CHAPTER **19**

Allenyl and polyenyl cations

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I. INTRODUCTION

Allenyl cations **1** are a stabilized form of vinyl cations[1−3] in which the β-carbon atom of the vinylic structure is part of the substituent which effects the stabilization of the ion via its electron-donating ability. This leads to a resonance hybrid having formally the alkynyl cation structure **2**. Allenyl cations should be distinguished from the allenyl substituted carbenium ions **3** formulated as the mesomeric structures of the vinyl cations **4** (dienyl cations) stabilized by an α-vinyl group (equation 1).
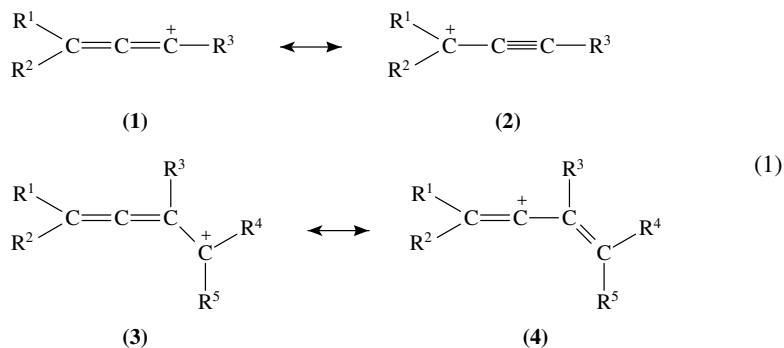
Similar to the allyl cation[4] the stabilization in the allenyl cation **1** occurs by overlap of the incipient vacant p orbital with the allenyl π-system as shown in **5**. The allylic π-orbitals are geometrically constrained to the most favored geometry for overlap with the p orbital due to the orthogonality of the two double bonds and the conjugation is not accompanied by any loss of ground state conjugation.
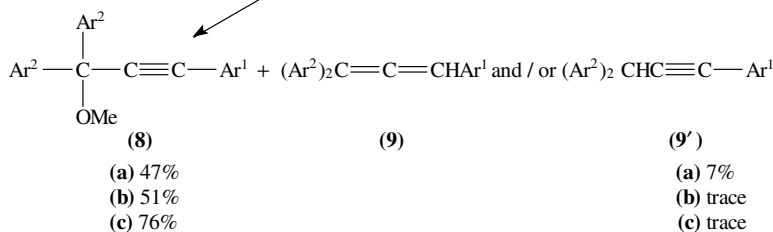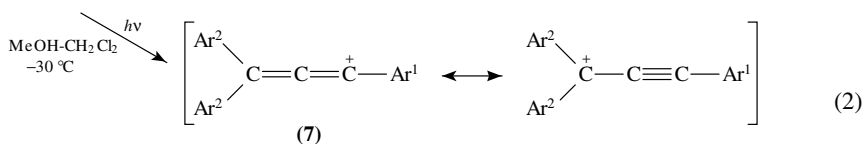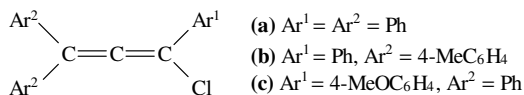

(5)

Allenyl cations have been generated by solvolysis of allenic derivatives, by photolysis of allenyl halides and by reaction of metal salts with allenyl and propargyl halides. This review will delineate these reactions. The related butatrienyl cations are not many and they will be only briefly described.

II. ALLENYL CATIONS

A. Generation by Photolysis

Photolysis of the carbon–halogen bond to give carbenium ions[5,6] has been extended to the formation of vinyl cations by Taniguchi, Kobayashi and coworkers[7]. In this context several chlorotriarylallenes **6** were photolyzed in a mixed solvent system of methanol and dichloromethane[8]. The photolysis was carried out at $-30\,°C$ to prevent a thermal solvolysis of the substrate. The major product of the reaction is the 1,3,3-triaryl-3-methoxypropyne **8** with a small amount of the reduced compounds **9** and/or **9'** as the side product. Photolysis of **6** ($Ar^1 = Ar^2 = Ph$) in ethanol and 2-propanol gave the corresponding 3-alkoxy-1,3,3-triphenylpropynes (**8a**-OEt and **8a**-OPr-i) in 33 and 37% yields, respectively, together with a small amount of the reduced product **9'** ($Ar^2 = Ar^1 = Ph$)[8].

(6)

(a) $Ar^1 = Ar^2 = Ph$
(b) $Ar^1 = Ph,\ Ar^2 = 4\text{-}MeC_6H_4$
(c) $Ar^1 = 4\text{-}MeOC_6H_4,\ Ar^2 = Ph$

(2)

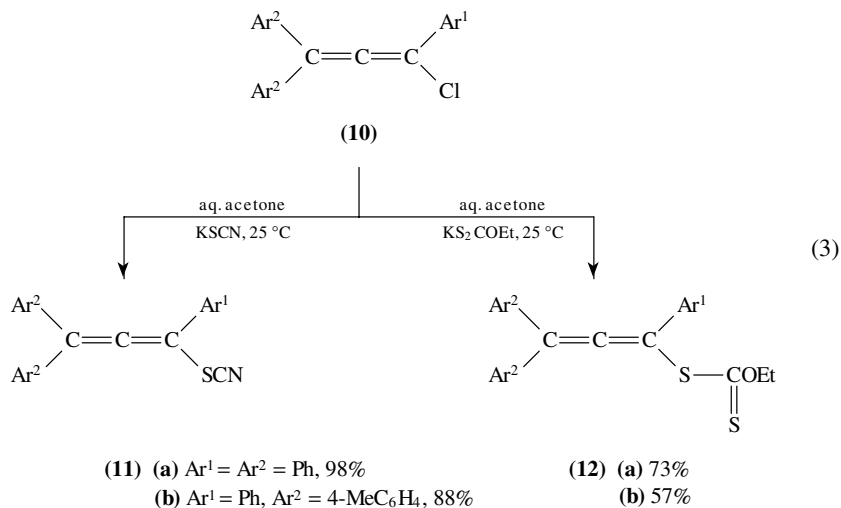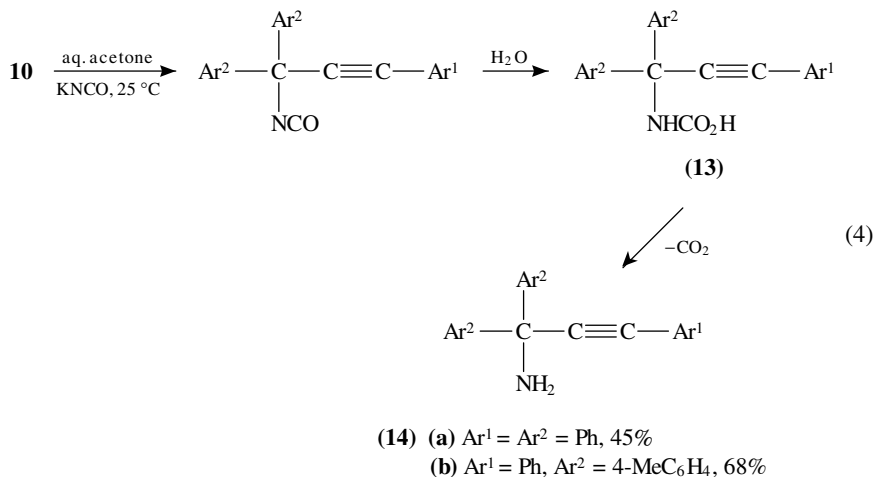|	(8)	(9)	(9')
(a)	47%		7%
(b)	51%		trace
(c)	76%		trace

The formation of solvent-incorporated products **8** suggested that triarylallenyl cations **7** are formed by photolysis of the corresponding chloroallenes **6** (equation 2). However, the products **8** obtained by photolysis were attributed to attack by nucleophiles at γ-positions of the allenyl cation. Although allenyl cations are ambident cations and can produce allenyl or propargyl derivatives by attack at the α- or γ-position, respectively, only γ-attack was observed in this photolysis of triarylchloroallenes. This result is parallel to that observed by Schiavelli and coworkers[9] in the solvolysis of these systems (*vide infra*) which therefore supports the formation of allenyl cations in the photolysis.

B. Generation by Solvolysis

The intermediacy of allenyl cations in the solvolysis of allenic derivatives was first shown by Jacobs and Fenton[10]. However, the main work on the mechanism of the reaction is that of Schiavelli and coworkers[11−17], who showed with the aid of kinetics and substituent, solvent, salt and isotope effects that the reactions proceed via an initial cleavage of the bond to the leaving group with the formation of the allenyl cations **1**. Chlorotriarylallenes have been shown to solvolyze with convenient rates and even a primary allenyl cation was generated solvolytically. Extensive coverage of earlier work on the solvolytic behavior of allenyl systems are given elsewhere[1b−d]. One of the most interesting features is the ambident character of allenyl cations, which can provide, on reaction with a nucleophile, the allenyl and/or propargyl derivatives. However, most work on solvolysis of allenyl halides indicates that nucleophiles attack at the γ-position of the resulting allenyl cations, unless bulky substituents are present on the γ-position[12].
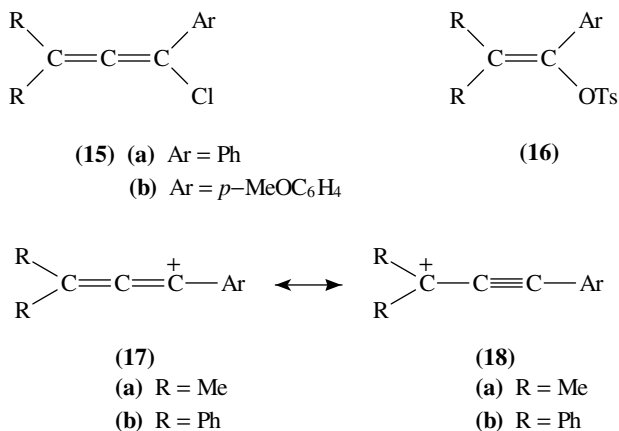
Recently, the solvolyses of 1-chloro-1,3,3-triarylallenes **10** (and of 1-butyl-3,3-diphenyl-allenyl chloride) were carried out in the presence of thiocyanate and *o*-ethyl dithiocarbonate anions as nucleophiles and found to give the corresponding allenyl derivatives **11** and **12** in good yield (equation 3)[18]. However, when potassium cyanate was used as a nucleophile, the cyanate ion attacked at the γ-position to give the propargyl amines **14** after decarboxylation of the unstable intermediate **13** (equation 4).

(3)

(10)

aq. acetone
KSCN, 25 °C

aq. acetone
KS_2COEt, 25 °C

(11) **(a)** $Ar^1 = Ar^2 = Ph$, 98%
(b) $Ar^1 = Ph$, $Ar^2 = 4\text{-MeC}_6H_4$, 88%

(12) **(a)** 73%
(b) 57%

$$\mathbf{10} \xrightarrow[\text{KNCO, 25 °C}]{\text{aq. acetone}} \underset{\underset{\text{NCO}}{|}}{\overset{\overset{\text{Ar}^2}{|}}{\text{Ar}^2-\text{C}-\text{C}\equiv\text{C}-\text{Ar}^1}} \xrightarrow{\text{H}_2\text{O}} \underset{\underset{\text{NHCO}_2\text{H}}{|}}{\overset{\overset{\text{Ar}^2}{|}}{\text{Ar}^2-\text{C}-\text{C}\equiv\text{C}-\text{Ar}^1}}$$

(13)

$\swarrow \quad -\text{CO}_2$ (4)

$$\underset{\underset{\text{NH}_2}{|}}{\overset{\overset{\text{Ar}^2}{|}}{\text{Ar}^2-\text{C}-\text{C}\equiv\text{C}-\text{Ar}^1}}$$

(14) **(a)** $\text{Ar}^1 = \text{Ar}^2 = \text{Ph}$, 45%
          (b) $\text{Ar}^1 = \text{Ph}$, $\text{Ar}^2 = 4\text{-MeC}_6\text{H}_4$, 68%

These results indicate that the reaction outcome can be controlled by the choice of nucleophile. From the kinetic[12] and theoretical[19] (*vide infra*) studies, it is predicted that nucleophiles react at the propargyl position of the allenyl cation. However, when the γ-position bears a sterically hindered substituent, a nucleophile should attack on the allenyl position[13]. Such a steric factor may be also operative for a bulky nucleophile. Among the nucleophiles used, thiocyanate and *o*-ethyl dithiocarbonate anions are larger than cyanate anion because sulfur atom has a much larger van der Waals radius than that of nitrogen or oxygen atom[20]. The larger nucleophile prefers to attack the less sterically congested allenyl position, while the smaller nucleophile prefers the propargyl position, which is more reactive than the allenyl position[12,19].

The kinetic studies on the solvolysis of 1-aryl-1-chloro-3-methylbuta-1,2-dienes (**15**, Ar = Ph, *p*-MeOC$_6$H$_4$) showed that the ρ values ($\rho^+ = -2.8$ in 80% aqueous ethanol and -2.9 in aqueous acetone)[21] are much lower than those of the correspondingly substituted vinyl derivative **16** ($\rho^+ = -4.3$ in aqueous ethanol)[22]. This result indicates that the α-substituent effect in cations **17a** is much smaller than in the vinyl cations, suggesting

$$\underset{\text{R}}{\overset{\text{R}}{>}}\text{C}=\text{C}=\underset{\text{Cl}}{\overset{\text{Ar}}{\text{C}<}} \qquad\qquad \underset{\text{R}}{\overset{\text{R}}{>}}\text{C}=\underset{\text{OTs}}{\overset{\text{Ar}}{\text{C}<}}$$

(15) **(a)** Ar = Ph   **(16)**
          (b) Ar = *p*−MeOC$_6$H$_4$

$$\underset{\text{R}}{\overset{\text{R}}{>}}\text{C}=\text{C}=\overset{+}{\text{C}}-\text{Ar} \quad\longleftrightarrow\quad \underset{\text{R}}{\overset{\text{R}}{>}}\overset{+}{\text{C}}-\text{C}\equiv\text{C}-\text{Ar}$$

(17)   **(18)**
(a) R = Me   **(a)** R = Me
**(b)** R = Ph   **(b)** R = Ph

that the contribution of the propargyl structure **18a** in the transition state is important. Furthermore, from these values and comparison of the *m* values (0.88 in aqueous EtOH) for the chloroallene **15a** and the ρ values of the 1-chloro-1,3,3-triarylallenes **10** ($\rho^+ = -2.0$ in aqueous acetone)[10], it was concluded that in the 1-aryl-3,3-dimethyl-substituted allenyl derivative **15** (R = Me) the contribution of the propargyl structure **18a** is greater in the transition state in comparison with the allenyl structure **17a**.

Reaction of 1-chloro-1,3,3-triphenylallene (**19**) with *p*-toluidine in the presence of silver triflate gave 2,3,4-triphenylbuta-1-aza-1,3-diene derivative **22a** via a novel 1,2-phenyl shift not reported earlier in the solvolysis of allenyl chlorides[23]. The reaction takes place via the formation of the allenyl cation, which is captured as its canonical propargyl cation, first affording the protonated amine **20** (R = Me). Proton transfer[24] from the nitrogen to the acetylenic carbon is followed by migration of a phenyl group in the intermediate vinyl cation **21** (R = Me) to afford the iminium triflate **22a**. The latter is hydrolyzed by aqueous sodium hydroxide to the azabutadiene **23** (equation 5). Similar reaction of **19** with aniline and silver triflate afforded the corresponding iminium triflate **22b**[23].
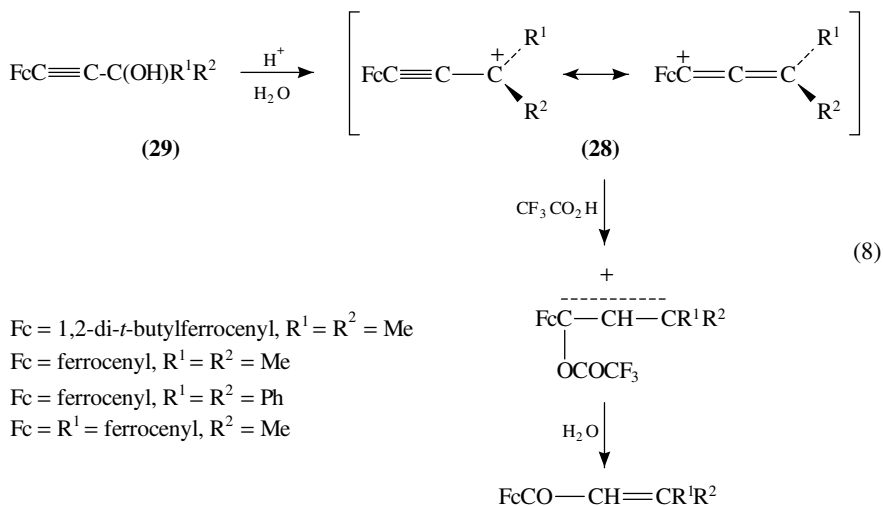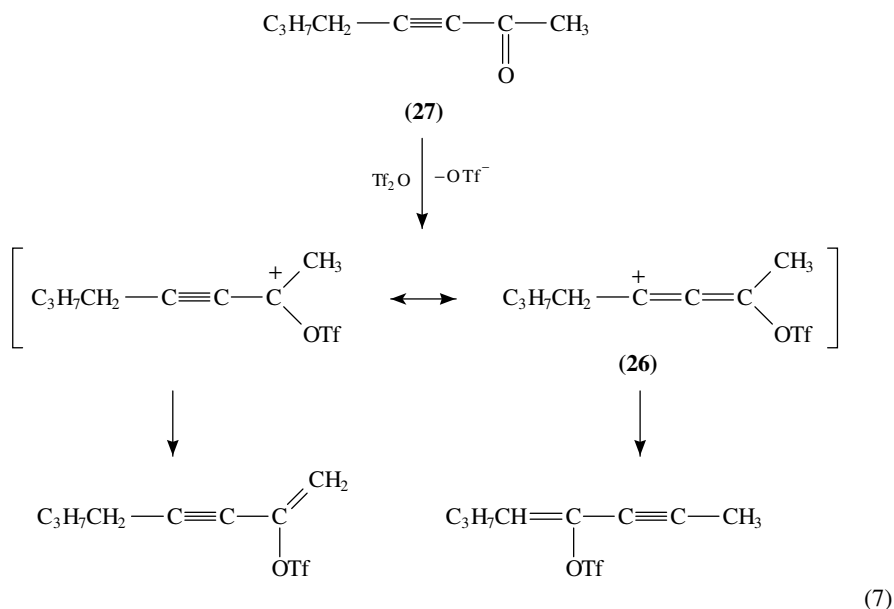

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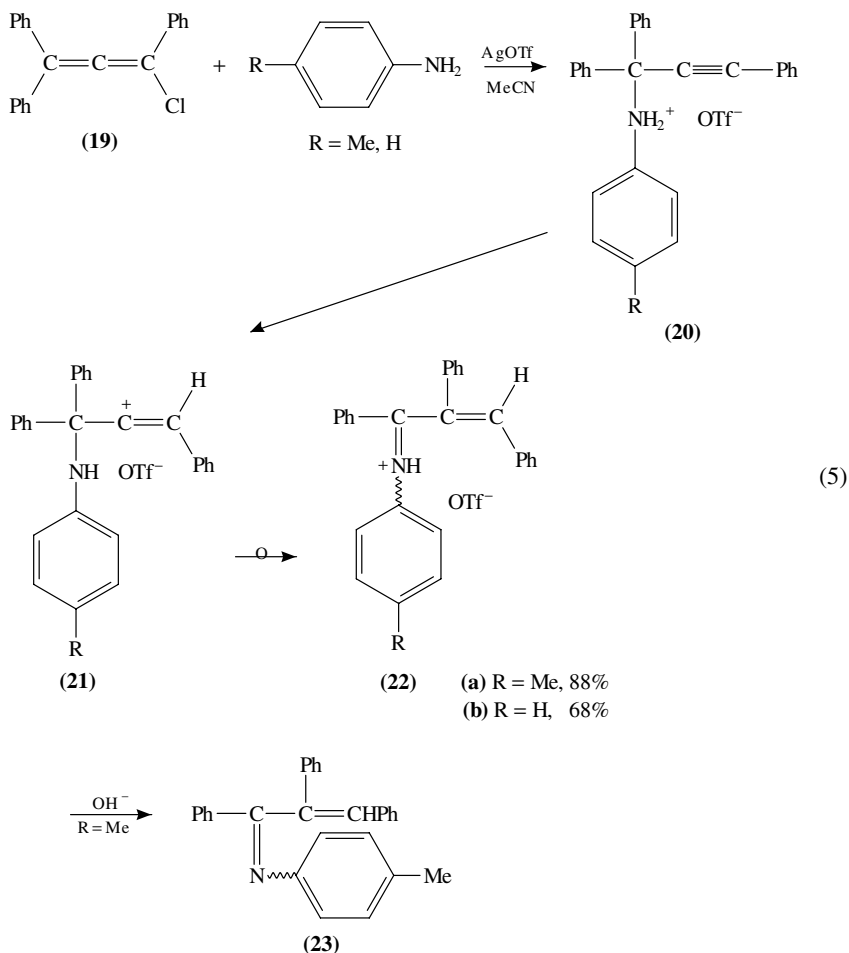
Solvolysis of the propargyl chlorides *E*- and *Z*-**24** (stereochemistry based on Cl and Ph[25]) in 80% aqueous ethanol at 50 °C gave, besides the corresponding solvent captured substituted propargyl products, the allenyl chlorides *E*- and *Z*-**25** formed with complete retention via the allenyl cation intermediate (equation 6)[25].
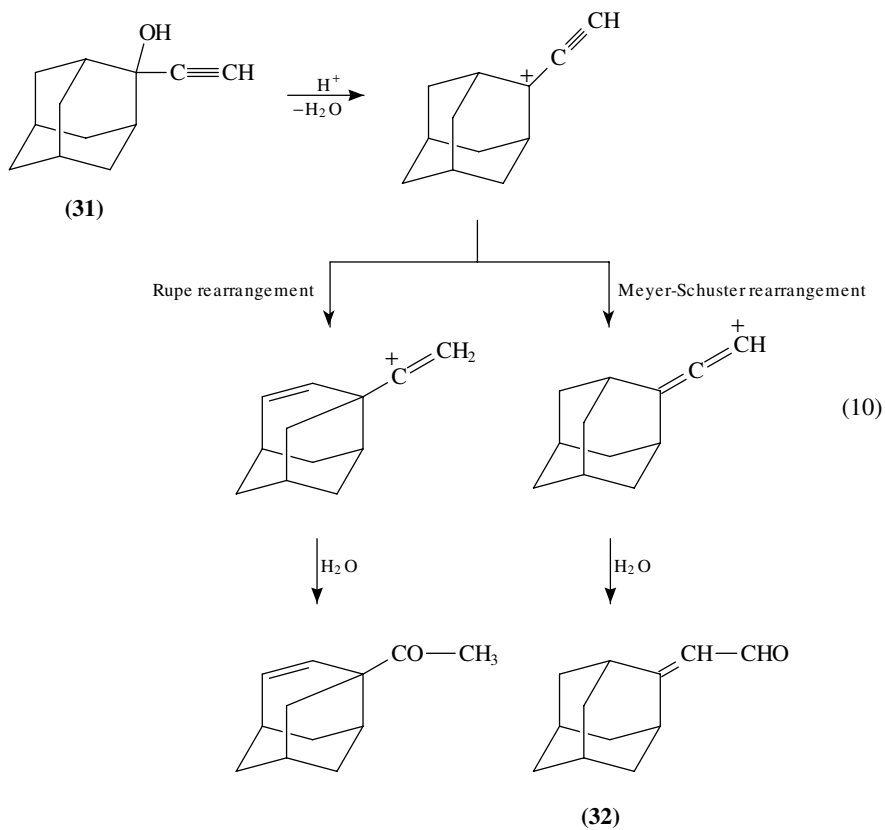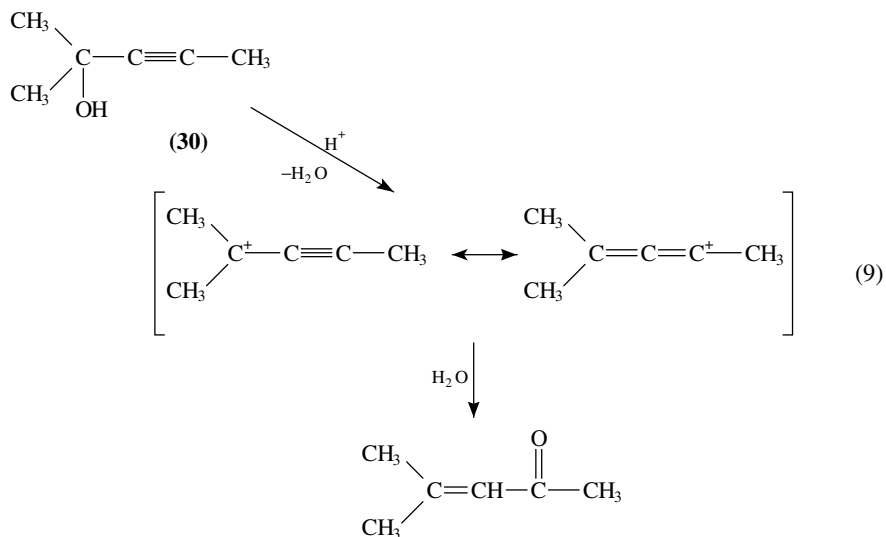

(*E*-**24**)

(*Z*-**24**)

80% EtOH

(6)

for *E*-**24**   for *Z*-**24**

(*E*-**25**)   (*Z*-**25**)
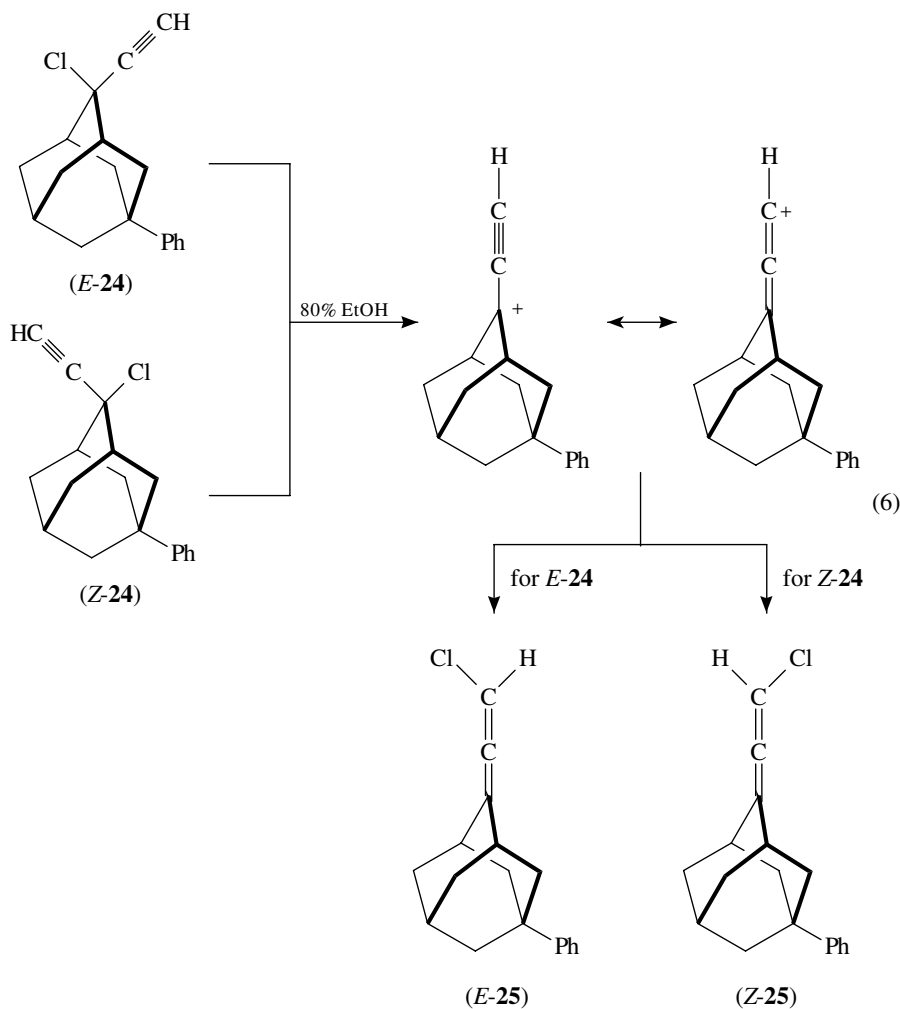
Intermediate allenyl cation **26** has been implied in the reaction of oct-3-yn-2-one (**27**) with trifluoromethanesulfonic anhydride, which forms vinyl triflates (equation 7)[26].

Ferrocenyl-substituted allenyl cations **28** were generated when 1,3-diferrocenyl-substituted secondary and ferrocenyl-substituted tertiary alcohols **29** were treated with trifluoroacetic acid[27]. These were rapidly converted into trifluoroacetoxyallylic ions by solvent addition; the ions gave ferrocenyl-substituted enones by reaction with water (equation 8).

$$C_3H_7CH_2 - C\equiv C - \underset{\underset{O}{\|}}{C} - CH_3$$

(27)

Tf$_2$O $\Big|$ $-OTf^-$

$$\left[C_3H_7CH_2 - C\equiv C - \overset{+}{C} \overset{CH_3}{\underset{OTf}{\diagdown}} \quad \longleftrightarrow \quad C_3H_7CH_2 - \overset{+}{C}=C=C \overset{CH_3}{\underset{OTf}{\diagdown}} \right]$$

(26)

$$C_3H_7CH_2 - C\equiv C - \underset{OTf}{\overset{CH_2}{\overset{\|}{C}}} \qquad\qquad C_3H_7CH=C - C\equiv C - CH_3$$
$$\underset{OTf}{|}$$

(7)

$$FcC\equiv C\text{-}C(OH)R^1R^2 \quad \underset{H_2O}{\overset{H^+}{\longrightarrow}} \quad \left[FcC\equiv C - \overset{+}{C}\overset{R^1}{\underset{R^2}{\diagup}} \quad \longleftrightarrow \quad Fc\overset{+}{C}=C=C\overset{R^1}{\underset{R^2}{\diagup}} \right]$$

(29)   **(28)**

CF$_3$CO$_2$H $\Big|$

(8)

$$\overset{+}{\underset{\text{-----------}}{}}$$
$$FcC - CH - CR^1R^2$$
$$\underset{OCOCF_3}{|}$$

H$_2$O $\Big|$

$$FcCO - CH=CR^1R^2$$

Fc = 1,2-di-*t*-butylferrocenyl, R^1 = R^2 = Me
Fc = ferrocenyl, R^1 = R^2 = Me
Fc = ferrocenyl, R^1 = R^2 = Ph
Fc = R^1 = ferrocenyl, R^2 = Me

The products from the acid-catalyzed hydration of α-tertiary alcohols **30** (Meyer–Schuster and Rupe rearrangements) are formed via the mesomeric propargyl-allenyl cation (equation 9) and have been extensively investigated[28].

When 2-ethynyl-2-hydroxyadamantane (**31**) was treated with 95% formic acid or dilute sulfuric acid only a Meyer–Schuster rearrangement took place to give 95% of 2-(formylmethylene)adamantane (**32**) (equation 10). No Rupe rearrangement took place[29].
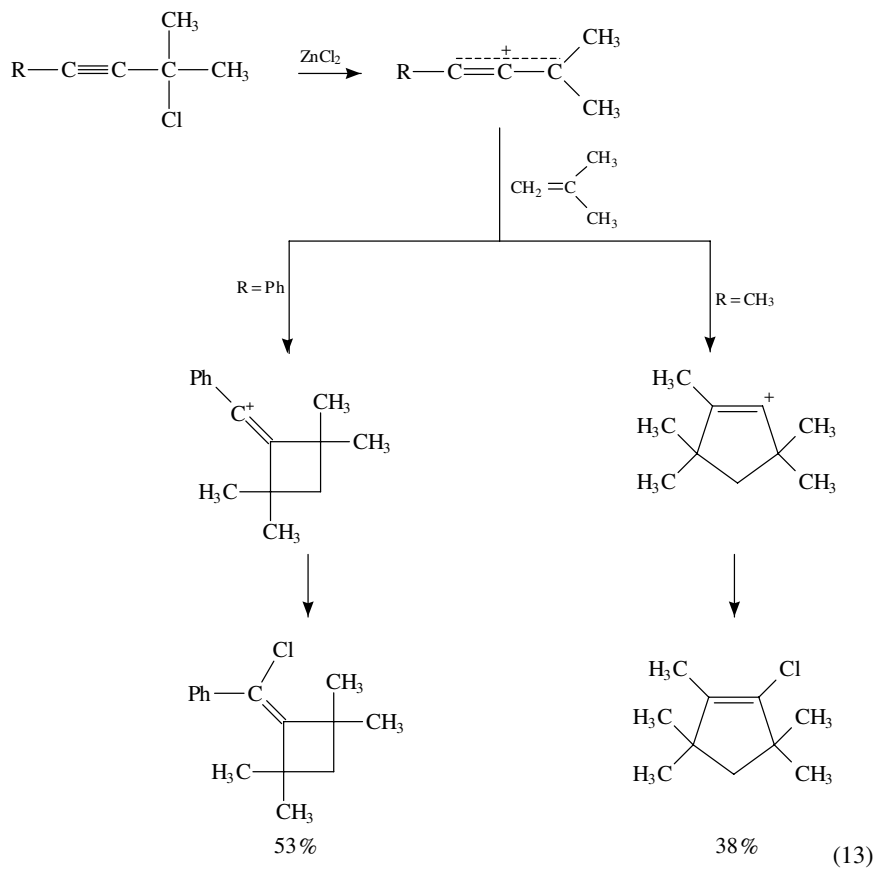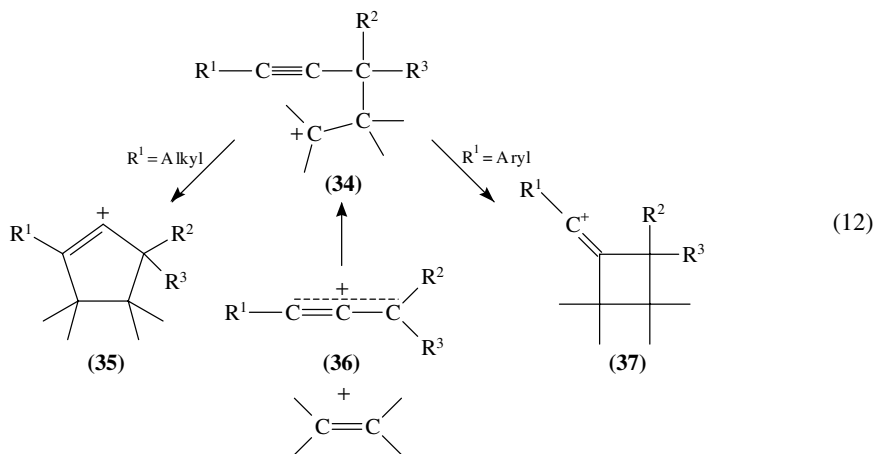
$$CH_3 \\ \quad \ \ C-C\equiv C-CH_3 \\ CH_3 \ \ | \\ \qquad OH$$

(30)

H⁺
−H₂O

$$\left[\begin{array}{cc} CH_3 & CH_3 \\ \ \ \ C^+-C\equiv C-CH_3 & \ \ \ C=C=C^+-CH_3 \\ CH_3 & CH_3 \end{array} \right] \quad \longleftrightarrow \quad$$

(9)

H₂O

$$CH_3 \qquad \qquad O \\ \quad \ \ C=CH-C-CH_3 \\ CH_3$$

(31)

$$\overset{OH}{\underset{}{\big|}} C\equiv CH$$

H⁺
−H₂O

C≡CH

Rupe rearrangement   Meyer-Schuster rearrangement

(10)

$$\overset{+}{C}=CH_2$$

$$C=\overset{+}{CH}$$

H₂O   H₂O

CO—CH₃   CH—CHO

(32)

2-Chloro-2-ethynyladamantane (**33**) was the major product when **31** was reacted with concentrated hydrochloric acid. If 1,4-dioxane was used as the solvent, 82% of 2-(formylmethylene)adamantane (**32**) was obtained together with only 3% of the chloro product **33** (equation 11). It is remarkable that no reaction takes place even under reflux conditions with ethereal hydrogen chloride[29].

(11)
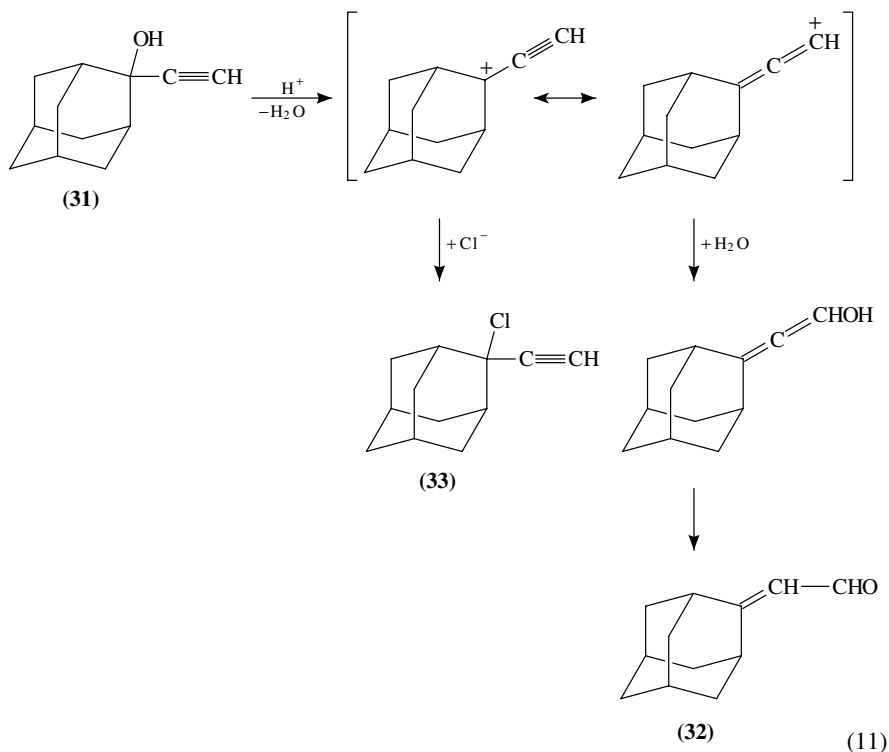
Similar to the cycloaddition of allyl cations[30], allenyl cations have been found to undergo cycloadditions with alkenes to afford bicyclic compounds[31]. The allenyl cations were generated from propargyl chlorides by treatment with Lewis acids. This reaction sequence proceeds via the cyclization **34** $\longrightarrow$ **35**[32], in spite of the fact that 1-cyclopentenyl cations are highly unstable and are not formed during solvolysis of cyclopent-1-enyl triflates[33]. The reaction takes place by a stepwise cycloaddition of the intermediate allenyl cation **36** to an olefinic C=C bond proceeding via cation **34** to afford vinyl cation **37** (equation 12)[34].

The cycloaddition of allenyl cations with monoolefins lead to [2 + 2]- or [3 + 2]-cycloadducts based on the substituents in the allenyl cations as exemplified in equation 13[32].

The cycloaddition of allenyl cations with 1,3-dienes results in a number of intermediate cations from which different products result. The allenyl cations **38** are generated first by the reaction of propargyl chlorides with zinc chloride and are then allowed to react with cyclopentadiene or other 1,3-dienes. The products of cycloaddition depend on the substituents on the allenyl cations[32,35]. The products formed with cyclopentadiene are given in equation 14.
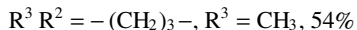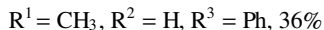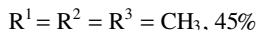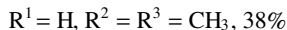
$$R^1 - C \equiv C - \underset{\underset{\scriptstyle \overset{+}{C}}{|}}{\overset{\overset{\scriptstyle R^2}{|}}{C}} - R^3$$

(34)

$$R^1 = \text{Alkyl} \qquad \qquad R^1 = \text{Aryl}$$

$$R^1 - \underset{\scriptstyle \overset{+}{C} = C - \underset{\scriptstyle R^3}{\overset{\scriptstyle R^2}{|}}}{C}$$

(35)   (36)   (37)

$$\underset{\scriptstyle C = C}{\overset{+}{}}$$

(12)

$$R - C \equiv C - \underset{\underset{\scriptstyle Cl}{|}}{\overset{\overset{\scriptstyle CH_3}{|}}{C}} - CH_3 \qquad \xrightarrow{\text{ZnCl}_2} \qquad R - C = \overset{+}{C} - \underset{\scriptstyle CH_3}{\overset{\scriptstyle CH_3}{C}}$$

$$CH_2 = \underset{\scriptstyle CH_3}{\overset{\scriptstyle CH_3}{C}}$$

R = Ph   R = CH₃

53%   38%

(13)
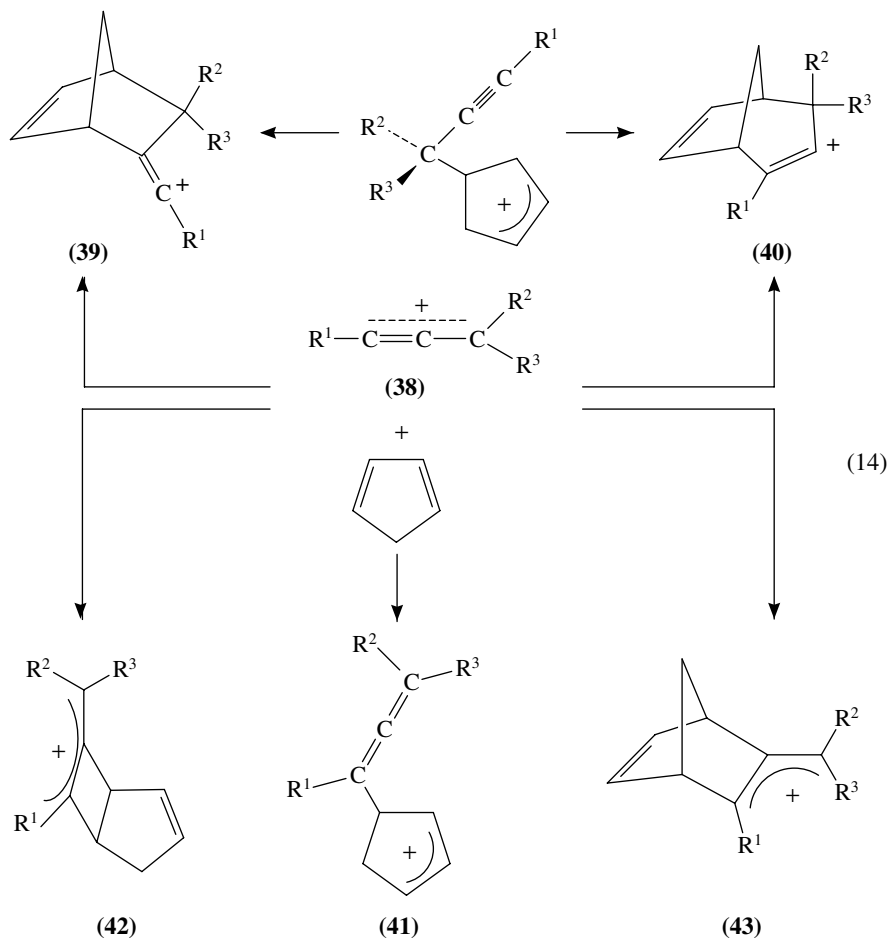
In general, allenyl cations **38** attack at the sp^2-carbon atom of 1,3-dienes and form vinyl cations **39** and **40** ($R' = H$, alkyl) or ($R' = $ aryl). Although a concerted cycloaddition mechanism is possible, a stepwise mechanism is preferred[34]. If a nucleophilic attack at the sp-carbon atom of the allenyl cation takes place, then cation **41** and the resulting cations **42** and **43** are formed. Some examples of bicyclic products obtained from cyclic 1,3-dienes and propargyl chlorides are given in equation 15[34].

