
(300)	H	H	H	CN

irradiation of **296b** affords the semibullvalene **299** as the main product (63% direct, 30% sensitized). Again, in this example the route to the semibullvalene is different, depending on which irradiation mode is employed. Labelling studies have provided evidence for this divergence of reaction path. Direct irradiation involves a 1,2-shift path while sensitization utilizes only the di-π-methane path[162]. The corresponding semibullvalene **300** is obtained from irradiation of **296c** but only in 5% yield. Again the dual paths to this have been demonstrated to be operative[163]. The ester-substituted derivatives, e.g. **301**, are also photochemically reactive and follow the di-π-methane rearrangement path to afford the semibullvalene **302**[164].



(301)



(302)

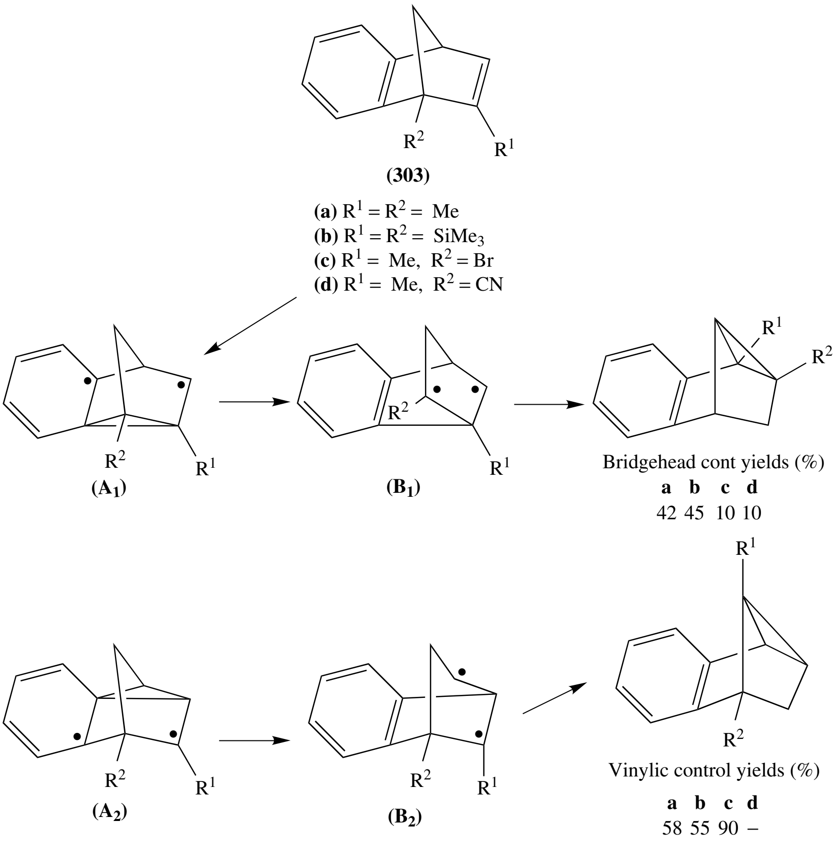
2. Benzonorbornadienes

The di-π-methane rearrangement is also operative within the benzonorbornadiene system. In these cases the interaction within the excited state will involve the vinyl group and the benzo moiety. Considerable detail has been recorded for the rearrangement of such systems such as the triplet state reactivity of the derivatives **303**. This work focused upon the influence of the bridgehead substituents on the outcome of the reactions and the control that these substituents have on the stability of the radicals formed on excitation. The result indicate that there is either bridgehead (intermediates $\mathbf{A}_1$ and $\mathbf{B}_1$) or vinylic control (intermediates $\mathbf{A}_2$ and $\mathbf{B}_2$) and the results are shown in Scheme 7[165]. Both acetone and acetophenone sensitization as well as direct irradiation bring about the cyclizations of **304**. The triplet state processes are more efficient. The reactions encountered show some regiospecificity, as illustrated by the transformation of **304a–c** quantitatively into **305**. Only with **304d** is a mixture of products **305d** and **306d** obtained. The influence of substituents within this system is also evidenced by the fact that some derivatives are unreactive or poorly reactive, as in **307**[166]. Other studies have also examined the influence on the outcome of the reaction of the inclusion of substituents within the arene ring, in this instance a pyridine group. Again, the ratio of products obtained appears to be dependent upon the nature of the substituents and perhaps also on the stability that these exercise on the biradical intermediates (Schemes 8 and 9)[167].

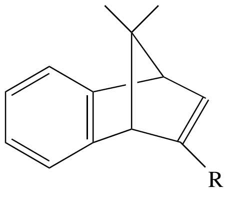
In more recent times interest has been shown in the effects of constrained environment on the outcome of such reactions. Some enantioselectivity in the product **308** has been reported following the irradiation of benzonorbornadiene **309** in a TlY zeolite. (−)-Ephedrine was used as the chiral inductor and sensitization brought about the reaction in 30 min. An ee of about 14% was obtained[168].

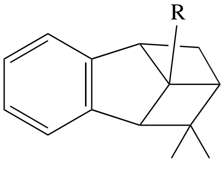
3. Bicyclo[2.2.2]octadienes

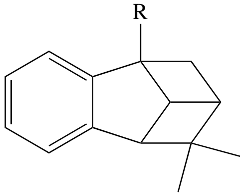
The increase in ring size from the norbornadiene-type to bicyclo[2.2.2]octadiene systems appears not to affect the overall reaction outcome. Again the interaction involves



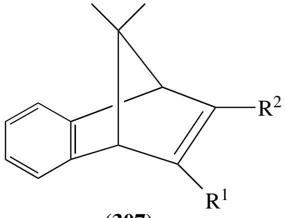
SCHEME 7





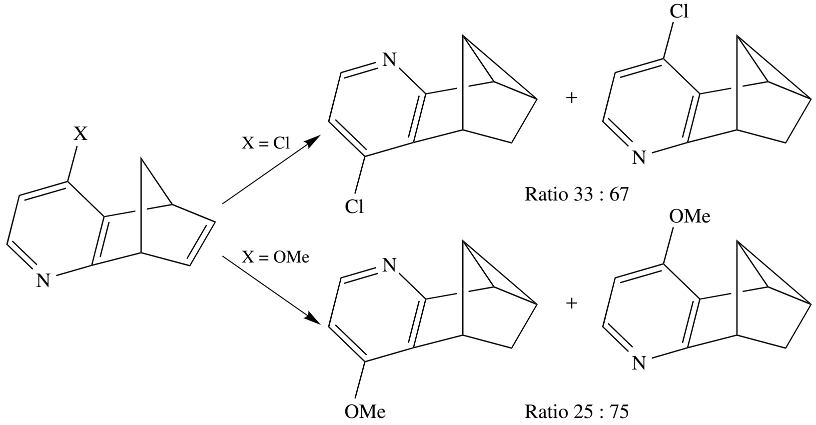


(304)	**(305)**	**(306)**
(a) R = CN	**(a)** 100 %	**(a)** —
(b) R = MeO	**(b)** 100 %	**(b)** —
(c) R = CO_2Me	**(c)** 100 %	**(c)** —
(d) R = Me	**(d)** 70 %	**(d)** 30%



(307)

R^1	R^2
Cl	H
CN	CN
CO_2Me	CO_2Me



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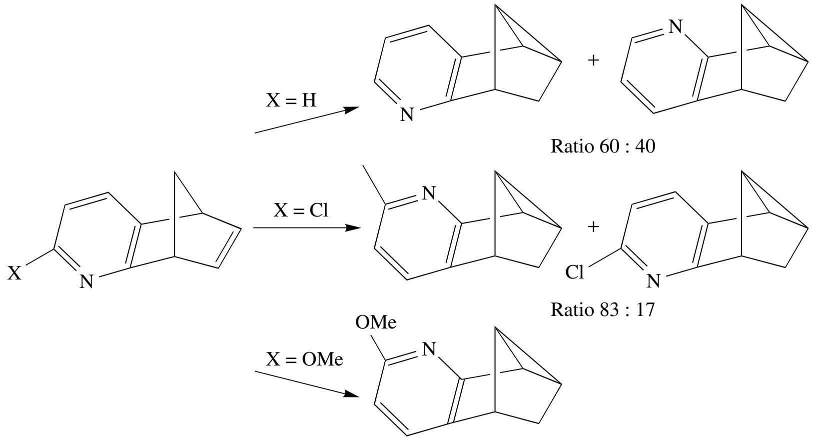
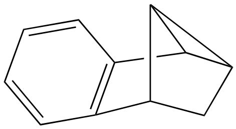


SCHEME 9



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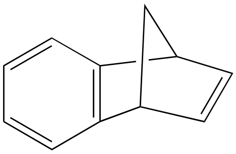
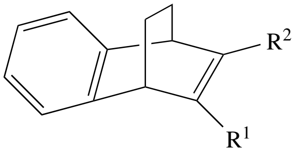


(309)

benzo/vinyl bridging. For example, the derivatives **310** can be effectively cyclized, with some evidence for regiospecificity, into the products **311** and **312**. There is obviously some control upon the reaction from substituents since the derivatives **310** (R^1 = OMe, Cl, CN or CO_2Me, R^2 = H, CN or CO_2Me) fail to cyclize[166].



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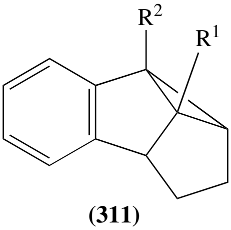

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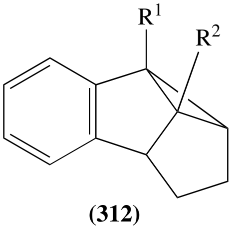
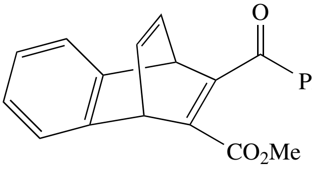


(312)

	R^1	R^2		
(a)	CN	H	**(a)** 100%	**(a)** 0%
(b)	Me	H	**(b)** 73%	**(b)** 27%
(c)	CF_3	H	**(c)** 86%	**(c)** 14%
(d)	Me	Me	**(d)** 50%	**(d)** 50%
(e)	CN	Me	**(e)** 100%	**(e)** 0%

4. Benzobarrelenes

Benzobarrelenes are an important class of molecule where the di-π-methane rearrangement is operative. Clearly, within this class there is a possibility that benzo–vinyl interactions can be in competition with vinyl–vinyl processes. The direct irradiation ($\lambda > 330$ nm) of the benzobarrelene **313** in a variety of solvents (benzene, acetonitrile, methanol or hexane) affords two principal products **314** and **315** in a ratio of 1 : 1. The products are formed via a di-π-methane process involving vinyl–vinyl bridging which



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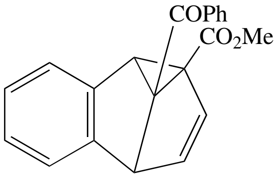

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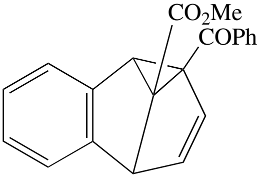
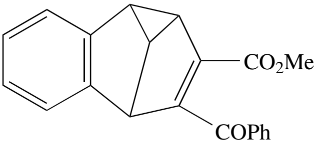


(315)

yields the more stable biradicals. Interestingly, the process is dependent on environment and, in the crystalline phase, different reactions are encountered. Thus, irradiation in the solid state using $\lambda > 290$ nm yields the three products **316**, **317** and **318**, which are produced in ratios of 5 : 3 : 2. The major product again arises by the di-π-methane path but involves less stable biradicals. The involvement of the less stable radicals is thought to be due to topochemical restrictions of molecular movement in the crystalline phase[169]. Not all such systems undergo the di-π-methane rearrangement and this is illustrated in the direct irradiation of **319** in benzene or acetonitrile which affords only a cyclooctatetraene derivative[170,171]. Benzophenone sensitization is required to activate this compound and irradiation under these conditions gives the semibullvalene **320**[172]. Vinyl benzo-bridging is the path followed on direct irradiation of **321** in benzene or acetonitrile. This again yields a 1 : 1 mixture of a cyclooctatetraene and the semibullvalene **322**. The authors[173] suggest that steric influences play a major part in determining the outcome of the reaction. In these examples an unusual example of Me–Me strain relief is operative. Other substituted barrelenes **(323)** are also reported to rearrange readily to the corresponding semibullvalenes[174].