Highly alkylated 1-chloro-2-(trimethylsilyl)cyclopentenes **44**, which are of interest as possible cyclopentyne precursors, were prepared by reacting 3-chloro-3-methyl-1-(trimethylsilyl)but-1-yne (**45**) with 1,1-dialkylated or 1,1,2-trialkylated ethylenes in the presence of titanium tetrachloride[35]. Because of the low S_N1 reactivity of **45**, the yields of the products were moderate. The stepwise $[3 + 2]$-cycloaddition mechanism discussed above was proven by the isolation of the intermediate acyclic adduct (in 74% yield) when **45** and isobutene were reacted in the presence of BCl$_3$. Under these conditions, the intermediate **46** could be trapped by Cl$^-$ since BCl$_4^-$ is more nucleophilic than TiCl$_5^-$ (equation 16).
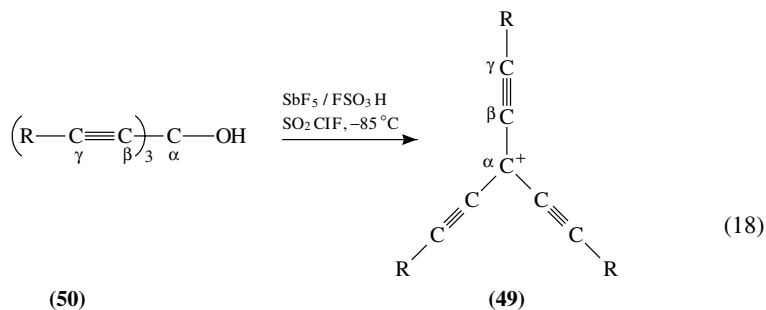
(15)

$$(CH_3)_3Si \!-\! C\!\equiv\! C\!-\!\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}\!-\!CH_3 \quad \xrightarrow[\text{CH}_2\text{Cl}_2,\,0\,^\circ\text{C}]{\text{TiCl}_4} \quad \left[(CH_3)_3Si\!-\!C\!=\!C\!\cdots\!\overset{+}{C}\!\!\begin{array}{c}CH_3\\ \\CH_3\end{array} \right]$$

(45)   **(46)**

$R^1 = H$, $R^2 = R^3 = CH_3$, 38%

$R^1 = R^2 = R^3 = CH_3$, 45%

$R^1 = CH_3$, $R^2 = H$, $R^3 = Ph$, 36%

$R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, 16%

$R^3 R^2 = -(CH_2)_3-$, $R^3 = CH_3$, 54%

$$\xrightarrow{\underset{R^2}{\overset{R^3}{\diagdown}}C\!=\!C\underset{R^1}{\overset{H}{\diagup}}} \quad (16)$$

(CH$_3$)$_3$Si, Cl structure **(44)** with R^3, R^2, R^1, CH$_3$, CH$_3$
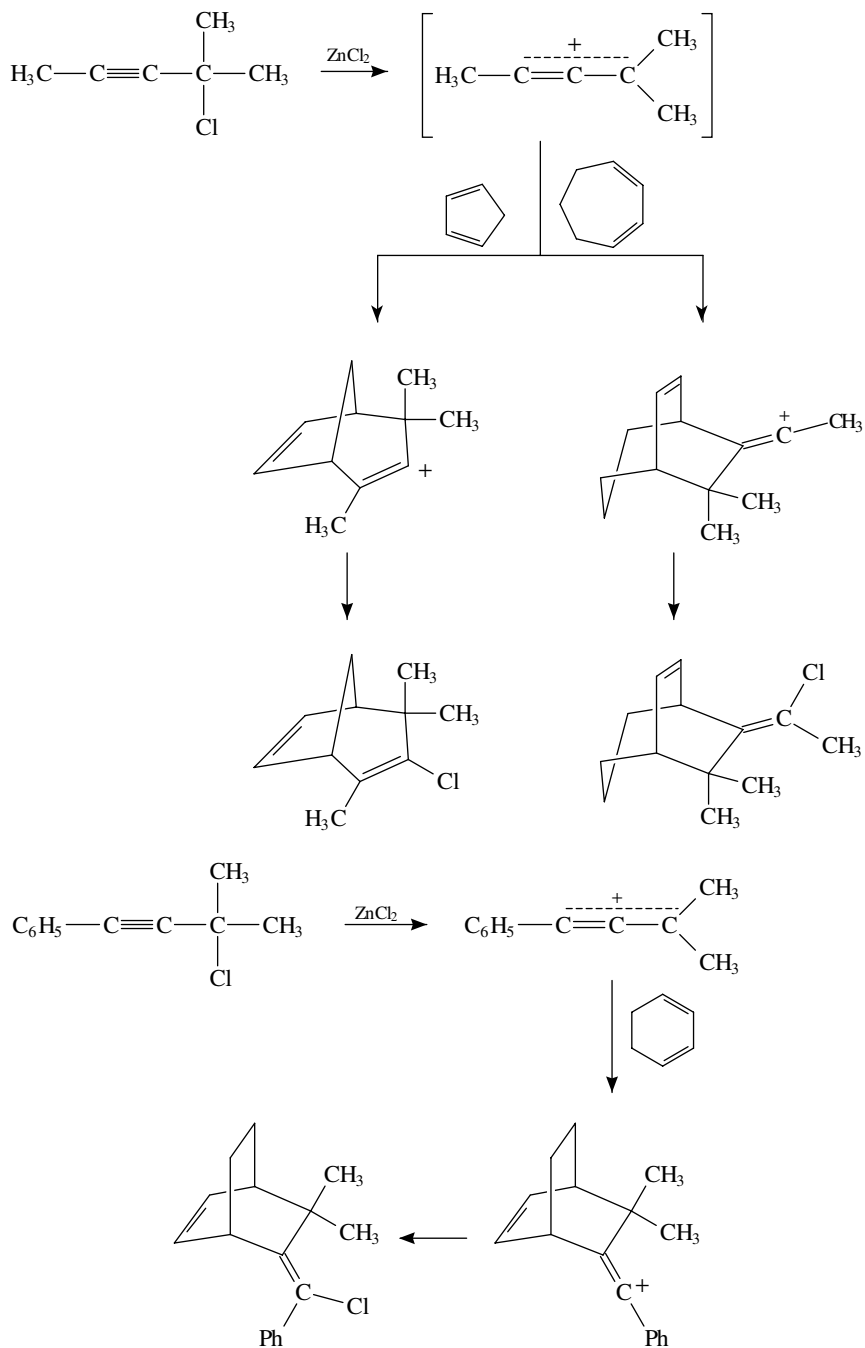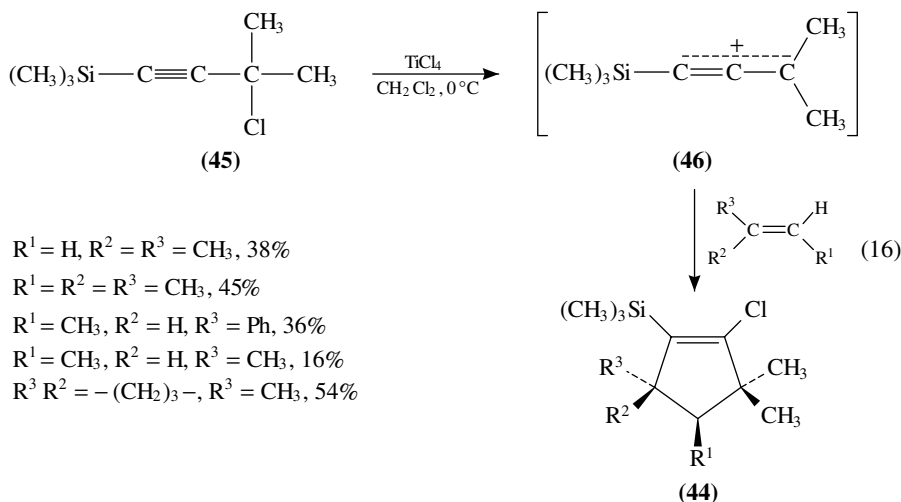
C. Spectroscopic Identification of Allenyl Cations

Substituted allenyl cations **47** have been generated from propargyl alcohols **48** under stable carbocation conditions (SbF_5/FSO_3H in SO_2ClF) (equation 17). On the basis of ^{13}C-NMR chemical shifts, the positive charge has been found to be extensively delocalized with the mesomeric allenyl cations contributing highly to the total ion structure[36,37].

$$\underset{R^2}{\overset{R^1}{\diagdown}}\underset{OH}{\overset{|}{C}}\!-\!C\!\equiv\!C\!-\!R^3 \quad \xrightarrow[\text{SO}_2\text{ClF} -130\,^\circ\text{C}]{\text{SbF}_5 \,/\, \text{FSO}_3\text{H}} \quad \underset{R^2}{\overset{R^1}{\diagdown}}C\!=\!\overset{+}{C}\!=\!C\!-\!R^3$$

(48)   **(47)**

(a) $R^1 = R^2 = R^3 = CH_3$

(b) $R^1 = R^2 = Ph$, $R^3 = CH_3$

(c) $R^1 = R^2 = CH_3$, $R^3 = Ph$

(d) $R^1 = R^3 = Ph$, $R^2 = CH_3$

(e) $R^1 = R^2 = R^3 = Ph$

(17)
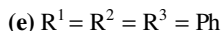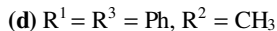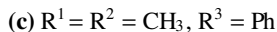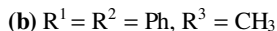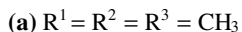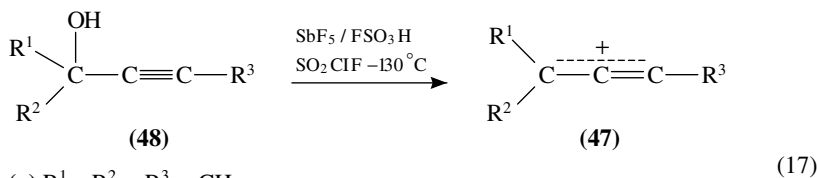
^{13}C-NMR spectroscopic studies on α-substituted tris(ethynyl)methyl cations **49** prepared from alcohols **50** (equation 18) provided evidence for the participation of resonance structures with allenyl cationic character[38]. The parent tris(ethenyl)methyl cation (**49**, R = H) cannot be generated under stable carbocation conditions (SbF_5/FSO_3H) presumably due to the highly reactive unsubstituted termini of the three ethynyl groups and the resulting low kinetic stability. The chemical shift data (Table 1) give evidence that in all cases C_α and C_γ are deshielded more than C_β (relative to their precursor alcohols).

Recently, the ^{13}C-NMR spectrum of 1-mesityl-3,3-dimethylallenyl cation (**51**) generated from the propargyl alcohol was measured (equation 19)[39]. The cation exhibits strong shielding for the C^+-atom (192 ppm).

$$\left(R{-}\underset{\gamma}{C}{\equiv}\underset{\beta}{C}{-} \right)_3 \underset{\alpha}{C}{-}OH \quad \xrightarrow[\text{SO}_2\text{ClF}, -85\,^\circ\text{C}]{\text{SbF}_5 / \text{FSO}_3\text{H}} \quad (49) \tag{18}$$

(50)   **(49)**

(a) R = CH$_3$
(b) R = t-C$_4$H$_9$
(c) R = Si(CH$_3$)$_3$
(d) R = Ph
(e) R = H

$$ -130\,^\circ\text{C} \Big| \text{FSO}_3\text{H} / \text{SbF}_5 \tag{19}$$

(51)
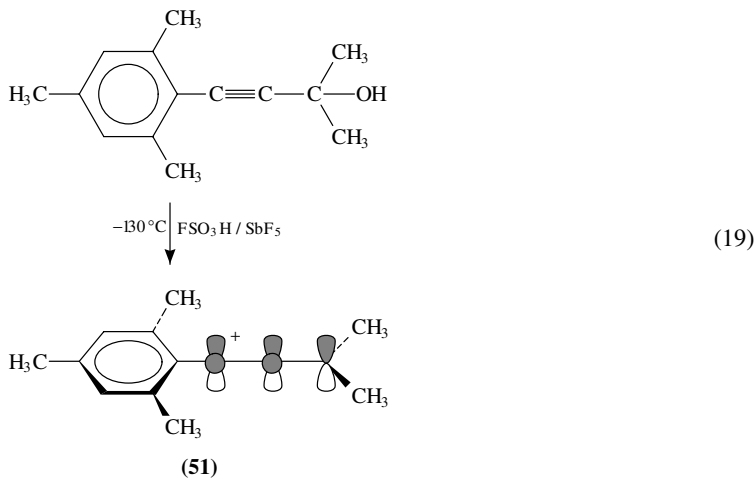
TABLE 1. ^{13}C-NMR Chemical Shifts of Tris(ethynyl)methyl Cations (**49a–d**) and Their Precursor Alcohols **50a–d**[a]

Compound	C_α	C_β	C_γ	Other carbons
49a	164.4	105.6	157.6	9.2
49b	162.6	105.3	164.1	33.1, 27.6
49c	166.3	101.3	144.9	−2.2
49d	140.7	110.5	137.9	118.9, 130.0
				137.2, 137.5
50a	54.0	77.9	78.8	3.4
50b	54.5	78.2	90.4	27.2, 30.3
50c	54.7	88.1	101.6	−0.8
50d	55.6	83.1	86.6	121.5, 128.2
				129.0, 132.0

[a]In ppm, referenced to TMS. The spectra of cations **49a–d** were measured in SO$_2$ClF at −60 °C using (CD$_3$)$_2$C=O (29.8 ppm) in a coaxial capillary tube. The spectra of the precursors were recorded in CDCl$_3$.

III. BUTATRIENYL CATIONS

The homologue of allenyl cation, butatrienyl cation **53** is the mesomeric form of α-ethynyl stabilized vinyl cation **52**. Such a species was generated for the first time by Kobayashi, Sonoda and Taniguchi in 1977[40], by the solvolysis of the butatrienyl halides **54a** and **54b** in aqueous ethanol. The first-order kinetics, the leaving-group effect ($k_{Br}/k_{Cl} = 52$) and the Grunwald–Winstein's *m* value of *ca* 0.5 show that **54a** and **54b** solvolyze by an S_N1 mechanism with the mesomeric butatrienyl cation **55** as the intermediate.

Both the butatrienyl halides **54a** and **54b** gave the alkyne (**56**) as the sole product in 97–100% yield[41]. The kinetics described above fit the mechanistic sequence shown in equation 20 for the formation of the product **56**. The mesomeric butatrienyl vinyl cation **55**

(20)
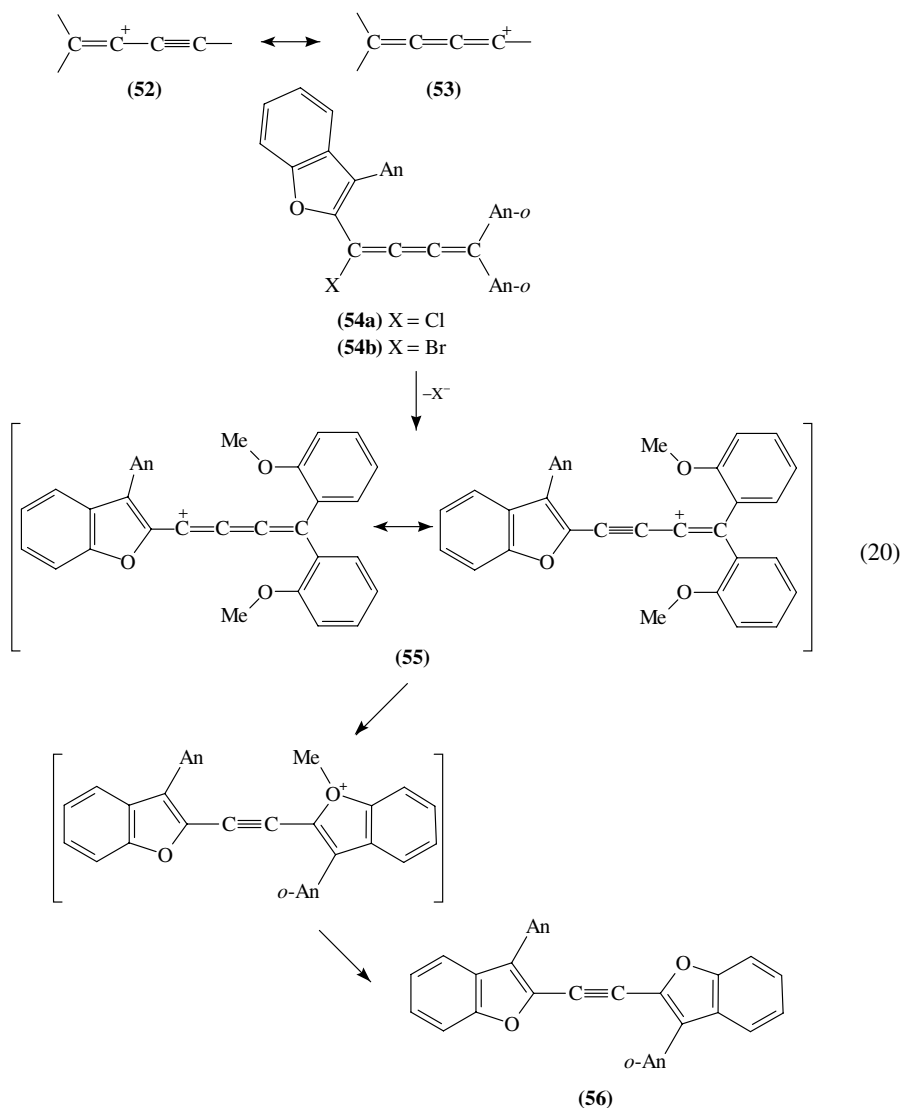
generated during the solvolysis is intramolecularly attacked by the methoxy group, which is located in a suitable position to form the five-membered ring, followed by elimination of the methyl group.

$$
\begin{array}{ccc}
\underset{\substack{Ph \\ Ph}}{>}C=C\underset{Br}{\overset{C\equiv C-An}{<}} & \underset{\substack{Ph \\ Ph}}{>}C=C=C=C\underset{X}{\overset{An}{<}} \\
\textbf{(57)} & \textbf{(58)} \\
& X = Br, Cl
\end{array}
$$

$\downarrow -Br^{-}$ $\qquad$ $\downarrow -X^{-}$

$$
\left[\underset{\substack{Ph \\ Ph}}{>}C=\overset{+}{C}-C\equiv C-An \longleftrightarrow \underset{\substack{Ph \\ Ph}}{>}C=C=C=\overset{+}{C}-An \right] \qquad (21)
$$

(59)

$\downarrow$ EtOH

$$
\underset{\substack{Ph \\ Ph}}{>}C=C=C=C\underset{OEt}{\overset{An}{<}}
$$

(60)

$$
H_3C-C\equiv C-\underset{OTf}{\overset{\displaystyle |}{C}}=CH_2
$$

(62)

$H_3C-C\equiv C-C\equiv CH$

$\nwarrow -H^{+}$

$H_3C-C\equiv C-\overset{+}{C}=CH_2$

(63)

$\swarrow H_2O$

$$
H_3C-C\equiv C-\underset{\overset{\displaystyle ||}{O}}{\overset{\displaystyle |}{C}}-CH_3
$$

$\updownarrow$

$H_3C-\overset{+}{C}=C=C=CH_2$

(61)

$\qquad$ $\underset{EtOH}{\nearrow}$ $H_3C-C\equiv C-\underset{OEt}{\overset{\displaystyle |}{C}}=CH_2$

$\underset{CF_3CH_2OH}{\searrow}$ $H_3C-C\equiv C-\underset{OCH_2CF_3}{\overset{\displaystyle |}{C}}=CH_2$ $\qquad (22)$

$\downarrow H_2O$

$$
H_3C-\underset{\overset{\displaystyle ||}{O}}{\overset{\displaystyle |}{C}}-CH=C=CH_2
$$

(64)
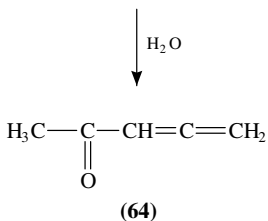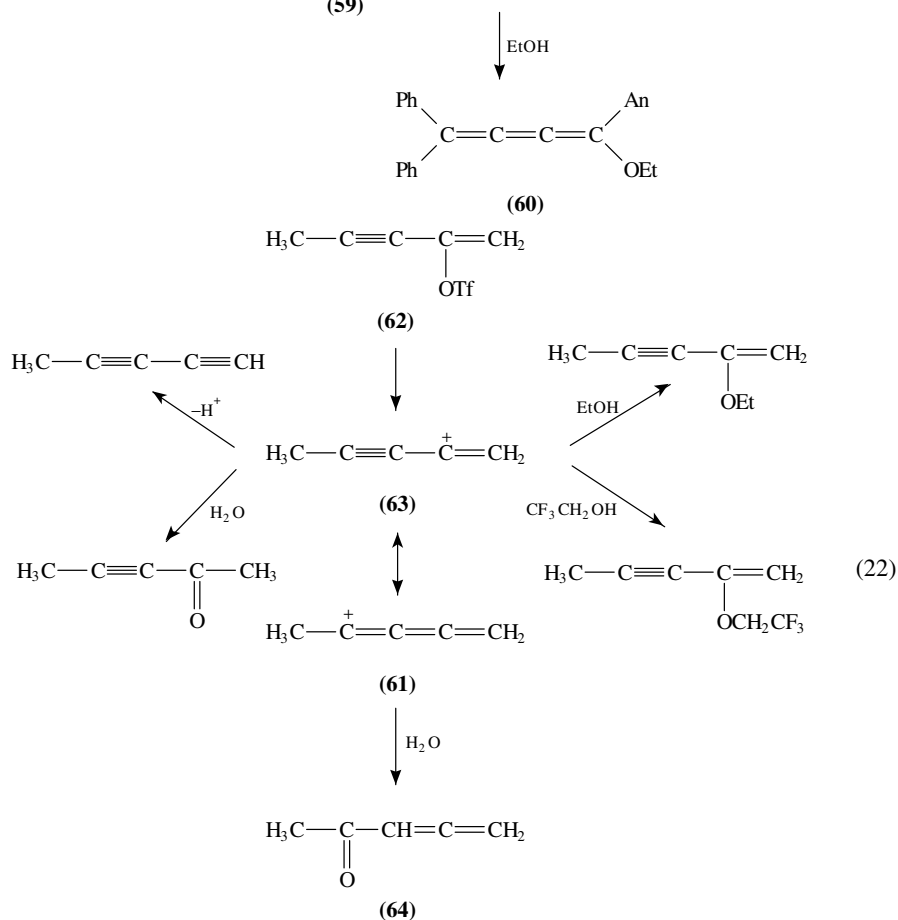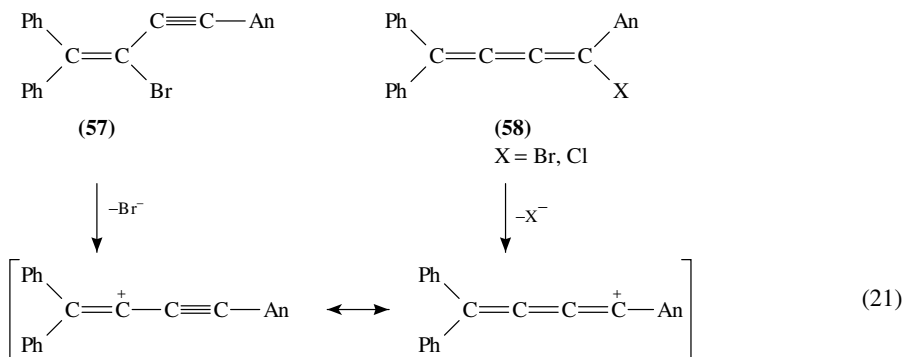
If one compares the solvolyses of 2-bromo-1,1-diphenyl-4-(p-methoxyphenyl)-but-1-en-3-yne (**57**) and 4,4-diphenyl-1-bromo-1-(p-methoxyphenyl)-buta-1,2,3-trienes (**58**, X = Br) in aqueous ethanol (equation 21), the destabilization of the intermediate cation **59** by the large inductive effect of the triple bond as compared to its conjugative effect is evident[42]. Only in the case of **58** could the substitution product butatrienyl enol ether **60** be isolated in 40% yield, while it was only detected by UV and IR spectroscopy in the solvolysis product of **57**. The faster observed reaction rate of **58** as compared to **57** was ascribed to a difference in their ground-state energies[42].

Butatrienyl cations **61** were also implied in the solvolysis of the α-propynyl vinyl triflate **62**[43]. The vinyl triflate solvolyzes 35–70 times faster than the corresponding simple vinyl analogues and gives products resulting mainly from the α-alkynyl vinyl cation **63**. A small amount of the allenic ketone **64** derived from the butatrienyl cation is also detected (equation 22).

An allenyl cation **65** is involved as an intermediate in the room-temperature isomerization of 1-chloro-1,4,4-tris(4-methylphenylthio)butatriene (**66**) to the tris(4-methylphenylthio)butenyne (**67**)[43] (equation 23).

$$R = 4\text{-}CH_3C_6H_4 \qquad (23)$$
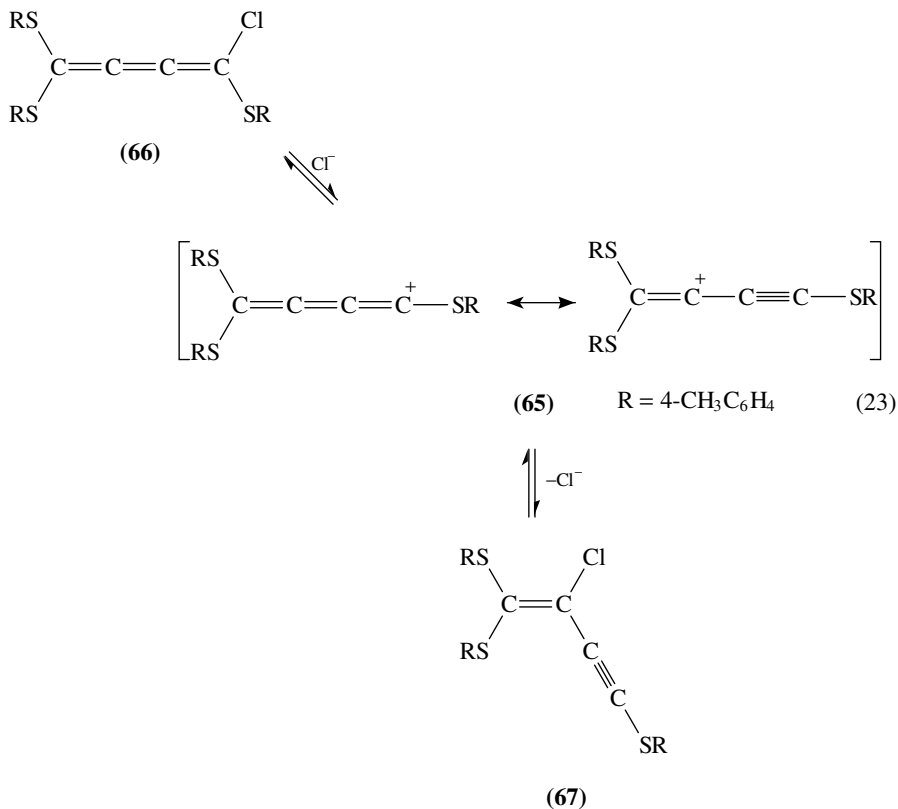
Higher homologues than the butatrienyl cations are not known to the best of my knowledge. The summary given here provides strong evidence for the existence of the cumulated vinyl cations, i.e. allenyl and butatrienyl cations. A leap into the preparatory domain, harvesting the potentials of these cations, should definitely be a fruitful venture.

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CHAPTER **20**

Oxidation of dienes and polyenes

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I. INTRODUCTION

The functionalization of a carbon–carbon double bond is a basic procedure in organic chemistry. Oxidation is one of the many different ways in which such a double bond may be transformed. Although the term oxidation is rather a general one, we will mostly concern ourselves in this review with oxygenations, i.e. reactions in which oxygen is added to the substrate with or without cleavage of the carbon–carbon bond. Only some mention will be made of other formally oxidative procedures such as dehydrogenation.

Although oxidation in general and of alkenes in particular is very well documented, it is rather surprising that there has been no systematic description of the oxidation of dienes or polyenes in the literature. In fact, more often than not an early literature example of the oxidation of a diene will be part of or an extension of a report dealing with the oxidation of monoalkenes. Only in recent years has oxidative functionalization of di- and polyenes become an important procedure in itself in fields such as natural product synthesis.

For the purpose of this review, one may view a diene in two ways depending on the structure of the substrate and the specific oxidation reaction to be carried out. The first point of reference is to consider the substrate as a compound having two *independent* monoalkene units. Often but not always this means that the double bonds are non-conjugated. In this case, the relative reactivity of the various carbon−carbon double bonds will usually form the basis of the research described and will deal with the selective formation of a specific product. In the most simple case, such as in substrates with two identical but independently reactive alkene units, for example *cis,cis*-1,5-cyclooctadiene (**1**), this translates into selectivity based on mono- vs di- or poly-oxidation. In a more complicated substrate, two different double bonds, neither of which are further influenced by additional functional units, may be considered. Such a case is typified by substrates such as limonene (**2**) where the question of regioselectivity and/or stereoselectivity is paramount. The third, more complicated example includes substrates which have additional functional groups such as geraniol (**3**) where one double bond is *cis (Z)* and allylic to a primary alcohol and the other is independent of a functional unit or ligand. In such compounds questions of chemoselectivity as well as regioselectivity and stereoselectivity are the important factors to be considered. For compounds with additional functional groups, we will only discuss in detail examples where one of the double bonds actually react although there are numerous oxidation reactions where dienes are inert in the presence of other reactive centers.

(1)   (2)   (3)
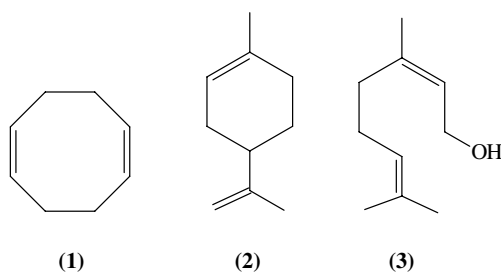
In the literature, there are also several examples where the specific oxidation reaction is *dependent* on the presence of a diene. Often the substrates are conjugated dienes where there is simultaneous oxidation of both double bonds. An important prototype of this reaction is the well-known singlet oxygen oxidation of dienes to endoperoxides, for example the oxidation of α-terpinene (**4**) to ascaridole (**5**) (equation 1).

(1)

(4)   (5)
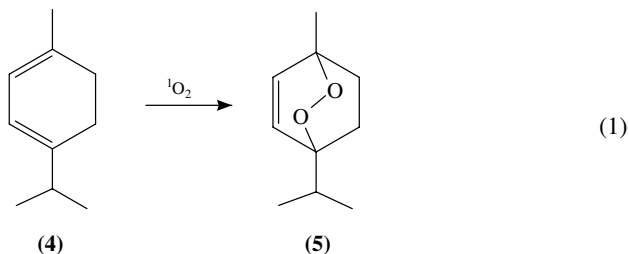
There are many ways to categorize the oxidation of double bonds as they undergo a myriad of oxidative transformations leading to many product types including epoxides, ketones, diols, endoperoxides, ozonides, allylic alcohols and many others. Rather than review the oxidation of dienes by substrate type or product obtained, we have chosen to classify the oxidation reactions of dienes and polyenes by the oxidation reagent or system used, since each have a common reactivity profile. Thus, similar reactions with each specific oxidant can be carried out on a variety of substrates and can be easily compared.

II. OXIDATION WITH METAL-OXO COMPOUNDS AND INTERMEDIATES

High-valent metal-(M)-oxo compounds have often been used in the oxidation of dienes and polyenes. There are oxidants of alkenes which are exclusively stoichiometric reagents. Especially noteworthy is the use of permanganate but chromium-based reagents such as pyridinium chlorochromate (PCC) have also been used. Others, especially osmium and ruthenium tetraoxide, are known stoichiometric reagents; however, reactions are often carried out catalytically using terminal oxidants such as N-methylmorpholine oxide (NMO), ferricyanide, peroxides, periodate and hypochlorite. Finally, there are purely catalytic reactions, where the active intermediate metal-oxo compound is unstable and/or unknown under normal conditions. Most prominent in this last group are the metalloporphyrins and the metal-salen compounds as catalysts, where the metal is most often manganese(III). There are also reports using iron(III). A wide range of terminal oxidants have also been employed. The former reagents, MnO_4^-, OsO_4 and RuO_4, can provide an alkene with two oxygen atoms. Reactions with these oxidants therefore lead to *cis*-diols, α-ketols, diketones and oxidative cleavage. Both [2 + 2] and [3 + 2] cycloadditions, where the alkene adds to either one or both of the metal-oxo bonds, have been cited as the pathway to the key intermediates (equation 2)[1]. On the other hand, manganese-oxo intermediates of salen or porphyrin complexes contribute only one oxygen to the carbon–carbon bond yielding epoxides as initial product (equation 3)[1]. The intermediate and the mechanism in this reaction has been the subject of much research and discussion and is still disputed.

$$(2)$$

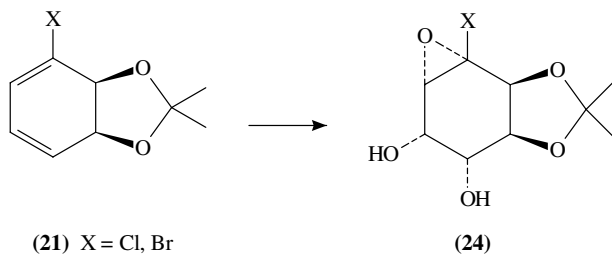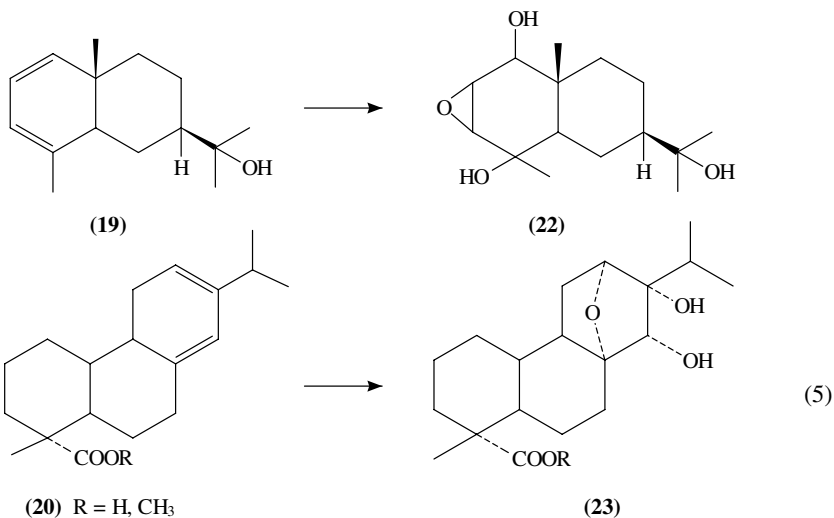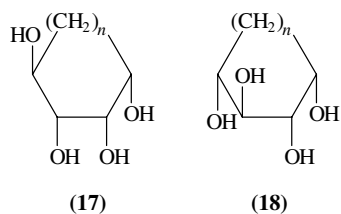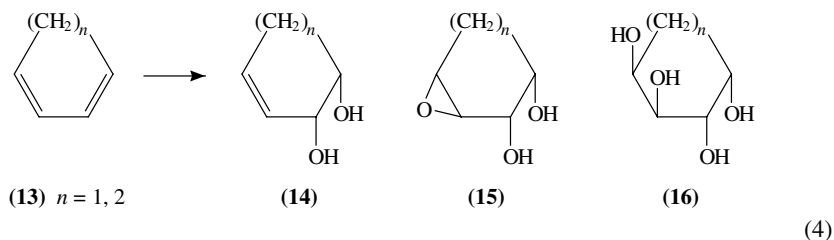

$$(3)$$
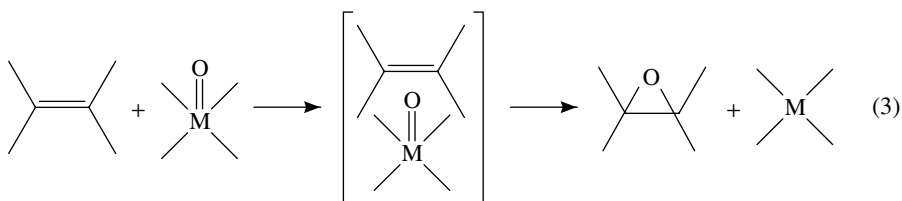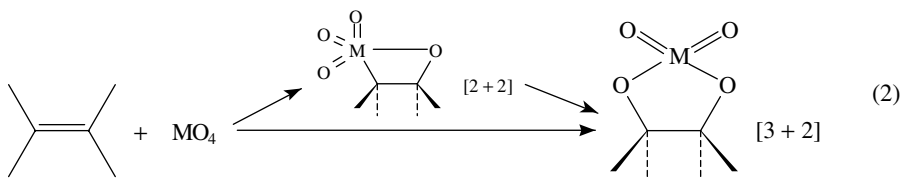
A. Oxidation with Permanganate

Some of the earliest work in the oxidation of alkenes was performed by oxidation with potassium permanganate. Under acidic and neutral conditions the intermediately formed glycols are oxidized, generally leading to cleavage of the carbon–carbon bond. Thus, such procedures have seldom been synthetically applied to diene oxidation. One notable

exception is the oxidative cleavage of pimaric (6) and sandaracopimaric (7) esters at the terminal vinylic bond to yield the acids **8** and **9**, respectively[2]. Under basic conditions the oxidizing strength of the permanganate is reduced and it is possible to prepare *cis*-diols and α-ketols. Diol formation is favored by low permanganate and relatively high base concentration and α-ketol formation is favored by high permanganate and low base concentration[3]. Early use of permanganate and base in the oxidation of dienes was first reported in the previous century by Wagner[4] who oxidized limonene (2) to the correspond-ing tetraol. Later on Wallach[5,6] similarly oxidized the 1,4 dienes, γ-terpinene (10) and terpinolene (11) whereas the 1,3 diene, α-terpinene (4), was ring cleaved. Subsequently, 1,4 cyclohexadiene (12) was oxidized in the same manner to both the diol and the *cis, anti,cis* tetraol[7,8]. The *cis,anti,cis* tetraol was preferred over the *cis,syn,cis* tetraol product because of the steric hindrance to the second addition[9].

(6)   (7)   (8)

(9)   (10)   (11)   (12)
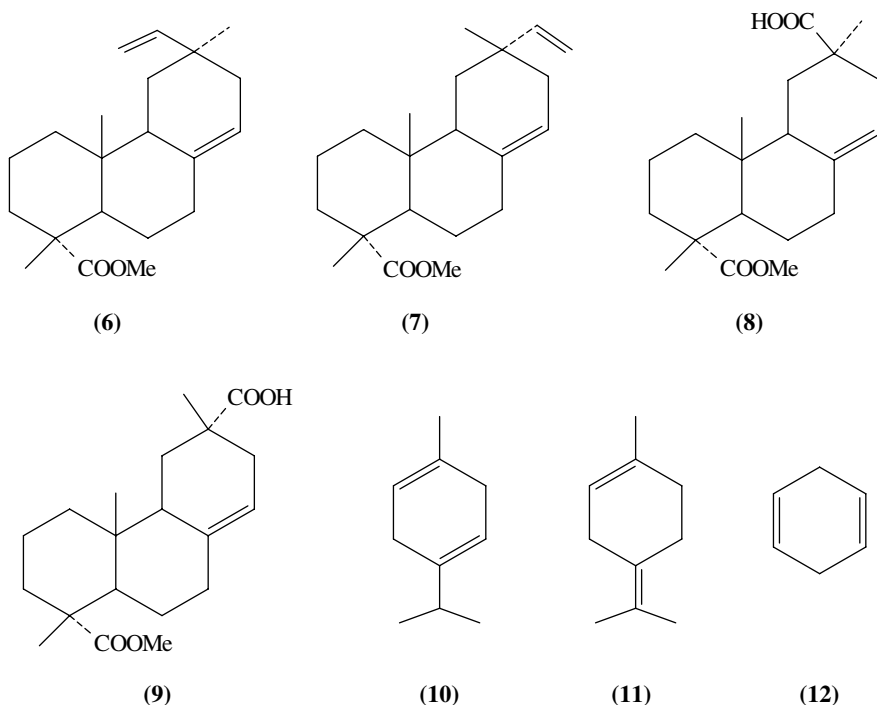
   The basic permanganate oxidation of conjugated 1,3-dienes is different from those reported for the 1,4-dienes above. Therefore, in the oxidation of cyclopentadiene and 1,3-cyclohexadiene (13) a mixture of five products **14–18** is obtained (equation 4)[10,11]. In this reaction **14** and **16** are derived from the 'normal' *cis* hydroxylations whereas **17** and **18** were said to be formed from **15** by hydration in what the authors[9] term an epoxidic pathway. Formation of epoxy-diols under similar permanganate oxidations has been found for occidentalol[12] (19), levopimaric acid[13] (20) and a 1-chloro- or 1-bromo-1,3-diene[14] (21) as an intermediate step in the synthesis of (+)-D-*chiro*-3-inosose and (+)-D-*chiro*-3-inositol (equation 5). The explanation for the epoxide formation in the oxidation of 1,3-dienes (13, **19–21**) is not clear but may be connected to the fact that other additions of permanganate to dienes are possible beyond those commonly observed

(equation 2). Other unusual additions are clearly observed in the oxidation of 1,5-dienes described below. Other 1,3-dienes, such as ergosterol[15] and abietic acid[16], have also been oxidized with permanganate but yield a complicated mixture of products whose identity is somewhat questionable.

(13) n = 1, 2   **(14)**   **(15)**   **(16)**

(4)

(17)   **(18)**

(19)   **(22)**

(20) R = H, CH₃   **(23)**

(5)

(21) X = Cl, Br   **(24)**

A most fascinating and remarkably high-yield permanganate oxidation of 1,5-dienes to stereospecifically form the *cis*-isomers of 2,5-bis(hydroxymethyl)tetrahydrofurans (equation 6) was discovered by Klein and Rojahn thirty years ago[17]. Two groups have suggested mechanisms to explain the stereochemistry of the tetrahydrofuran product. The first introduced a metallaoxetane intermediate, i.e. a [2 + 2] cycloaddition, followed by alkyl migration with retention of configuration, reductive elimination, oxidation and hydrolysis[18]. The second began with a [3 + 2] cycloaddition of one alkene bond with permanganate, and requires oxidation with another permanganate anion followed by intramolecular cycloaddition of the double bond and hydrolysis[19]. Isotopic experiments with ^{18}O-permanganate suggest that neither of these mechanisms is correct, but no further discussion has been presented[20]. In any case the stereochemistry of the cyclization is predictable and controlled by the geometry (*E* or *Z*) of the double bonds. This steroselective transformation has since been used in the synthesis of the tetrahydrofuran unit of ionomycin[21] and the bis-tetrahydrofuran unit of monesin[22]. Also, a high degree of enantioselectivity has been achieved in the neroate diene system functionalized with a chiral auxillary ligand in the total synthesis of ionophores[23]. Finally, this reaction has also been modified using a combination of potassium permanganate and copper sulfate to form butanolides (equation 7)[24].

$$\text{R}^1 - \text{R}^6 = \text{H}$$
$$\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{Me}; \ \text{R}^3 = \text{R}^6 = \text{H}$$
$$\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{Me}; \ \text{R}^3 = \text{R}^6 = \text{H}; \ \text{R}^5 = \text{CH}_2\text{OAc}$$

(6)

(7)
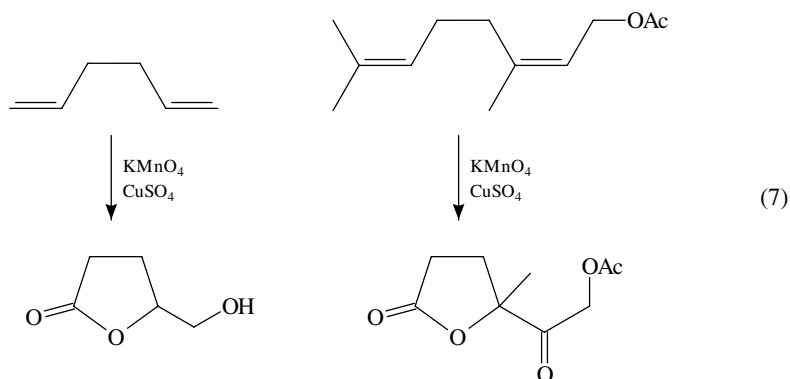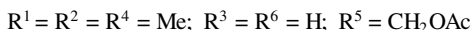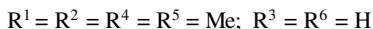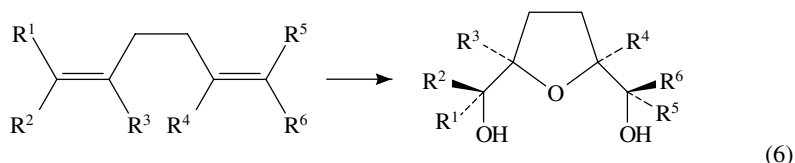
## B. Oxidation with Osmium Tetraoxide

Oxidation of alkenes with osmium tetraoxide is much more moderate than similar oxidations with permanganate. This makes OsO_4 a very reliable reagent for *cis* dihydroxylation.