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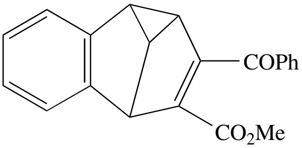

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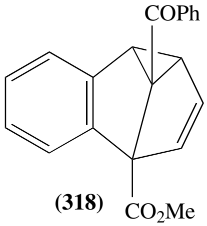

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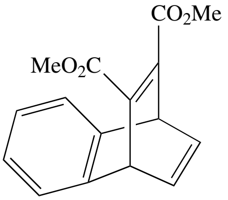

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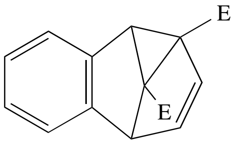
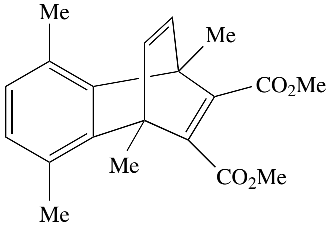


E = CO_2Me

(320)



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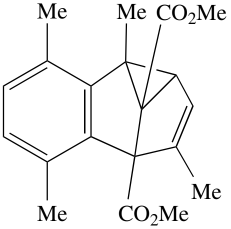

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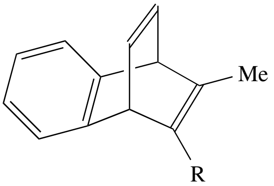
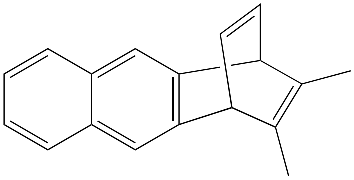


(323)

R = CN, CO_2H or CO_2Me

Vinyl–vinyl bridging reactions are also operative in the barrelene derivatives **324**. The reaction arises from the triplet and is brought about by xanthene sensitizaion[175]. The semibullvalenes **325** and **326** are formed in a ratio of 8.3 : 1 in this rearrangement. Even when hetero-atoms are present, there are some instances when vinyl–vinyl bridging is operative. This is demonstrated by the conversion of **327**, R = H, into **328**. This reaction mode is in competition with the pyrazino–vinyl bridging path that yields **329**, R = H, and **330**, R = H[176]. Others have also examined the reactivity of such pyrazine derivatives[177]. The pyrazino–vinyl system is an example of the aza-di-π-methane system originally discovered by Armesto and his coworkers and reviewed recently by Zimmerman and Armesto[148].



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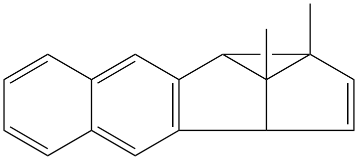

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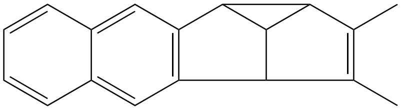

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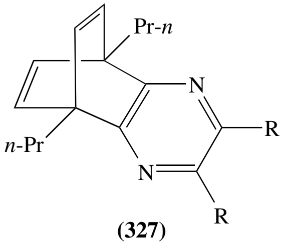

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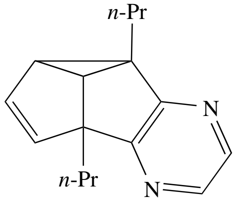

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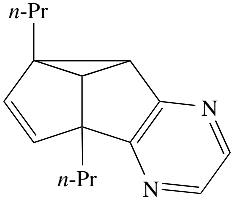

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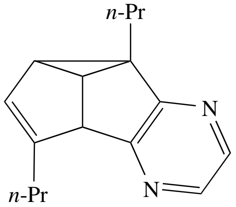
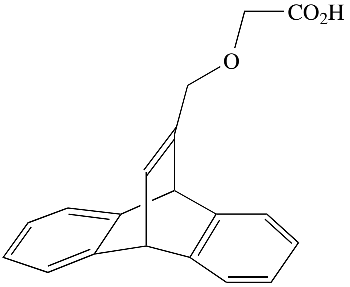


(330)

5. Dibenzobarrelenes

The influence of radical stabilization on the outcome of the rearrangement reactions of a variety of dibenzobarrelenes has been evaluated[178]. A detailed analysis of the acetophenone-sensitized conversion of the cyano-substituted barrelenes into the corresponding semibullvalenes has been presented[179]. The outcome of the irradiation of the dibenzobarrelene **331** is dependent upon the excited state involved. Thus direct irradiation affords a cyclooctatetraene and sensitized irradiation converts it into the two semibullvalene derivatives **332** and **333** in a ratio of 3 : 1[180]. The diol **334** can be photochemically converted (by irradiation at 254 nm) into the semibullvalene **335** in ethanol solution. Acetone sensitization is also effective, affording the same product[181].



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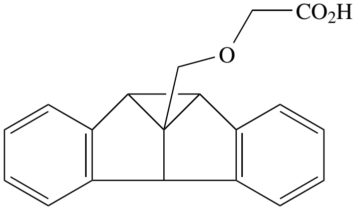

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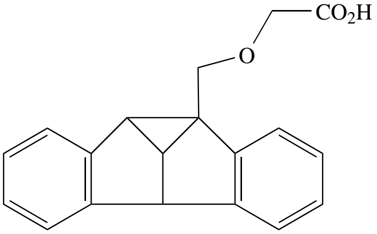

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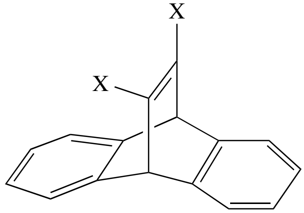
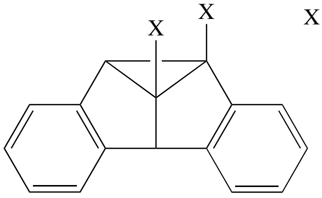


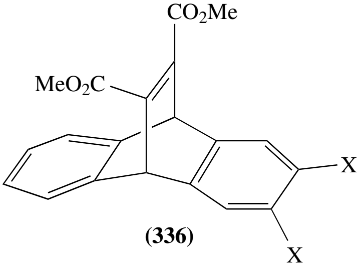
(334)

X = C(OH)Ph_2



(335)

The di-π-methane rearrangement of **336** arises from both the singlet and the triplet excited states and affords the regioisomeric products **337** and **338**[182]. The influence of substituents on the di-π-methane rearrangement of the dibenzobarrelene **339** has been studied. All the compounds undergo photoconversion into the corresponding dibenzosemibullvalenes. Where the substituents on the ester groups were different, two regioisomeric paths were observed[183]. Previous studies on the photochemical rearrangement of the dibenzobarrelene **340** had shown that acetone-sensitization affords the two products **341** and **342** by way of the two possible biradicals formed by benzo–vinyl bridging[184]. Other more heavily substituted derivatives **343** have also been studied and both direct irradiation and acetone sensitization affords the di-π-methane product **344**[185]. Variations in the substituents do not appear to affect adversely the outcome of the reaction. Thus the irradiation of **345**, as a solution in deuteriochloroform, brings about efficient di-π-methane rearrangement, $\phi = 0.28$, affording the corresponding semibullvalene[186]. Demuth and his coworkers[187] have described the design of a 'solar' reactor for carrying out photochemical reactions. The reaction demonstrated is the *p*-hydroxyacetophenone sensitized conversion of the barrelene derivative **346** into **347**. IR studies of **348**, show that hydrogen-bonded structures, both monomeric and dimeric, are present. In non-polar solvents irradiation of **348** afforded two products, **349** and **350**, in a ratio of 4 : 1 formed by a di-π-methane rearrangement. The ratio of the products from the irradiation are in accord with the ratio of the hydrogen-bonded species detected in the IR work[188]. Scheffer and coworkers[189] have also studied the di-π-methane reactivity of a series of dibenzobarrelenes in an attempt at establishing the features which controlled the regiospecificity of the conversion into semibullvalene derivatives. Associated with this they[190] have demonstrated with some molecules, e.g. **351**, that only one product **(352)** is obtained. When substituents are introduced into the lactone ring, as in **353**, only two photo-products **354** and **355** are obtained. From these results the authors[189,190] reason that the relief of steric crowding is the principal factor governing regioselectivity in such transformations.



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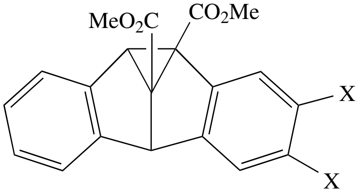
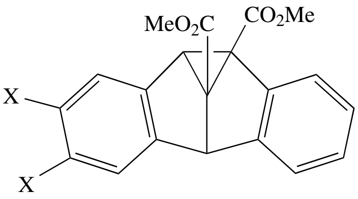


(337)

X = alkyl



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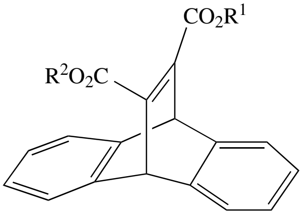

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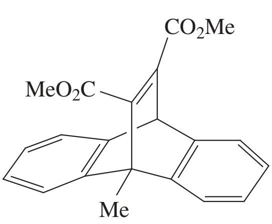

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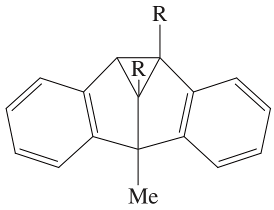
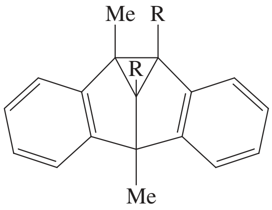


(341)

R = CO_2Me



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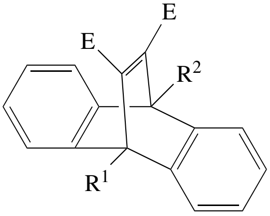

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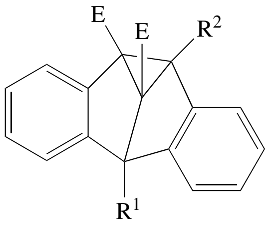

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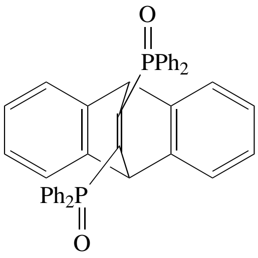
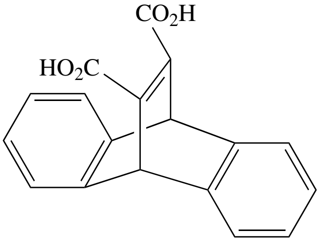


(345)

(a) $E = CO_2Me$, $R^1 = R^2 = Me$
(b) $E = CO_2Me$, $R^1 = Me$, $R^2 = Ph$
(c) $E = CO_2Me$, $R^1 = Ph$, $R^2 = H$



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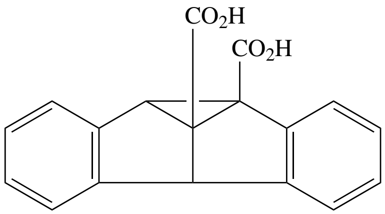

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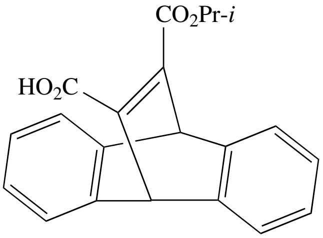

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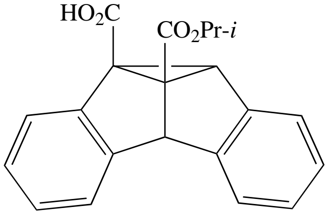

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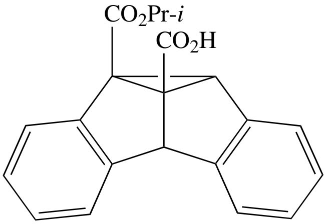

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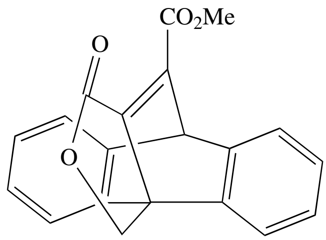

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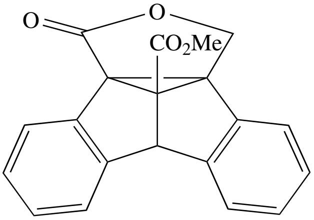

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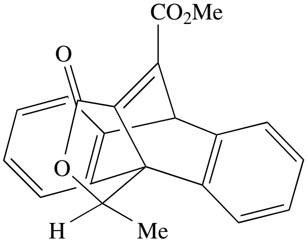

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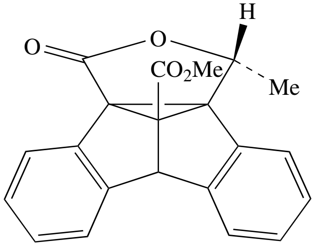

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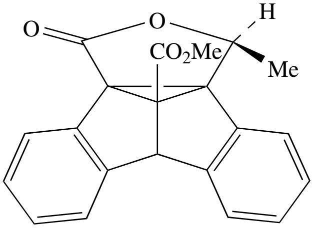
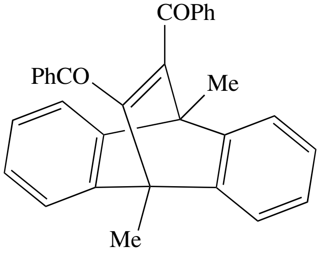


(355)

In some instances the semibullvalene product is not isolated and alternative routes are operative. Related to this is the work of George and his coworkers[191] who reported the results of the irradiation of the dibenzobarrelene **356**. The original structural assignments were shown to be incorrect by Scheffer and his coworkers[192]. A reinvestigation has shown that the products from the reaction are a cyclooctatetraene, and the products **357** and **358**[193]. The compound **358** is formed by a secondary photo reaction: **356** is converted into the usual semibullvalene product. Thus, under the conditions of the reaction it undergoes bond fission. Trapping of the resultant biradicals by oxygen eventually results in the production of the isolated product **358**. The transformation arises by way of a semibullvalene derivative involving the di-π-methane transformation of the starting material. A further example of such a process is shown in the steady state and laser-flash photolysis of the barrelene derivative **359**. Irradiation of this in a variety of solvents (benzene, acetone or methanol) results in its efficient conversion (70%) into the dibenzopentalene ketone **360**[194].