Both stoichiometric[25,26] and catalytic[27,28] oxidations were developed more or less at the same time. The stoichiometric methods involve reductive cleavage of the intermediate osmium complexes. The most effective reducing agents appear to be bisulfite, hydroxide, hydrogen sulfide and lithium aluminum hydride. Reactions in the presence of a nitrogen ligand, e.g. pyridine (Pyr), often allows the isolation of a $OsO_2(OR)_2Pyr_2$ complex before reductive cleavage. The catalytic methods are now generally considered more applicable due to the high price and toxicity of the osmium tetraoxide reagent. Common terminal oxidants include hydrogen peroxide, tert-butylhydroperoxide, N-methylmorpholine oxide (NMO), metal chlorates, hypochlorite and, most recently, potassium ferricyanide. Among the substrates in the original work of Milas and Sussman[27] in the hydrogen peroxide catalytic system, limonene (2) and 1,5-hexadiene were both oxidized to the corresponding tetraols at moderate yields in reactions carried out at subambient temperatures. Criegee and coworkers[26], on the other hand, prepared cis-diols from cyclopentadiene and 1,4-cyclohexadiene using one equivalent of OsO_4 and pyridine. Yields in this case were quantitative. Much later on 1,4-cyclooctadiene was similarly oxidized to the diol; however, in this case the intermediate complex was identified by its ^{1}H NMR, IR and Raman spectra[29]. 1,4-cyclooctadiene (1) was also oxidized to the diol in the first reported use of NMO as terminal oxidant[30]. The preference for oxidation at a trans-double bond vs a cis-double bond was first demonstrated in oxidation of cis,trans,trans-1,5,9-cyclododecatriene (25) in a non-catalytic system[31]. Cis-5-trans-9-cyclododecadiene-1,2-diol is formed exclusively. Further reaction of this product in a second step, again selectively, yields the cis-9-cyclododecene-1,2,5,6-tetraol.

Osmium tetraoxide has also been used in the oxidation of bicyclic and polycyclic dienes. Thus, oxidation of norbornadiene (26) in a stoichiometric reaction was found to yield the exo-cis diol exclusively[32]. On the other hand, in the NMO catalytic system a mixture of the exo-cis and endo-cis products was reported[30]. However, by use of the NMO catalytic procedure for the substituted norbornadiene 27, the exo-diol was formed exclusively at the sterically crowded unsubstituted double bond and this product was utilized in the synthesis of pentalenolactone[33]. Somewhat surprisingly, oxidation of hexamethyl Dewar benzene (28) exclusively gave the endo-cis diol as sole product[34]. The tricyclic compound 29 gave the usual cis-diol oxidation product of one of the double bonds[35].

(25)   (26)   (27)


(28)   (29)
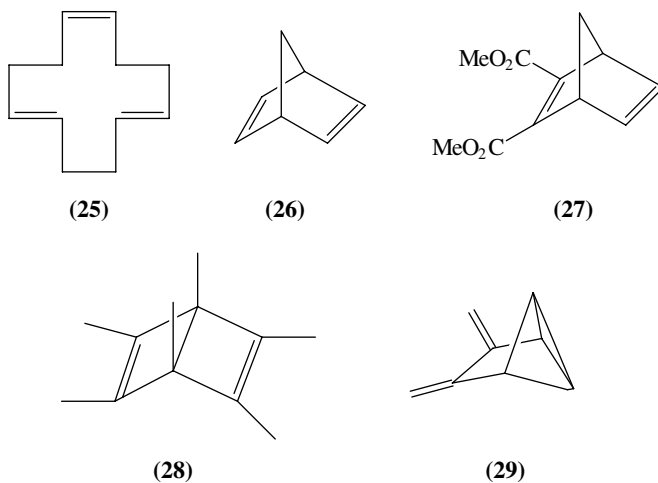
The use of osmium tetraoxide has also played an important part in the earlier research carried out on the functionalization of steroids. Already in their first reports[26], Criegee and his colleagues oxidized ergosterol (30) at the Δ^5 double bond only to form the $5\alpha,6\alpha$-dihydroxy compound. At the same time others similarly oxidized 5,17(20)-pregnadiene-3β-ol (31, R = H) at the same position. Protection of the hydroxy group by preparation of the acetate (31, R = Ac) reverses the regioselectivity and brings about formation of the 17,20-diol[36]. In a further example intermediate 32 was selectively oxidized at the Δ^3 double bond, a useful position for the preparation of steroids methylated at the C-14 position[37]. Interestingly, a series of 4-pregnen-3-ones 33 were all exclusively functionalized at the C-17(20) position[30,38−40]. The enone double bond was much less reactive than the non-functionalized double bond. Finally, the directing effect of C-11 substituents on the addition of OsO$_4$ to steroidal $\Delta^{1,4}$-3-ketones (34) was investigated[41]. Substituents with an α-geometry (11α-hydroxy, 11α-acetoxy and 11α-methyl) brought about addition at the Δ^4 position to form 4β,5β-diols. The same was found for 11-oxo substitution. On the other hand, 11β-hydroxy substitution gave a mixture of diols.
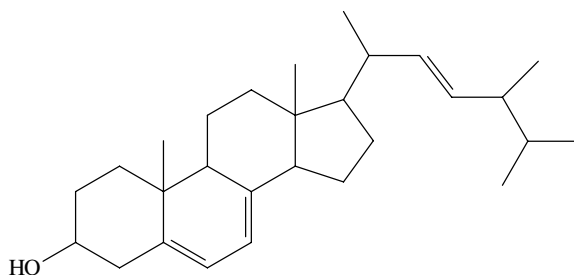
(30)
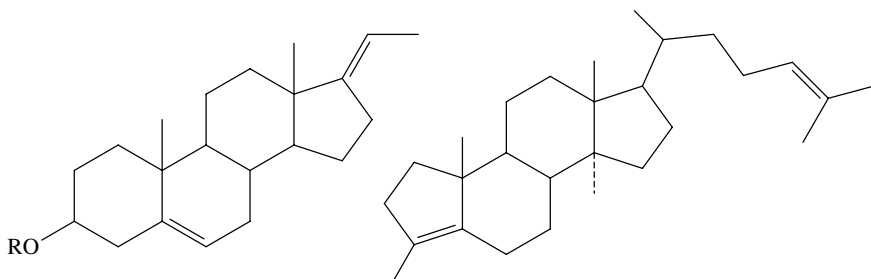
(31)

(32)

The effect of an allylic hydroxy group was first observed in divinylglycol (1,5-hexadiene-cis-3,4-diol and 1,5-hexadiene-trans-3,4-diol). It was shown that the hydroxy substitutions directed the addition of the osmium tetraoxide to syn addition, so that the cis-diol yielded allitol (all cis-hexaol) and the trans-diol yielded mannitol[42]. The oxidation of the dienol 35 yielded a lactone ring 36 by cis-dihydroxylation and transesterification

$$R^1 = R^2 = H, \quad R^3 = OAc, \ Br$$
$$R^1 = H, \ Me \quad R^2 = OH, \quad R^3 = C$$

(33)

(34)
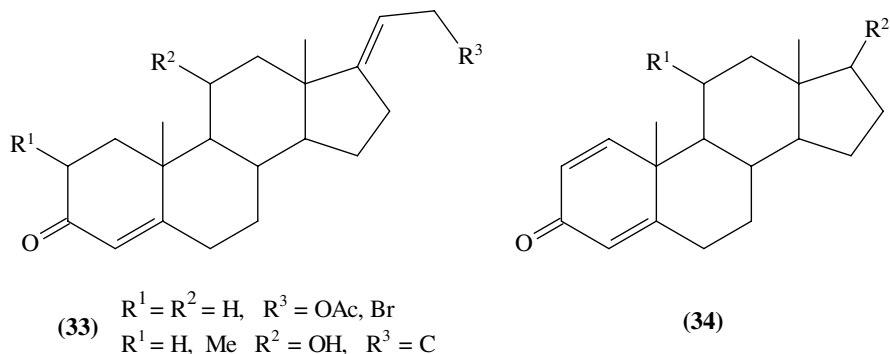
(equation 8), a key intermediate in the synthesis of verrucosidin[43].

$$\text{(8)}$$

(35)   **(36)**
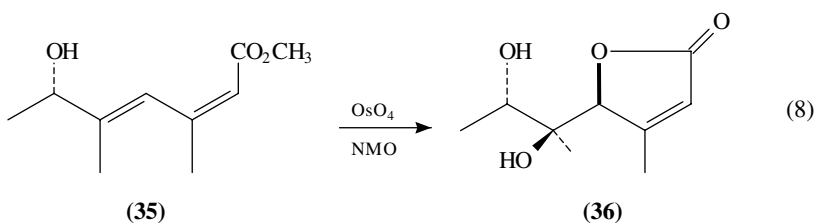
A very important breakthrough in the use of osmium tetraoxide oxidations was made by Sharpless and his group a few years ago. They discovered that by use of chiral cinchonia derivatized alkaloids as nitrogen-containing ligands, the osmylation reaction could be carried out in unprecedented levels of enantiomeric excess[44]. As concerns the use of this technique for the oxidation of dienes, there have been two reports by this group using NMO[45] or potassium ferricyanide[46] as terminal oxidants. In the oxidation of a model compound, *trans,trans*-1,4-diphenyl-1,3-butadiene with NMO, the tetraol was obtained as the major product with only a trace of the diol being obtained. The tetraol was obtained in a diastereomeric ratio of 16:1 (as determined by X-ray diffraction) in favor of the 1,2-*syn*-2,3-*anti*-3,4-*syn* isomer **(37)** vs the all-*syn* isomer **(38)**. Less substituted or *cis*-double bonds gave lower diastereomeric ratios. Use of ferricyanide as terminal oxidation yielded diol **(39)** as the product. Further work in the ferricyanide system showed that for unsymmetrical dienes, osmylation occurred preferentially at the more electron-rich double bond. For example, in 2-methyl-2,7-heptadiene, only the diol at the 2,3 position was formed. Selectivity is less substantial in conjugated dienes. Thus, for 1,3-hexadiene the ratio of products was 3:1 in favor of the more substituted Δ^3-double bond. The preference of

(37)   **(38)**   **(39)**
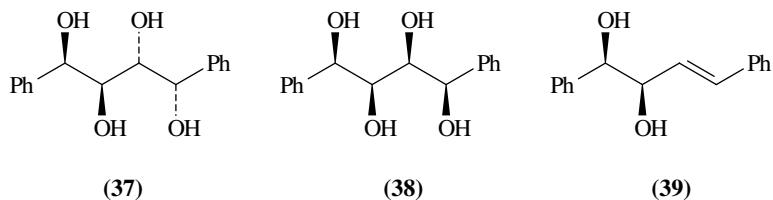
a *trans* over *cis* alkene is significant as was observed in *trans*-2-*cis*-4-hexadiene, where osmylation at the *trans* bond was favored by 15:1. The selective asymmetric dihydroxylation of dienes has recently been applied by others in the very elegant asymmetric syntheses of WCR sex pheromone and antibiotic (−) A26771B[47] and naturally occurring polyethers of the annonaceous acetogenin family[48].

## C. Oxidation with Ruthenium Tetraoxide and Chromate Based Oxidants

Both dichromate and ruthenium tetraoxide, but especially the latter, are very strong oxidizing agents and therefore have been usually only used in synthetic procedures requiring double-bond cleavage. Recently, however, a few synthetic procedures have been described in the oxidation of dienes using these oxides. Thus, a 1-alkylated 1,4-cyclopentadiene **40** was oxidized to an enone **41** using the milder oxidizing agent 2-cyanopyridinium chlorochromate[49]. Pyridium dichromate has also been used in the oxidative rearrangement of dienols although the double bonds themselves are not actually oxidized[50]. Ruthenium tetraoxide has been used in the ring contraction of an oxepine to a furan[51]. An interesting use of RuO_4 in the oxidation of the steroidal diene **42** was recently reported where oxidation takes place exclusively at the 9(11) double bond forming a mixture of three separable products[52].

(40)   **(41)**

(42)
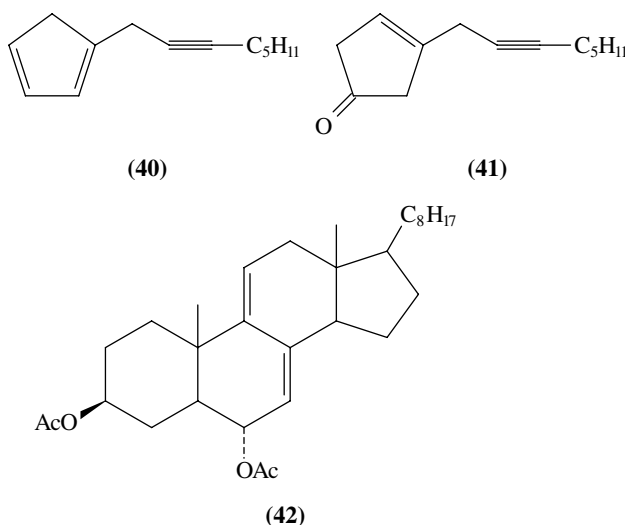
## D. Catalytic Oxidation with Metalloporphyrins and Metal Salen Complexes

Starting in the early 1980s a great deal of research in the oxidation chemistry of metalloporphyrins became of interest, motivated by a biomimetic approach to the understanding of the unique activity of the cytochrome P-450 enzyme. The initial interest was in the iron porphyrins; however, it became obvious that sometimes, but not always for synthetic purposes, the manganese porphyrins were more effective. The activity of the manganese porphyrins led also to the realization that manganese-salen type compounds would be similarly reactive because of the similar nearly square-planar coordination of the metal in both cases. The complexes in the presence of oxygen donors such as

iodosobenzene, hypochlorite and many others are thought to form highly active intermediate manganese(IV) or more probably manganese(V) oxo intermediates, which can easily react with alkenes to form epoxides in high yields. Turning first to the work with metalloporphyrins, the oxidation of limonene (2) led to regioselective epoxidation at the endocyclic position. Endocyclic/exocyclic ratios varied from 7:1[53] to 19.6:1[54] for the manganese and iron porphyrins, respectively. Similar preferred endocyclic oxidation was observed for 4-vinylcyclohexene. In a similar iron-cyclam catalyzed reaction, somewhat lower regioselectivities were observed[55]. In the reaction of 2-methyl-1,3-butadiene (isoprene), there was also a preference, though significantly lower, for epoxidation at the more substituted double bond[53]. The oxidation of the trimethylsilylated derivative of geraniol (3) yielded the 6,7-epoxygeranyl−OSiMe$_3$ and only traces of the 2,3-epoxygeranyl−OSiMe$_3$ compound[53]. The reactivity of *cis* vs *trans* olefins is also of importance. Oxidation of *cis, trans, trans*-1,5,9-cyclododecatriene (25) showed little preference for either geometry in nonsterically hindered porphyrin ligands although *cis*-stilbene is much more reactive than *trans*-stilbene[54,56]. However, using a more sterically crowded porphyrin ligand, very significant *cis/trans* regioselectivity was observed. The synthetic manipulation of the porphyrin ligand was further used in comparison of epoxidation of dienes with manganese porphyrins. As steric crowding at the manganese center was increased by use of tetraphenyl- < tetramesityl- < tetra(triphenyl)phenyl porphyrin ligands (43), R = H, Me, Ph, respectively, the natural tendency towards epoxidation at the more substituted double bond could be inverted[57]. Dramatic effects were observed for 1,4- and 1,3-hexadiene, 4-vinylcyclohexene and limonene (2). Another approach to obtain regioselectivity in a porphyrin-mediated epoxidation was to prepare a vesicular assembly and positioning
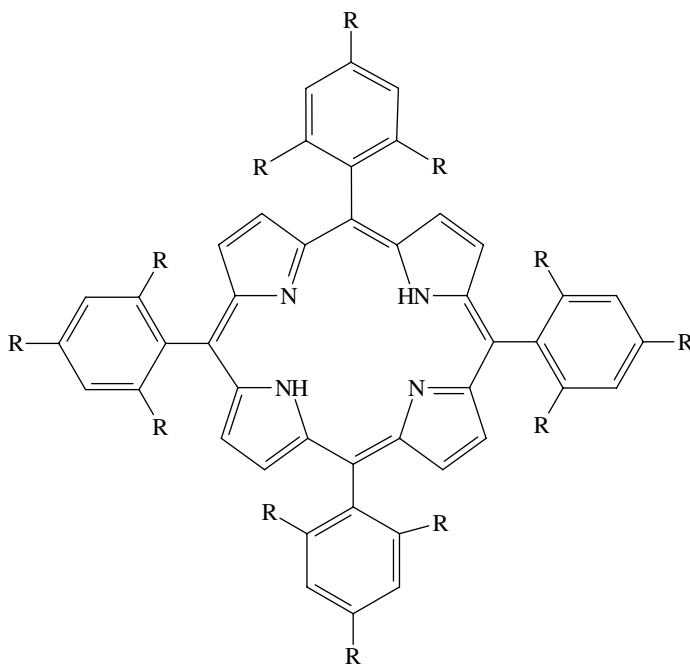

(43)

the metal active site in the center of the lipid bilayer[58]. Then using the hydropho-
bic/hydrophilic orientation of a substrate within such a biomimetic membrane, regios-
electivity of epoxidation of selected substrates such as steroids and fatty acids could be
controlled. In this way the normal epoxidation of stigmasterol (44) at the Δ^5-double bond
in homogeneous solution was reversed to selective epoxidation in the side chain[59]. Simi-
larly, the epoxidation of the Δ^{12}-double bond was preferred over the Δ^9 double bond in
linoleic acid (45), otherwise equally reactive in homogeneous solution.
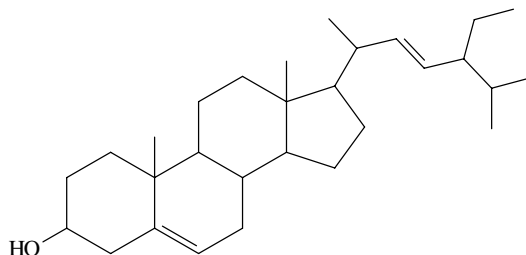
(44)
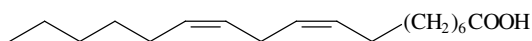
(45)

The regioselectivity of epoxidation of 1,3-conjugated dienes using manganese salen
complexes 46 (R = H or t-Bu) was compared to that using the mangenese porphyrins[60].
Similar regioselectivities were found in four different dienes (isoprene, 2,4-dimethyl-1,3-
pentadiene, 1,3-hexadiene and 1,4-diphenyl-1,3-butadiene). A very significant stride was
also made recently in the use of a chiral Mn(salen) compound (47) for asymmetric cat-
alytic epoxidation of non-functionalized alkenes[61]. This method utilizes steric control in
the approach of the prochiral double bond to the metal-oxo site, forcing preferred epoxi-
dation at one face of the double bond and therefore formation of epoxides in significant
enantiomeric excesses. Jacobsen and his coworkers found early on that in the epoxida-
tion of 1,3-cyclohexadiene and the *tert*-butyl ester of 2,4-hexadienoic acid enantiomeric
excesses of up to *ca* 60% could be obtained[62]. In a later and much more complete study[63]

(46)

$R^1 = COOEt, \ R^2 = n\text{-Hex}$

$R^1 = n\text{-Hex}, \ R^2 = Me$

$R^1 = OH, \ R^2 = n\text{-Hex}$
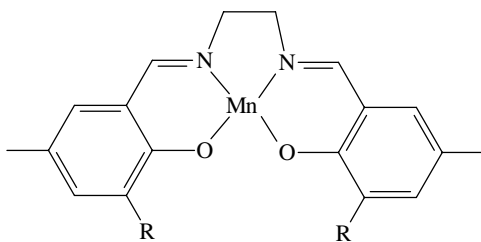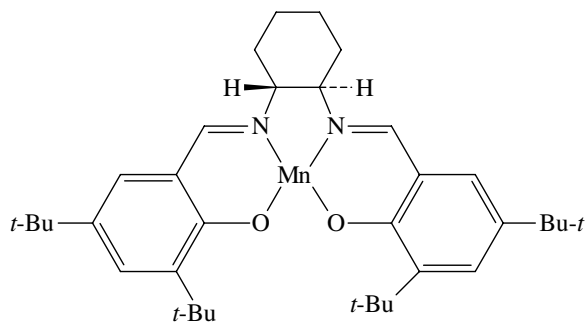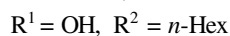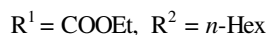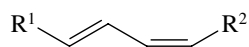
**(47)**   **(48)**

on a series of *E, Z*-conjugated dienes **48**, they found that epoxidation at the *Z* double bond was much preferred. *E*-Epoxides were formed in excess over the *Z*-isomers although ratios varied significantly with no apparent reason. Enantioselectivities were moderate to high. Other substrates such as 3-methylenecyclohexene, 1,3-cyclohexadiene and 1,3-cycloheptatriene were also epoxidized with high enantioselectivities[64]. It is important to note at the conclusion of this section that both the manganese porphyrins and salens react preferably at *cis* vs *trans* double bonds in contrast to what was found for permanganate and osmium tetraoxide. In this sense, these former compounds react in a manner similar to the peroxo compounds to be discussed below.

E. Miscellaneous

Selenium dioxide is also an oxygen donor to alkenes. In this case, however, the initial reaction of the double bond is with the selenium center followed by two pericyclic steps. After hydrolysis of the organo-selenium intermediate, the result is a hydroxylation at the allylic carbon position[65]. Thus, limonene (**2**) yields racemic *p*-mentha-1,8(9)-dien-4-ol[66]. The high toxicity of selenium intermediates and prevalence of many rearrangements has limited the widespread use of the reagent in synthesis.

III. OXIDATION WITH PEROXO COMPOUNDS

The susceptibility of a nucleophilic double bond to an electrophilic oxygen found in peroxo compounds to yield epoxides as products is a very common reaction that was first discovered by Prileschajew at the beginning of the century[67]. For much of this period the epoxidation reaction had been carried out using organic peracids as the epoxidizing agent. Much of the early research has been detailed in a very extensive and encompassing review[68] and later on in a book by Swern[69]. In the earliest years, epoxidation reactions were generally carried out using peracetic, performic, perbenzoic and perphthalic acids, although often the reaction conditions were such that the epoxide was not isolated as primary product. Usually the epoxide would react further with the acid to form glycol monoesters or with water to form diols. Later on, greater control and understanding of the reaction conditions allowed preparation of epoxides in higher yields. The oxygen transfer mechanism is generally considered to be concerted as first proposed by Bartlett (equation 9)[70]. The epoxidation of dienes as a distinct class of compounds with peracids has not been specifically reviewed, but many examples have been given in the early manuscripts[68,69].

$$\text{(9)}$$
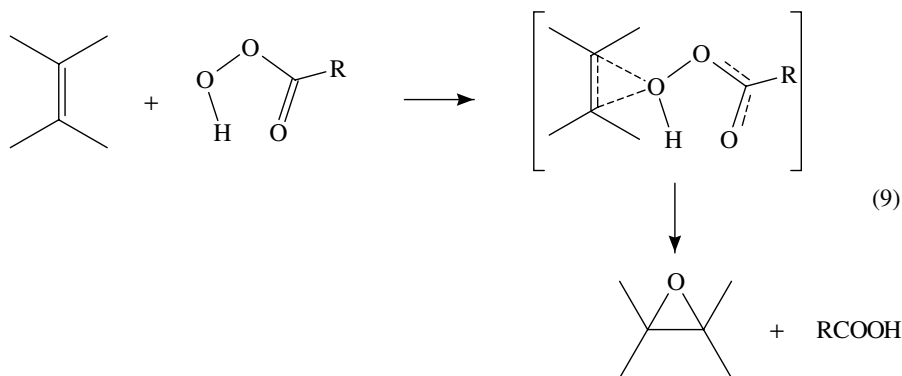
Although the use of peracids in alkene oxidation is simple, it has several drawbacks, especially in large-scale and industrial situations. As indicated above reaction control *vis a vis* selectivity can be problematic; however, additionally and perhaps more seriously, peracids are dangerous and explosive compounds which introduce stringent safety considerations when carrying out such reactions[71]. One possible remedy that is being explored is the use of safer peroxygen compounds. Another possible approach in remediation of this concern is to use alkylhydroperoxides and hydrogen peroxide as oxidants. These compounds are significantly safer and practically inert to double bonds. Their use, however, requires catalytic activation which is generally achieved by use of high-valent (d^0) transition metals with high Lewis acidity and low oxidation potentials. Most commonly used are Ti^{IV}, V^V, W^{VI}, Mo^{VI}[72] and, more recently, Re^{VII} compounds[73]. In the activation process it is commonly accepted that a M−OOH peroxo intermediate (sometimes termed an inorganic peracid) is formed which is the real epoxidizing agent. Oxygen transfer takes place by a heterolytic cleavage of the O−O bond in a manner similar to peracid oxidation. Thus, reagents prepared by mixing metal oxides such as WO_3, V_2O_5 and MoO_3 with hydrogen peroxide yield what were originally termed Milas reagents[74]. These original reagents are poor epoxidizing agents and have not been realized at large scales. However, much recent research is being aimed at improving catalytic hydrogen peroxide activation due to its great perceived ecological and economic advantages. Similarly, there have been considerable efforts in the activation of alkylhydroperoxides, most prominently *t*-BuOOH. This activation was first realized by Hawkins in 1950[75] and since has been investigated by many groups. As in the case of organic peracids, there has been no systematic review on the catalytic oxidation of dienes with hydroperoxides.

A. Oxidation with Organic Peracids

The most widely accepted method for epoxidation of alkenes remains oxidation with organic peracids. The early work (up to 1970) in this field shows that a large number of dienes and polyenes were oxidized in this manner[69]. The most commonly used peracids are peracetic, monoperphthalic and perbenzoic acids which are most dominant in industrial applications. On the other hand, in laboratory procedures *m*-chloroperbenzoic acid, MCPBA, is often used, with trifluoroperacetic acid cited in more difficult transformations. Recently, the transportation of *m*-chloroperbenzoic acid has been restricted and the use of other peroxygen agents has been gaining acceptance as a general alternative. Among the substrate types epoxidized it would be especially worthy to point out polyunsaturated

steroids, fatty acids, terpenes and diesters as well as many simpler di- and poly-ene hydro-carbons. The easiest way to summarize the vast pre-1970 literature (over 600 substrates) would be to note the following general conclusions which may serve as a guideline for reactivity in polyfunctionalized compounds. First and foremost, reactions are most strongly affected by the nucleophilicity of the double bond. Therefore, the higher the alkyl sub-stitution at the double bond the higher the reactivity. On the other hand, the presence of electron-withdrawing groups such as carbonyl, carboxylic acids and esters strongly decreases the likelihood of reaction at proximate double bonds. Furthermore, *cis*-alkenes are more reactive than *trans*-alkenes, strained double bonds are more reactive than alkenes without strain, cycloalkenes react more easily than dialkyl substituted alkenes and aryl substituents have little effect. Finally, in conjugated dienes, the epoxidation of the second double bond is slower than the epoxidation at the first double bond. Using these guidelines, the expected regioselectivity in a diene epoxidation can be easily determined. In addition, almost without exception, the epoxidation is stereospecific, i.e. *cis*-double bonds yield *cis*-epoxides whereas *trans*-double bonds yield *trans*-epoxides[76]. In certain cases neighboring groups may effect direction of the peracid attack at the double bond by steric interaction.

As the oxidation of alkenes with organic peracids is so prevalent, little has been researched over the past two decades at an academic level, especially as concerns epoxida-tion of di- and poly-enes. It is important, however, to point out that organic peracids have, despite safety considerations, been applied in a number of industrial applications[77]. As concerns polyunsaturated substrates, the most important are the epoxidized vegetable oils (naturally occurring mixtures of unsaturated triglycerides) which are important stabilizers and plasticizers for PVC. Synthetic polymers such as polyisoprenes and polybutadiene containing various percentages of 1,4-*cis*, 1,4-*trans* and 1,2-vinyl olefinic units are avail-able which can be epoxidized easily to a level of 6–8% oxirane oxygen. More recently natural rubber has been epoxidized to form a new polymer, epoxidized natural rubber ENR. Both types of the epoxidized polymers may compete with natural rubber in non-tire applications. An interesting monomeric diepoxide is **49**, which is both a thermosetting and UV curable cross-linking agent used in the electronics industry.
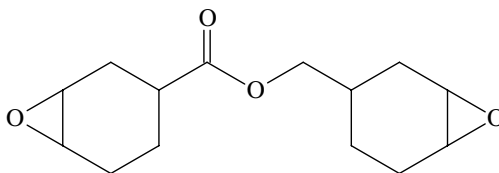

**(49)**

B. New Peroxygen Reagents

Safety considerations concerning the organic peracids described above have led to a search for possible new peroxygen agents with reduced hazard in their use. Despite this trend MCPBA is still often used in the laboratory. For example, one may note its use in the triepoxidation of barrelene[78]. Some recently developed organic peroxygen compounds include magnesium monoperoxyphthalate hexahydrate, MMPP **(50)**, DABCO-di-*N*-oxide-di-perhydrate **(51)** and urea hydrogen peroxide, UHP **(52)**. The oxidation of 1,2-dimethylcyclohexa-1,4-diene **(53)** and 4,7-dihydroindane **(54)** with MMPP[79] proceeds in an identical manner to that with MCPBA[80], i.e. epoxidation at the more electron-rich double bond is preferred. Similar preference for epoxidation at the more substituted double bond was observed in the reaction of **55** carried as one of the stages in the synthesis of the quinone antibiotic frenilicin[81].

(50)

(51)

(52)

(53)   **(54)**   **(55)**
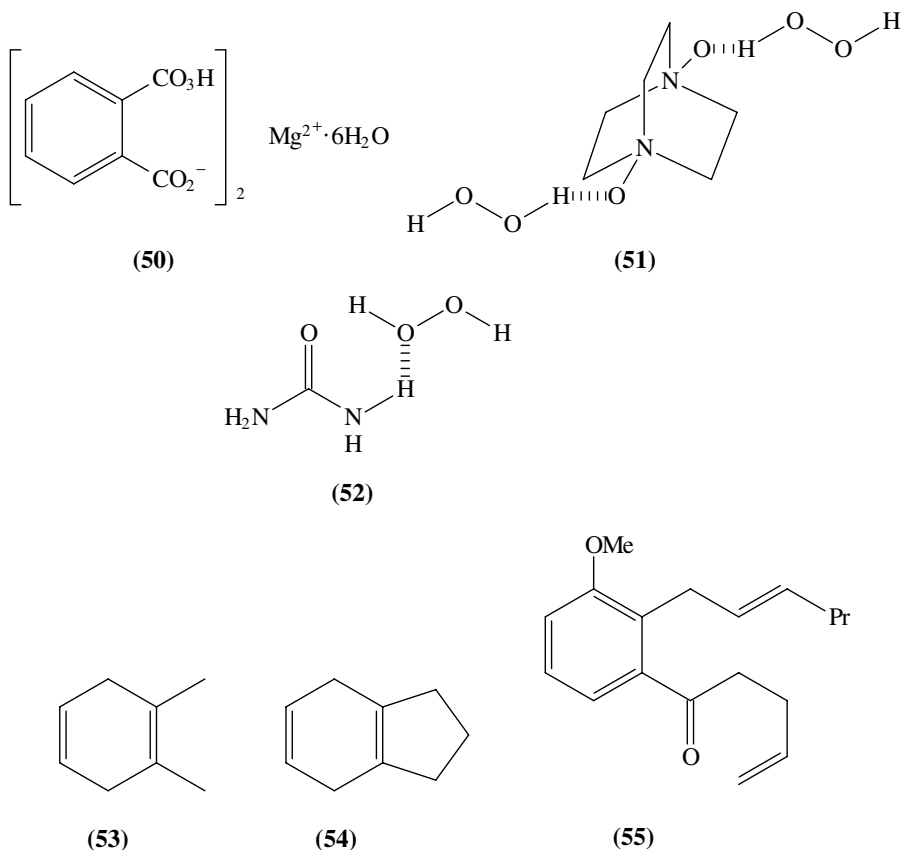
Epoxidation of limonene (2) with both MMPP and UHP proceeded preferentially at the endocyclic double bond with a 4:1 ratio of regioisomers being observed[82]. The presence of electron-withdrawing groups also has in general the predictable effect. Therefore, ger-anyl acetate (3 with OH replaced by OAc) is epoxidized mostly at the 6,7-double bond with both UHP and MCPBA[83]. Notably, this selectivity can be reversed by using an emulsion technique where the more hydrophobic 6,7-double bond is kept from the water-dissolved oxidant in the hydrocarbon or oil phase. Selectivity of 93% to the 2,3-epoxide was obtained[84]. Normal regioselectivity was obtained in the epoxidation of the substituted diene esters 56 and 57 with MMPP. The former yielded the α-epoxide, 58, exclusively vs 3:1 mixture of α versus β-epoxide with 3,5-dinitroperbenzoic acid[85], whereas the latter gave, upon acid-catalyzed cyclization, a tetrahydrofuran intermediate 59 as a key step in the total synthesis of (+)-altholactone (equation 10)[86]. Worth noting also is the good diastereofacial selectivity obtained with MMPP, 3.5:1, in favor of the β-face vs poor selectivity with MCPBA. In the oxidation of α-ionone (60) with UHP, the endocyclic double bond was exclusively epoxidized[78]. This selectivity could be inverted by using basic conditions where a nucleophilic HOO^- species is formed and is known to attack the more electrophilic double bond[87].
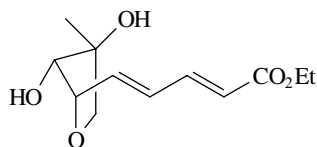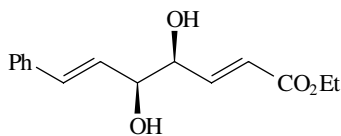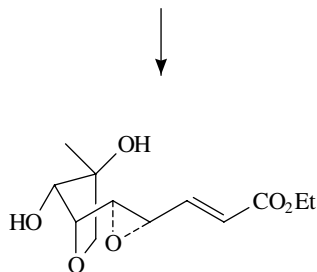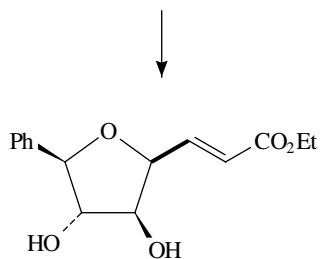
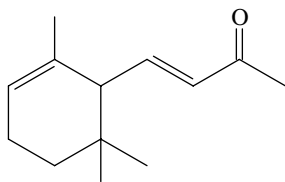**(56)**   **(57)**

(10)

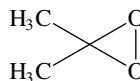**(58)**   **(59)**


**(60)**   **(61)**

Another interesting new class of peroxygen compounds relevant to the oxidation of alkenes are the dioxiranes, especially the dimethyldioxirane **(61)** only recently isolated[88]. Although almost no specific research has been carried out in diene oxidation, research into the oxidation of various alkenes has revealed that the dioxirane reagent is less sensitive to substitution effects than peracids, thereby leading to greater reactivity with less nucleophilic substrates[89]. One important example worth pointing out is the epoxidation of allenes, **62**, to the corresponding diepoxides, **63**[90,91]. An interesting comparison may be made when investigating similar oxidations with MCPBA[92]. In certain cases formation of a monoepoxide may be followed by a cyclization reaction[93]. Another highlight in the use of dimethyldioxirane is the epoxidation of aflatoxin B$_1$ to form the 8,9 epoxide, **64**, a well-known carcinogen which could not be prepared by other methods[94].

Inorganic peroxygen compounds have also been mentioned as possible organic peracid substitutes. Most noteworthy are potassium monopersulfate, oxone, as a triple salt 2KHSO$_5$ · KHSO$_4$ · K$_2$SO$_4$, sodium perborate and sodium percarbonate. The direct use of oxone has been limited because of the high acidity of this reagent, although it is most often used in the presence of ketones to form dioxiranes as discussed above[95]. 4-Vinylcyclohexene was predominately oxidized at the endocyclic double bond with this

(62)   **(63)**   **(64)**
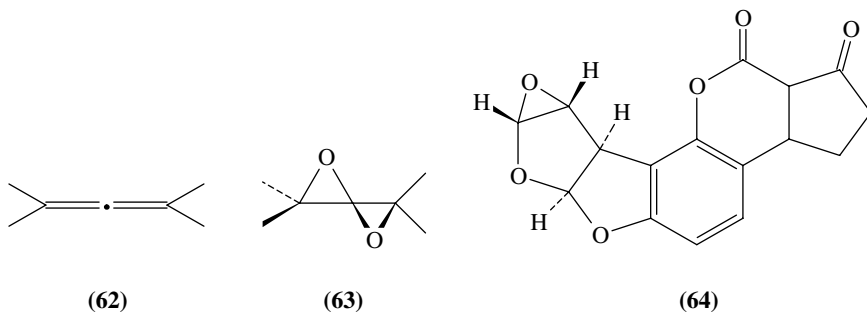
reagent[96]. In a somewhat unusual reaction oxone gave higher yields than MCPBA in the oxidation of the dienyl ethers **65** (R = Me, Et), a key step in the total synthesis of bruceantin[97]. A 2-nitrobenzenesulfonyl peroxide is active in diene epoxidation at $-30\,^{\circ}\text{C}$ with normal regioselectivity[98]. Sodium perborate has been used to epoxidize the tricyclic diene **66** at a 50% yield to the diepoxide[99]. Oxidation of the α, β-enone **67** to **68** at high yields would seem to indicate that the perborate has a reactivity profile more similar to basic hydrogen peroxide[100]. In summary, in recent years we have seen the advent of new peroxygen reagents, developed to overcome inherent safety problems in the use of organic peracids. Selectivity profiles are often near to those found for the peracids.

(65)   **(66)**

(67)   **(68)**
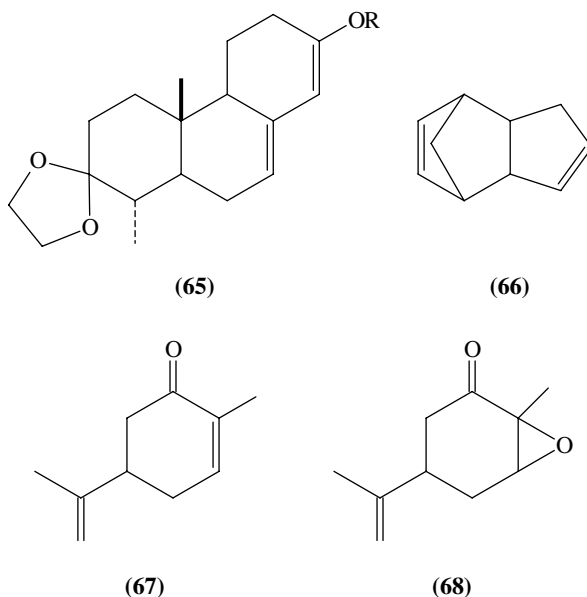
C. Catalytic Activation of Hydroperoxides

As stated above, one of the alternatives to using organic peracids for the oxidation of alkenes is the use of hydroperoxides[72]. Since the latter are practically inert to double

bonds, it is necessary to activate the hydroperoxide with high-valent transition metals. Use of main group oxides such as selenium dioxide has also been documented. The majority of research has been in the use of *tert*-butyl hydroperoxide and aqueous hydrogen peroxide. Although the exact mechanism of oxygen transfer is not known for all cases, one may generalize by saying the reaction proceeds by formation of a complex between the metal center and the hydroperoxide forming a so-called 'inorganic peracid'. The oxygen transfer occurs via heterolysis of the oxygen–oxygen bond aided by polarization of electron density to the high-valent metal. As concerns synthetic applications, it is important to point out that as the oxidation potential and Lewis acidity of the metal catalysts increase, the selectivity of the reaction often is decreased, due to homolysis of the hydroperoxide. This leads both to non-productive decomposition of the hydroperoxide and often unwanted side reactions due to the intermediate radical oxygen species formed.

1. Alkyl hydroperoxides

In agreement with the electrophilic nature of the metal-hydroperoxide intermediate, the rate of epoxidation increases with the nucleophilicity of the double bond and therefore closely parallels reactivity of organic peracids. The first in-depth study[101] with *tert*-butylhydroperoxide (TBHP) as oxidant with homogeneous vanadium and molybdenum compounds as catalysts revealed that the latter are more effective than the former by approximately two orders of magnitude. However, in the case of allylic alcohols this trend is reversed (see below). For example, oxidation of limonene[102] (**2**) and 4-vinylcyclohexene[96] exclusively yielded the epoxide at the endocyclic double bond with $Mo(CO)_6$ as catalyst. Similarly, 1,5-cyclooctadiene and *cis, trans, trans*-1,5,9-cyclododecatriene both yielded monoepoxides with the same catalyst, the latter preferably at the *cis*-double bond. Conjugated dienes such as 1,3-butadiene and isoprene[103] reacted more slowly. The latter reaction was not regioselective. Other molybdenum complexes have also been used[104]. Early on it was also found that functional groups such as acetates could bring about preferential attack at the double bond from the face of the molecule containing the functional groups, leading to excess formation of stereoisomers, in contrast to what was observed for organic peracids[105].