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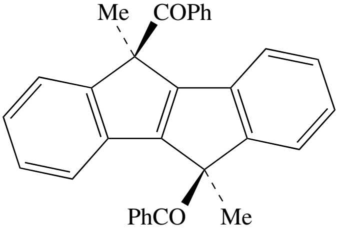

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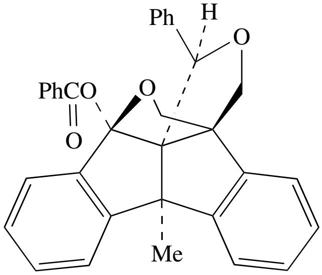

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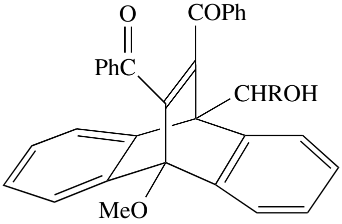
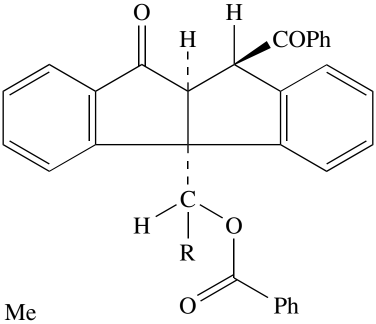


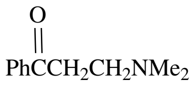
(359)

R = H or Me



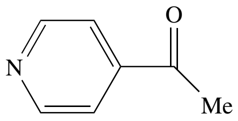
(360)

a. Phase effects. Considerable interest has been shown in the influence of phase on the outcome of the irradiation of dibenzobarrelene derivatives. For example, the ammonium salts of the acid function of **331**, using the amines **361**, **362** and **363**, have been used to study triplet energy transfer in the solid state. Under these conditions the amine groups were irradiated specifically (at $\lambda > 330$ nm) and gave only the two semibullvalenes **332** and **333** with no evidence for the formation of the cyclooctatetraene that is formed from the singlet state. The semibullvalenes were obtained in ratios of 6 : 1, 5 : 1 and 15 : 4, respectively. This is indicative of triplet energy transfer within the solid state[180]. In another example crystals of **334** were shown to have close interactions of the hydroxy groups. Irradiation in the solid resulted in the suppression of the di-π-methane process and intramolecular proton transfer results in the formation of the ether **364**[181]. Other detailed studies have shown that a variety of paths can be operative in the crystalline phase. In this regard an analysis has indicated that the photochemical cyclization of the dibenzobarrelene **365** to the semibullvalene **366** can occur by four possible paths only involving vinyl/benzo bridging. These paths are bridging between carbons 9a and 11 and between 4a and 12 on one side of the molecule, and between 8a and 11 and 10a and 12. It is possible to differentiate between paths by determining the absolute configuration in the reactant crystal. The crystal of the barrelene **365** is homochiral and irradiation in the solid gives laevorotatory **366**. This means that there is a preference for the path using 9a/11or 10a/12 interaction. It is argued that within this pair of routes the interaction between 10a/12 is favoured[195]. Dibenzobarrelene **343a** also shows different reactivity in the crystalline phase. Irradiation does afford the same semibullvalene **344** as is obtained from the solution-phase reaction, but a new product **367** is also obtained. This is reminiscent of the reactivity of **356** previously mentioned. A re-investigation of this has suggested that the biradical **368** is involved in the formation of this new product. The formation of the biradical such as **368** must involve a possible tri-π-methane intermediate **369**[185].



$\mathrm{Ph\overset{\overset{O}{\|}}{C}CH_2CH_2NMe_2}$

(361)



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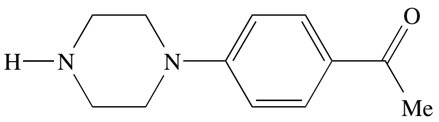

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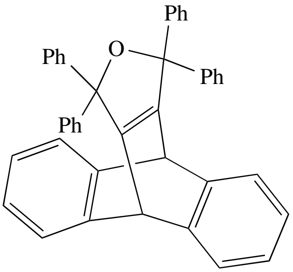

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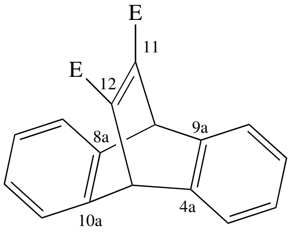
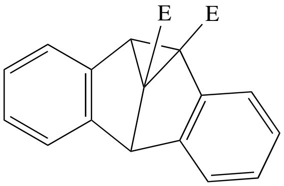


(365) E = CO_2Pr-*i*



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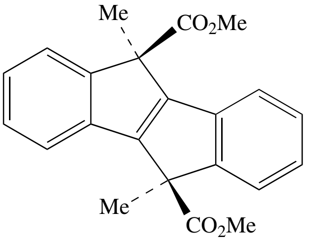

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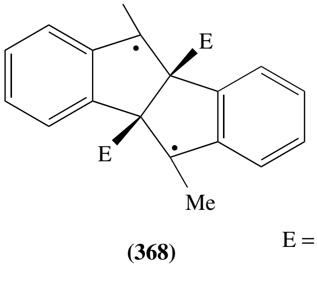
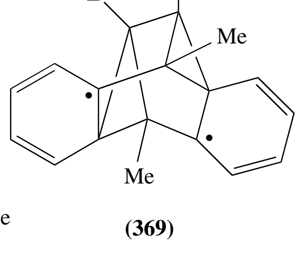


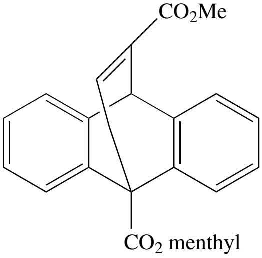
(368)

E = CO_2Me



(369)

Asymmetric induction in the di-π-methane rearrangement is also of interest and studies on this have examined the influence of chiral esters. Thus the irradiation of **370** yields a cyclooctatetraene **371** and a diastereoisomeric mixture of the semibullvalenes **372** and **373** in a ratio of 60 : 40 in solution and 20 : 80 in the solid phase. The position of attachment is vital and the diastereoselectivity shown by the barrelene **374** is very poor and yields a 1 : 1 mixture of products[196]. Further examples of the control exercised when dibenzobarrelenes are irradiated in the crystalline phase have used the derivatives **375** and **376** as the acid salts formed with chiral amines. Irradiation affords the products **377** and **378** respectively, obtained after esterification with MeOH, with an ee of >95%[197]. The influence of a chiral crystal lattice on the outcome of the di-π-methane reaction of achiral **379** has been studied. The irradiation in the crystalline phase gives two chiral di-π-methane products **380** and **381**. The former of these is racemic but the latter is obtained in high enantiomeric excess which, under the best conditions, i.e. at −20 °C, approaches 100%[198]. The irradiation of crystals of **345**, as an ethanol complex, affords **382** with an ee of 94%. Carrying out the irradiation at temperatures lower than ambient enhances the specificity of the reaction[186].