The strong rate acceleration observed in allyl alcohol oxidation with vanadium compounds, usually $VO(acac)_2$, despite the electron-withdrawing effects observed in peracid epoxidation, was attributed to the strong coordination of the alcohol ligands to the metal. This use of $VO(acac)_2$ and TBHP was utilized to selectively epoxidize both geraniol and linalool at the double bond allylic to the alcohol group with very high selectivity, in contrast to what was found with organic peracids[106]. The principle of preferred oxidation at an allyl alcohol double bond was further utilized almost immediately. Examples include the oxidation of the multifunctionalized alcohol, **69**, to the diepoxide, **70**, in the synthesis of a juvenile hormone[107], and regioselective epoxidation of **71** to **72** (equation 11)[108]. The reactions are also stereospecific to *syn* addition. Therefore, the regioselectivity along with the stereospecificity of addition was also used in the epoxidation of 1,5-cyclohexadiene-4-ol[109] and the cyclic dienol, **73**, which led to **74** via transannular rearrangement of the initially formed *syn*-epoxide (equation 12)[110]. The stereoselectivity of the epoxidation was also applied in the preparation of the antibiotic methyl pseudomonate A[111]. Homoallylic alcohols can also be epoxidized very effectively[112]. In compound **75** having both an endocyclic and an exocyclic homoallylic double bond, the former was oxidized much more easily to yield **76** (equation 13)[113].
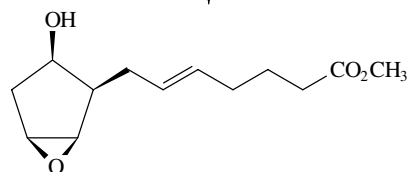
**(69)**

(70)   (11)

(71)

(72)

(73)   (12)

(74)
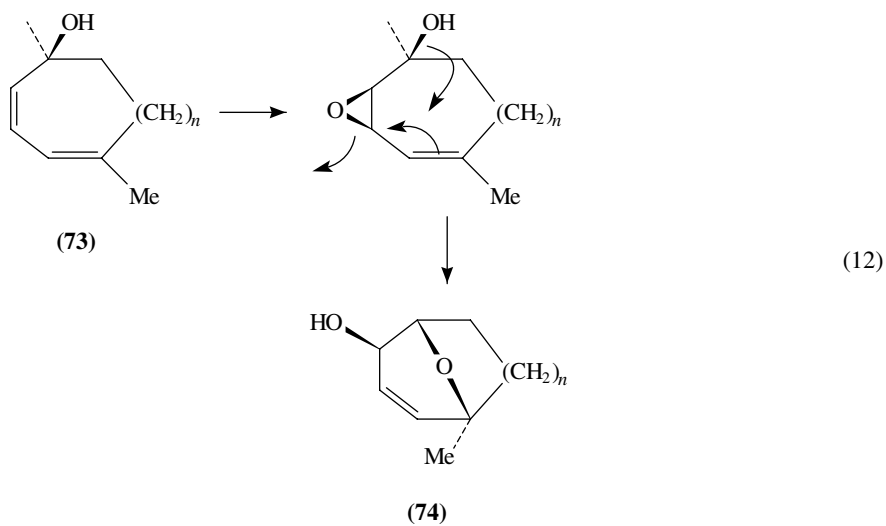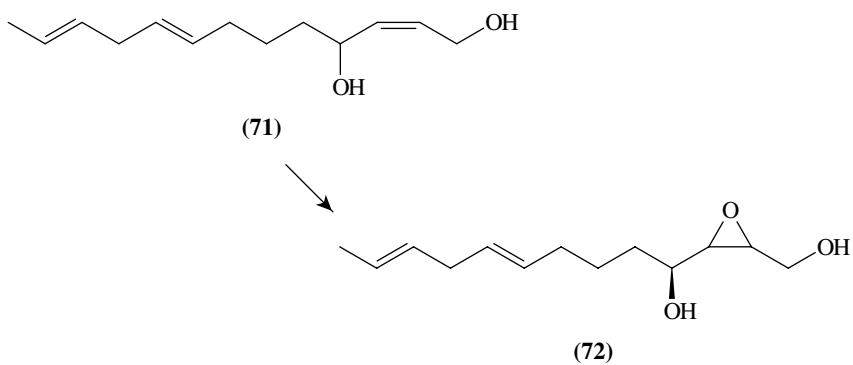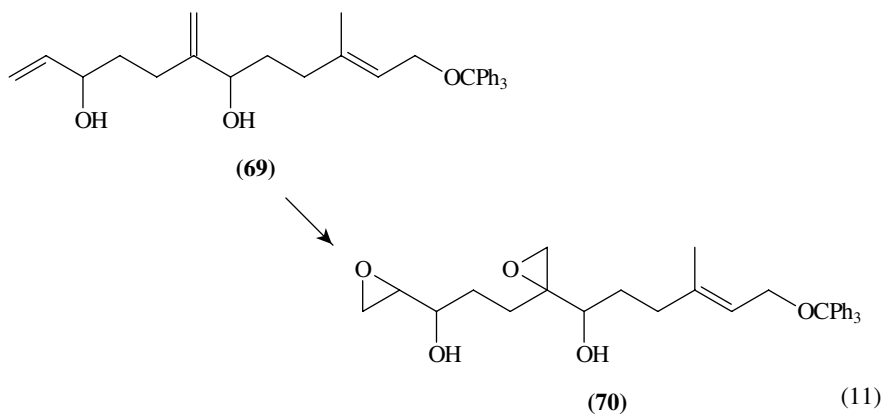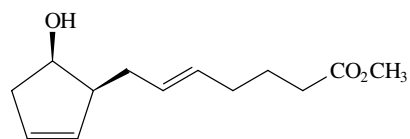
(75)

(13)

(76)

A very interesting way to control alkene epoxidation was introduced by Breslow and Meresca[114]. In the steroid diene, **77**, epoxidation takes place exclusively at the 4,5 double bond using $Mo(CO)_6$ and TBHP. However, by attaching a template, as in **78**, to the alcohol, the regioselectivity could be inverted so that epoxidation takes place only at the 17,20 double bond. It was concluded that the appendage did not act as a steric shield, but the remote tertiary alcohol moiety was transformed *in situ* to a hydroperoxide resulting in the observed selectivity by intramolecular epoxidation. This approach was then extended to other functionalized polyenes, such as farnesol and geranylgeraniol[115].
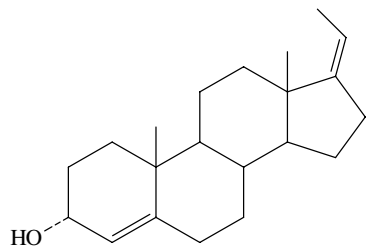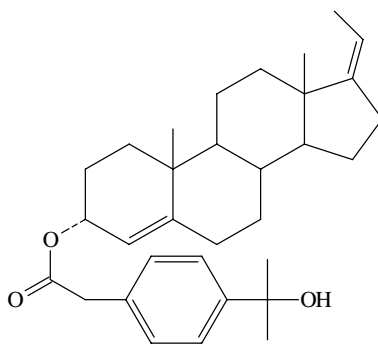

(77)   **(78)**

The use of alkylhydroperoxides as epoxidizing agents for allylic alcohols under catalytic conditions was soon expanded into enantioselective epoxidation with use of the more mild titanium alkoxides in the presence of chiral tartaric esters[116]. As concerns the epoxidation of functionalized dienes, these now so-called Sharpless conditions [$Ti(OPr^i)_4$, dialkyl tartrate, TBHP] have been utilized to enantioselectively epoxidize 1,4-pentadiene-

3-ol[117] **(79)**, 2,8-nonadiene-4-ol[118] **(80)** (equation 14), geraniol and linalool at the allylic position[119] as well as many others which have been complied in a recent review[120]. Steric factors may also play a role in the enantioselective formation of epoxy alcohols. Therefore, in the case of the optically active alcohol **81**, use of (+) diisopropyl tartrate, (+)-DIPT, yields the desired epoxy alcohol in a 92% ee ('matched pair') whereas with (−) diisopropyl tartrate, (−)-DIPT, only a 50% ee was observed in a 'mismatched pair' (equation 15)[121]. The triene **82** was also epoxidized with very high enantioselectivity[122]. Other important epoxy alcohols formed include squalene oxide analogs[123], intermediate in the synthesis of marmine[124] and virantmycin[125]. Recent examples of inverse enantioselectivity[126] and the use of different chiral auxiliaries have been reported[127].


(14)

(15)
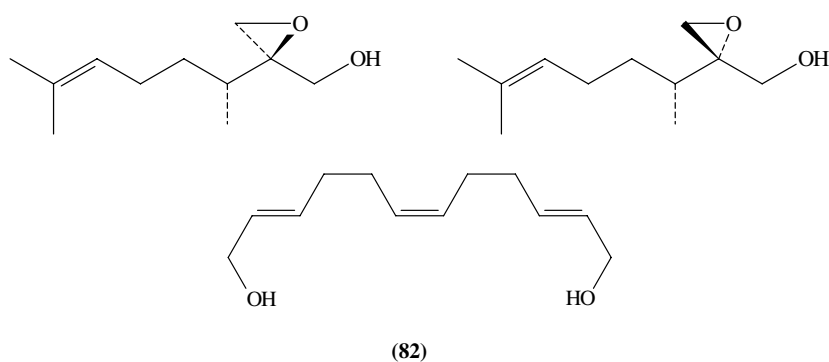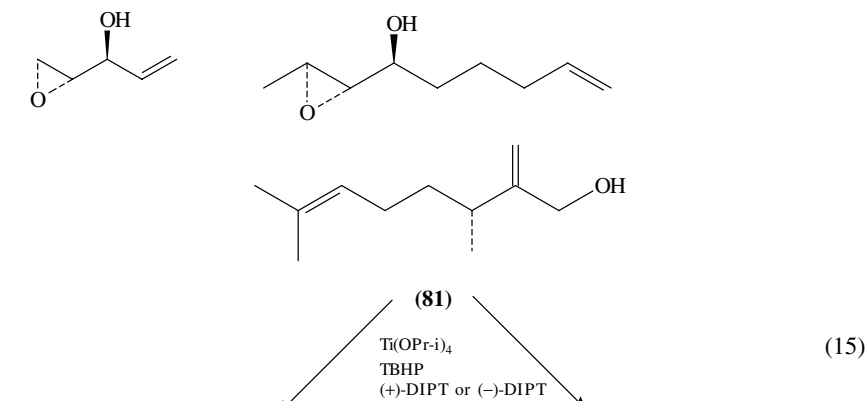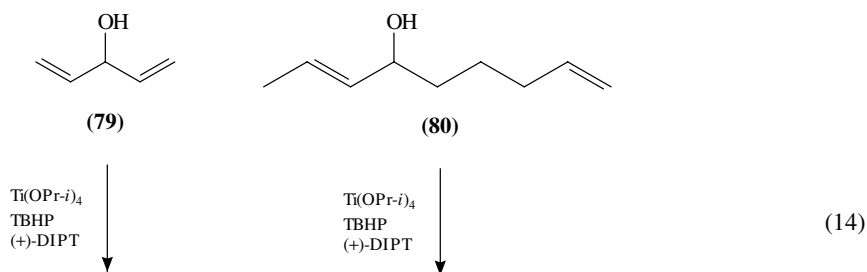
A further interesting extension of the allyl alcohol epoxidation reaction is the metal-catalyzed direct hydroxy-epoxidation of alkenes. In such a reaction an ene reaction with singlet oxygen, $^1O_2$, or Schenk reaction forming an allylic hydroperoxide is combined with metal-catalyzed intramolecular epoxidation to form epoxy alcohols[128]. For example, with 2,5-dimethyl-2,4-hexadiene (83) two different isomers, 84 and 85, were obtained with Ti(OPr-i)$_4$ and VO(acac)$_2$, respectively (equation 16)[129]. Similar reactions were also carried out on dicyclopentadiene[130] and α-ionone (60)[131]. Recently, a large pore bifunctional titanium-aluminosilicate was used to epoxidize and then cyclize linalool (86) to a mixture of furan and pyran derivatives in one step (equation 17)[132]. Other titanium-substituted silicates have also been used for the epoxidation of limonene[133].
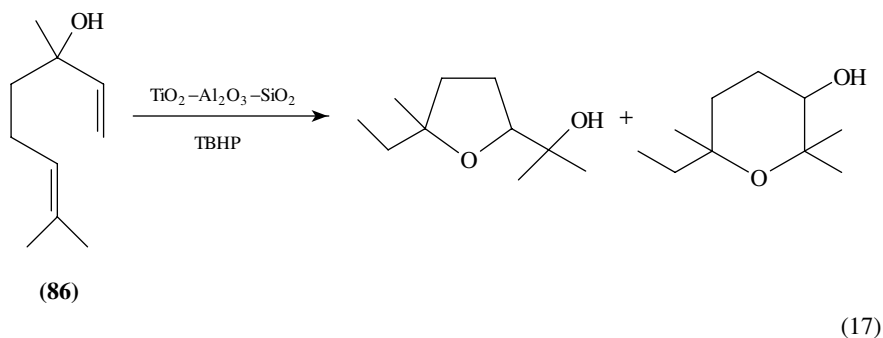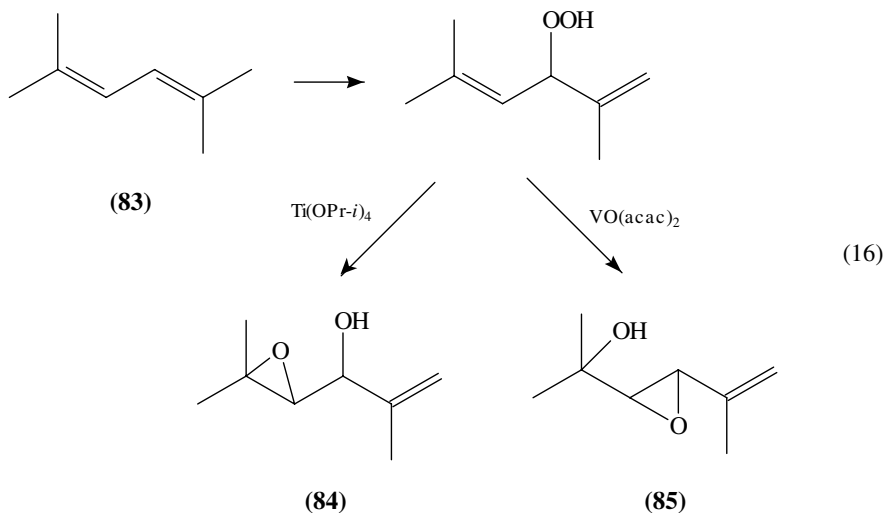
Towards the end of this section it may be worthwhile to point out some new reactions with high-valent metals and TBHP. The first is a pyridinium dichromate PDC−TBHP system[134]. Nonsubstituted or alkyl-substituted conjugated dienes, such as 1,3-cyclooctadiene (87) and others (also linear dienes), yield keto allyl peroxides 88 (equation 18), whereas phenyl-substituted dienes such as 1,4-diphenylbutadiene (89) gave diketo compounds, 90 (equation 19). In further research into a GIF-type system[135] with iron and TBHP, limonene gave a mixture of products with carvone as the major product. The mechanism is thought to proceed initially by formation of a Fe(V)−carbon

intermediate, followed in the presence of air to a peroxo intermediate, from which products are formed[136].

(87)   (88)   (18)

(89)   (90)   (19)
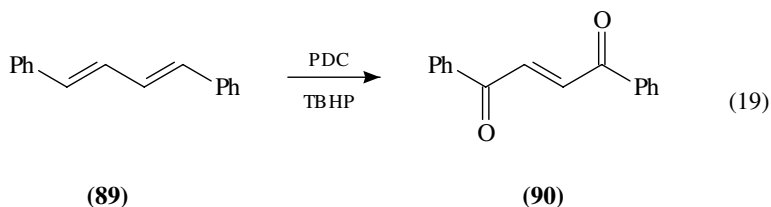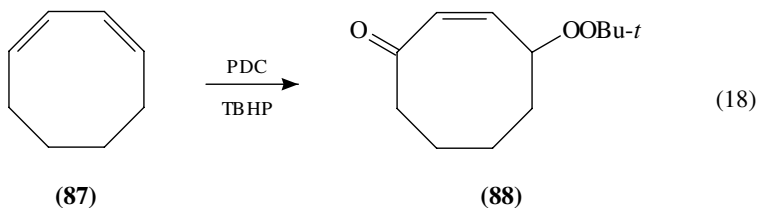
2. Hydrogen peroxide

The use of hydrogen peroxide in catalytic oxidation of dienes is highly desirable from an economic and ecological point of view. However, there are relatively as yet few results in this still rather virgin field, especially compared to the significant success that has been obtained with TBHP and other alkyl hydroperoxides. Some of the earlier results showed that 1,5,9-cyclododecatriene, 1,4-cyclooctadiene and 1,3-cyclooctadiene could all be epoxidized in the range of 80–90% epoxide vs diol selectivity with simple oxides such as WO_3, MoO_3 and V_2O_5[137]. More recently, peroxotungstates of the type $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ have been used to oxidize 4-vinylcyclohexene exclusively at the endocyclic double bond and the steroid 4,20-pregnadiene-3-one (91) at the 20,21 double bond[138]. Another pertungstate salt which has been used advantageously is the $W_2O_{11}{}^{2-} \cdot 2Ph_3PCH_2Ph^+$ compound[139] which has been shown to catalyze the oxidation of limonene, geraniol, nerol and carvone (92). For limonene the endocyclic position is
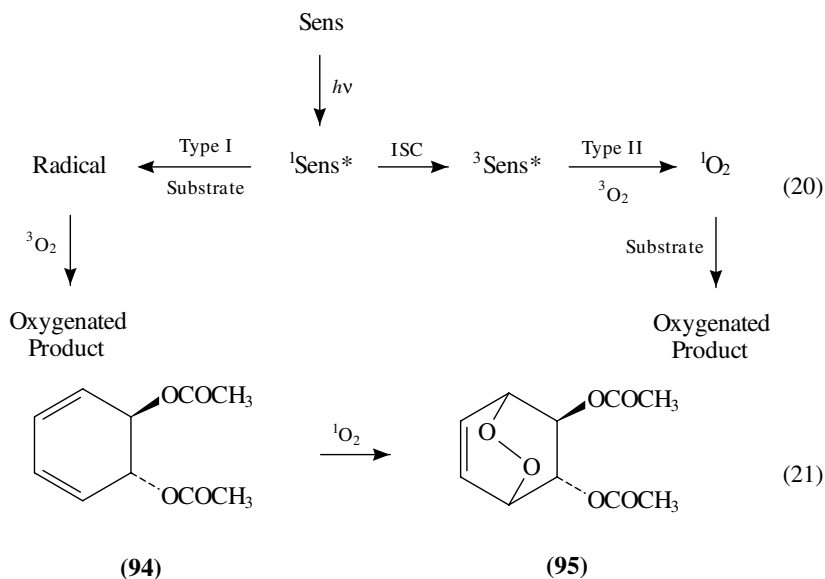

(91)   (92)   (93)
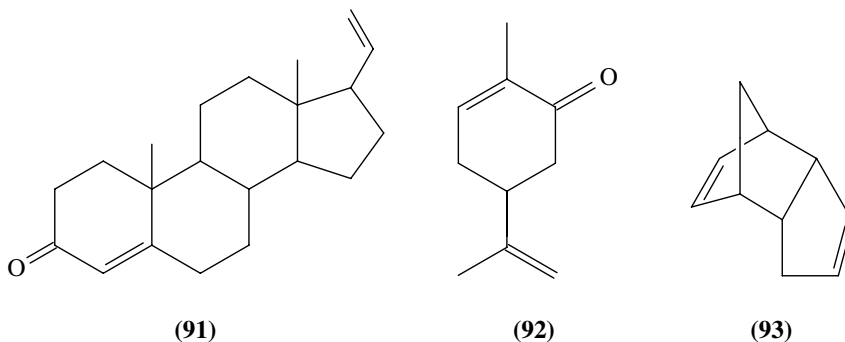
highly preferred, for nerol and geraniol the allylic position is most reactive whereas, in carvone, the α-keto group causes strong deactivation of the neighboring double bond leading to epoxidation at the 9,10 position. Use of the phosphotungstate, $PW_{12}O_{40}^{3-}$, leads to a mixture of mono- and di-epoxides in the epoxidation of the tricyclic **93**[140]. Similarly, $PMo_{12}O_{40}^{3-}$ has been used in the oxidation of dienes with one allylic alcohol unit. The α-epoxy alcohols are the preferred products[141]. Recently, our group has also used a manganese-substituted polyoxometalate as catalyst for diene epoxidation with hydrogen peroxide[142].

IV. OXIDATION WITH OXYGEN

The oxidation of organic compounds with molecular oxygen is a highly desirable goal stemming from its availability. From a thermodynamic point of view combustion products are of course always to be preferred, therefore specific methods and catalysts must be found to bring about selective reactions. Molecular oxygen is a triplet in its ground state making the direct reaction with the majority of organic substrates which are singlets, among them of course dienes and polyenes, a disallowed process. Only upon the input of a large amount of thermal energy, as in gas-phase reactions, can one bring about oxidation of organic substrates, but this has never been successfully done with dienes or polyenes. The use of molecular oxygen, therefore, in essence requires indirect methods for its activation and use in synthetic organic chemistry. In this section, we will discuss these methods. The first possibility is to excite the ground state molecular oxygen to an excited state forming singlet oxygen, $^1O_2$. This is commonly done with light radiation using photosensitizers[143]. The singlet oxygen thus formed is highly reactive with organic substrates and has been especially and successfully used in the formation of numerous endoperoxides from conjugated dienes[143]. A second method commonly employed to use molecular oxygen in organic chemistry is to form hydrocarbon radicals[144]. These radicals react at a diffusion-controlled rate with molecular oxygen, forming peroxides. These intermediates can propagate a radical chain reaction, termed autooxidation, by formation of more hydrocarbon radicals and intermediate hydroperoxides. Initial formation of hydrocarbon radicals occurs occasionally due to thermal carbon–hydrogen bond disassociation, although for most practical applications thermally sensitive initiators are employed. Alternatively, photoactivation as well as use of catalysts of sufficient oxidation potential may be considered in order to initialize radical formation. A third method to utilize molecular oxygen is to form metal–dioxygen bonds which, under appropriate conditions, form highly active metal-oxo intermediates[145]. In nature, monooxygenase enzymes such as cytochrome P-450 or methane monooxygenase utilize reducing agents in order to split the oxygen–oxygen bond. Dioxygenases are also known. Although many enzymatic systems have been discovered, they are as yet relatively poorly understood and have not been translated by comparable synthetic or biomimetic systems to diene oxidation. A fourth way to use molecular oxygen is as the secondary oxidant in a catalytic cycle. In such a cycle a primary oxidant, often a metal catalyst, is used to carry out the original oxidative transformation of the organic substrate. The reduced primary oxidant or metal catalyst can then be reoxidized by molecular oxygen. The most important prototype of this reaction is the palladium-catalyzed oxidation of alkenes, commonly termed the Wacker process or reaction[146]. A fifth and final method for employing molecular oxygen is to pass it between two electrodes at high voltages thereby producing ozone, O_3. The latter is a highly potent oxidizing agent[147].

A. Singlet Oxygen

Singlet oxygen may be produced chemically by reaction of hydrogen peroxide and hypochlorite. The most useful procedure, however, is via sensitized photooxidation (equation 20). Light absorption of the sensitizer leads to formation of a sensitizer in the excited singlet state. In some cases, especially with electron-poor aromatics and ketones, a type I photooxidation will take place whereby electron transfer between the substrate and the excited state singlet sensitizers will yield a radical ion. The latter will react with ground triplet oxygen. These types of reactions will be discussed in the next section. More commonly, the excited singlet sensitizer, most commonly rose bengal, methylene blue and porphyrins, undergoes intersystem crossing to the triplet state and then reacts in a type II photooxidation with ground state oxygen to form singlet oxygen, which then reacts with the organic substrate to form product. The reaction of singlet oxygen with conjugated dienes forms endoperoxides as the initial product by a Diels–Alder type reaction where singlet oxygen reacts as a dienophile[148]; the reaction of **94** to **95** (equation 21) is simply a fairly recent example[149]. Reactions are most efficiently selective to the endoperoxides at low temperatures in halogenated or deuterated solvents.

$$\text{Sens}$$

$$\downarrow h\nu$$

$$\text{Radical} \xleftarrow[\text{Substrate}]{\text{Type I}} {}^{1}\text{Sens*} \xrightarrow{\text{ISC}} {}^{3}\text{Sens*} \xrightarrow[{}^{3}\text{O}_2]{\text{Type II}} {}^{1}\text{O}_2 \qquad (20)$$

$$\left. {}^{3}\text{O}_2 \right\downarrow \qquad\qquad\qquad \text{Substrate} \downarrow$$

$$\begin{array}{cc}\text{Oxygenated} & \text{Oxygenated} \\ \text{Product} & \text{Product}\end{array}$$

$$(21)$$

(94)   **(95)**

Kinetic measurements showed the following relative rates for oxidation with singlet oxygen with representative conjugated dienes: 1,3-cyclooctadiene < 2-*cis*-4-*trans*-hexadiene < 2-*trans*-4-*trans*-hexadiene ∼ 1,3-pentadiene < 1,3-cycloheptadiene < 1,3-cyclohexadiene < 1,3-cyclopentadiene[150]. The slow reactions of the eight-membered and larger rings are attributed to the lack of planarity of the diene[151]. The slower rate of addition for acyclic dienes vs cyclic dienes often causes formation of byproducts such as dioxetanes and hydroperoxides in the reaction of the former, which are rarely observed in the latter. An interesting example showing both formation of the hydroperoxide in acyclic dienes and endoperoxide formation in cyclic hexadienes was observed in the oxidation of neoabietic acid **(96)** to the endoperoxide **97** (equation 22)[152].

(96) **(22)**

(97)
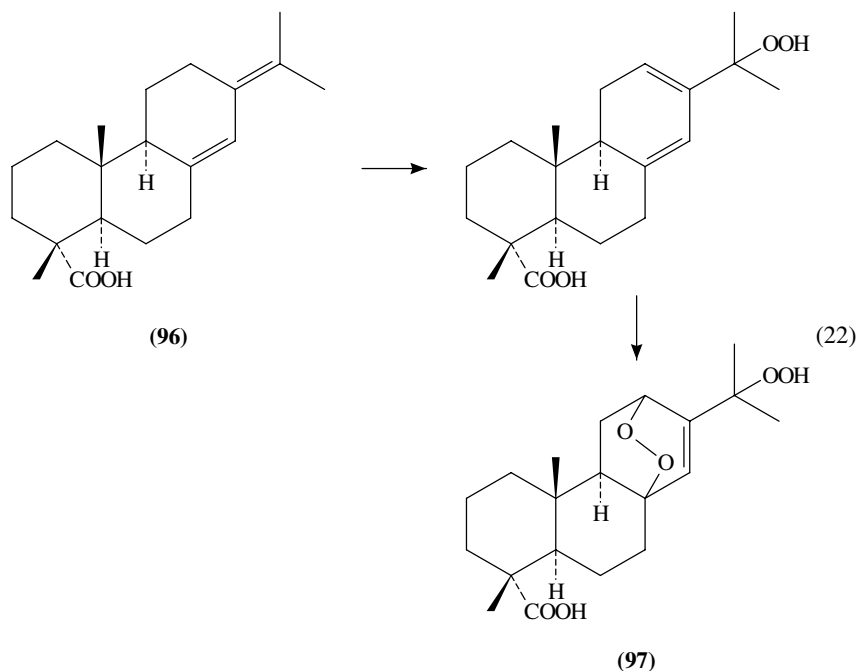
The literature on the oxidation of dienes with singlet oxygen is very voluminous and only recently both the mechanistic and synthetic aspects of this reaction have been very thoroughly reviewed and therefore will not be repeated here[153]. It is worth pointing out that the stable endoperoxides formed in the addition of singlet oxygen to conjugated dienes may be manipulated in many ways to form further interesting products, for example by reduction[154] or rearrangement[155]. Products which may be obtained include acids, ketones and aldehydes, alcohols, epoxides and others depending on the specific additional conditions applied during or after the singlet oxygen reaction.

Non-conjugated dienes react differently with singlet oxygen. In such substrates each alkene reacts as a separate entity with allylic hydroperoxides being the predominant product via the Schenk reaction[156]. Regioselectivities in such reactions vary to a great degree. The general rule of thumb is that the hydroperoxide is most easily formed at the allylic hydrogen orthogonal to the alkene plane[157] due to the electronic requirement for overlap between p orbitals of the developing double bond in the transition state[158]. It has been shown that functional groups may affect regioselectivity, for instance in the oxidation of α, β-unsaturated ketones[159]. Stereoselectivity in reactions of non-conjugated dienes with singlet oxygen is a newly found phenomenon. In connection with the synthesis of calcitriol (dihydroxyvitamin D_3) both remarkably high regio- and stereoselectivities were observed[160]. A further investigation has shown that the selectivities obtained are due to a combination of electronic and steric effects where addition of carboxylic acid substituents lead to selectivity[161].

Finally, another interesting use of singlet oxygen in the oxidation of dienes concerns the reactivity of allenes. Besides the formation of endoperoxides by addition to dienes and hydroperoxide formation via the ene reaction, singlet oxygen reacts with electron-rich

alkenes to form dioxetanes. Allenes react in this manner[162]. Thus, the triene **98** yields **99** (equation 23)[163]. Similarly, an adamantane disubstituted allene also yields the same type of product[164]. Dioxetane formation was also observed in the reaction of the norbornene derivative **100** to yield **101** (equation 24)[165].

$$\text{(23)}$$

(98) **(99)**

$$\text{(24)}$$

(100) **(101)**
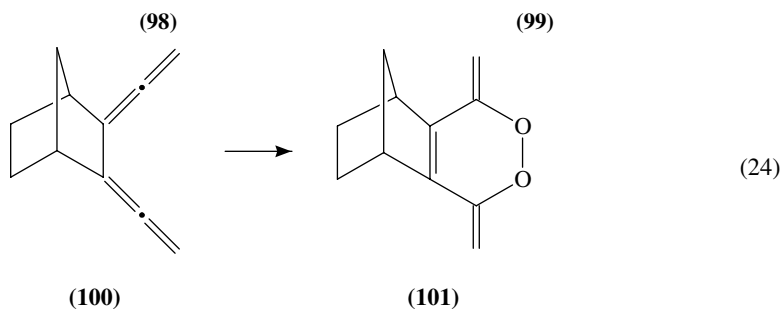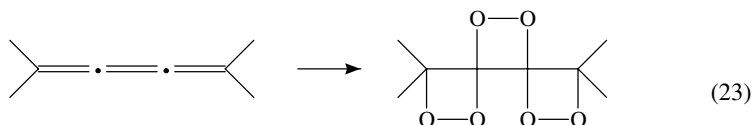
B. Triplet Ground State Oxygen

As stated above, reaction of triplet ground state molecular oxygen with a singlet organic substrate requires formation of a radical (atom transfer) or cation radical (electron transfer) from the former to an initiator or catalyst. This type of chemistry has been realized in a variety of ways. One common scheme is to mix an aldehyde, alkene and dioxygen often in the presence of a catalyst[166]. Since aldehydes are relatively sensitive to hydrogen abstraction, peracids are easily formed in this manner (equation 25). The peracids may then quickly react with the alkenes, also dienes and polyenes, in the reaction mixture to form epoxides. Although these are technically reactions with molecular oxygen, the reactivity and mechanism is more similar to that of organic peracids. A recent example of the use of this technique is in the oxidation of 3-hydroxy-7-methyl-1,6-octadiene to the expected epoxide at the nonallylic position[167]. There has been no further systematic study of diene oxidation using these systems.


$$\text{(25)}$$
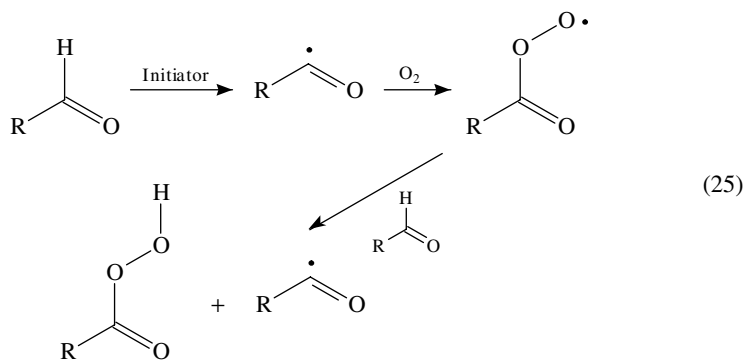
Reaction of molecular oxygen with radicals formed directly from dienes is a subject of chemical, medicinal and biological interest[168]. The polyenes of most interest are the fatty acids, linoleic acid (*cis,cis*-9,12-octadecadienoic acid), γ-linolenic acid (*cis,cis,cis*-6,9,12-octadecatrienoic acid), α-linolenic acid (*cis,cis,cis*-9,12,15-octadecatrienoic acid), arachidonic acid (*cis,cis,cis,cis*-5,8,11,14-eicosatetraenoic acid) and polyenes from the prostaglandin family of compounds. The polyunsaturated acids are important components of membranes and the prostaglandins are important regulatory compounds. The autooxidation of these compounds has often been associated with aging and disease. Using linoleic acid as a model it has been found that carbon–hydrogen bond strengths are 82, 87 and 95 kcal mol^{-1} for the bisallylic, allylic and nonallylic secondary carbons, respectively[169]. Therefore, autooxidation using free radical initiators will predominantly, but not only, yield hydroperoxides at the bisallylic positions. A report on a unified mechanism of polyunsaturated acid autooxidation including kinetic measurements has been carried out for linoleic[170] and triene and tetraene acids[171]. Enzymatic oxidation using lipoxygenase enzymes, however, yields specific products. Thus, for example, using maize lipoxygenase, hydrogen abstraction at the bisallylic position of linoleic acid (**102**) is accompanied by isomerization of the double bond and stereospecific formation of 9-*d*-hydroperoxy-*trans,cis*-10,12-octadecadienoic acid (**103**). Soybean lipoxygenase will similarly yield the hydroperoxide at the C-13 carbon, i.e. 13-*l*-hydroperoxy-*cis,trans*-9,11-octadecadienoic acid (**104**) (equation 26)[172].

(26)
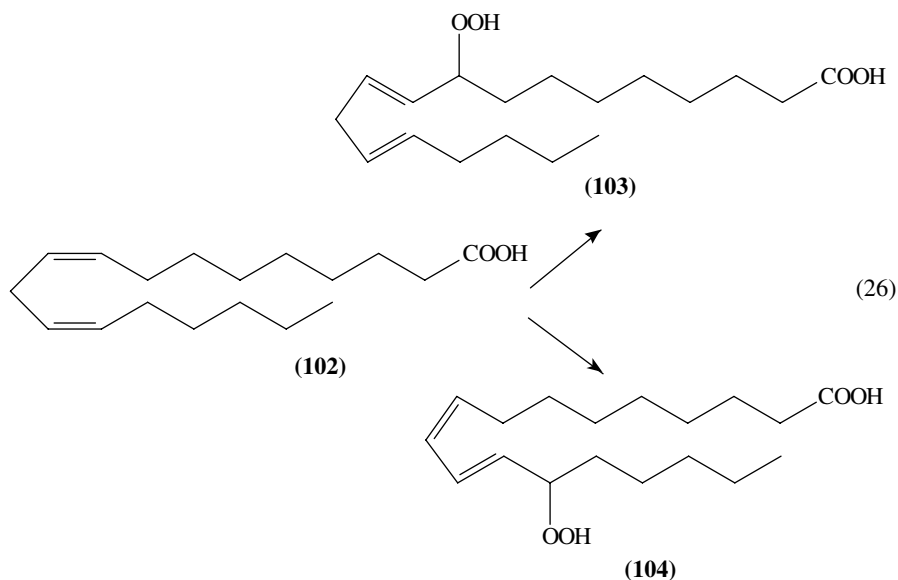
In the case of arachidonic acid, lipoxygenase enzymes will yield hydroperoxye-icosatetraenoic acids (HPETEs), which may then be enzymatically manipulated to leukotrienes by controlled dehydration or to endoperoxide prostaglandins such as PGG$_2$ by cyclooxidation[173]. The non-enzymatic reaction of diene hydroperoxides, for example **105** to form the hydroperoxide-endoperoxide **106**, has been studied (equation 27). Many additional substrates have been studied including 1-hydroperoxy-3,5-hexadiene and 1-hydroperoxy-4,8-undecadiene[174]. Similarly, the reaction of the fatty acid hydroperoxides under acid conditions (Hock rearrangement) gives both carbon–carbon bond cleavage and

ether formation[175], e.g. colneleic acid[176] via intermediate epoxides. These product types are associated with formation of organic volatiles in food degradation.

(27)

(105)   (106)
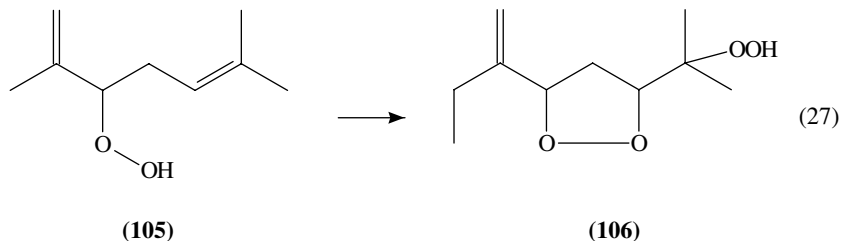
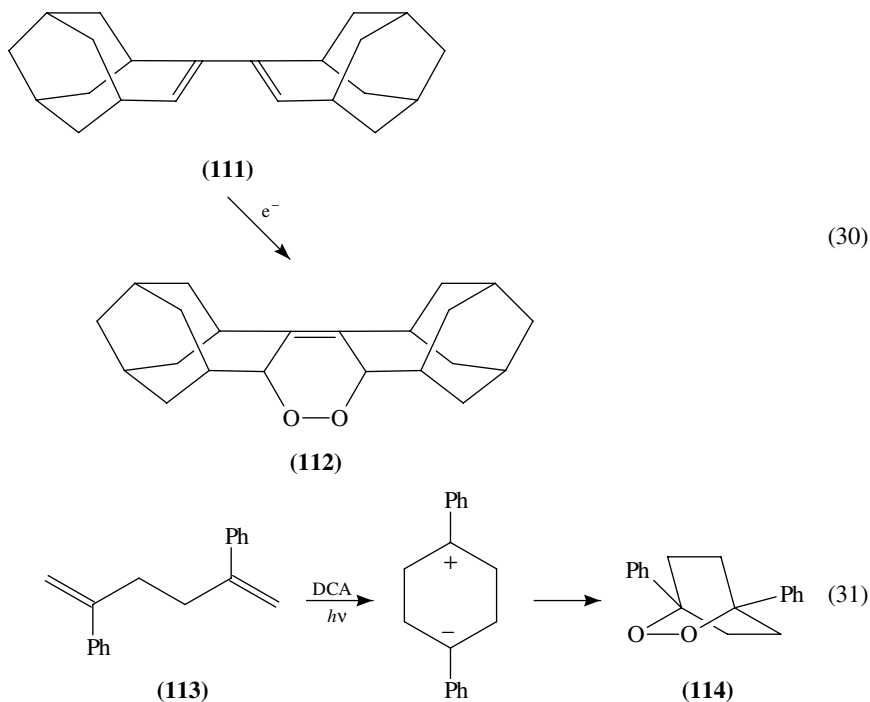Another interest in the use of triplet oxygen lies in the oxidation of dienes with photochemical activation (Type I, above) with formation of endoperoxides as products. The first example of this reaction was observed in the early 1970's. Thus, reaction of ergosteryl acetate (107) in the presence of trityl tetrafluoroborate[177] and Lewis acids[178] in the presence of light yielded the endoperoxide 108 (equation 28). With certain Lewis acids this reaction could be thermally, rather than photochemically, activated. Cation radicals were shown to be the intermediate active species, as was borne out by a comparative oxidation of the isomeric lumisteryl acetate which was inactive under these conditions but reacted easily with singlet oxygen[179]. This reaction was later extended to other substrates. Thus, the intermediacy of cation radicals was also indirectly observed by the fact that the *t*-butyl substituted 1,3-cyclodiene 109 gave a 'dimeric' product 110 (equation 29) via the cation radical intermediate in addition to the usual endoperoxide 110a[180].

(28)

(107)

(108)

(29)

(109)   (110)   (110a)
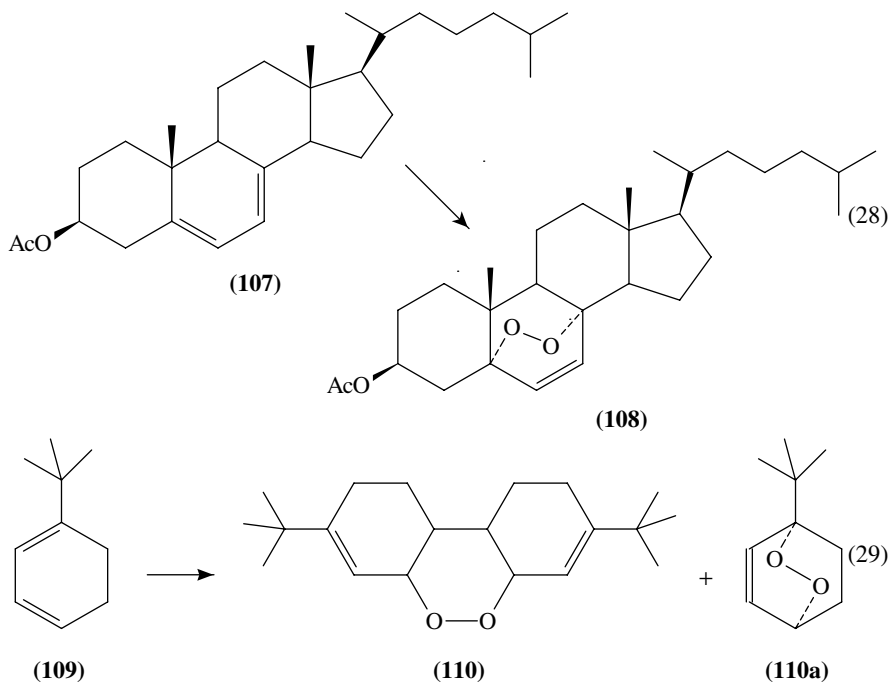
In an electrochemical transformation of **111**, **112** was obtained as product (equation 30)[181] and 9,10-dicyanoanthracene (DCA) was used to photochemically initiate the reaction of 2,5-diphenyl-1,5-hexadiene **(113)** to **114** (equation 31)[182].

(111)

e^-

(30)

(112)

(31)

(113) **(114)**

Above, we have discussed some methods for the use of triplet oxygen via interaction with organic radical intermediates. There is a natural interest in the 'activation' of molecular oxygen using transition metal complexes[183]. Excluding examples where the function of the transition metal, most often cobalt, is to form free radicals, the nonradical activation of molecular oxygen is a poorly developed field. As concerns diene oxidation, two rather exceptional examples are worth pointing out. The first is the use of a μ_3-oxo triiron catalyst in the presence of molecular oxygen to epoxidize geraniol acetate at the 6,7 position only, as found for peracid epoxidation[184]. The mechanism is unknown although the interim formation of a radical could not be discounted. Although dioxygen complexes of transition metals are often unreactive, a rhodium complex, $[(COD)_2Rh(O_2)]_2$ (COD = 1,5-cyclooctadiene), heated without any additives in benzene, resulted in oxidation of the 1,5-cyclooctadiene ligand to a mixture containing mostly cyclooctanone and cyclooctanone-4-ene[185]. Addition of $^{18}O_2$ showed that this was an intramolecular reaction.

Although there are indeed only few reported methods of direct activation of molecular oxygen via transition metals, there are many reports of indirect oxidation. The majority of this research is based on palladium-based oxidation as summarized in equation 32. The palladium complex catalyzed oxidation reactions have been reviewed previously[186] and also only very recently[187] and in this book the palladium catalyzed oxidation of dienes and polyenes will be discussed separately and therefore will not be discussed

further[188]. Molecular oxygen has also been used as a secondary oxidant in other metal-catalyzed systems. As concerns the subject of this review, it is possible to oxidatively dehydrogenate cyclic dienes to the corresponding aromatic products using the polyoxometalate, $H_5PV_2Mo_{10}O_{40}$, as catalyst. In such a way anthracene is obtained from 9,10-dihydroanthracene and *p*-cymene is the product of limonene dehydrogenation. In the latter case, dehydrogenation is preceded by isomerization of the exocyclic double bond[189].

H_2O ← reoxidant → Pd(0) ← Product

(32)

O_2 → reduced reoxidant ← Pd(II) → Substrate
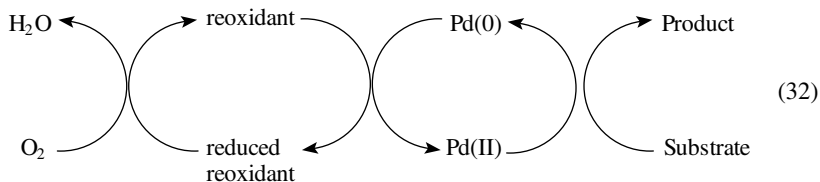
C. Ozone

Ozonolysis as used below is the oxidation process involving addition of ozone to an alkene to form an ozonide intermediate which eventually leads to the final product. Beyond the initial reaction of ozone to form ozonides and other subsequent intermediates, it is important to recall that the reaction can be carried out under reductive and oxidative conditions. In a general sense, early use of ozonolysis in the oxidation of dienes and polyenes was as an aid for structural determination wherein partial oxidation was avoided. In further work both oxidative and reductive conditions have been applied[190]. The use of such methods will be reviewed elsewhere in this book[191]. Based on this analytical use it was often assumed that partial ozonolysis could only be carried out in conjugated dienes such as 1,3-cyclohexadiene, where the formation of the first ozonide inhibited reaction at the second double bond[192]. Indeed, much of the more recent work in the ozonolysis of dienes has been on conjugated dienes such as 2,3-di-*t*-butyl-1,3-butadiene[193], 2,3-diphenyl-1,3-butadiene[194], cyclopentadiene[195] and others[196,197]. Polyethylene could be used as a support to allow ozonolysis for substrates that ordinarily failed, such as 2,3,4,5-tetramethyl-2,4-hexadiene, and allowed in addition isolation of the ozonide[198]. Oxidation of nonconjugated substrates, such as 1,4-cyclohexadiene and 1,5,9-cyclododecatriene, gave only low yields of unsaturated dicarboxylic acids. In a recent specific example 1,4-cyclohexadiene yields mostly malonic acid or esters as product depending on the solvent[199]. In oxidative ozonolysis use of a emulsion with aqueous hydrogen peroxide allowed higher yields[200]. Later on, use of silver oxide allowed formation of **115** from norbornadiene[201] and **116** from vinylcyclohexene[202]. Treatment of the dicyclopentadiene (**117**) gave the dicarboxylic acid **118**[203]. Use of selenium dioxide after the ozonolysis of 1,4-cyclohexadiene and 1,5,9-cyclododecatriene yielded stereospecific formation of lactones **119** and **120**, respectively[204]. Reductive ozonolysis has been useful in formation of

(115)   **(116)**   **(117)**   **(118)**

(119)

(120)

(121)
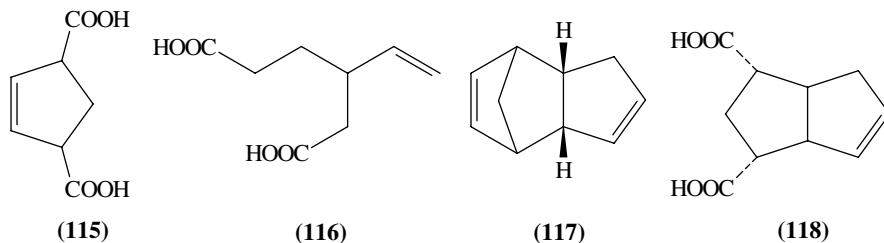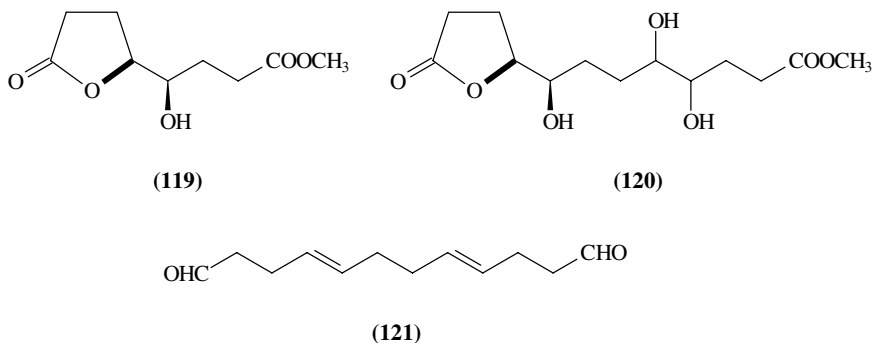
unsaturated dialdehydes, ketones and even alcohols. For example, the intermediate mono-
ozonide of 1,5,9-cyclododecatriene could be catalytically reduced with H_2 to yield the
dialdehyde **121**[205]. Other similar reactions have been reviewed[206]. Ozonolysis of di-vinyl
ethers yielded keto-ethers or keto-alkenes, depending on the solvent[207].

Reaction of ozone with a double bond is not surprisingly a function of the
nucleophilicity or electron density of the double bond. Therefore, in ozonolysis
of octamethylsemibullvalene[208] **(122)** as well as for hexamethylbicyclo[2.2.0]-2,5-
hexadiene[209] and octamethyltricyclo-octadiene[210] the diozonides, e.g. **123**, are formed as
the major product (equation 33). On the other hand, for hexachlorobicyclopentadiene[211]
(124), hexachlorobicycloheptadiene[212] and 2-chloro-3-methyl-1,3-butadiene[213] attack
takes place at the nonchlorinated double bond only to form the ozonide **125** (equation 34).

$$(33)$$

(122)   **(123)**

$$(34)$$

(124)   **(125)**
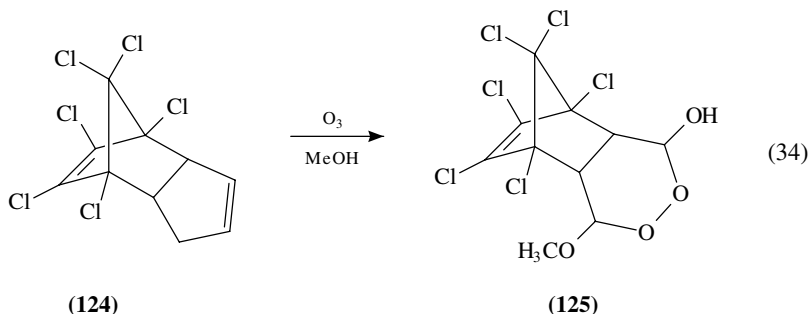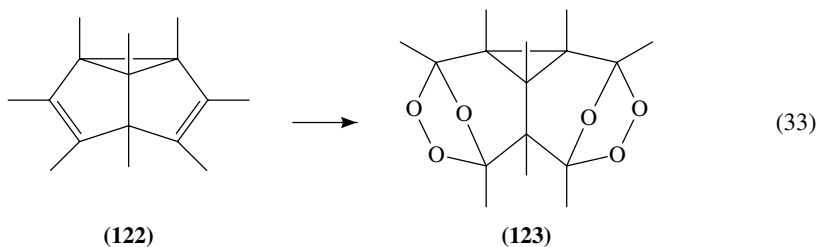
Finally, there has also been research into the ozonolysis of allenes. Thus sterically
hindered allenes react by transfer of one oxygen atom, forming a mixture of reaction
products[214]. Recently, the ozonolysis of a cyclopropylallene has been shown to yield a
diastereomeric mixture of cyclopropyl esters[215].

V. SUMMARY AND CONCLUSIONS

In the review presented above, we have tried to point out the major pathways for oxidation of dienes and polyenes useful for organic synthesis. It is apparent that the many different methods bring about different product types allowing great flexibility in the functionalization of dienes and polyenes. Emphasis has been placed on the synthetic aspects with the adjutant kinetic and mechanistic questions receiving less attention, the latter often reviewed in connection with alkene oxidation, wherein dienes and polyenes are a specific subgroup. Not discussed were the many possibilities for oxidizing substrates containing both dienes and other functional groups where, in fact, the other functionality is reactive and the diene inert. An attempt has been made to give a complete spectrum of samples reported in the literature, although it is certain that some examples have surely missed our attention. This is true especially concerning specific examples mentioned, among many others, in papers dealing with the oxidation of monoalkenes and also for examples reported in the patent literature. There are other reports which were beyond the scope of this paper. For example, isoprene (2-methyl-1,3-butadiene) is a natural hydrocarbon emitted from plants at a level of 4.4×10^6 ton year^{-1} in the USA alone. Research has been carried out on the reaction of isoprene with several oxidants such as ozone[216,217], the hydroxyl radical and atomic oxygen simulating its reaction in the troposphere[218]. This type of research has even been expanded to other substrates, including other terpenes[219].

It would appear that the oxidation of dienes and polyenes has reached a stage of maturity in the context of available oxidants as to the type of transformations and product types accessible. Future work with known oxidants and oxidation systems, however, will surely enable advances in the synthesis of complex organic molecules. On the other hand, new oxidants and oxidation systems will certainly also find their way to application in transformation of dienes and polyenes.

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CHAPTER **21**

Synthesis and transformation of radialenes

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I. INTRODUCTION

A. Nomenclature and Classification

Radialenes are alicyclic compounds in which all ring carbon atoms are sp^2-hybridized and carry as many exocyclic double bonds as possible. The general term for the parent

molecules is [n]radialenes where $n \geqslant 3$ and stands both for the ring size and the number of double bonds involved. Thus the hydrocarbons **1–4**, with the general formula C_nH_n ($n = 3,4,5,6$) are [3]-, [4]-, [5]-, and [6]radialene.


(1)   (2)   (3)   (4)
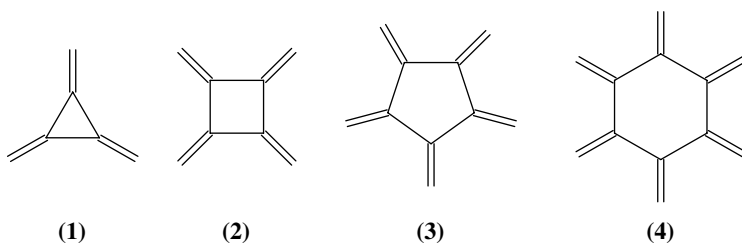
It is obvious that these compounds have in common an uninterrupted cyclic arrangement of cross-conjugated π-systems. Compound **5** likewise contains the maximum number of exocyclic double bonds at a perimeter consisting only of sp^2-hybridized carbon atoms. Thus, our definition allows one to call it a radialene, i.e. naphtharadialene; on the other hand, it excludes hydrocarbons such as **6** [3,4,5,6-tetrakis(methylene)cyclohexene]. Although in the latter molecule all carbon atoms are indeed sp^2-hybridized, the number of exocyclic double bonds has not reached its maximum. In **5**, however, the number of double bonds cannot be increased further.

(5)   (6)
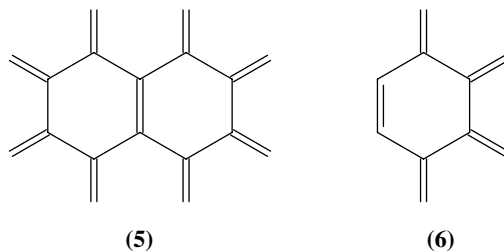
It is of course possible to name individual radialenes according to IUPAC rules [e.g. per(methylene)cycloalkanes **1–4**]. However, the descriptiveness of the term 'radialene' may some day pave its way into the 'official' nomenclature. For substituted [n]radialenes we have proposed[1] a 'pragmatic' numbering system, in which an 'inner ring' is numbered first, followed by an 'outer ring'. The numbering of substituents should follow IUPAC rules. Thus, the hydrocarbon **7** is 4,4-diethyl-5,5-dimethyl[3]radialene, the ester **8** should be called 7-methoxycarbonyl-5,5-dimethyl[4]radialene, the nitrile **9** which can exist in four diastereomeric forms is (6Z,7Z)-6-cyano-5,5,7-trimethyl[4]radialene and the difunctionalized [5]radialene **10** is (7E,6Z)-7-bromo-6-formyl-6-methyl[5]radialene.

(7)   (8)   (9)   (10)
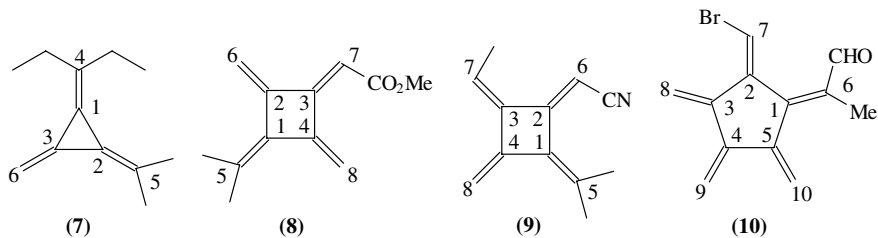
We are aware that these simple rules must and will be extended as the structural complexity of the known radialenes evolves. Unfortunately, however, the 'catchiness' of the term radialene has led to its inflationary use in recent years. Although we think it is justified to call molecules such as **11** and **12** 'expanded' [4]- ($n = 1$) and [6]radialenes ($n = 3$) — by widening our above definition, since sp-hybridized carbon atoms are 'allowed' — we hesitate to call compounds of the type **13** heteroradialenes.

X = SiR$_2$, NH, PH, S, $\cdots$

**(11)**   **(12)**   **(13)**
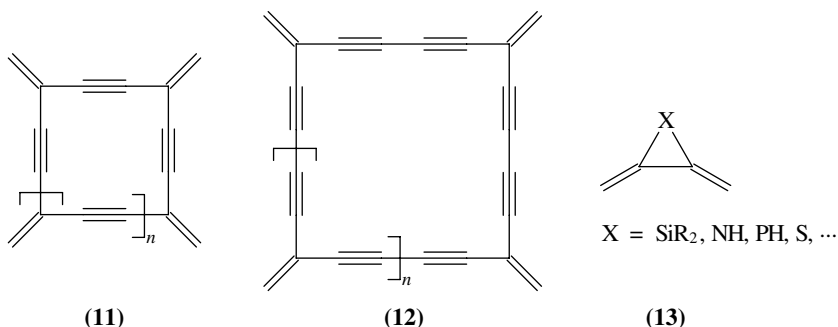
If one were to call compounds **13** radialenes, one would have to include molecules such as **14** and **15** as well. Although this has been done in the chemical literature we prefer to regard these latter unsaturated ring systems as polyalkylidene heterocycles. One reason for this is that they are lacking the characteristic cross-conjugation encountered in the radialenes (see above).

X = SiR$_2$, SnR$_2$, BR

(14)   **(15)**
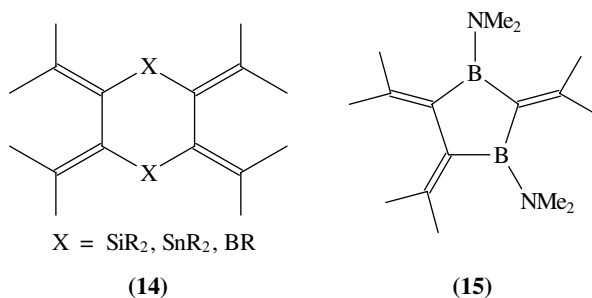
On the other hand, radialenes whose methylene groups have been replaced partially or totally by heteroatoms or heteroorganic groups — as examples, the (unknown) 'oxocarbons' **16** and **17** may be quoted as well as the tetraaza[4]radialene **18** and 'mixed' systems such as **19–21** — are clearly covered by the above definition if 'sp^2-hybridized carbon atom' is replaced by the appropriate isovalent group. Such heteroradialenes, however, will

(16)   **(17)**   **(18)**

(19)   **(20)**   **(21)**
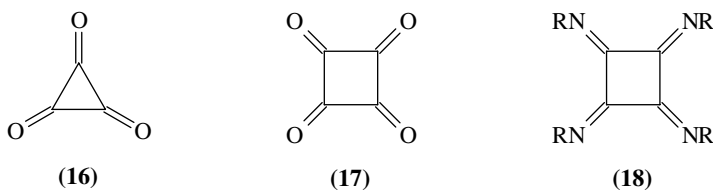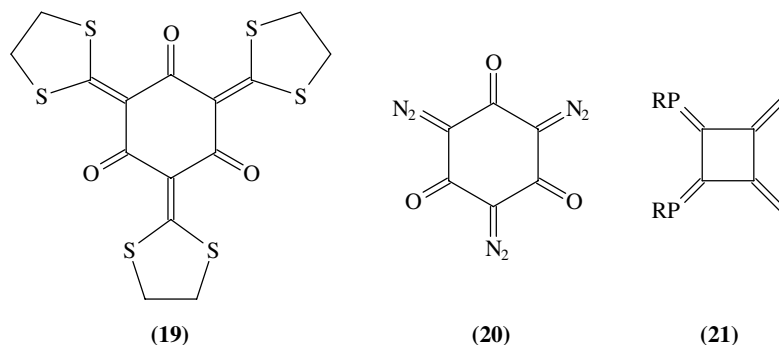
not be presented here in detail, since this volume deals with the chemistry of C=C double bond systems.

B. Significance of the Radialenes

Among the olefins — and unsaturated systems in general — the radialenes were the last to attract the interest of the chemists. Although the number of publications dealing with these cross-conjugated molecules has been growing rapidly during the last decade, they still cannot compete in importance with many of the other classes of dienic and polyenic π-systems discussed in this Volume. In fact, it appears likely that they will always play a specialized role among the numerous unsaturated hydrocarbon systems and their derivatives. However, many of the reactions employed to prepare the radialenes are useful in other fields of synthetic chemistry, the structural data obtained are of importance in comparsion to those of other π-structures, and for the development of computational methods the radialenes are also important reference structures. The radialenes are hence not only of importance for their own sake.

The last review on radialenes — which is also the first ever published and still the only available one — was published by the authors just a few years ago[1]. This, of course, raises the question of whether the present summary is really necessary. We believe it is — not only for the sake of completeness but also since especially during the last five-year period there has been significant progress in the radialene area. The main reason for this lies outside of radialene chemistry and has to do with the development of fullerene chemistry on the one hand, and various attempts to synthesize novel carbon allotropes and networks on the other. For example, C_{60} may be regarded as a cyclic dodecamer of (the still unknown) [5]radialene hydrocarbon — the six-membered ring of the former being produced 'automatically' when the hydrogen atoms of the latter are 'removed' (on paper). Correspondingly, partial structures of C_{60} containing five-membered rings may be regarded as derivatives of [5]radialene also. The so-called 'exploded' radialenes (see below) are other examples of the extension of a basic radialene structural element to a larger molecular framework or scaffold.

C. Scope of the Review

Since our earlier review[1] appeared not so long ago, it makes no sense to repeat here all facets of the radialene family. Therefore, we focus here on the synthesis and chemical transformation of the radialenes, and we suggest the reader consult our earlier review for information on structural and spectroscopic data as well as the use of radialenes as building blocks for organic conductors and organic ferromagnets, as these topics will not

be discussed in this chapter any more. We have tried to include in the present review the material published in the primary literature until the end of 1995. Besides using our own literature files we carried out both a Chemical Abstract and Beilstein Crossfire[TM] literature search.

II. SYNTHESIS AND TRANSFORMATION OF RADIALENES

A. [3]Radialenes

The parent [3]radialene **1** has been generated from variously functionalized cyclopropane precursors by classical β-elimination reactions (Scheme 1)[2−6]. All these reactions have been carried out as gas-phase reactions, and the radialene has been collected at $-63\,°C$ or below. At $-78\,°C$, the pure compound is stable for several days, but polymerization occurs when the vapor is exposed to room temperature as well as in carbon tetrachloride at 273 K[2], or in contact with oxygen[3].

Attempts to prepare **1** from some other precursors were largely unsuccessful: N, N', N''-(cyclopropane-1,2,3-trimethyl)-tris(dimethylamine oxide) decomposed unspecifically above $250\,°C$[3] and pyrolysis of 1,2,3-tris(acetoxymethyl)cyclopropane gave mainly benzene[3]; its gas-phase pyrolysis at $570−580\,°C$ produced a mixture of at least fifteen compounds containing perhaps a small amount of **1**[7].
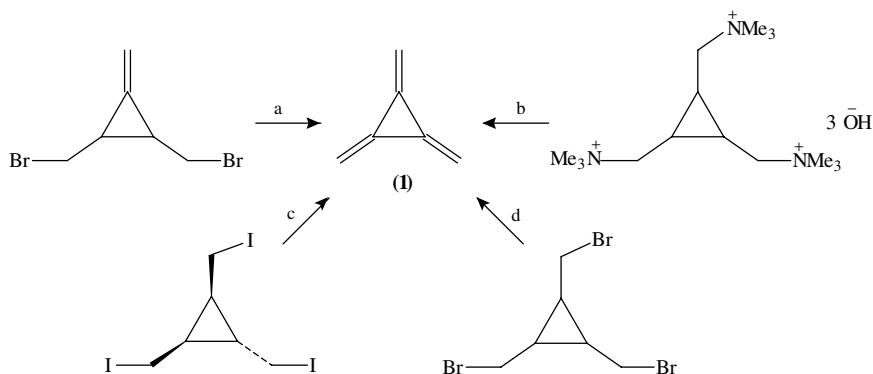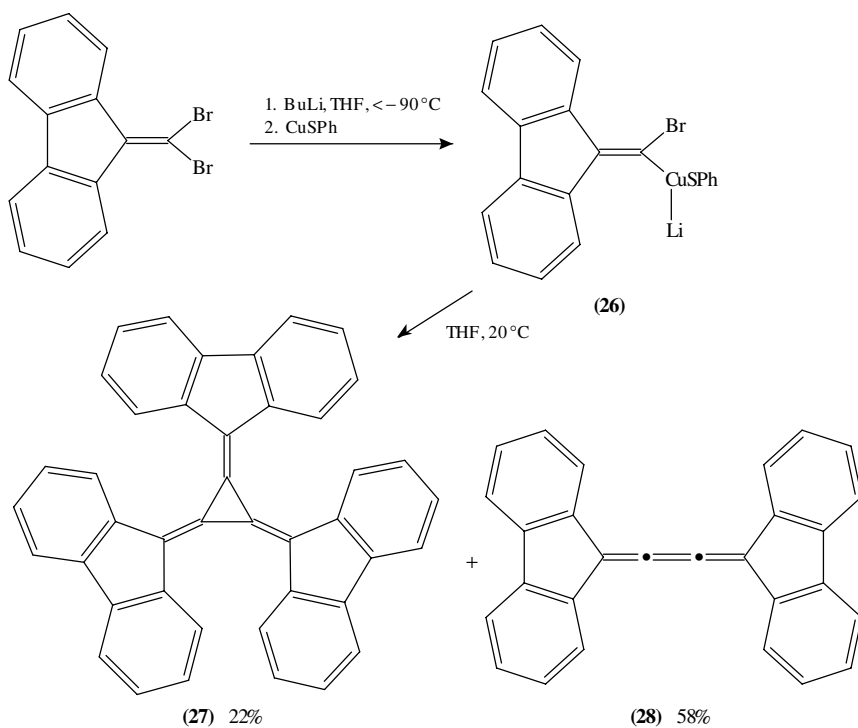

SCHEME 1. Reagents: (a) KOH, $150\,°C$, 47% yield[2]; (b) $160−170\,°C$, 4.5 Torr, 1.5% yield[3,4]; (c) KOH, $140\,°C$, *ca* 20% yield[3,4]; (d) powdered KOH, CaO, $150\,°C$, 1 Torr, no yield given[5,6]

Various alkyl- and aryl-substituted [3]radialenes could be prepared from 1,1-dihaloalkenes using organometallic pathways. Hexamethyl-[3]radialene **(25)**, the first [3]radialene to be synthesized, was obtained in a very low yield by treatment of 1,1-dibromo-2-methyl-1-propene **(22)** with butyllithium[8,9]. The lithium carbenoid **23** and the butatriene **24** are likely intermediates of this transformation (Scheme 2), the former being the source of an unsaturated carbene moiety which is transferred onto the latter. However, the outer double bonds of **24** are more readily cyclopropanated than the central one.
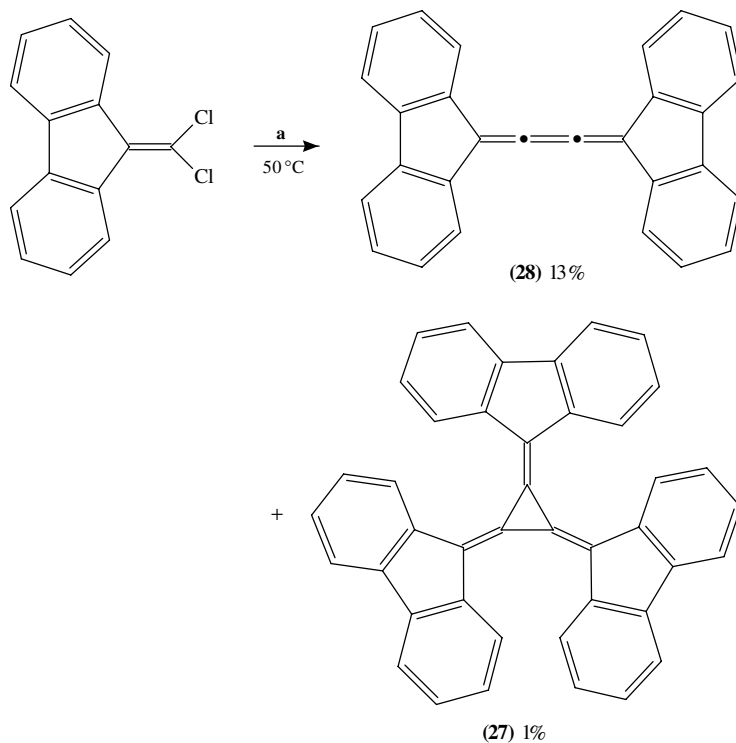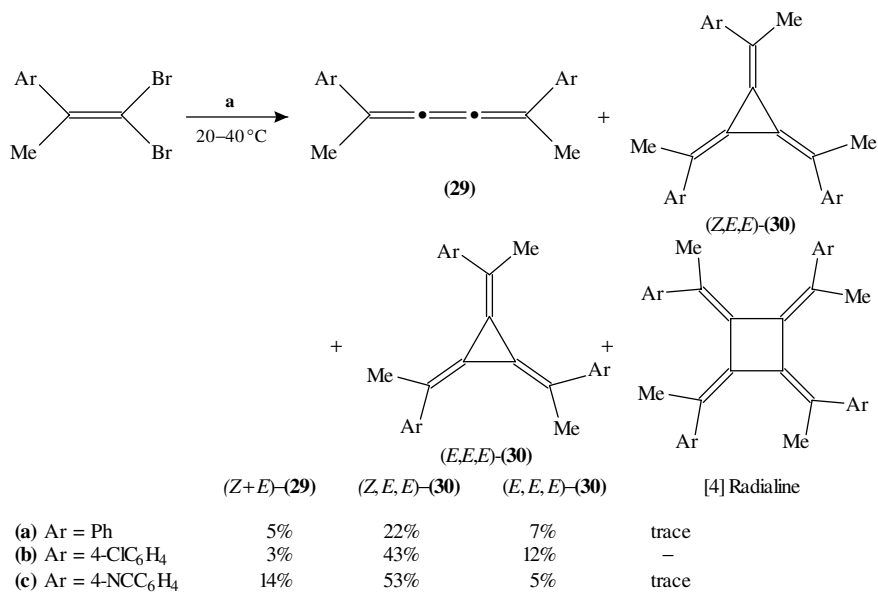
It appears that neither the lithium carbenoid pathway nor the cyclopropanation of butatrienes are general routes to [3]radialenes. More successful is the cyclotrimerization of 1,1-dihaloalkenes via copper or nickel carbenoids, provided the substituents at the other end of the C=C double bond are not too small. Thus, tris(fluoren-9-ylidene)cyclopropane **27** was formed besides butatriene **28** from the (1-bromo-1-alkenyl)cuprate **26** generated *in situ* from (9-dibromomethylene)fluorene (Scheme 3)[10]. The cuprate complexes formed

(25) 0.3−2 %
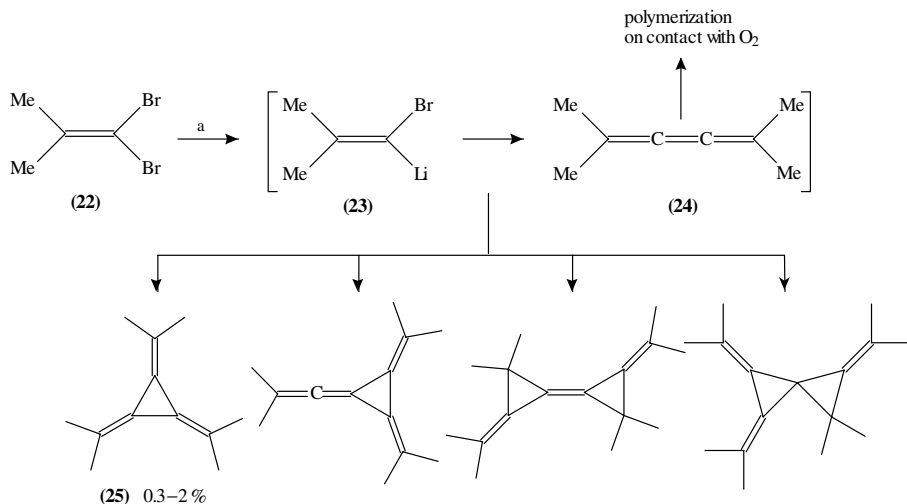
SCHEME 2. Reagents: (a) 2 equiv. of **22**; 1. BuLi (1.25 equiv.), THF, −110 °C; 2. −110 °C → −65 °C;
3. BuLi (0.75 equiv.), −65 °C → 20 °C

(27) 22%   **(28)** 58%

SCHEME 3

	(Z+E)–(29)	(Z, E, E)–(30)	(E, E, E)–(30)	[4] Radialine
(a) Ar = Ph	5%	22%	7%	trace
(b) Ar = 4-ClC$_6$H$_4$	3%	43%	12%	–
(c) Ar = 4-NCC$_6$H$_4$	14%	53%	5%	trace

SCHEME 4. Reagents: (a) Ni (5−10 equiv.), THF, ultrasound; (b) NiI$_2$, Li, 4,4′-di-*tert*-butylbiphenyl, THF, 50 °C

(31) 17%

(32) 2%

(31) 6% + **(32)** trace +

(33) 10%

(34) 54%
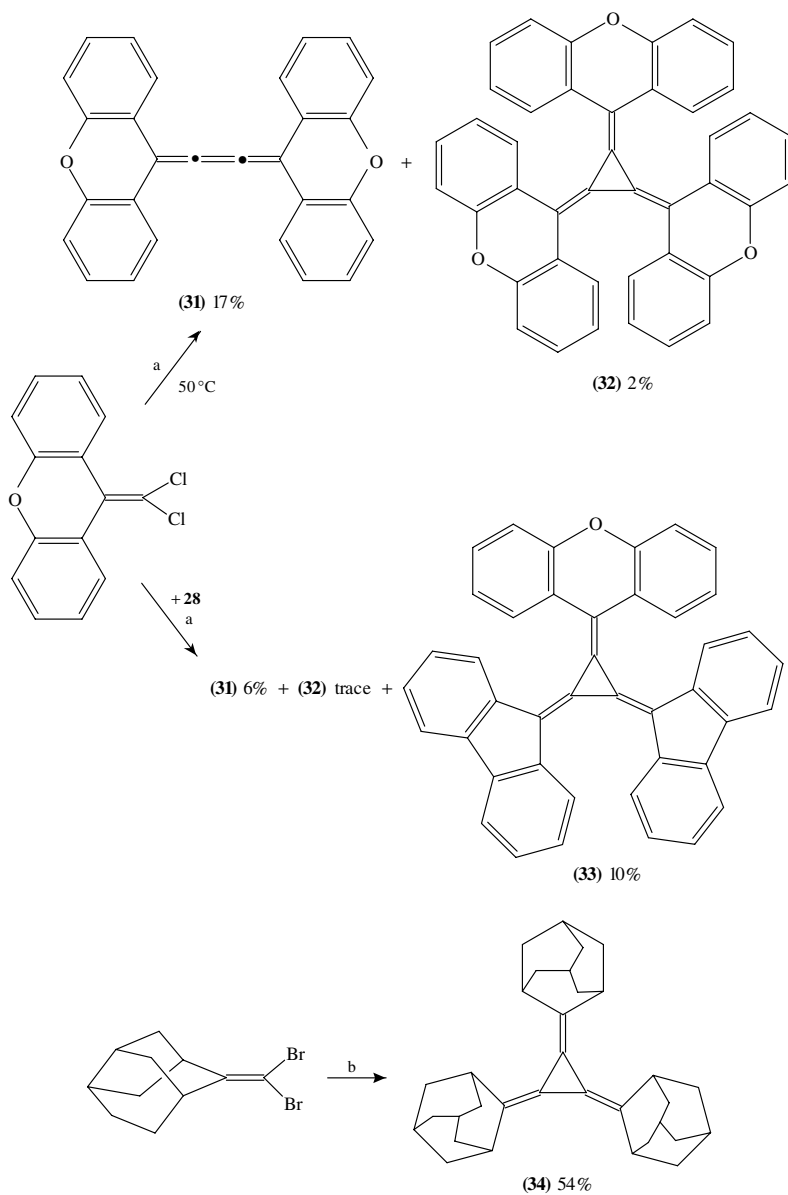
SCHEME 4. (*continued*)

with CuI·PBu$_3$ or CuBr·Me$_2$S gave the radialene in only 2–3% yield together with **28** (76–85%), and with CuCN only traces of **27** were found. Furthermore, decomposition of the cuprate obtained with CuI·PBu$_3$ in the presence of butatriene **28** did not result in an improved yield of **27** which suggests that the cumulene is not an intermediate in the radialene formation, in contrast to the lithium carbenoid pathway shown in Scheme 2.

While no [4]- and [5]radialenes were formed in the decomposition of cuprate **26**, the analogous cuprate generated from 1,1-dibromo-2,2-diphenylethene led to the corresponding [4]radialene, and [4]- and [5]radialenes were obtained from the cuprate derived from **22** (see Section II.B and II.C). These findings point to a steric influence on these cyclooligomerization reactions, with sterically demanding substituents favoring the formation of [3]radialenes.

The most recent strategy to prepare [3]radialenes is the treatment of 1,1-dihaloalkenes with activated nickel. Thus, the aryl-substituted [3]radialenes (*Z,E,E*)-**30** and (*E,E,E*)-**30**, **27** and **32** were obtained together with the corresponding butatrienes (**29**, **28**, **31**) from the 1,1-dibromo- or 1,1-dichloroalkenes with the help of nickel activated by ultrasound (Scheme 4)[11]. It is worth mentioning that the mixed-substituted radialene **33** was produced, when the nickel carbenoid derived from 9-(dichloromethylene)xanthene was generated in the presence of butatriene **28**[11].

Treatment of 2-(dibromomethylene)adamantane with Ni(0) generated from $NiBr_2$-$(PPh_3)_2$, Zn and PPh_3 in DMF gave the corresponding butatriene as the main product, but no tris(2-adamantylidene)cyclopropane **34**. However, when the activated nickel was generated from NiI_2 and Li powder with 4,4′-di-*tert*-butylbiphenyl as electron carrier
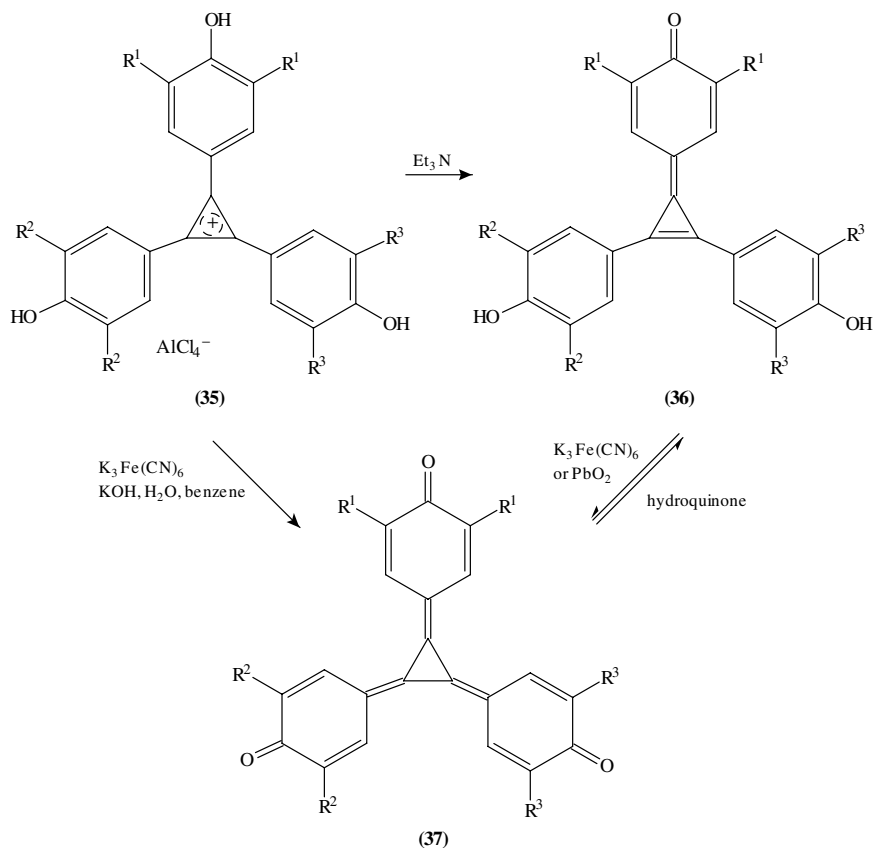
SCHEME 5. **35**–**37**: (**a**) $R^1 = R^2 = R^3 = Me$; (**b**) $R^1 = R^2 = R^3 = i$-Pr; (**c**) $R^1 = R^2 = R^3$ *t*-Bu; (**d**) $R^1 = R^2 = t$-Bu, $R^3 = Me$; (**e**) $R^1 = R^2 = t$-Bu, $R^3 = i$-Pr; (**f**) $R^1 = i$-Pr, $R^2 = R^3 = t$-Bu

in THF, radialene **34** was the sole product in 54% isolated yield (Scheme 4)[12]. These results show that the success of the Ni(0)-mediated cyclotrimerization reactions depends on many factors, including the nickel activation, as well as electronic (cf **30a–c**; electron-withdrawing aryl substituents give better yields) and steric factors (successful formation of **34** as opposed to [4]- and [5]radialene formation from 1,1-dibromo-2-methylpropene, see Sections II.B and II.C).

A variety of functionalized [3]radialenes have been prepared starting from the appropriately substituted cyclopropanes or cyclopropenes. West and Zecher have pioneered the chemistry of [3]radialenes with quinoid substituents. The general strategy of this synthesis is outlined in Scheme 5[13]. A tris(4-hydroxyphenyl)cyclopropenylium


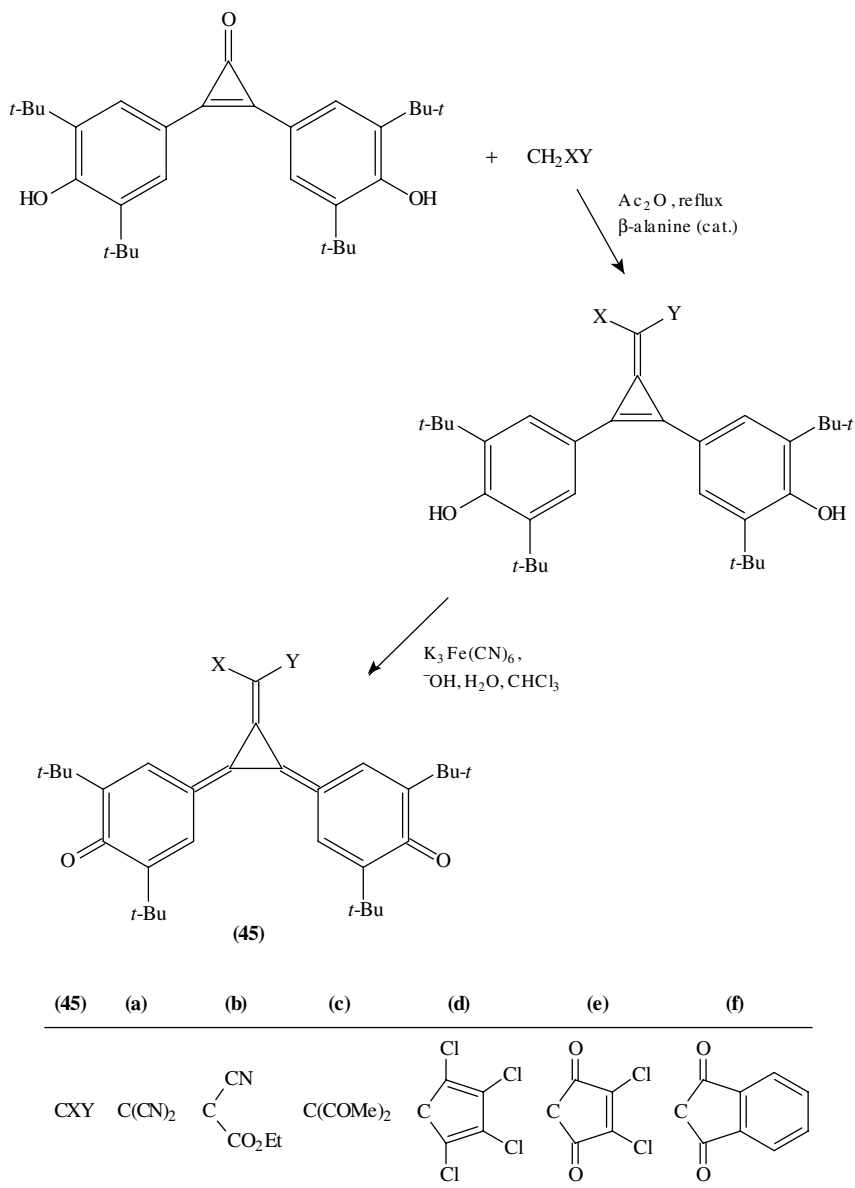**(38)**

(39) X =

(9-anthron-10-ylidene)

(40) X =

(41)
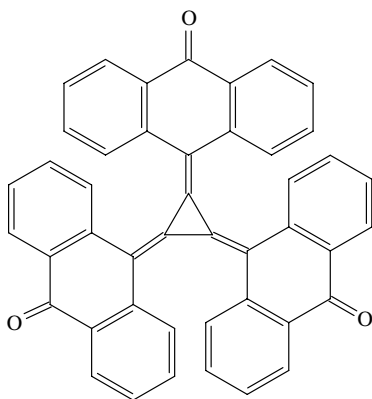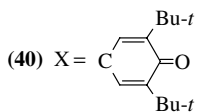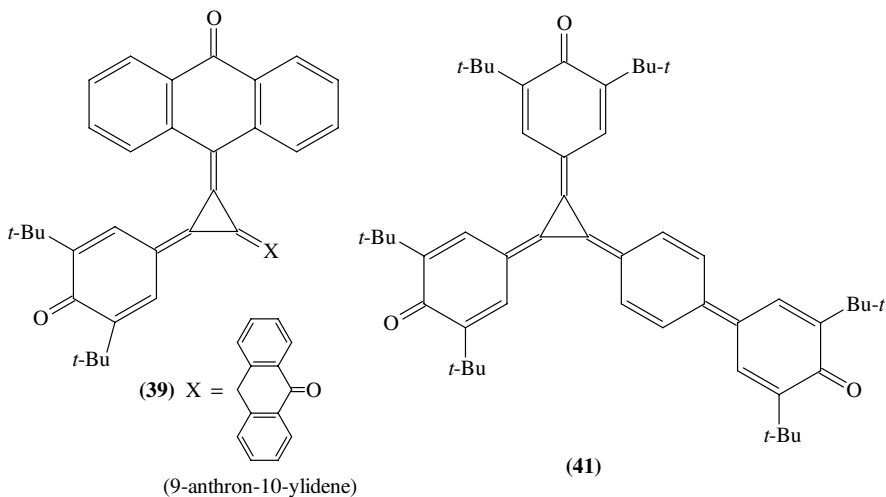
salt **35**, which is obtained from the trichlorocyclopropenylium salt $CCl_3^+ \cdot AlCl_4^-$, is deprotonated to give a methylenecyclopropene **36**. Oxidation of the latter provides the desired tris(quino)cyclopropane **37**. The deprotonation/oxidation sequence can also be carried out in a two-phase system as a one-pot reaction.

The thermal stability in air of the deeply colored radialenes **37** increases with the efficiency of steric shielding of the carbonyl groups. Thus, **37a** was only detected in solution by its UV/Vis spectrum, whereas **37b** and **37c** are reduced to their precursors, **36b** and **36c**, when heated in air at 133 and 280 °C, respectively. In solution, this reduction is readily accomplished with hydroquinone[13].

Various other [3]radialenes bearing quinoid substituents have been synthesized analogously, for example **38**[14], **39**[14], **40**[15], **41**[16], **42**[15], and the rather unstable **43**[17]. In contrast to most other tris(quino)cyclopropanes, reduction of tris(anthraquino)cyclopropane **38** does not succeed with hydroquinone, but requires more forcing conditions (Sn/HCl or Zn/HCl). Compound **44** represents the only tropoquino-substituted [3]radialene known so far[18]; the black-blue crystals of this strongly electron-accepting radialene are stable to air and light.

(42)

(43)

(44)
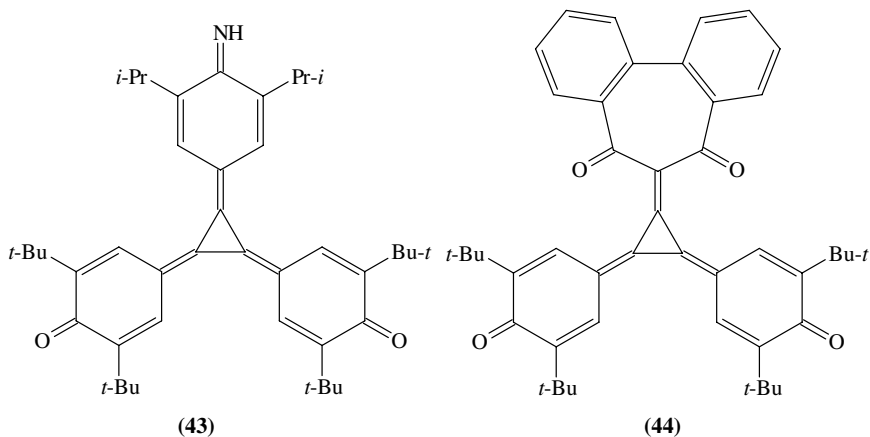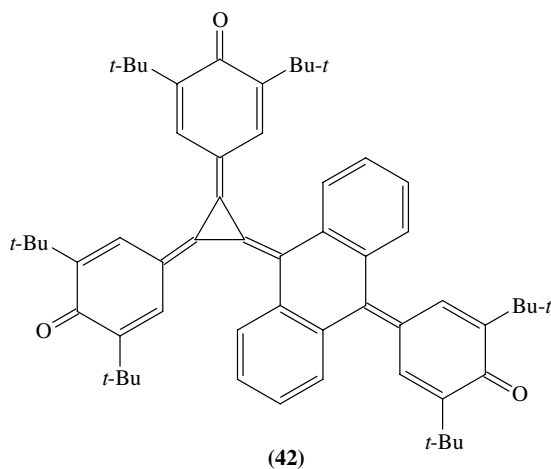
[3]Radialenes which are structurally related to **44**, i.e. cyclopropanes bearing two quinoid and another acceptor-substituted methylene substituent, were obtained by condensation of bis(4-hydroxyphenyl)cyclopropenones with active methylene compounds, followed by oxidation (Scheme 6)[19]. Radialenes **45a–f** are brilliantly colored solids that are blue or blue-violet in solution but appear metallic gold or red in reflected light. Instead

(45)

(45)	(a)	(b)	(c)	(d)	(e)	(f)
CXY	C(CN)$_2$	C with CN and CO$_2$Et	C(COMe)$_2$	tetrachlorocyclopentadiene-ylidene	tetrachloro-quinone-ylidene	phthalimide-ylidene

SCHEME 6

of active methylene compounds, arenologous malononitriles such as 9-anthryl-, 2-thienyl- or 2-selenienyl-malononitrile can be employed in the condensation step which gives access to the [3]radialenes **46**[20], **47**[21] (R = *t*-Bu: quite stable in the solid state and in solution; R = Me: stable in solution at room temperature) and **48**[22].