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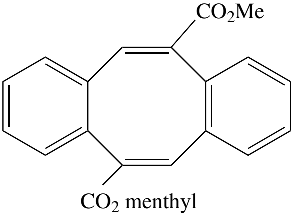

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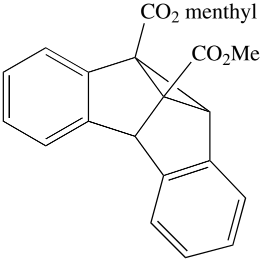

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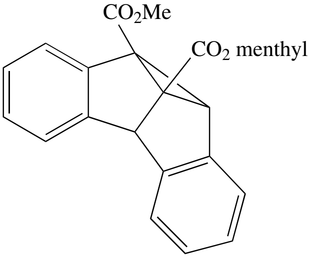

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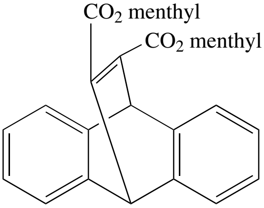

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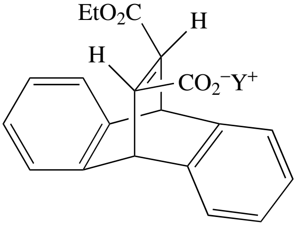

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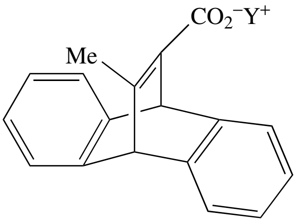

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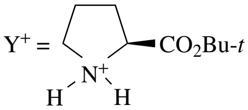

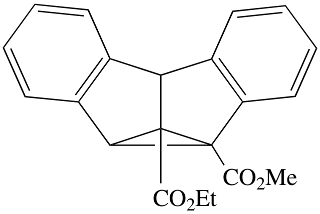

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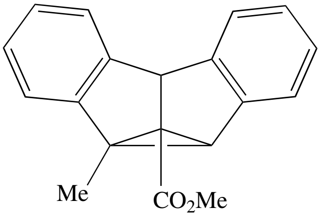

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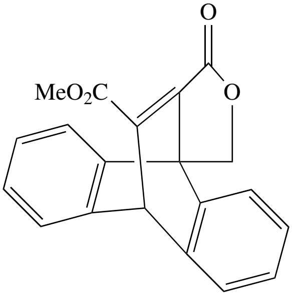

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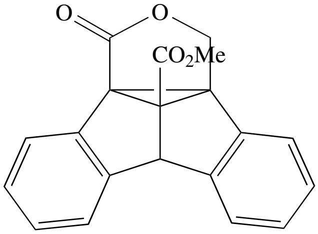

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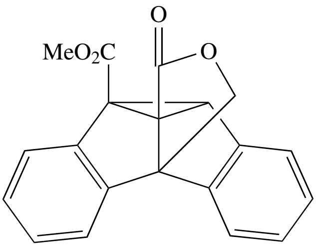

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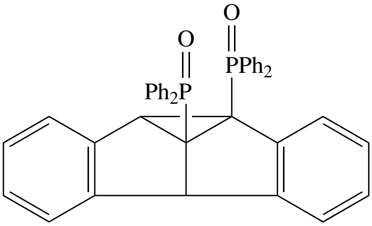
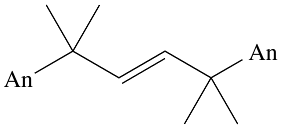


(382)

6. Other systems undergoing the di-π-methane rearrangement

a. All-carbon systems. The triplet state of **383** is also reactive by the di-π-methane rearrangement yielding **384**. This involves an aryl/vinyl bridging reaction. Direct irradiation has a completely different outcome and yields four products that are probably formed by secondary reaction of the cyclopropane **384**[199]. A vinyl–aryl interaction is also found in the irradiation of the alkenes **385** under nitrogen in benzene and results in the formation of the cyclopropanes **386**[200]. Both direct and sensitized irradiation of the biphenylylbutene **387** brings about the formation of the cyclopropane **388** with a quantum yield of 7.6×10^{-3}. The authors[201] suggest that the low reactivity of this substrate in the di-π-methane rearrangement is a result of localization of the excitation energy within the biphenyl moiety. The irradiation of the alkene **389** affords the cyclopropanol **390** by a di-π-methane rearrangement. The dienol **391** is also reactive in this mode and affords the isomeric cyclopropanes **392**[202].



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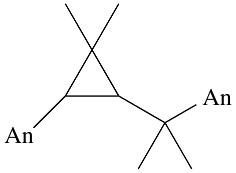
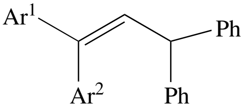


(384)

An = p-MeOC$_6$H$_4$



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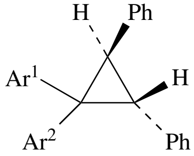
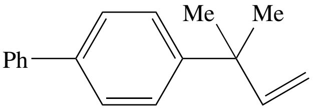


(386)

Ar^1 = Ar^2 = Ph
Ar^1 = p-tolyl, Ar^2 = Ph
Ar^1 = Ar^2 = p-tolyl
Ar^1 = p-MeOC$_6$H$_4$, Ar^2 = Ph
Ar^1 = Ar^2 = p-MeOC$_6$H$_4$



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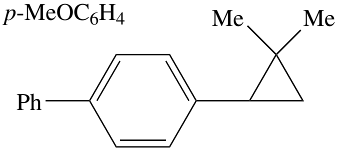
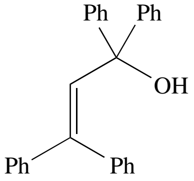


(388)

As pointed out earlier, there is a growing interest in the control that can be exercised on the reactions of molecules constrained within the solid state. The previous focus on this dealt with rearrangements of dibenzobarrelenes, but control has also been demonstrated for open-chain systems. This has been shown by Demuth and his coworkers[203] in a study



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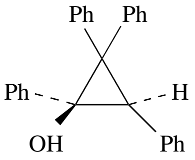

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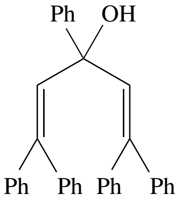

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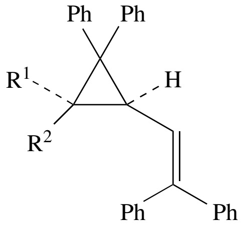
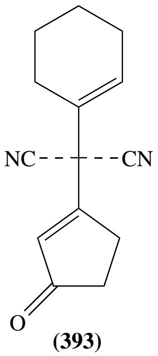


(392)

$R^1 = Ph, R^2 = OH$
or *vice versa*

of the homochiral crystals of the enone **393**. This is converted into the two products, **394** with 44% ee and **395** with 96% ee. Here again the outcome of the reaction is dependent on the amount of available space within the crystal. X-ray analysis has shown that there is more movement for the cyclohexene moiety in the crystal than there is for the cyclopentenone and it is this which controls the stereochemical outcome of the reaction. In solution phase, other enone systems such as **396** are also reactive. This undergoes di-π-methane rearrangement into the two products **397** and **398**[204]. The related furanone **399** is also reactive and is converted into the cyclopropane derivative **400**. The route to this product involves the biradical **401**; bond-breaking brings about re-aromatization and the formation of a primary radical[205]. The cyclic-1,4-dienes **402** all undergo the di-π-methane rearrangement affording bicyclic products, as illustrated for **402a** in Scheme 10[206].



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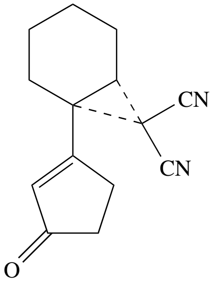

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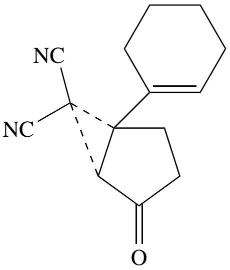

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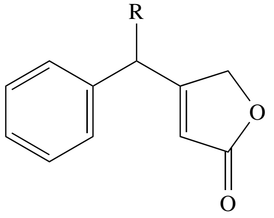
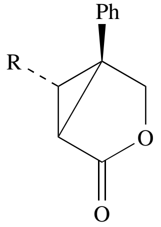
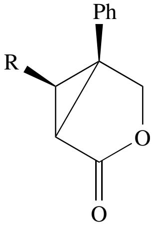


(**396**)

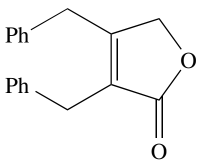


(**397**)

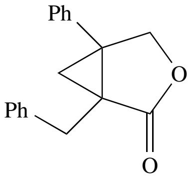


(**398**)

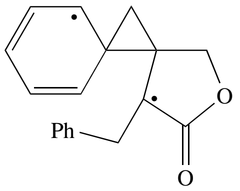
R = Me, Ph or cyclohexyl



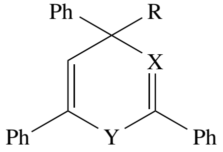
(**399**)



(**400**)

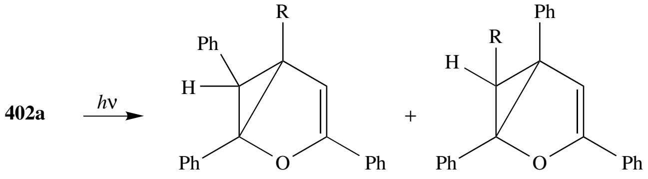


(**401**)



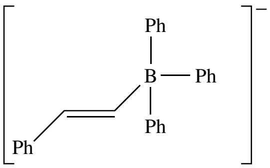
(**402**)

(**a**) X = CH, Y = O, R = Ph, 4-BrC$_6$H$_4$ or 4-MeC$_6$H$_4$
(**b**) X = CH, Y = S, R = Ph, 4-BrC$_6$H$_4$ or Me
(**c**) X = N, Y = O, R = Ph

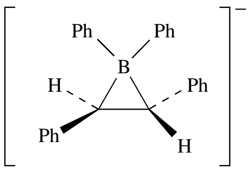


SCHEME 10

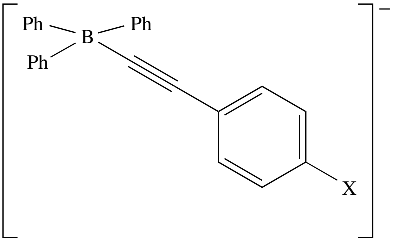
b. Hetero-di-π-methane systems. The di-π-borate process has also been investigated. This concerns the conversion of **403** into **404** by direct irradiation at 254 nm. The reaction is efficient and involves a vinyl–phenyl interaction, similar to that encountered in the all-carbon system. The product **404** is formed in a reasonable yield of 60%[207]. An alkynyl–phenyl interaction is also observed in the photochemical conversion of the ethynyltriphenyl borate salts **405** which undergo the rearrangement to yield unstable cyclopropene derivatives **406**[208–210]. Earlier studies had suggested that the irradiation of such compounds gave only *cis*-stilbene and biphenyl[211]. Phenyl–phenyl bridging is also possible as in the conversion of **407** into **408**[212]. A review has highlighted aspects of the photochemical behaviour of unsaturated borane chemistry[213].



(**403**)

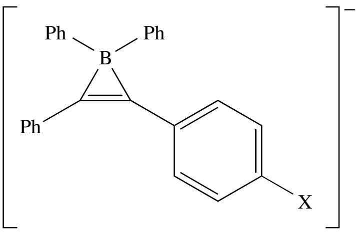


(**404**)

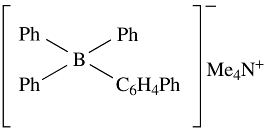


(**405**)

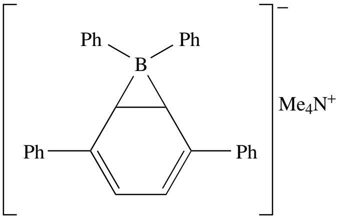
X = H, F or MeO



(**406**)



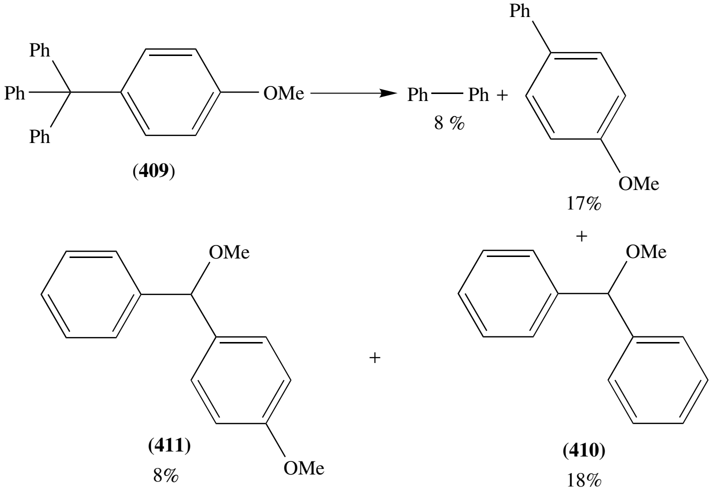
(**407**)