Tetrachlorocyclopropene is another building block for [3]radialenes (Scheme 7). Its reaction with anions of active methylene compounds such as malononitrile

(46)

(47) X = S; R = *t*-Bu, Me
**(48)** X = Se; R = *t*-Bu

(49)

(50) X = CN
(51) X = CO₂Me

(52) 5 %
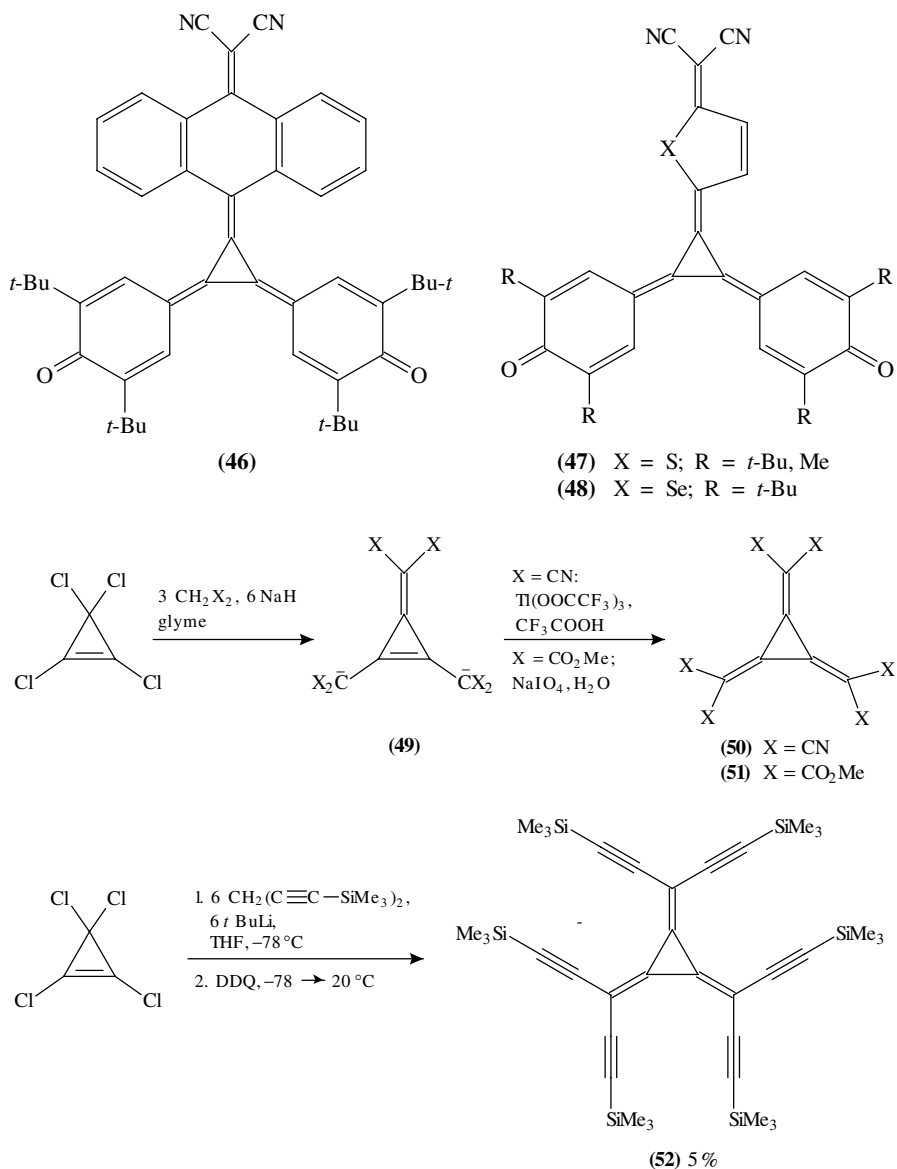
SCHEME 7

and dimethyl malonate yields the dianions **49**, which could be isolated as tetrabutylammonium or sodium salts[23]. Subsequent oxidation of the respective salts provides hexacyano[3]radialene **(50)** and hexamethoxycarbonyl[3]radialene **(51)**[24,25]. Hexakis(trimethylsilylethynyl)[3]radialene **(52)** was prepared analogously, but without isolation of the intermediate dianionic salt[26a]. The corresponding (i-Pr$_3$Si)-derivative could not be obtained in this manner, probably because of steric overcrowding.

In contrast to **51**, hexacyano[3]radialene **(50)** proved difficult to obtain in pure form. Freshly prepared samples are bright-yellow, but turn brown on exposure to air and blue on contact with many solvents. Potassium bromide and sodium iodide reduce **50** to the radical anion and the dianion, respectively[24].

Radialene **52** has been envisaged as a precursor to hexaethynyl[3]radialene, a potential building block for carbon networks. However, desilylation under very mild conditions led to an unstable product of so far unknown identity. In this context, it should be mentioned that according to thermochemical calculations, the still unknown hexaethynyl[3]radialene has an increased conjugation energy with respect to vinylacetylene, probably because of partial relief of strain in the radialene core[26b]. A remarkable aspect of **52** is its color: the crystals are deep-red and a hexane solution has a purple color. In this respect, **52** differs from the yellow radialenes **50** and **51** and resembles [3]radialenes such as **27** and **38**, which have much more extended π-systems.

The condensation of hexachlorocyclopropane with three equivalents of the active methylene compound thioxanthene has been used for the synthesis of the electron-rich, blue [3]radialene **53**[27] (equation 1).

**(53)** 21%   (1)
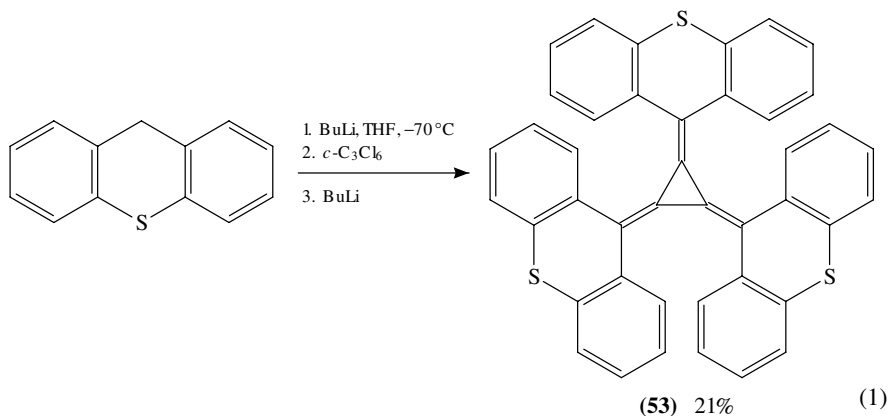
[3]Radialenes have not received much attention with regard to the classical chemical transformations of polyolefins. While the parent [3]radialene **(1)** is difficult to handle because of its extreme oxygen-sensitivity and its propensity to polymerize under various conditions (see above), increasing substitution of the skeleton leads to a kinetic stabilization, but at the same time it renders intermolecular addition reactions more difficult. Catalytic hydrogenation of **1** with Pd/C as catalyst furnishes a mixture of 3-methylpentane and 3-methyl-2-pentene; with Rh−Al$_2$O$_3$ as catalyst, however, 3-methylpentane, all-cis-1,2,3-trimethylcyclopropane, 2-ethyl-1-butene, and (E)- and (Z)-3-methyl-2-pentene (in a 6:2:1:7:3 ratio) were found[3]. The hydrogenation products from hexamethyl[3]radialene **(25)** (H$_2$, Raney−Ni, EtOH, consumption of 2.94 equivalents of H$_2$) have not been identified[9].

In trifluoroacetic acid, **25** is protonated to form the cyclopropylium cation **54** (UV/Vis: $\lambda_{max} = 480$ nm) (equation 2)[28]. Protonated **1** could not be prepared cleanly in the same

manner due to the extreme propensity of this radialene to undergo cationic polymerization[28]. The remarkable stability of **1** towards dilute mineral acids is worth mentioning, however.


$$(2)$$

(25)   **(54)**
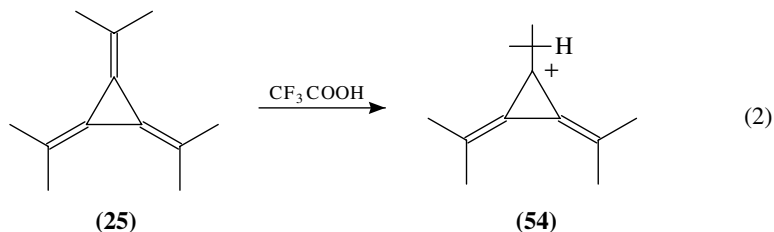
Hexamethyl[3]radialene **(25)** does not undergo Diels-Alder-reactions with the typical electron-poor dienophiles, probably because of the full substitution at the diene termini. With TCNE, however, a violet-blue charge-transfer complex is formed which disappears within 30 min at room temperature to form a 1:1 adduct (82% yield) to which structure **55** was assigned[9]. Similar observations were made with tris(2-adamantylidene)cyclopropane **(34)**, but in this case cycloaddition product **56** (81% yield) was identified; its allenic moiety is clearly indicated by IR and ^{13}C NMR data[12].

(55)   **(56)**
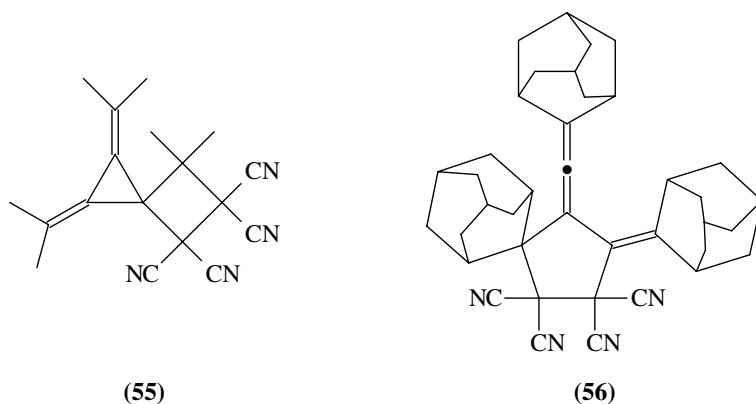
Virtually all of the [3]radialenes known so far have been evaluated with respect to their reduction/oxidation properties. Electron-donating [3]radialenes can be oxidized to the radical cation and the dication, electron-accepting ones are reduced to the radical anion and the dianion, depending on the substituents. The parent [3]radialene **(1)** has been transformed into the molecular ion only by photoionization in the gas phase[6]. For its permethylated derivative **25**, the ionization potential has also been determined from the photoelectron spectrum[29]; furthermore, the radical cation (formed by γ-irradiation in an organic matrix at 77 K, characterized by the UV/Vis spectrum[28]) and the radical anion (formed by K in DMF at $-70\,^\circ$C; characterized by ESR spectrum[30]) have both been generated. Tris(2-adamantylidene)cyclopropane **(34)** undergoes a rather easy, irreversible one-electron oxidation in acetonitrile–dichloromethane solution[12]. The cyclic voltamogram of tris(thioxanthen-9-ylidene)cyclopropane **(53)** in dichloromethane consists of two pairs of reversible waves at $+0.67$ and $+0.80$ V vs Ag/AgCl, corresponding each to a one-electron oxidation[27]. The radical cation **53**$^{\bullet+}$ and the dication **53**$^{2+}$ were also generated by

chemical oxidation with thallium(III) trifluoroacetate and characterized by their UV/Vis and ESR spectra. The dark-blue salt $53^{2+} \cdot 2\ CF_3COO^-$ could be isolated; analysis of its ESR spectra at various temperatures points to the existence of a triplet state that is only 0.07 eV higher in energy than the singlet ground state[27]. So far, **53** is the [3]radialene with the best electron-donating qualities.

[3]Radialenes with electron-accepting substituents (**57**) are typically reduced in two one-electron steps via the radical anion **57**$^{\bullet-}$ to the dianion **57**$^{2-}$ (equation 3). MO calculations and ^{13}C NMR data for **27**$^{2-}$[31], **33**$^{2-}$[31], **50**[23] and **51**[23] suggest that resonance structure **57**$^{2-}$ **A**, with a cyclopropenylium core and negative charges delocalized in the electron-accepting substituents, contributes considerably to the ground states of the dianions **57**$^{2-}$. Experimentally determined bond geometries of such dianions are not yet available. However, X-ray crystal structure analyses of several transition metal salts formally containing the radical anion $C_6(CN)_6^{\bullet-}$ (**50**$^{\bullet-}$)[32−34] reveal the bond length equalization between the ring and exocyclic C−C bonds in these [3]radialene anions [12 individual values; average bond length of C−C (ring): 1.393 ± 0.028 Å; exocyclic C−C: 1.375 ± 0.031 Å].

$$(3)$$

(57)   (57$^{\bullet-}$)

(57^{2-})   (57^{2-}A)

X = electron-accepting group
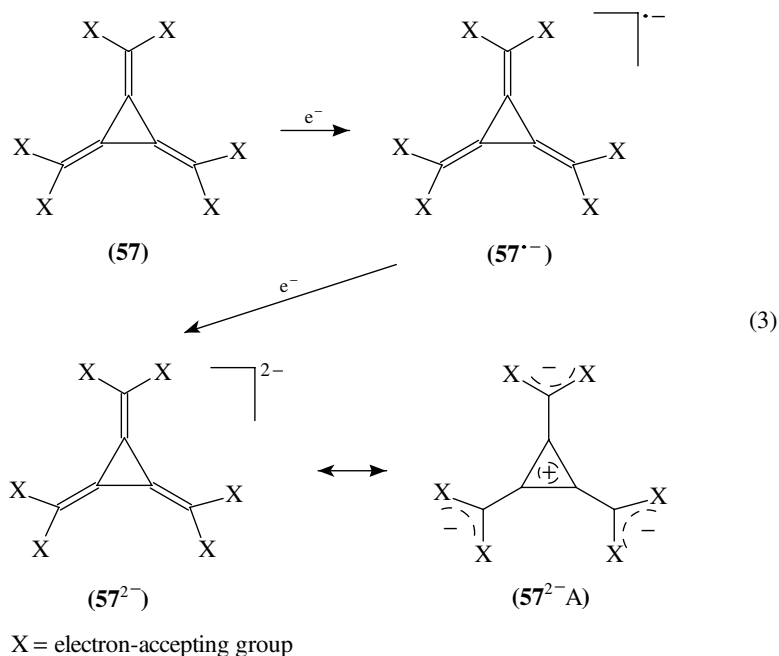
Hexacyano[3]radialene (**50**) is a very powerful electron acceptor according to both experiment[23,24,35] and MNDO calculations of LUMO energy and adiabatic electron affinity[25]. The easy reduction to the stable species **50**$^{\bullet-}$ and **50**$^{2-}$ by KBr and NaI, respectively, has already been mentioned. Similarly, the hexaester **51** is reduced to **51**$^{2-}$ by LiI[24]. Most [3]radialenes with two or three quinoid substituents are reduced in two subsequent, well-separated, reversible one-electron steps. As an exception, an apparent two-electron reduction occurs for **46**[20]. The reduction potentials of some [3]radialenes of this type, as determined by cyclic voltammetry, are collected in Table 1. Due to the occurrence of the first reduction step at relatively high potential, all these radialenes

TABLE 1. Reduction potentials of [3]radialenes ($E_{1/2}$, V) with quinoid substituents and of some related compounds, as determined by cyclic voltammetry (in CH_2Cl_2 vs SCE)
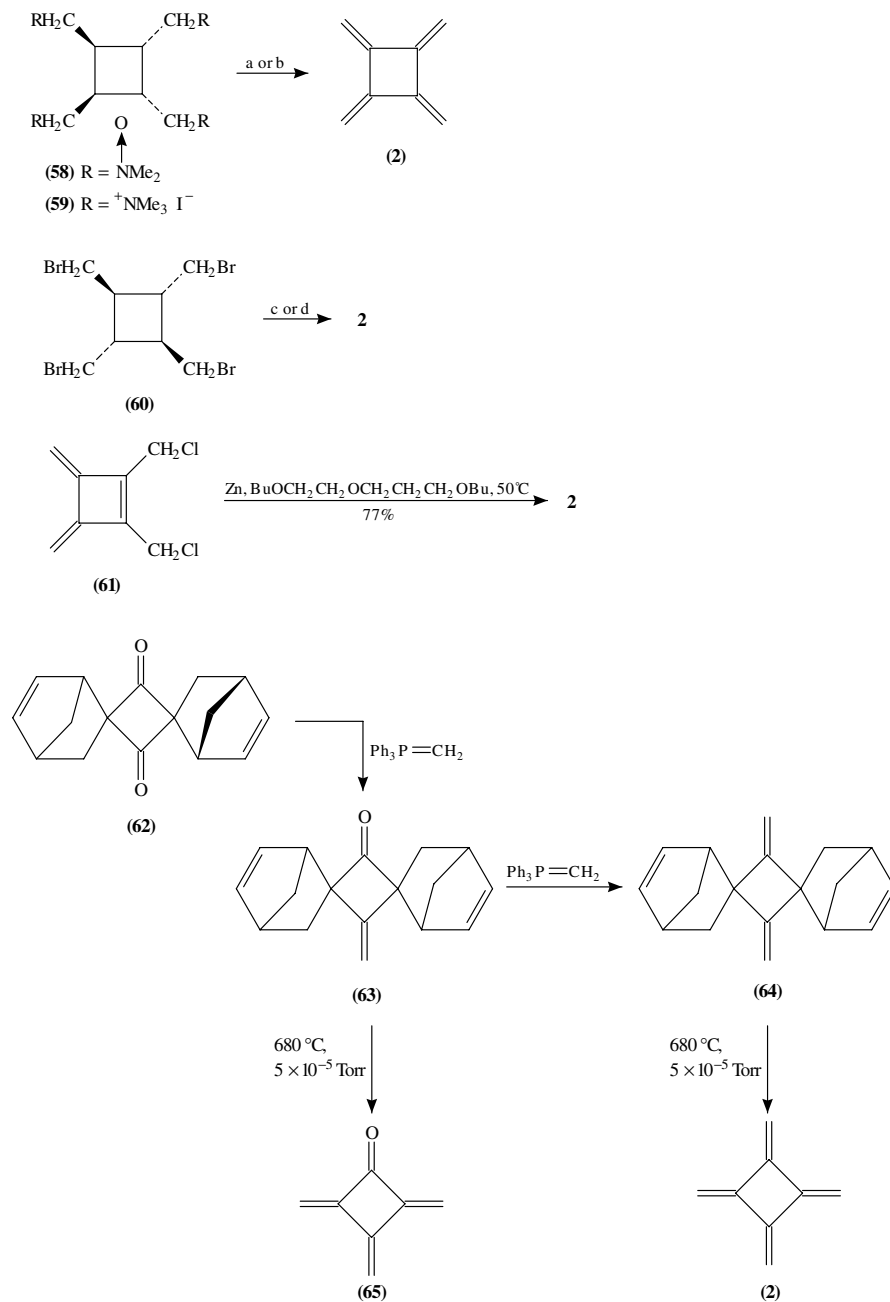

Compound	**37c**	**39**	**43**	**45a**	**45d**
Q					

Compound	**46**	**44**	**47**	**48**
Q				

Compound	$E^1_{1/2}$	$E^2_{1/2}$	Reference
37c	+0.05	−0.27	36
38	+0.02	−0.28	14
39	+0.02	−0.27	14
43	−0.08	−0.51	17
45a	+0.30	−0.24	19
45d	+0.25	−0.14	19
46	0.00	−0.04	20
44	+0.17	−0.20	18
47	+0.20	−0.12	21
48	+0.19	−0.13	21
TCNQ	+0.22	−0.36	21
DDQ	+0.57	−0.32	35b
Chloranil	0.00	−0.78	35b

represent strong oxidants. For example, the oxidizing power of **44**, **45a**, **45d**, **47** and **48** is comparable to that of TCNQ, whereas in most other cases the first reduction step is comparable to that of chloranil, and the second one to that of DDQ. As we have mentioned already, these radialenes in general are indeed reduced quite easily to the corresponding bis(4-hydroxyaryl)cyclopropenes (e.g. **37** ⟶ **36**). In several cases, persistent radical anions have also been generated by chemical reduction and characterized spectroscopically. For example, reduction of **47** with LiI provides **47**[•−] quantitatively[21], and radical anion **46**[•−] can be obtained by treatment of the radialene with Na/K alloy[20].

Because of the stability of their reduced forms, in combination with remarkable and reversible color changes, these quinoid radialenes have been suggested as materials for electrochromic display devices[18,35b].

(58) R = NMe_2

(59) R = $^+NMe_3$ I^-

(60)

$$\xrightarrow[77\%]{Zn, BuOCH_2CH_2OCH_2CH_2CH_2OBu, 50°C} 2$$

(61)

(62)

$Ph_3P = CH_2$

(63)

$Ph_3P = CH_2$

(64)

680 °C,
5×10^{-5} Torr

680 °C,
5×10^{-5} Torr

(65)

(2)

SCHEME 8. Reaction conditions: (a) 250 °C, vacuum, 1–2% yield; (b) 115 °C, no pure product; (c) NaOEt, EtOH, 0 °C, <50% yield; (d) solid KOH, 150 °C

The two-step reduction of tris(9-fluorenylidene)cyclopropane **27**[31] and of hexakis(tri-methylsilylethynyl)cyclopropane **52**[26a] requires increasingly more negative potentials than in the cases listed in Table 1; this is, of course, a consequence of the presence of less electron-accepting substituents. Nevertheless, dianion **27**$^{2-}$ has been generated by reduction with sodium or lithium; the lithium salt could be kept in THF solution for up to one year at 20 °C without detectable decomposition[31].

Electron-rich and electron-poor [3]radialenes have received much attention as components of molecular π donor−acceptor complexes; for information on this subject, see elsewhere[1,21,22].
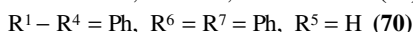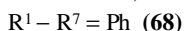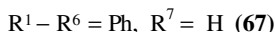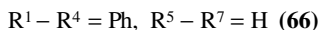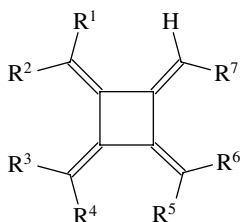
B. [4]Radialenes

[4]Radialenes represent the biggest and best known subset of the radialene family; this is not surprising in view of the fact that more methods to prepare them exist than for any other class of radialenes. The major strategies are the transformation of appropriate cyclobutane derivatives, the thermal or Ni(0)-catalyzed cyclodimerization of butatrienes or higher cumulenes and the cyclotetramerization of (1-bromo-1-alkenyl)cuprates.
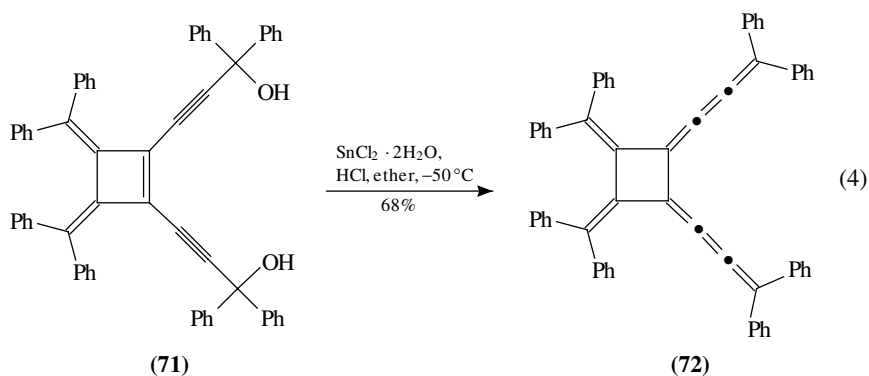
Cyclobutane derivatives are involved in all known syntheses of the parent [4]radialene (Scheme 8). The first approaches used β-elimination reactions on compounds **58**[36], **59**[36] and **60**[36−38] to introduce all four exocyclic C=C bonds in one operation.

A more recent approach is the reductive 1,4-dechlorination of 1,2-bis(chloromethyl)-3,4-dimethylenecyclobutene (**61**), which is prepared in five steps from 1,5-hexadiyne in good overall yield[39]. Finally, **2** has been generated by flash vacuum pyrolysis of **64** in a twofold retro-Diels-Alder reaction[40]. Dispiro compound **64** is prepared from the cyclobutane-1,3-dione **62** in two Wittig olefination reactions via **63**; notably, the thermal fragmentation of **63** provides the radialene-like trimethylencyclobutanone **65**, a compound which polymerizes already at −95 °C.

Radialene (**2**) can be stored at −78 °C, but undergoes dimerization and polymerization reactions in solution at room temperature; neat **2** may even start to burn at this temperature[39]. It is also very sensitive towards oxygen; exposure to air leads to an intractable material containing up to 40% oxygen.

[4]Radialenes bearing four to seven phenyl substituents have been prepared from 3,4-bis(diphenylmethylene)cyclobutane-1,2-dione (**66−68**) and 2,3-bis(diphenylmethylene)-4-benzylidenecyclobutan-1-one (**69**, **70**), respectively, by standard synthetic operations[41]. While octaphenyl[4]radialene could not be prepared analogously[41], a cumulenic homologue thereof (**72**) was obtained (equation 4) by reductive 1,8-elimination from **71**, which itself came from a palladium-catalyzed cross-coupling reaction of 1,2-bis(diphenyl)methylene-3,4-dibromocyclobutene and 3,3-diphenylpropynol[42].

$R^1 − R^4 = Ph, \ R^5 − R^7 = H$ (**66**)

$R^1 − R^6 = Ph, \ R^7 = H$ (**67**)

$R^1 − R^7 = Ph$ (**68**)

$R^1 − R^4 = Ph, \ R^6 = Ph, \ R^5 = R^7 = H$ (**69**)

$R^1 − R^4 = Ph, \ R^6 = R^7 = Ph, \ R^5 = H$ (**70**)

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

$$(4)$$

When 1,2,3,4-tetrakis(4-pyridinyl)cyclobutane is treated with ethyl chloroformate in the presence of ethyldiisopropylamine, radialene **74a** is formed and can be isolated as red crystals. Addition of $AgBF_4$ to a red solution of **74a** results in an immediate color change to deep blue caused by the formation of the dicationic species **75a** (equation 5)[43]. Undoubtedly, the tetrapyridiniocyclobutane **73a** is an intermediate in the formation of **74a**. By way of contrast, the fourfold deprotonation of the analogous tetrakis(*N*-methyl-4-pyridinyl)cyclobutane **(73b)** did not succeed in the presence of oxygen. Treatment with NaH/EtOH in the presence of oxygen produced the dication **75b**, which could be reduced to the [4]radialene only electrochemically[44]. Deprotonation of **73b** with sodium hydride
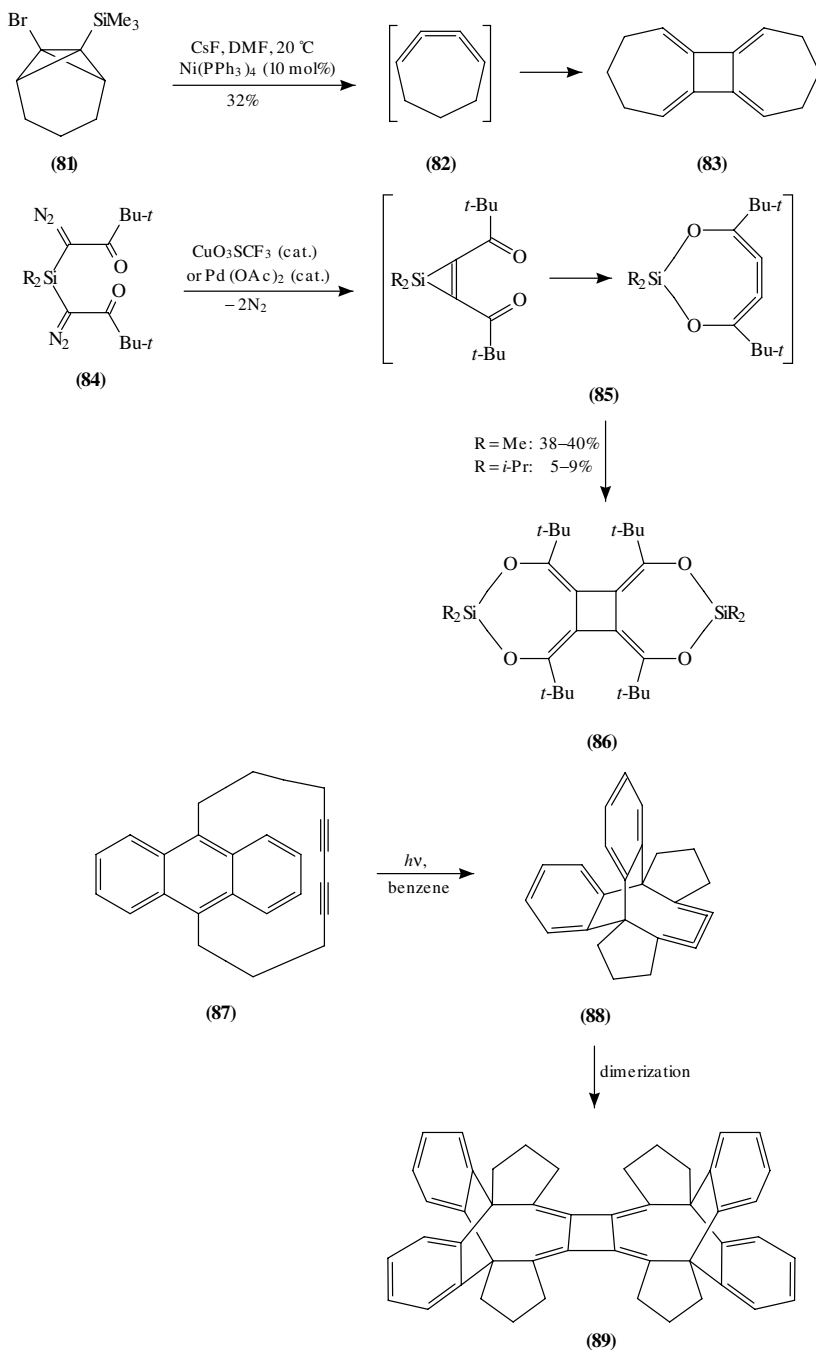

(73a)

(74a)   **(75a)**
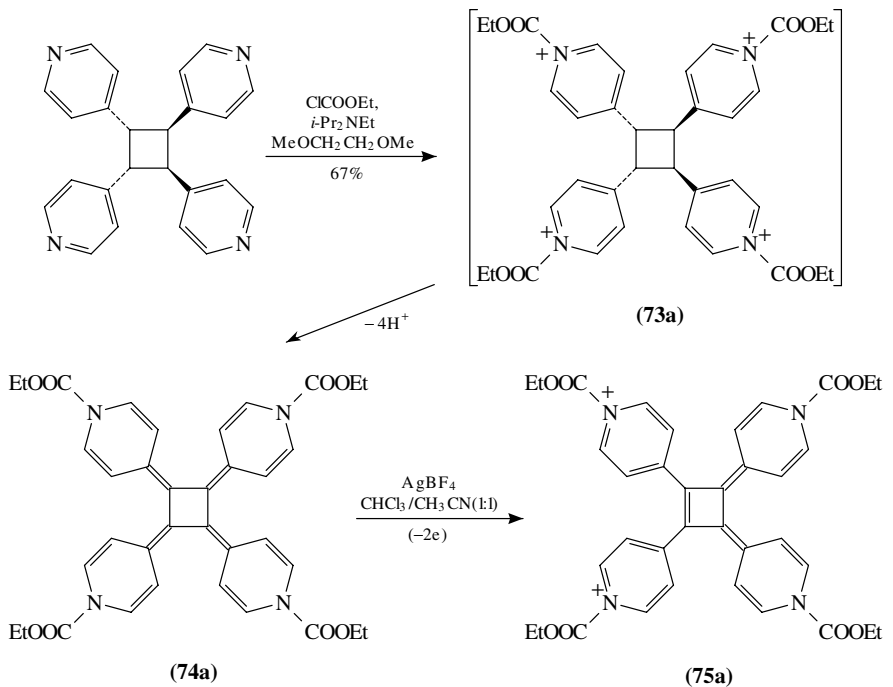
(73b) − **(75b)**: NMe instead of NCOOEt

$$(5)$$

in dimethylacetamide under an argon atmosphere gave a red solution, which had a similar absorption spectrum as radialene **74a** and turned blue on admission of air with formation of dication **75b**.

The thermally or photochemically induced $(2 + 2)$ cyclodimerization of butatrienes across the central C=C double bond, or of higher cumulenes at an inner double bond, appears as a reasonable route to [4]radialenes. However, success and failure of this approach have been reported about equally often. Butatriene itself yields 1,5-cyclooctadiyne and other products, but no [4]radialene, on heating[45]. Silyl-, stannyl- and germyl-substituted butatrienes seem to undergo no thermal dimerization at all[46]. In contrast to earlier assumptions, the photochemical dimerization of tetraphenyl- and tetrakis(4-methoxyphenyl)butatriene as well as the thermal dimerization of 7-(propadienylidene)tricyclo[4.1.0]heptane do not provide the respective [4]radialenes, but occur at one of the terminal C=C bonds to give a head-to-tail dimer in the former case[47] and a head-to-head dimer in the latter[48]. Some [4]radialenes which have been obtained by thermal (100–200 °C) cyclodimerization of [n]cumulenes are given below. It appears that only butatrienes bearing electron-withdrawing substituents are able to form [4]radialenes (e.g. **76**[49], **77**[50], **78**[51]). On heating, radialene **79** was obtained from a pentatetraene[52], and **80** from a hexapentaene[53,54], but it must be mentioned that different cyclodimers are formed when these cumulene systems bear other alkyl substituents[48,55,56].

(76)   (77)   (78)

(79)   (80)
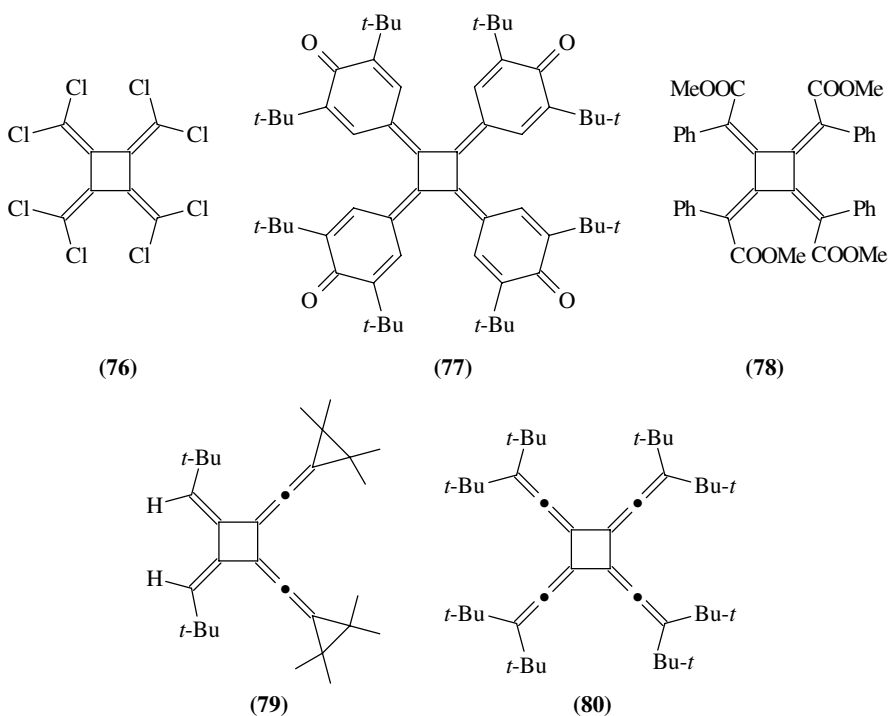
1,2,3-Cyclononatriene, the smallest cyclic [3]cumulene isolated so far, polymerizes when its solutions are concentrated[57]. On the other hand, several radialenes have been isolated which represent cyclodimers of seven- and eight-membered 1,2,3-trienes (Scheme 9).

(81) → **(82)** → **(83)**

CsF, DMF, 20 ℃
Ni(PPh₃)₄ (10 mol%)
32%

(84) → **(85)** → **(86)**

CuO₃SCF₃ (cat.)
or Pd (OAc)₂ (cat.)
− 2N₂

R = Me: 38–40%
R = i-Pr: 5–9%

(87) → **(88)** → **(89)**
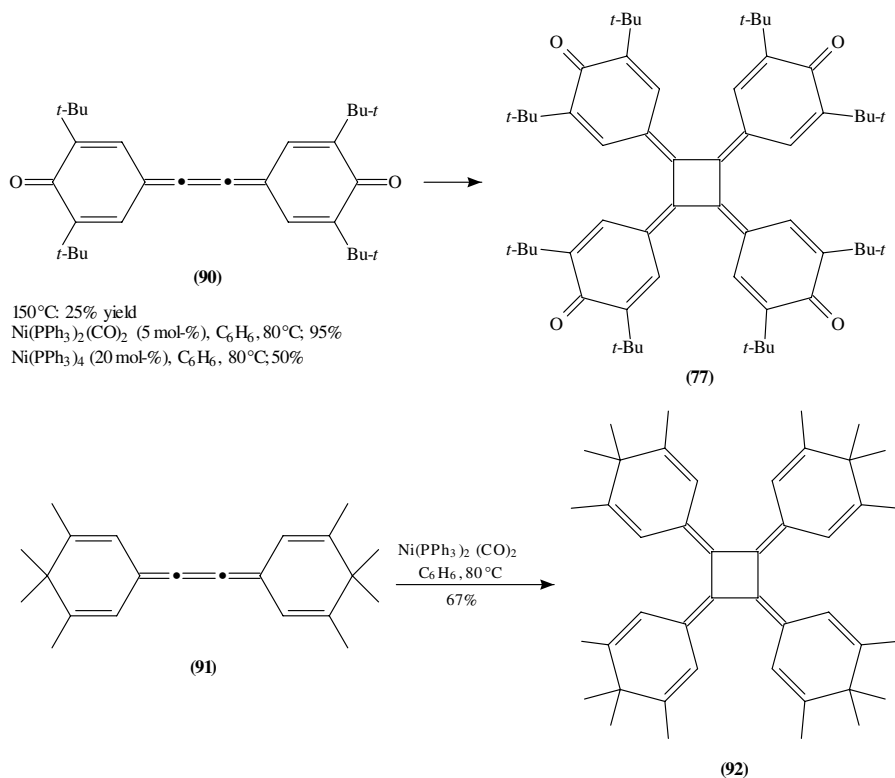
hν,
benzene

dimerization

SCHEME 9

The parent 1,2,3-cycloheptatriene **(82)**, generated as a reactive intermediate from tricyclus **81**, can be trapped with various dienes, but it does not dimerize[58]. In the presence of Ni(PPh$_3$)$_4$, however, the dimer, i.e. radialene **83** is formed[59]. Similar to the parent compound **(2)**, it polymerizes on contact with oxygen within a few hours.
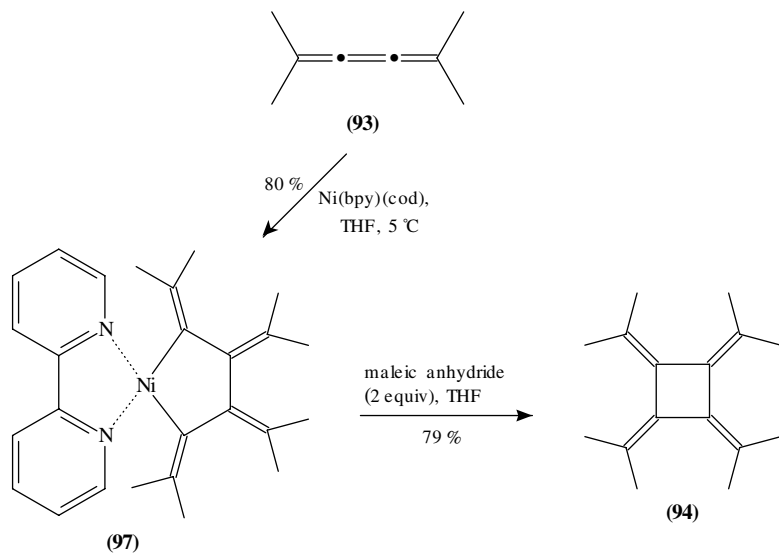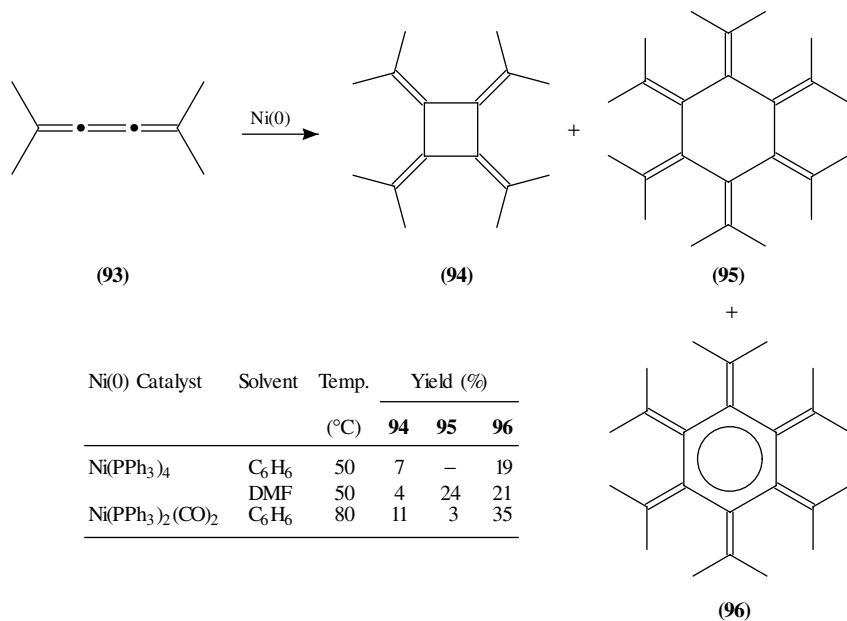
Radialenes **86** were obtained when bis(1-diazo-2-oxoalkyl)silanes **84** were decomposed with copper or palladium catalysts[60,61]. The assumption, that the heterocyclic [3]cumulene **85** is the immediate precursor of **86**, is corroborated by its trapping in a Diels-Alder reaction with furan.

Radialene **89**, a dimer of 1,2,3-cyclooctatriene derivative **88**, was isolated when the [10](9,10)anthracenophane-4,6-diyne **87** was exposed to sunlight[62]. In this case, the intermediate occurrence of **88** could not only be substantiated by isolation of (4 + 2) cycloadducts in the presence of furan or cyclopentadiene, but also by a UV/Vis spectrum obtained at 77 K in an organic glass.

The cyclodimerization of **82** to **83** is an example of a Ni(0)-mediated synthesis of [4]radialenes from [n]cumulenes. Applications of this method to butatriene derivatives **90**[50,63], **91**[64] and **93**[65,66] are shown in Scheme 10. The usefulness of Ni(0) catalysis for this transformation was first demonstrated by West and coworkers[63] and later explored in detail by Iyoda and coworkers[42,54,67]. In some cases, Ni(0) catalysis improves the efficiency of the process as compared to the purely thermal reaction (e.g. **90** ⟶ **77**); in other cases, it is a requirement for a successful [4]radialene synthesis (e.g. **82** ⟶ **83**

(90)

150°C: 25% yield
Ni(PPh$_3$)$_2$(CO)$_2$ (5 mol-%), C$_6$H$_6$, 80°C; 95%
Ni(PPh$_3$)$_4$ (20 mol-%), C$_6$H$_6$, 80°C; 50%

(77)

Ni(PPh$_3$)$_2$ (CO)$_2$
C$_6$H$_6$, 80°C
67%

(91)

(92)

SCHEME 10

(93)   **(94)**   **(95)**

Ni(0) Catalyst	Solvent	Temp.	Yield (%)		
		(°C)	**94**	**95**	**96**
Ni(PPh$_3$)$_4$	C$_6$H$_6$	50	7	–	19
	DMF	50	4	24	21
Ni(PPh$_3$)$_2$(CO)$_2$	C$_6$H$_6$	80	11	3	35

(96)

(93)

80 %   Ni(bpy)(cod),
        THF, 5 °C

maleic anhydride
(2 equiv), THF

79 %

(97)   **(94)**
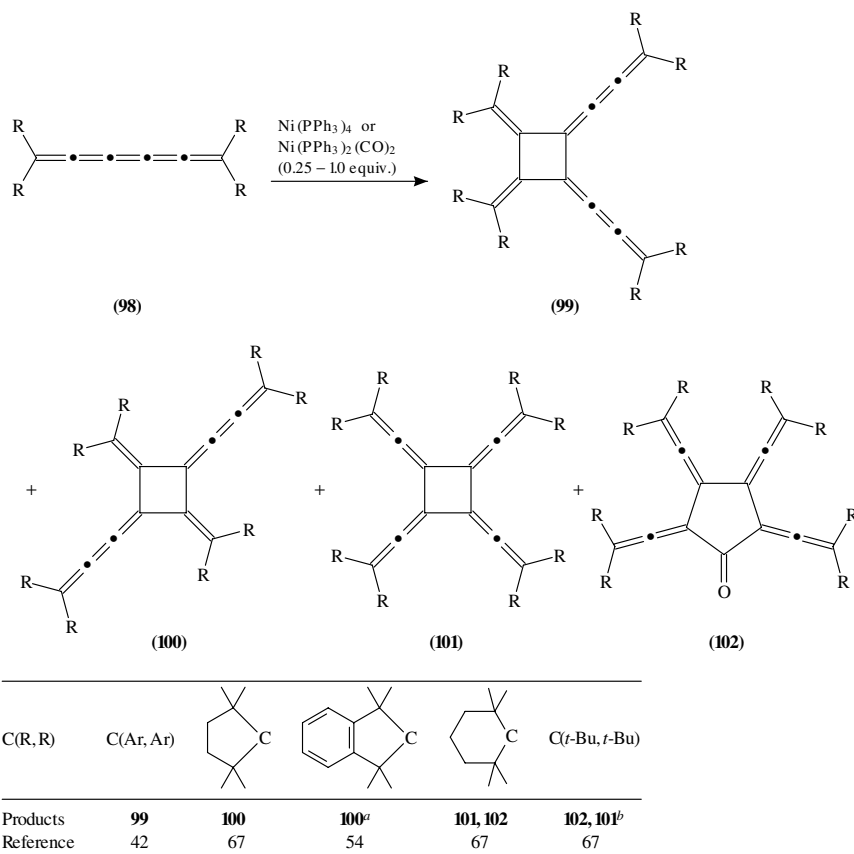
SCHEME 10. (*continued*)

and **93** $\longrightarrow$ **94**). On the other hand, tetraphenylbutatriene and 2,5-diphenylhexa-2,3,4-triene could not be cyclodimerized with catalytic Ni(PPh$_3$)$_4$ in benzene[66]. The examples shown in Scheme 10 also illustrate that different Ni(0) catalysts are in use, especially Ni(PPh$_3$)$_4$ [conveniently generated by *in situ* reduction of NiBr$_2$(PPh$_3$)$_2$, Ni(CO)$_2$(PPh$_3$)$_2$ and Ni(cod)$_2$, cod = 1,5-cyclooctadiene].

In the case of tetramethylbutatriene, Ni(0) catalyzes not only the cyclodimerization (formation of [4]radialene **94**), but also the cyclotrimerization, leading to [6]radialene **95** and its isomer **96** (see also Section II.D). The product pattern depends to some extent on the nature of the catalyst, but the choice of solvent seems to be more crucial[65,66]. This is illustrated impressively by the Ni(cod)$_2$-catalyzed reaction of **93**, which leads exclusively to the [4]radialene in toluene solution, but to the [6]radialene in DMF[68]. Interestingly, the stoichiometric reaction between **93** and (2,2′-bipyridyl)-(1,5-cyclooctadiene)nickel yields the nickel complex **97**, which has been isolated and characterized by X-ray diffraction[69]. On treatment of **97** with two equivalents of maleic anhydride, reductive elimination of nickel takes place and octamethyl[4]radialene **(94)** is formed in good yield. This reaction sequence sheds light on the mechanism of the Ni-catalyzed reactions mentioned above; further ideas on the mechanism of the cyclodimerization and cyclotrimerization reactions have been developed by Iyoda and coworkers[66].

The Ni(0)-mediated synthesis of [4]radialenes from hexapentaenes has also been investigated[42,54,67]. The regioselectivity of the cyclodimerization and the question of


C(R, R)	C(Ar, Ar)				C(t-Bu, t-Bu)
Products	**99**	**100**	**100**[a]	**101, 102**	**102, 101**[b]
Reference	42	67	54	67	67

[a] The thermal reaction (270 °C, 5 min) yields 101(51%).

[b] 101(R = t-Bu) = 80. The thermal reaction (200 °C, 15 min) also yields 101(90%)[53].

SCHEME 11

whether head-to-head or head-to-tail cycloaddition occurs depends obviously on the steric bulk of the substituents. It appears that cycloaddition across the C2=C3 bond of the [5]cumulene is normally favored, but bulky substituents induce reaction across the central double bond; in the latter case, a carbonyl ligand from the catalyst can be incorporated into the cyclodimer; see Scheme 11.

Zero-valent nickel complexes are known to reduce 1,2-dihalides to olefins and to mediate C,C-coupling reactions of vinyl halides. Based on these facts, Iyoda and coworkers developed a two-step, one-pot synthesis of alkyl-substituted [4]radialenes which starts from 2,3-dihalo-1,3-butadienes and 1,4-dichloro-2-butyne derivatives[65,66] and circumvents the isolation of the butatriene intermediates. Furthermore, the synthesis can be made catalytic in nickel when the Ni(0) complex is generated from $NiBr_2(PPh_3)_2$ with a more than stoichiometric quantity (based on the dihalide) of zinc. Again, the formation of radialene **94** must compete with that of **95** and **96**. With preformed $Ni(PPh_3)_4$ and $Ni(PBu_3)_4$, the [4]radialene is normally favored in benzene solution, but formation of **95** and/or **96** becomes important in the more polar solvents THF and DMF. With a catalyst


(**103**) 16%

+

(**104**) 37%

(**105**) 62%

SCHEME 12

E = COOMe
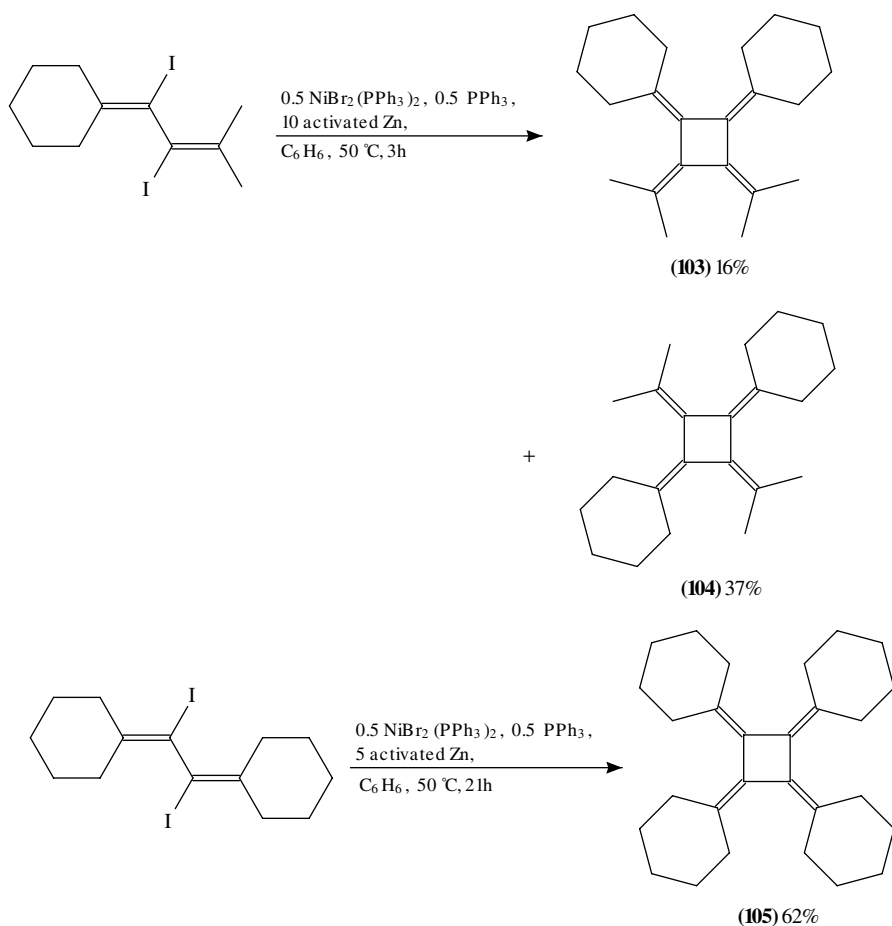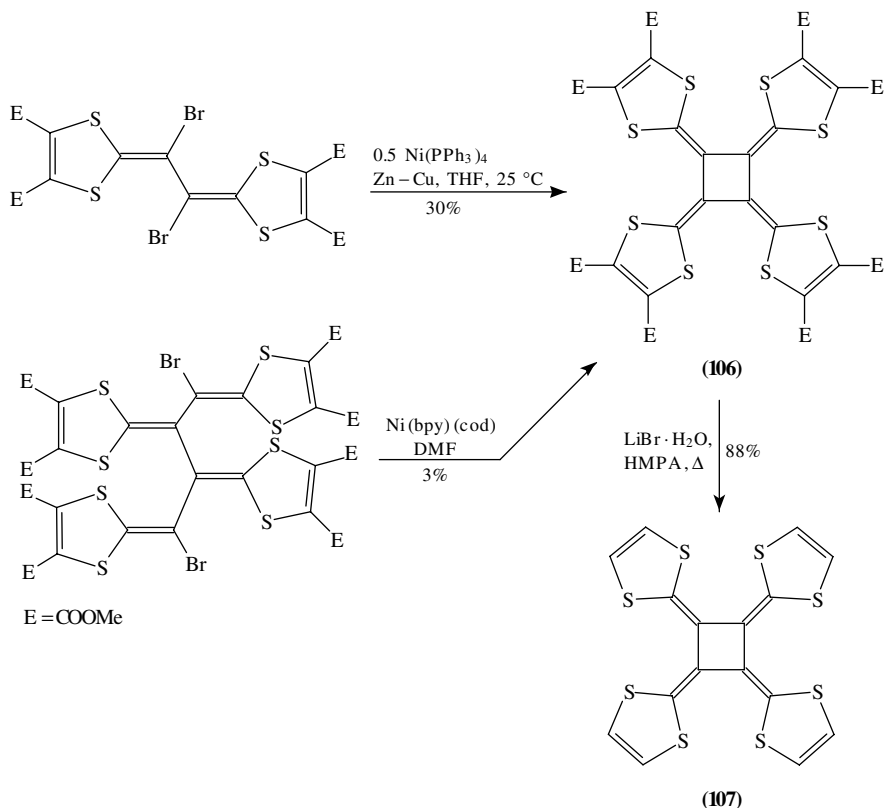
SCHEME 12. (*continued*)

generated *in situ* from $NiBr_2(PPh_3)_2$, Et_4NI and Zn (0.5:2:5 ratio) in THF solution, good yields of **94** can be obtained, and **95** and **96** are only minor products.

The scope of this method is illustrated by the preparation of other peralkylated [4]radialenes, such as **103–105**[66] and the functionalized radialene **106**[70,71] (Scheme 12). Removal of the carboxylate groups from the latter provided the very electron-rich radialene **107**.

As we have mentioned, octaphenyl[4]radialene **109** can be obtained neither by photochemical nor by Ni(0)-catalyzed cyclodimerization of tetraphenylbutatriene. However, **109** has been prepared from 1,1-dibromo-2,2-diphenylethene via organocuprate intermediates (Scheme 13)[72]. The correct choice of the added copper(I) salt is crucial for the success of this transformation, but even then, formation of tetraphenylbutatriene **(108)** from the bis(1-bromovinyl)cuprate intermediate limits the yield of **109**.

When the organocuprate methodology is applied to 1,1-dibromo-2-methylprop-1-ene, octamethyl[4]radialene **(94)** and decamethyl[5]radialene are the major products[73]. While this method does not offer any advantage over the Ni(0)-mediated syntheses of **94** (see above), it constitutes the only known synthesis of the permethylated [5]radialene (see Section II.C). For the sake of completeness, we mention that the Ni(0)-mediated dehydrohalogenation/cyclotetramerization of 1,1-dibromoalkenes is not an efficient route to [4]radialenes[66].

(108)   **(109)**
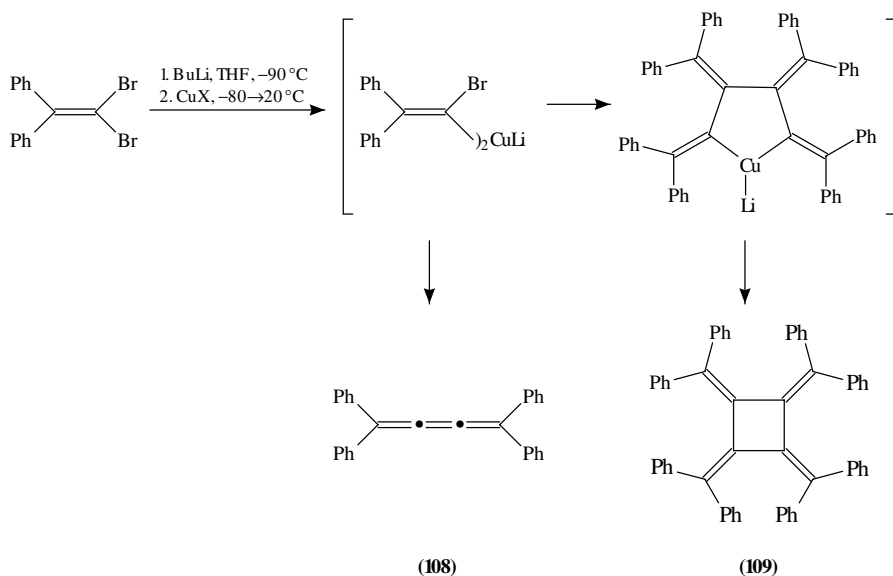
| CuX	Ratio			Yield of **108**	Yield of **109**
	alkene : BuLi : CuX			(%)	(%)
CuI · PBu$_3$	2 : 2 : 1			34	40
	4 : 2 : 1			48	29
CuCN	2 : 2 : 1			traces	41
CuI	2 : 2 : 1			Ph—≡—Ph (86%)	

SCHEME 13

An elusive [4]radialene synthesis has been reported by Sakurai. Irradiation of the 1,3,6,8,11,13,16,18-octasilacycloeicosan-4,9,14,19-tetrayne **110** in the presence of an equimolar amount of tricarbonyl(methylcyclopentadienyl)manganese initiates a skeletal rearrangement leading to **111**, whereas in the presence of an excess of the metal carbonyl, [4]radialene **112** is formed (Scheme 14)[74]. Although the mechanistic details of these rearrangements are not known, it is likely that the intramolecular version of the transformation of bis(trialkylsilyl)acetylene into a (2,2-disilylvinylidene)manganese complex is involved.

Concerning the transformation of [4]radialenes, the parent compound **(2)** has been studied best, despite its high instability in solution at room temperature or in the solid state (see above). We have already mentioned that **2** can be kept indefinitely at −78 °C, but undergoes dimerization and polymerization in solution at 20 °C. The dimerization leads to cyclooctadiene derivative **113**[36]. Trimethylenecyclobutane behaves analogously[75], and 5,5,6,6-tetraphenyl[4]radialene **66** reacts in the same manner to give **114** at 60 °C in chloroform solution (equation 6)[41]. Since thermal (4 + 4) cycloadditions should not occur in a concerted manner, it has been suggested that this reaction is a stepwise process in which the reacting 1,2-dimethylenecyclobutene unit exhibits 1,4-diradical character[39].
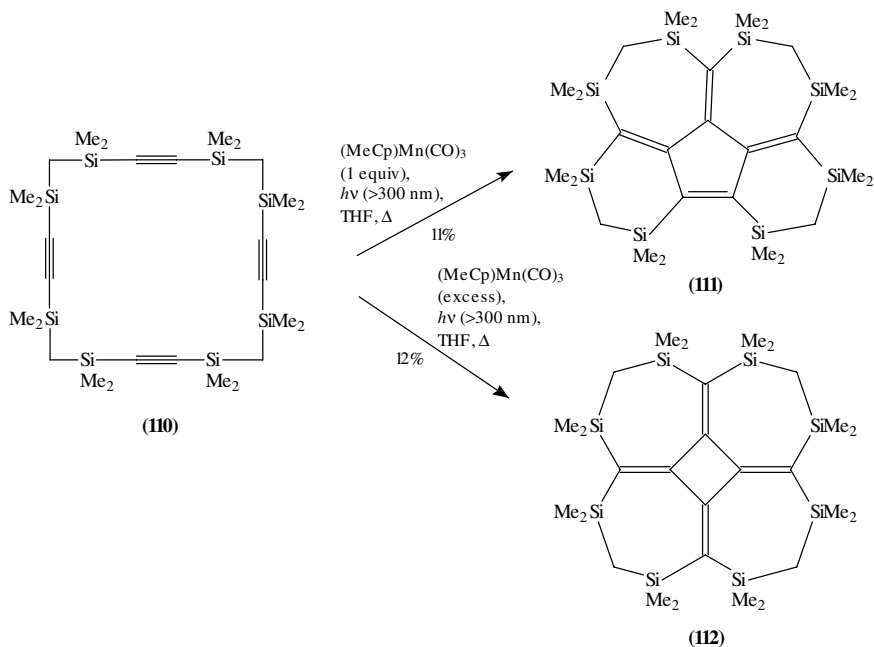
SCHEME 14

Notably, gas-phase thermolysis of **113** at 220 °C leads back to **2**[76].

R = H (**2**)
R = Ph (**66**)

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

$$ (6) $$
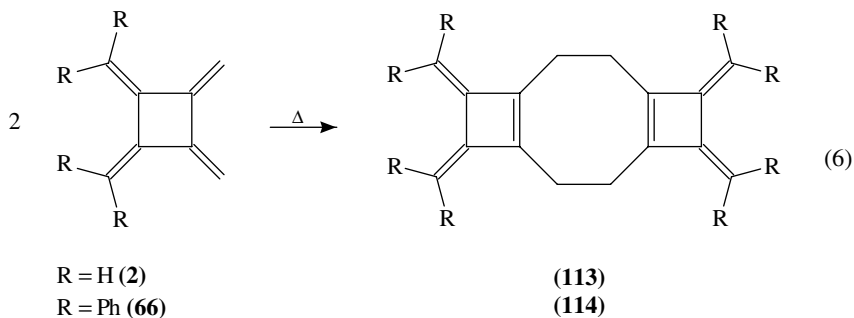
In the gas phase, **2** is a thermally very stable compound up to 850 °C. Pyrolysis at 880 °C/10^{-3} Torr generates styrene (55–62%) and *o*-xylene (6%) along with small amounts of phenylacetylene, benzene, toluene and unidentified hydrocarbons[39]. Cycloaddition reactions with dienophiles were among the first reactivity studies on **2**; they were of course driven by the expectation to generate a cyclobutadiene structure by a twofold (4 + 2) cycloaddition. However, while **2** reacts readily with electron-deficient alkenes such as TCNE[36], *N*-phenylmaleimide[36], 4-phenyl-1,2,4-triazolinedione[39] and diethyl azodicarboxylate[39] to form 1:1 adducts **115**, a second Diels-Alder reaction

producing cyclobutadienes **116** could never be realized with an excess of these powerful dienophiles. Obviously, the activation barrier on the way to the antiaromatic **116** is prohibitive. Octamethyl[4]radialene **(94)** also undergoes but a single (4+2) cycloaddition with TCNE[68]. With 4-phenyl-1,2,4-triazolinedione, however, not only the 1:1 adduct **117** but also the dipolar 2:1 adduct **118** is formed; again, the reacting system is reluctant to form a cyclobutadiene.

(2)   **(115)**   **(116)**

X	
‖	C(CN)$_2$
X	‖
	C(CN)$_2$

(94)   **(117)**

(118)
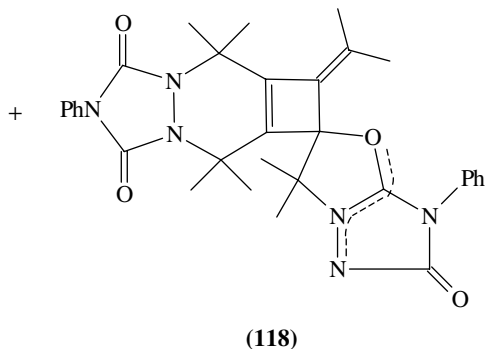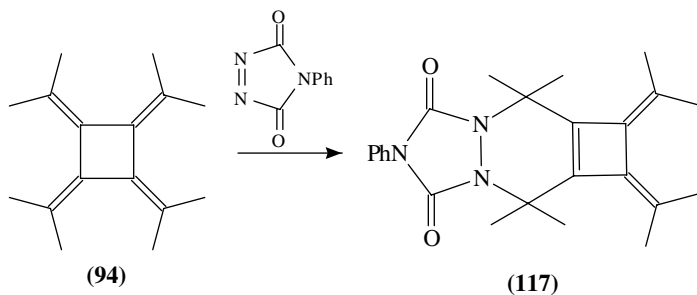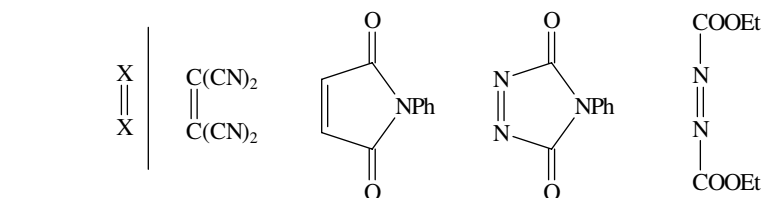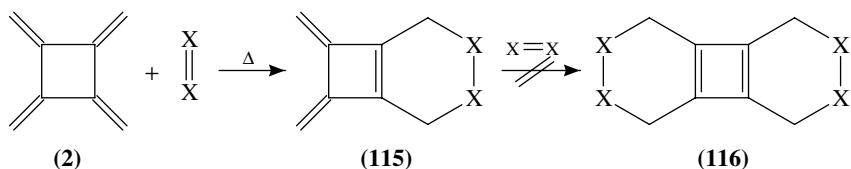
Diels–Alder reactions of **83** with various dienophiles occur regioselectively to form condensed tetra- or pentacycles of the type **119**[77]. (2+1) Cycloaddition reactions between **2** and carbenes are also known[78]. While exposure of **2** to diazomethane in the presence of CuCl leads to a mixture of mono-, di-, tri- and tetracyclopropanated products, transfer of

(119)

$X = O, NPh$
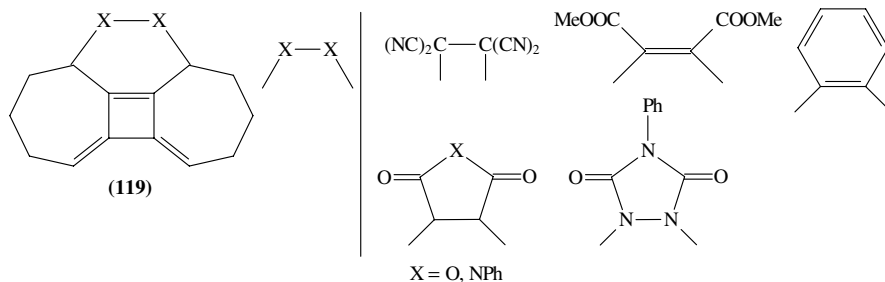
dichloro- or dibromocarbene becomes increasingly more selective. With dichlorocarbene, generated from chloroform under phase-transfer conditions, a diastereomeric mixture of the dispiro compounds **120a** and **120b** is formed. Treatment of this mixture with more dichlorocarbene provides the trisadduct **121** and the octachloro[4]rotane **122** (Scheme 15). In the second carbene transfer step, **120b** is obviously not cyclopropanated further and it can indeed be recovered. Addition of dibromocarbene proceeds slower and in lower yield, and the twofold cyclopropanated products analogous to **120a** and **120b** do not accept another carbene unit.
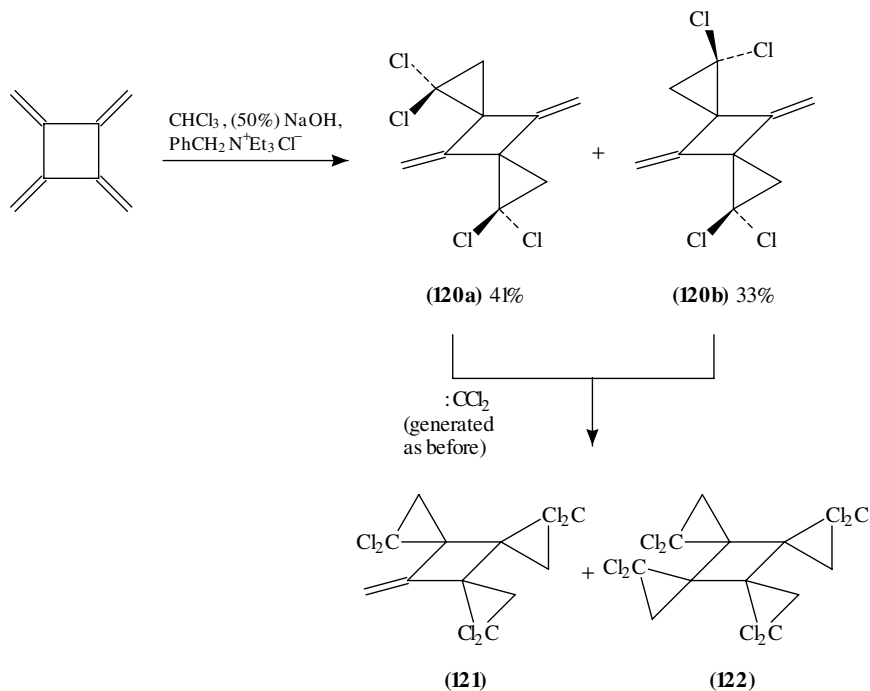
SCHEME 15

Although **2** was found to be remarkably stable towards dilute mineral acids and strong bases, some electrophilic addition reactions have been realized. With HCl, HBr and Br_2, trisadducts **123** and **124** were obtained (equation 7) which obviously result from one 1,4-

and two 1,2-addition reactions of the electrophile[39]. Again, formation of a cyclobutadiene, this time by a fourfold electrophilic 1,2-addition, is avoided.

(123)   **(124)** 68%
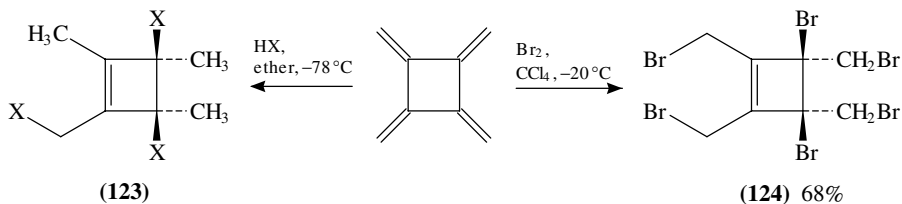
X = Cl (68%)
X = Br (50%)   (7)

Surprisingly little is known about isomerization reactions of [4]radialenes. 5,6,7,8-Tetravinyl[4]radialene **127** is certainly a unique case since it appears to be in equilibrium with its precursors in synthesis, **125** and **126**, by electrocyclic reactions (equation 8). As **127** has not been isolated in pure form and is unstable with respect to polymerization, no details on this possible equilibrium are known[79].

(125)   **(126)**

(8)

(127)
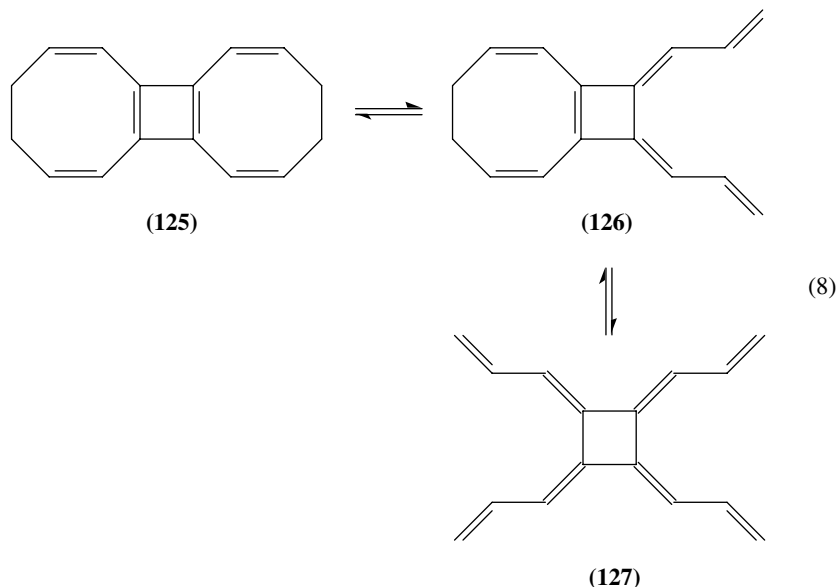
With the transition-metal-assisted ring-opening and isomerization of small rings in mind, it is astonishing that only one such study for a [4]radialene is known. The cobalt(I) complex $(C_5H_5)Co(H_2C=CH_2)_2$ catalyzes the isomerization **94** $\longrightarrow$ **128** in toluene solution, while a stoichiometric reaction takes place in THF solution from which the cyclohexadiene–cobalt complex **129** results (equation 9). The formation of **129** in the latter reaction suggests that this complex is also an intermediate in the catalytic reaction[80]. Notably, permethylated [6]radialene does not react with $(C_5H_5)Co(H_2C=CH_2)_2$.

(128)   **(94)**

(9)

(129)
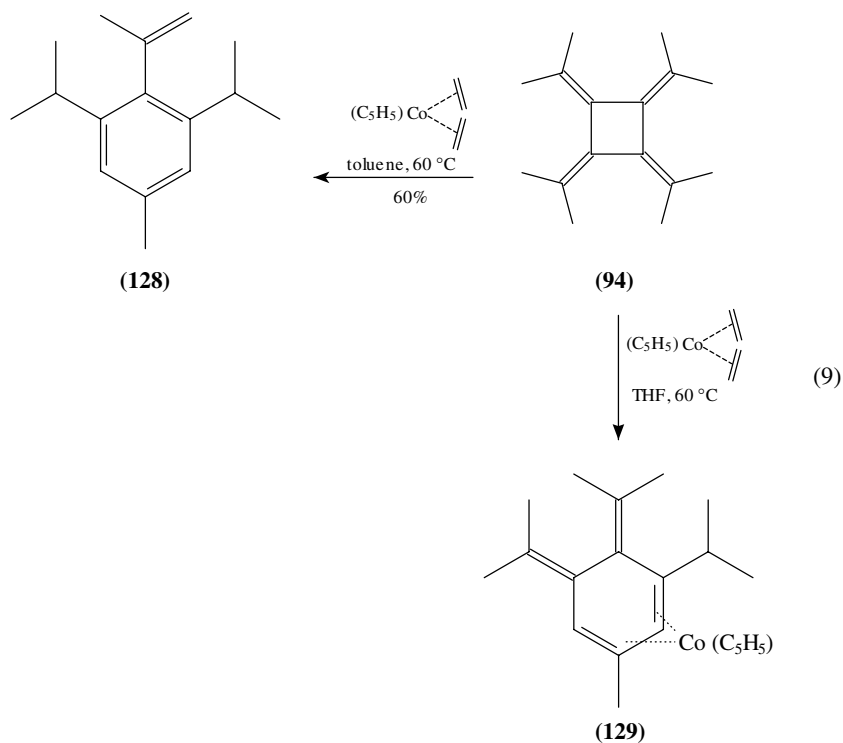
The functionalized [4]radialene **86** offers opportunities for further transformations by hydrolytic cleavage of the O-silylenol moieties and by oxidative desilylation (Scheme 16). Base- and acid-catalyzed hydrolyses lead to different products (**130** and **131**, respectively)[60]. By analogy with the formation of 1,4-diketones by oxidative coupling of two siloxyalkene molecules, treatment of **86** with the iodonium salt $PhI^+{-}O{-}^+I{-}Ph \cdot BF_4^-$ in dichloromethane leads to **132** which is immediately desilylated to provide cyclobutene **133**. If the reaction is carried out in carbon tetrachloride, the bicyclus **134** is obtained. Both the mechanism of this transformation and the influence of the solvent on the result are a matter of speculation[81]. 4-Methyl-1,2,4-triazolinedione, known as a powerful dienophile, does not undergo a Diels−Alder reaction with **86**. This is not unexpected, since the diene units of **86** are far from being planar and are sterically shielded at the termini by the t-Bu groups. Similar to the iodonium salt mentioned before, the triazolinedione brings about an oxidative desilylation of **86** leading to **132**[61]. A second transformation of this kind, which would provide tetrapivaloylcyclobutadiene, does not occur.

The redox chemistry of [4]radialenes shows similarities as well as differences with respect to [3]radialenes (see elsewhere[1] for a more detailed comparison). The simplest [4]radialene for which a redox chemistry in solution is known appears to be octa-methyl[4]radialene **(94)**. It has been converted into the radical anion **94**$^{\bullet-}$ (with potassium, [2.2.2]cryptand, THF, 200 K) and into the radical cation **94**$^{\bullet+}$ (with $AlCl_3/CH_2Cl_2$, 180 K)[82]. Both species are kinetically unstable, but the radical cation is less stable than the radical anion and disappears even at 180 K within 2 hours, probably by polymer-ization. For the success of the oxidation of **94** with the one-electron transfer system

(130)   NaOH,
             H₂O

             40%

             HCl, H₂O   (131)

                    65%

(86)

PhI⁺O⁺I Ph · 2 BF₄⁻   PhI⁺O⁺I Ph · 2 BF₄⁻
CH₂Cl₂   CCl₄

                                              toluene, Δ

(132)   (132) 45%

                            (134) 70%

H₂O, BF₄⁻

(133) 55%
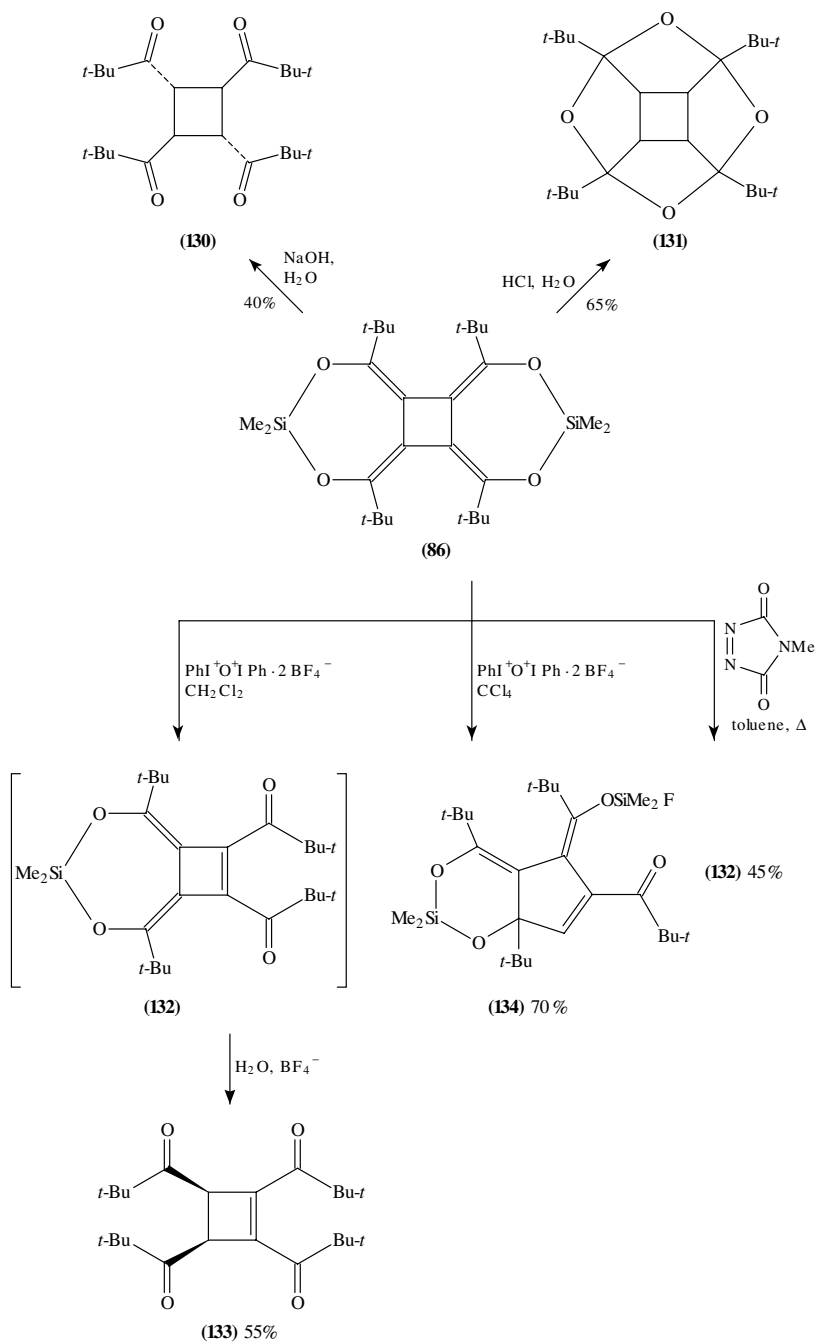
SCHEME 16
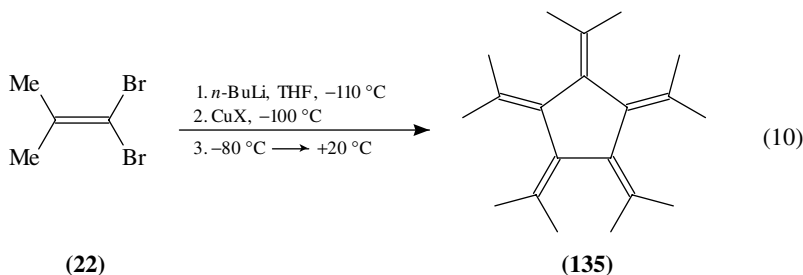
$AlCl_3/CH_2Cl_2$, it is important that the first vertical ionization energy of **94** is lower by more than 1 eV with respect to the parent [4]radialene **2** (7.30^{82} vs 8.35^{37} eV). The near congruency of the ESR and ENDOR spectra of **94**[•+] and **94**[•−] is a nice experimental proof of the topological prediction based on HMO theory that even-membered [n]radialenes have alternant π molecular properties. On the other hand, the corresponding spectra of the radical cation (generated with $Tl(OOCCF_3)_3/CH_2Cl_2$) and radical anion (formed with K, [2.2.2]cryptand) of octaphenyl[4]radialene (**109**) exhibit significant differences[83]; it has been suggested that structural differences of the two charged species account for this phenomenon.
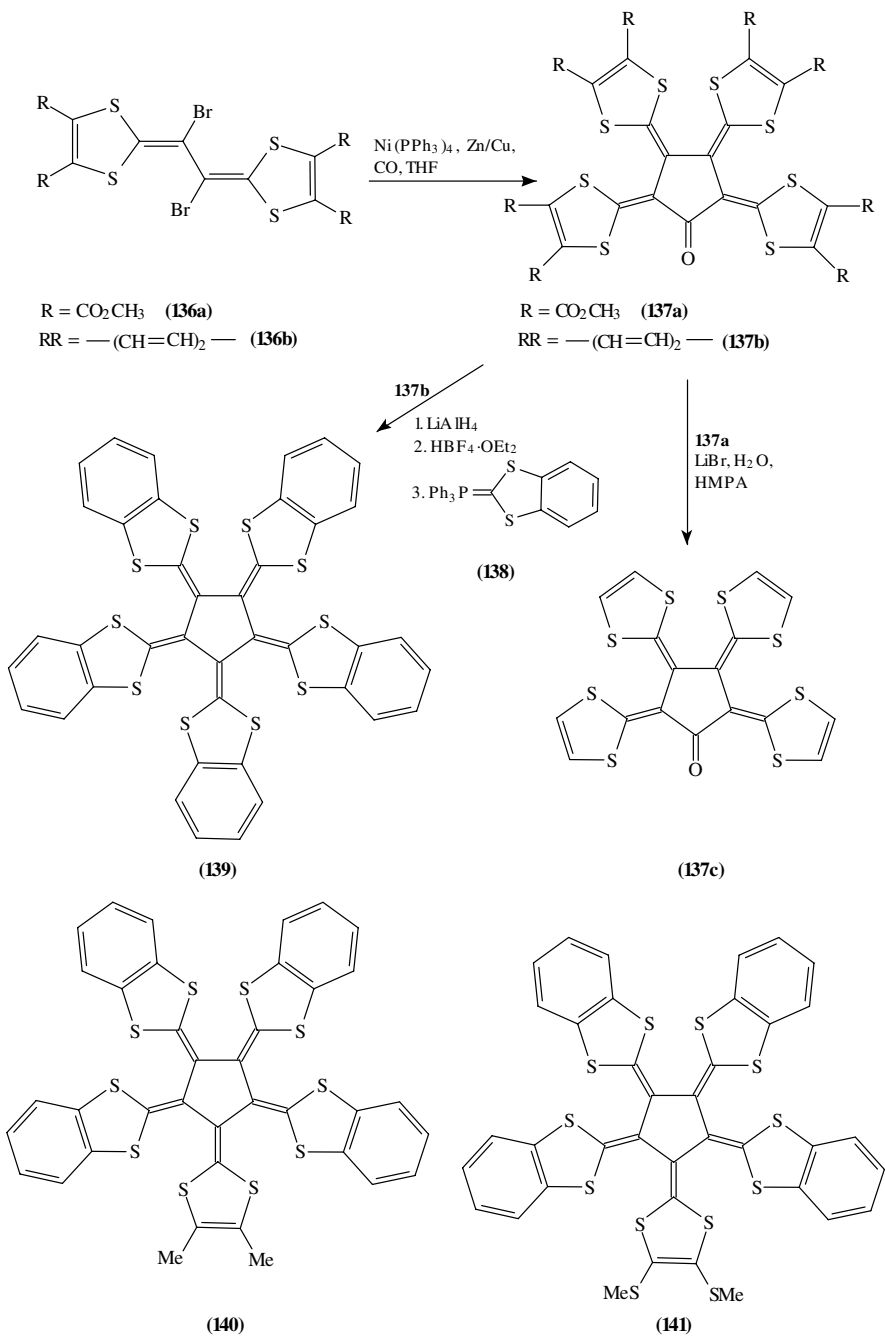
For appropriately substituted [4]radialenes, the range of accessible redox stages is wider than for [3]radialenes. While the latter can accept or give away up to two electrons (Section II.A, Table 1), the possibilities for [4]radialenes range from the dianion to the tetracation (see elsewhere[1] for a compilation). For example, the extremely electron-deficient octacyano[4]radialene, in contrast to the corresponding [3]radialene **50**, could not yet be generated. Its dianion was prepared from 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene and malononitrile and isolated as the tetrabutylammonium salt; only the one-electron oxidation to the radical anion could be achieved electrochemically[84]. Tetra(cyclohexadienylidene)cyclobutene **92** displays a fully reversible electrochemical transition from the dianion to the dication by subsequent one-electron steps[64], and the electron-rich tetrakis(1,4-dihydropyridin-4-ylidene)cyclobutane **74a**[43] and tetrakis(1,3-dithiol-2-ylidene)cyclobutanes **106** and **107**[70] can give away up to four electrons. It should be noted that this electrochemical four-electron oxidation converts the radialenes into energy-rich cyclobutadienes bearing four cationic substituents; these species are either present only in small equilibrium concentration (**74**[4+]) or undergo irreversible transformation (**106**[4+] and **107**[4+]).