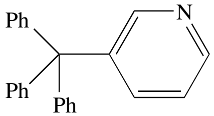
(**408**)

c. Triphenylmethyl derivatives. Phenyl–phenyl interactions are also the key processes in the photochemical rearrangements encountered with the tetraarylmethane derivatives such as **409**. As can be seen from Scheme 11, a variety of products are obtained on irradiation, usually in methanol as solvent and through a quartz filter. Here two types of bridging take place, one between two phenyl groups and one between a phenyl and the *p*-methoxyphenyl group, the di-π-methane type of interaction. Extrusion of the biphenyl moiety affords carbenes that are trapped as the ethers **410** and **411** when the reaction is carried out in methanol[214]. Analogous reactivity has been recorded for the pyridyl derivatives **412**[214], the esters **413**[215] and the phosphonate **414**[216]. The rearrangements within these compounds all involve the di-π-methane rearrangement accounting for the formation of the appropriate biphenyls and derivatives of the carbenes formed on extrusion of the biphenyl moiety. Thus methyl 2-methoxyphenylacetate is the carbene product from reaction of the ester **413**. Similar behaviour is seen on irradiation of the two derivatives **415** and **416** as shown in Schemes 12 and 13[217,218].

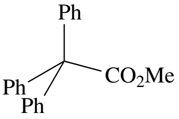
When one of the components of the molecule undergoing reaction is a double bond, an alternative reaction mode is operative. Thus it can be seen that **417** follows the usual path involving aryl–aryl bridging affording biphenyl and a carbene that is trapped by solvent. However, in addition a vinyl–aryl di-π-methane process is also operative and affords the



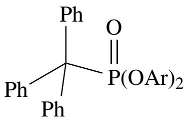
SCHEME 11



(412)

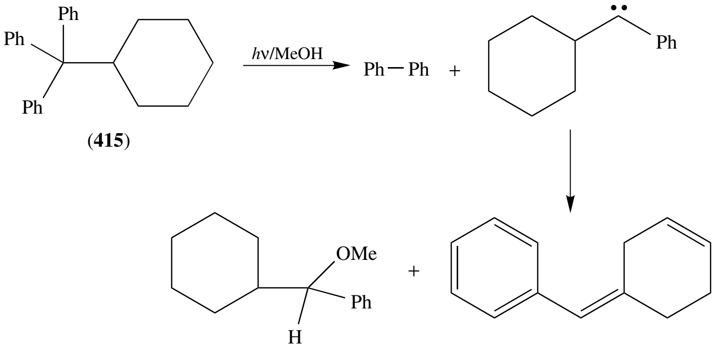


(413)



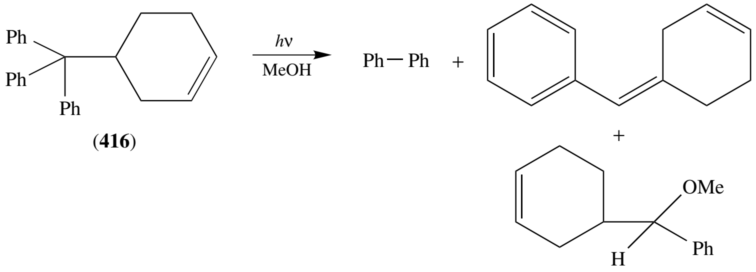
(414)

Ar = p-XC_6H_4, X = Me, MeO, Cl



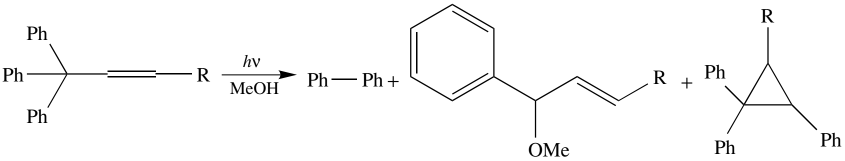
SCHEME 12

cyclopropanes **418** (Scheme 14)[219,220]. Shi and coworkers[221] have also reported the photochemical conversion of the alkyne **419a** into biphenyl and its derivatives (Scheme 15). The reaction is brought about by irradiation under argon in methanol solution. Again the reaction is a typical aryl–aryl di-π-methane interaction. It has been suggested that the proposed bridged intermediate is zwitterionic as shown in **420**. Such a postulate has been substantiated by substituent effects.



(**416**)

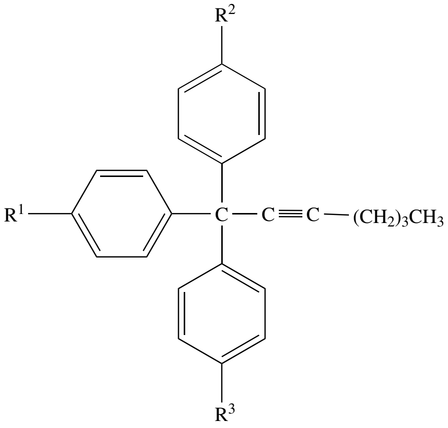
SCHEME 13



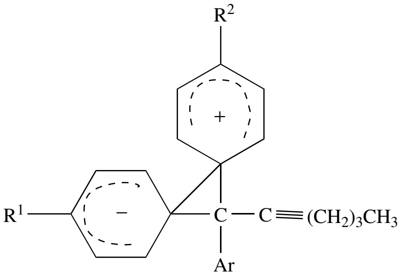
(**417**) (**418**)

R = H	8%	5%	14%
R = Me	16%	15%	8%
R = Et	24%	16%	9%

SCHEME 14

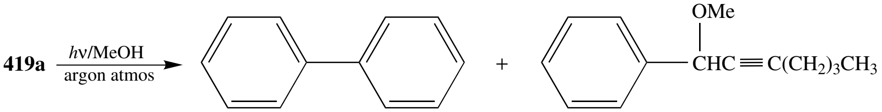


(419)



(420)

(a) $R^1 = R^2 = R^3 = H$
(b) $R^1 = R^2 = H$, $R^3 = Me$
(c) $R^1 = R^2 = R^3 = Me$
(d) $R^1 = R^2 = H$, $R^3 = MeO$
(e) $R^1 = R^2 = R^3 = MeO$



SCHEME 15

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