As in the case of [3]radialenes, the individual redox stages of [4]radialenes may have different colors. Based on these electrochromic properties, the application of **77** as a component in liquid crystal display devices was patented[85].

C. [5]Radialenes

Among the series of the parent systems **1–4**, [5]radialene (**3**) is still unknown. The simplest derivative described so far is decamethyl[5]radialene (**135**) which has been obtained from 1,1-dibromo-2-methylpropene (**22**) by low temperature metalation with n-butyllithium followed by a metal exchange reaction with nickel[11] or (better) copper[73] salts and the thermal decomposition of the carbenoid thus formed (equation 10). The yield of **135** varies: it is only 14% with $CuBr \cdot SMe_2$, but it more than doubles (32%) when $CuI \cdot PBu_3$ is employed[73]. The formation of **135** is accompanied by di-, tri- and tetramerization of the dimethylvinylidene unit derived from **22** leading to tetramethylbutatriene and the respective permethylated [3]- and [4]radialenes. It is unlikely, though, that this

$$(10)$$

(22)   **(135)**

R = CO$_2$CH$_3$ **(136a)**

RR = — (CH=CH)$_2$ —   **(136b)**

Ni(PPh$_3$)$_4$, Zn/Cu,
CO, THF

R = CO$_2$CH$_3$ **(137a)**

RR = — (CH=CH)$_2$ —   **(137b)**

137b

l. LiAlH$_4$
2. HBF$_4$·OEt$_2$
3. Ph$_3$P=

(138)

137a
LiBr, H$_2$O,
HMPA

(139)

(137c)

(140)

MeS   SMe

(141)

SCHEME 17

formally simple approach can be developed into a general method for the preparation of substituted [5]radialenes, since the amount of the [3]- and [4]radialenes produced increases with increasing bulkiness of the substituent (see Sections II.A and II.B).

In another metal-mediated coupling reaction, the highly functionalized dienes **136a** and **136b** were allowed to react with $Ni(PPh_3)_4$ in the presence of excess zinc/copper couple at 50 °C and 1 atm of carbon monoxide to provide the octakis(methoxycarbonyl) **137a** and the tetrabenzo derivatives **137b** in excellent yields (77 and 84%, respectively), (see Scheme 17; compare also Scheme 12 for the formation of the related [4]radialene **106**[86−88]). When **137a** was treated with excess $LiBr \cdot H_2O$ in HMPA at temperatures above 100 °C, the parent system **137c** was obtained in 88% yield[88]. The ketone **137b** was subsequently used to prepare the [5]radialene **139** by a condensation reaction employing the ylide **138**[87,89]. The [5]radialenes **140** and **141** were prepared analogously[89].

Another [5]radialene ketone, the tetraallene **102a**, has been prepared in 74% yield by treating the [5]cumulene **98a** with stoichiometric amounts of $Ni(CO)_2(PPh_3)_2$[67]; the sterically very shielded ketone **102b** is produced analogously in 32% yield from the corresponding 'terminally bridged' [5]cumulene **98b** (equation 11). In both cases the dimers of the [5]cumulenes, the peralkylated [4]radialenes are formed as well (see Section II.B, Scheme 11).

$$ (11) $$

98, 102	a	b
R, R	*t*-Bu, *t*-Bu	
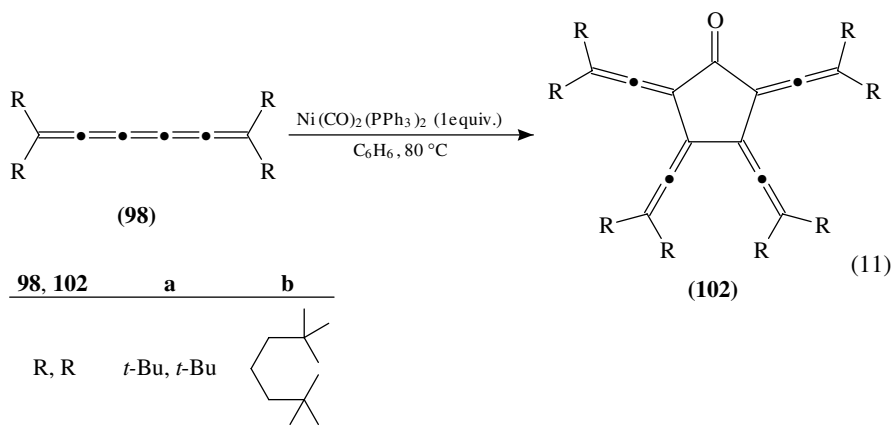
As already pointed out in the Introduction, [5]radialene **(3)** may be regarded as the 'monomer' of C_{60}[90a]. Likewise, hydrocarbon frameworks containing both six- and five-membered rings may be regarded as subunits of fullerenes if they are arranged in the proper geometric arrangement and are constructed from sp^2-hybridized carbon atoms only. In many of these subsystems—examples are provided by **142−144**—the aromatic character will clearly determine the chemical behavior. In other hydrocarbons, however, the radialenic, i.e. more polyolefinic, character might well begin to take over. This could, for example, be the case for the still unknown [5]radialenes **145** and **146**. For the 'totally benzannelated' compound **147**, corannulene, a tub-shaped molecule, which constitutes one-fourth of C_{60}, several ways of preparation are now known[90b].

Practically nothing is known about the chemical behavior of [5]radialenes. An exception is the electrochemistry of systems **139−141**. These potent electron-donating molecules show only one pair of reversible waves involving a net transfer of four electrons. In fact, these systems constitute the first examples of a single-wave four-electron transfer with only one macroscopic redox site in an organic redox system[87,89]. The corresponding tetracationic salts could be isolated.

(142)   **(143)**   **(144)**

(145)   **(146)**   **(147)**
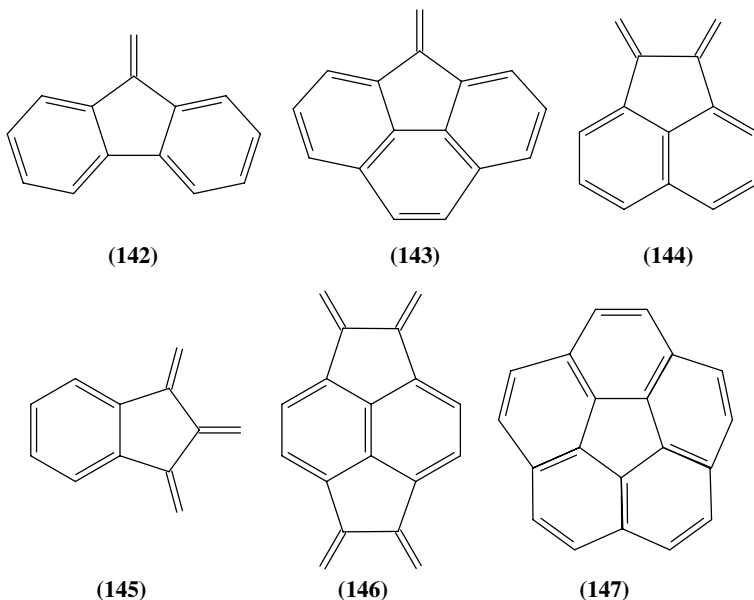
D. [6]Radialenes

Alkyl derivatives of [6]radialene **(4)** were the first members of this class of polyolefinic compounds ever to be reported (see below).

The parent hydrocarbon **4** has been obtained by several routes[91−93], with the thermal dehydrochlorination of the readily available 2,4,6-tris(chloromethyl)mesitylene (**148**, equation 12) being particularly valuable[92]. The yields of this process (close to 50%) are reproducible, making **4** a readily available, albeit difficult-to-handle, highly reactive starting material for further transformations (see below).

(12)

(148)   **(4)**
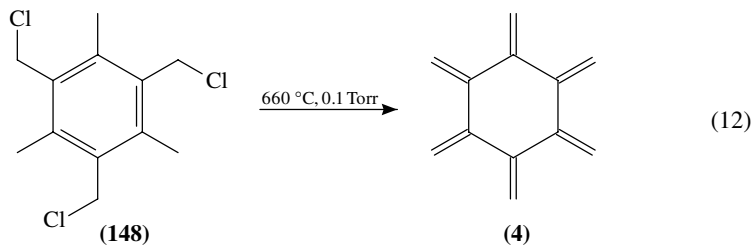
The hexamethyl derivative of **4**, all-(E)-7,8,9,10,11,12-hexamethyl[6]radialene (**150**), was the first [n]radialene described in the chemical literature. It was prepared in 1961 in 30% yield by treating either the hexabromide or the hexachloride **149** with magnesium in methanol/benzene (equation 13)[94,95]. The analogous hexaethyl[6]radialene was obtained by the same method from the corresponding hexakis(1-bromopropyl)benzene[96]. The two radialenes mentioned, which according to X-ray structural analysis[97] possess the so-called bucket wheel configuration, are the main elimination products. They crystallize particularly well and can hence be isolated easily. Besides these products there are other

diastereomers formed as well in low concentration.

$$(13)$$

(149) **(150)**
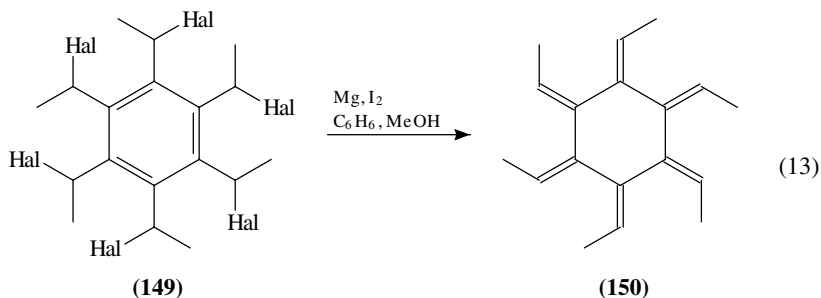
Hal = Cl, Br

Dodecamethyl[6]radialene **(95)** is obtained when *in situ* produced tetramethylbutatriene **(93)** is trimerized with a Ni(0) catalyst after debromination of the dibromide **151** with Ni(0) (equation 14)[65,66,68] (see also Section II.B). This approach was also successfully applied to the dibromides **136a** and **136b** which yield the electron-rich [6]radialenes **152a** and **152b** on treatment with [Ni(PPh$_3$)$_4$]/Zn–Cu in DMF (equation 15)[98].

(151) **(93)** **(95)** $$(14)$$

R = CO$_2$CH$_3$ **(136a)**
RR = —(CH=CH$_2$)$_2$ **(136b)**

(152a) 35%
(152b) 72%

$$(15)$$
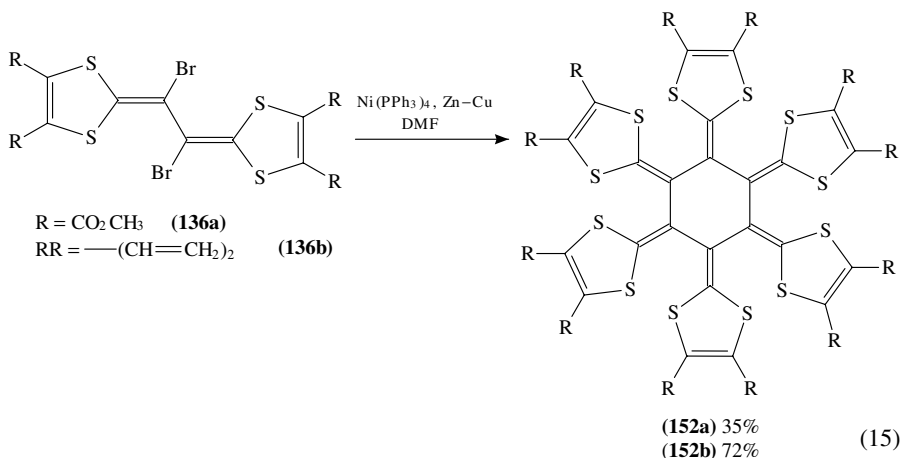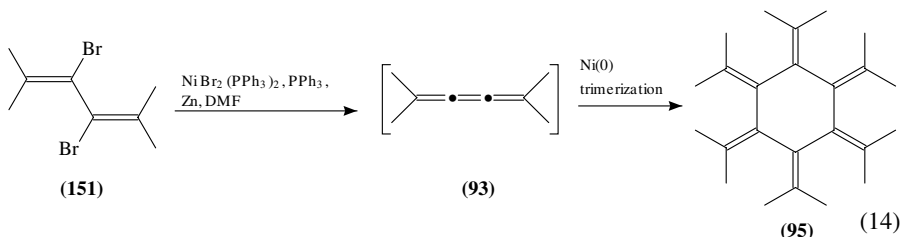
The parent [6]radialene has no stabilizing aromatic feature and is predicted to have a relatively low-lying HOMO as compared to the lower members of the series, **1–3**[99]. This may explain why it is so highly reactive that it is difficult to handle. As far as the chemical behavior of the [6]radialenes is concerned, it is the hexamethyl derivative **150**

which has been studied most thoroughly so far, undoubtedly due to its ready accessibility and its ease of handling.

Not unexpectedly, **150** reacts with electrophilic reagents such as HCl, HBr and Br$_2$, and also with H$_2$ in a 1,4- fashion, to give the hexa-substituted benzene derivatives **153a** and **153b** (which are synthetic precursors of **150**), **153c** and **153d**, respectively (equation 16)[94,95].

(153)	X	Y
(a)	Cl	H
(b)	Br	H
(c)	Br	Br
(d)	H	H

(150)   (153)   (16)
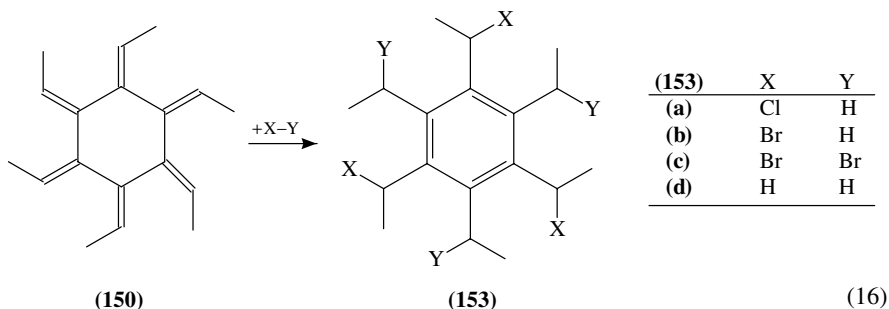
When **150** is thermolyzed at 230 °C it rearranges to at least three isomers, **155–157**, which comprise approximately 75% of the product mixture[100]. Very likely this process is initiated by two 1,5-hydrogen shift reactions providing the isomer **154** first. Before this can undergo a third 1,5-hydrogen migration process to the most stable isomer **155** — formally

230 °C, 1h

(150)   (154)

(17)

1,5 - H shift   disrotatory   conrotatory

(155)   (156)   (157)
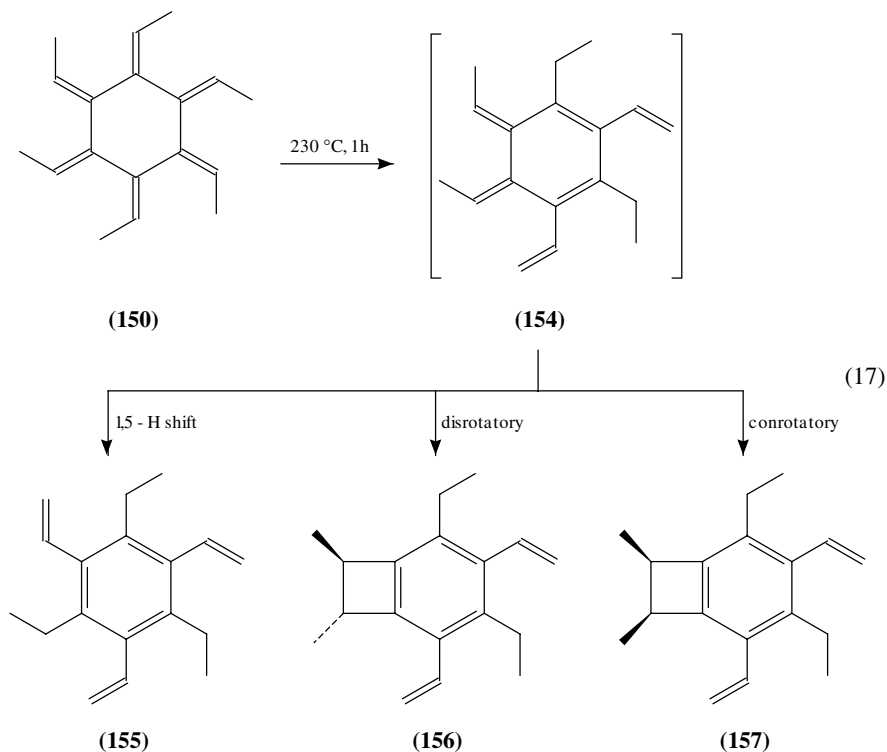
speaking, a threefold disproportionation product of **150** — it can also undergo electrocyclic ring-closure reactions at its remaining exocyclic butadiene system. This isomerization can take place either in a disrotatory or a conrotatory fashion leading to the benzocyclobutenes **156** and **157**, respectively (equation 17). Since the latter is the orbital symmetry-allowed process, it is not surprising that it is highly preferred (ratio **157/156** = 10 at 230 °C).

Dichlorocarbene adds to **150** to give the monoadduct **158** as well as the two bis-adducts **159** and **160** (equation 18)[101]. An 'ortho'-bis-adduct could not be detected among the cyclopropanation products — possibly because of steric hindrance in the immediate vicinity of **158**. The *anti*-arrangement of the two cylopropane rings in **159** and **160** was established by X-ray structural analysis[101]. Formally, the latter adducts represent hybrids of [6]radialenes and [6]rotanes ('rotaradialenes').

(150)   **(158)**   **(159)**

(18)

(160)
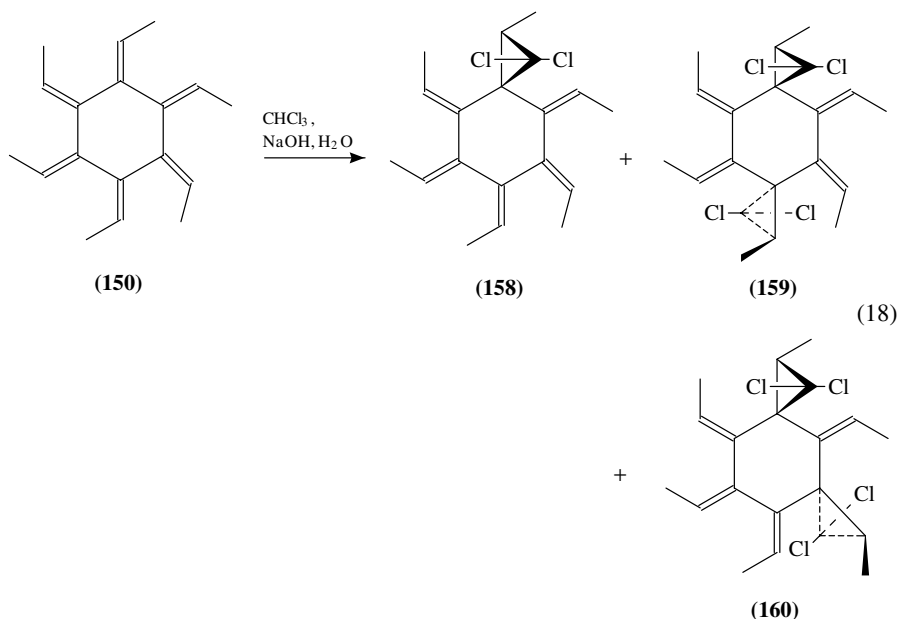
Since the [6]radialenes are triple-diene systems, it comes as no surprise that they have been used in multiple Diels–Alder reactions. In fact, after a first 1:1 addition with **150**, leading to **161**, has taken place, the reaction could proceed in two fashions — a linear course of addition leading to a *para*-xylylene **162**, and an angular route which produces an *ortho*-xylylene intermediate **163** (equation 19)[102,103].

Whereas for the hexamethyl compound **150** only products formed by the linear route have been detected with a sizeable number of dienophiles (X=X *inter alia* TCNE, maleic anhydride, benzoquinone, 1,4-naphthoquinone, acrolein, methyl acrylate[102]), the parent system **4** undergoes threefold Diels–Alder addition in a star-shaped manner leading to **164** with dimethyl acetylenedicarboxylate and to **165** with fumaroyl chloride followed by methanolysis (equation 20)[92].

That this difference in (4+2)-cycloaddition behavior most likely has steric origins — the methyl groups in **150** or the derived monoadduct preventing an 'ortho'-addition of two equivalents of the dienophile — is supported by the observation that permethyl[6]radialene **95** is inert even towards the extremely reactive dienophile 4-phenyl-1,2,4-triazolinedione[68].

(150)   **(161)**

(19)

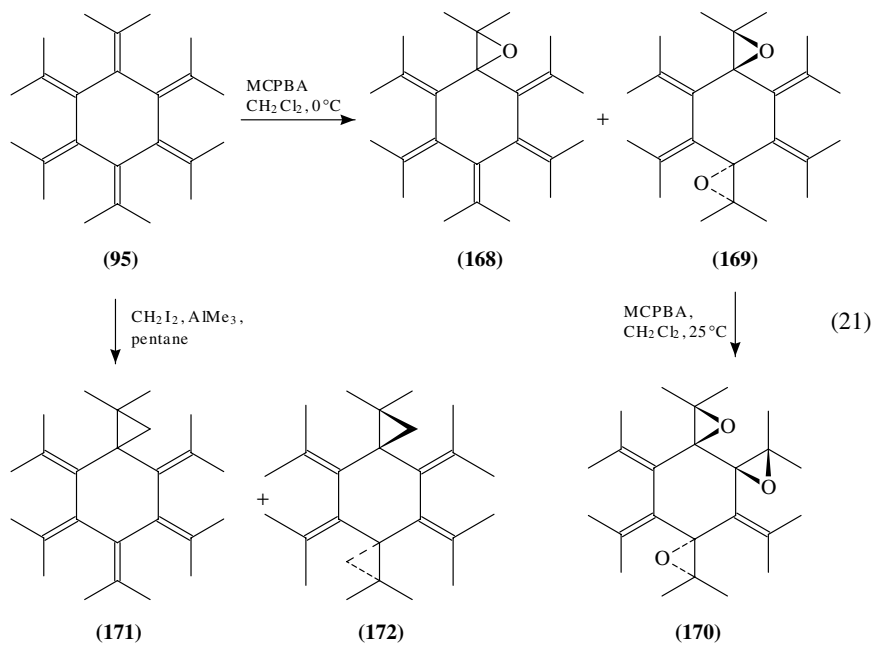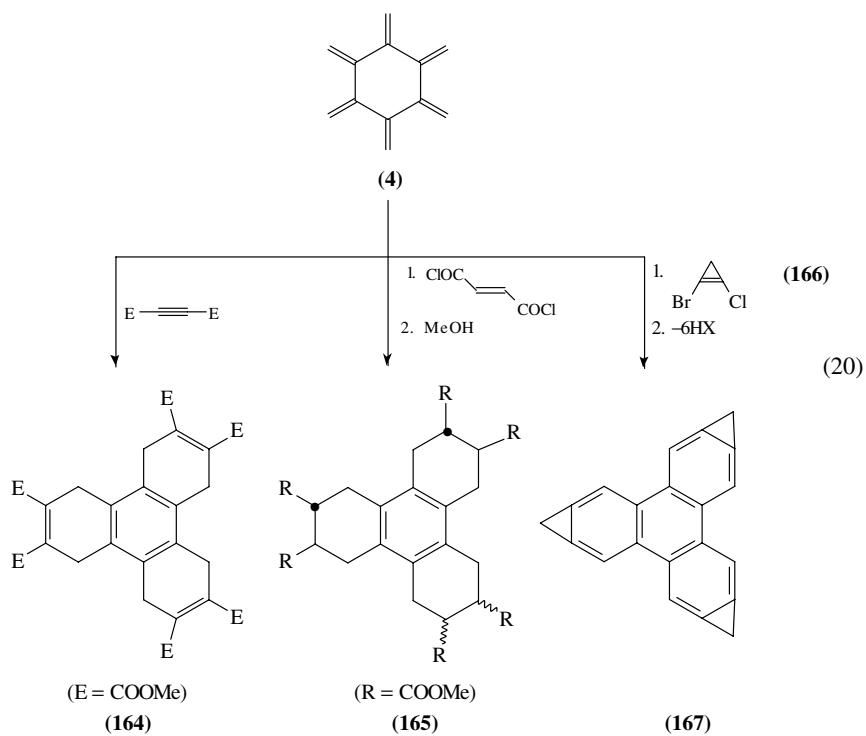**(162)**   **(163)**
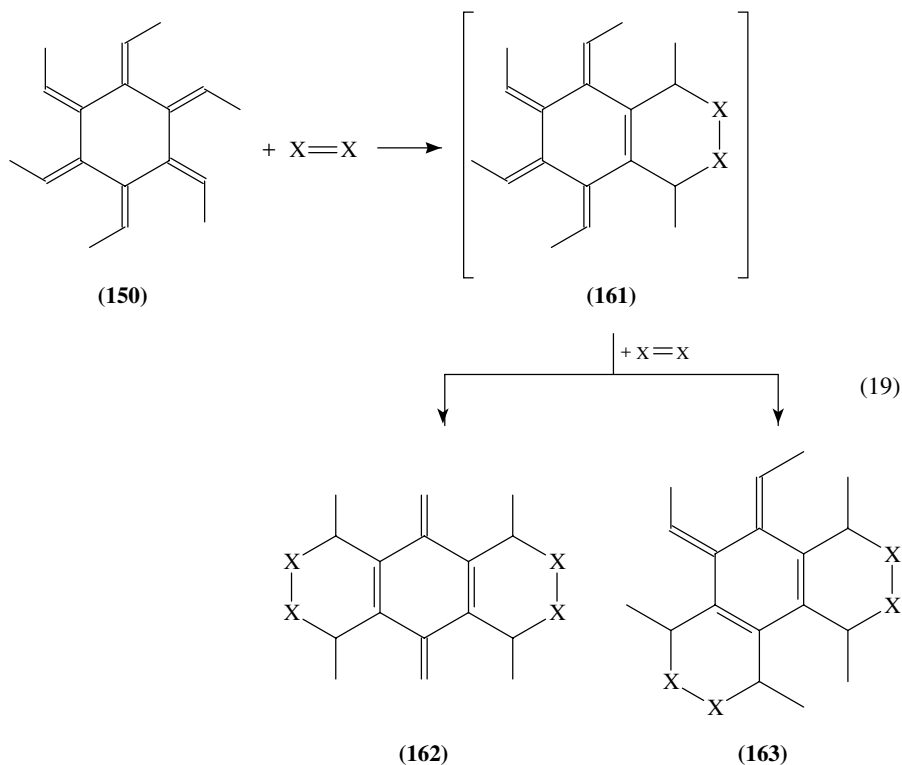
In a recent interesting application the 'tris-diene' **4** was first reacted with 1-bromo-2-chlorocyclopropene **166**, and the resulting *tris*-adduct was subsequently dehydrohalogenated to the tricycloproparene **167** (equation 20)[104].
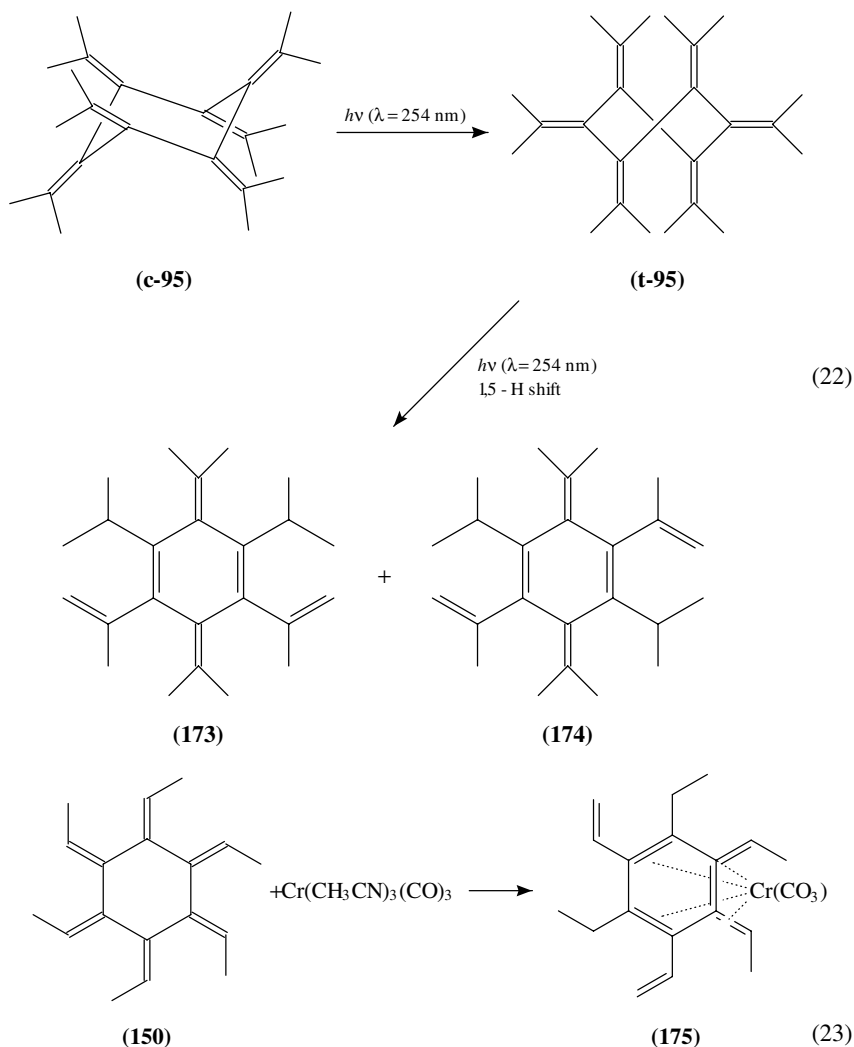
In very recent work the [6]radialene **95** has been epoxidized with *m*-chloroperbenzoic acid (MCPBA) to the mono- and the *bis*-epoxide **168** and **169**, respectively, at $0\,^{\circ}$C, and to the *tris*-epoxide **170** at room temperature[100]. Methylenation with $CH_2I_2/AlMe_3$ provides the 'rotaradialenes' **171** and **172** (equation 21)[101]. Again, the relative orientation of the three-membered rings in these adducts follows from X-ray and NMR data[100,101].

A series of remarkable transformations takes place when **95** is irradiated with 254-nm light. As has been shown by X-ray structure determination, this radialene adopts the chair configuration **c-95** in its ground state[68]. On irradiation **c-95** is first converted into the twist-isomer **t-95**, whose structure has been determined by X-ray analysis again[101]. In a second step, two photochemical 1,5-hydrogen shifts take place leading to the *para*-xylylenes **173** and **174** (equation 22). Normally, these all-carbon analogues of *p*-benzoquinone are very reactive and cannot be obtained in substance. In the present instance they can be handled easily under normal laboratory conditions[100]. Most likely this stability is caused by the complete substitution of the *para*-xylylene core of these hydrocarbons.

Whether [6]radialenes have a potential as novel ligands for metal complexes remains to be seen. A first example of a successful complexation is provided by **150**, which reacts with tris(acetonitrile)tricarbonylchromium in dioxane at room temperature to give the *ortho*-xylylene chromium complex **175** in excellent yield (83%) (equation 23)[105].

It should be noted that **175** is the chromium complex of **154**, the intermediate postulated in the thermal isomerization of hexamethyl[6]radialene (**150**).

(4)

1. ClOC
COCl
2. MeOH

1.
Br   Cl
2. –6HX

(166)

E ——— E

(20)

E
E
E
E
E
E

(E = COOMe)
(164)

R
R
R
R
R
R

(R = COOMe)
(165)

(167)

(95)

MCPBA
CH$_2$Cl$_2$, 0 °C

(168)

+

(169)

CH$_2$I$_2$, AlMe$_3$,
pentane

MCPBA,
CH$_2$Cl$_2$, 25 °C

(21)

(171)

+

(172)

(170)

(c-95)   (t-95)

(22)

(173)   +   (174)

(150)   +Cr(CH$_3$CN)$_3$(CO)$_3$ $\longrightarrow$ (175)   (23)
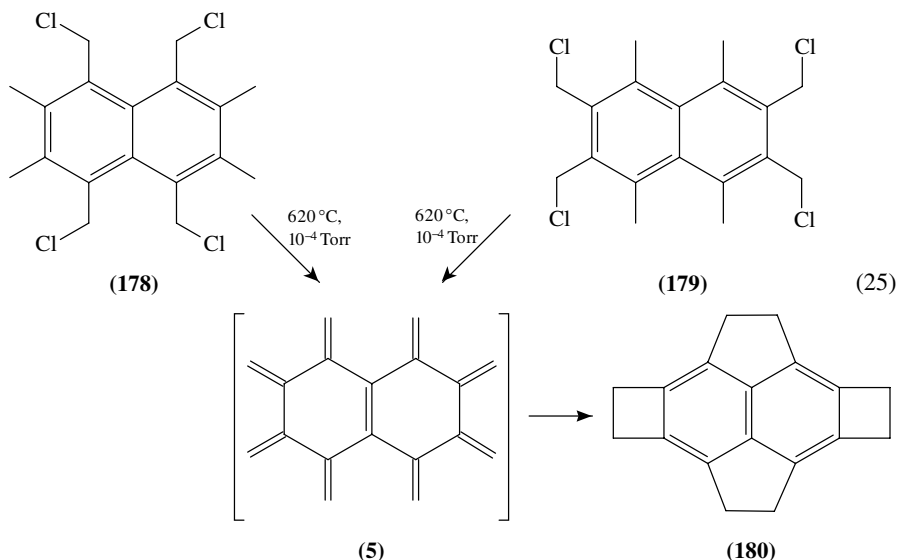
E. Higher Radialenes

Higher radialenes may be generated in several different ways. The most obvious one consists in just inserting additional exocyclic double bonds into the monocyclic ring system, thus generating [7]- **(176)** and [8]radialene **(177)** as the next members of the homologous series (e.g. as in equation 24). These compounds — which are unknown at the present time — are not only of interest in their own right and as targets of novel preparative routes which very likely have to be developed to prepare them. Based on the predicted first vertical ionization potential of only about 7.0 eV[99], these higher radialenes are expected to be extremely reactive and hence quite unstable, but they could in principle also serve as core units for extended π-systems in the same way in which [5]radialene plays this role in, e.g., corannulene **(147)** or C$_{60}$. Undoubtedly these cores will generate

topologies in these larger π-systems which are different from those produced by five-membered rings.

(176)   **(177)**   (24)
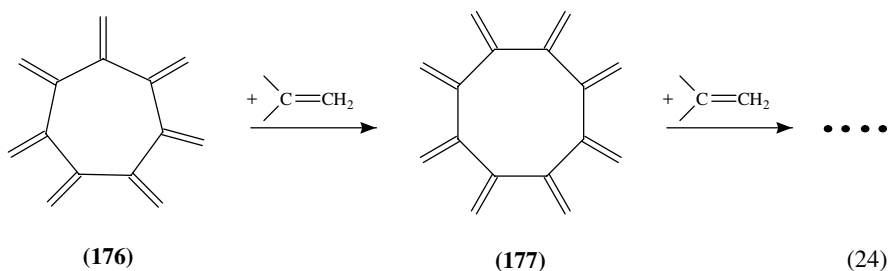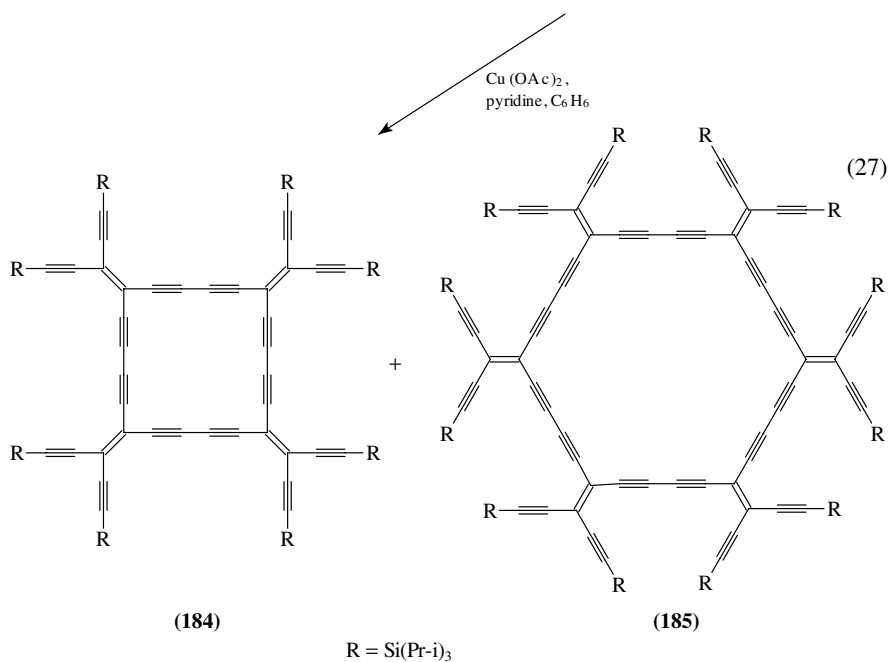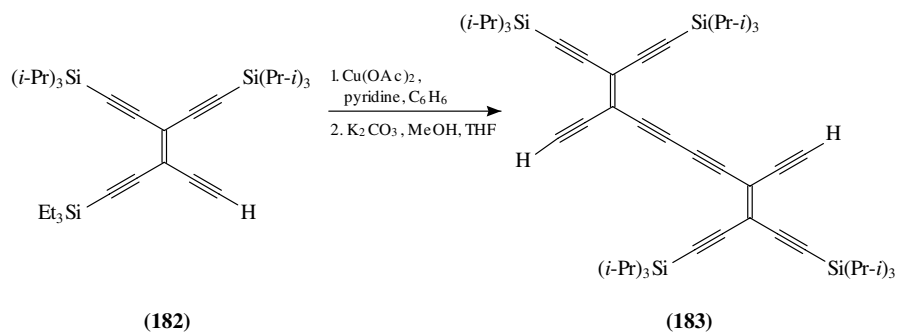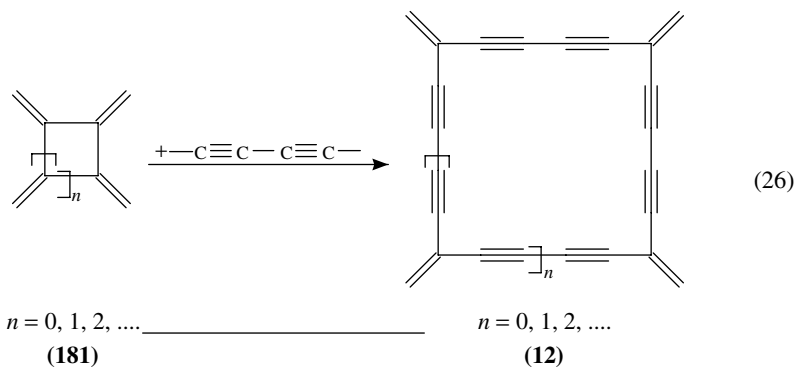
Secondly, the carbon framework 'holding' the exocyclic double bonds could be extended. This is demonstrated by naphtharadialene **5**, a highly reactive intermediate which has been generated by thermal dehydrochlorination from either the tetrachloride **178** or its isomer **179**[106]. Radialene **5** has not been detected as such in these eliminations; rather, its temporary formation was inferred from the isolation of the thermolysis product **180** which was isolated in 15% yield (equation 25). Formally, **5** may also be regarded as an [8]radialene into whose center an ethylene unit has been inserted. In principle, other center units — cyclobutadiene, suitable aromatic systems — may be introduced in this manner, thus generating a plethora of novel radialene structures.

(178)   **(179)**   (25)

(5)   **(180)**

A third route to higher or 'expanded' radialenes (see Introduction) also rests on an 'insertion principle'. It employs the rodlike butadiyne unit and inserts it between the neighboring double bonds of the basic radialene systems **181**, thus converting these into the boxlike molecules **12** (equation 26)[107,108].

The first representatives of these interesting π-systems have recently been described. In the even series (**12**, $n = 1,3,\ldots$) the synthesis of the square molecule **184** and the hexagonal one **185** starts from the building block **182**. This is first oxidatively dimerized

$$(26)$$

$n = 0, 1, 2, ...$ $n = 0, 1, 2, ...$

(181)   **(12)**

(182)   **(183)**

Cu(OAc)$_2$,
pyridine, C$_6$H$_6$

$$(27)$$

(184)   **(185)**

R = Si(Pr-i)$_3$

and the product formed is deprotected to give **183**, which possesses two 'free' triple bonds. Cyclization by oxidative coupling is hence possible, and it results in the formation of **184** and **185** which are produced in remarkably good yields (15 and 20%, respectively) (equation 27)[107,108].

To generate the pentagonal structure **188**, two equivalents of **182** were first coupled with the tetraethynylethene **186**. After deprotection of the appropriate ethynyl groups the resulting intermediate **187** could be 'roofed' with **183** to yield the desired product **188** (yield of last step: 15%) (equation 28)[107,108].

Clearly, this is a rich playground for chemists interested in novel π-structures and topologies, and it is likely that many novel radialene-derived compounds will be prepared in the not too distant future.

R = Si(Pr-i)$_3$ **(188)**
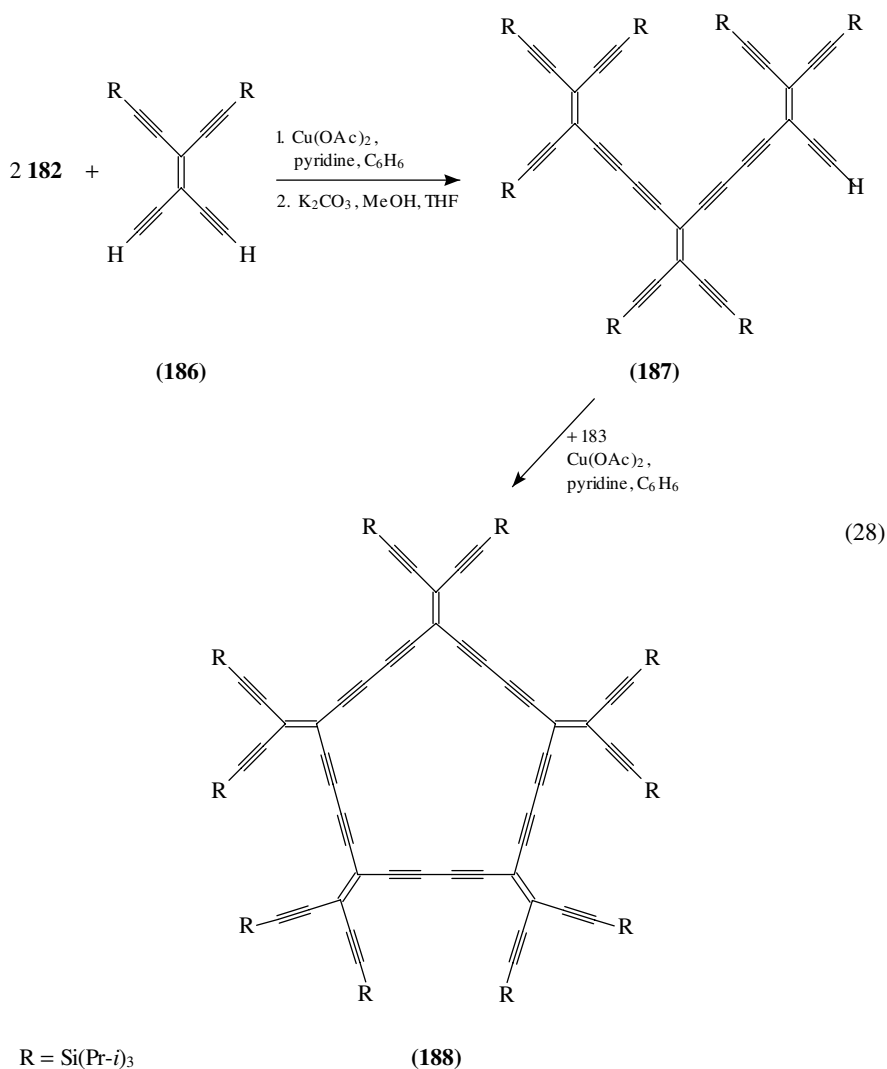
III. CONCLUDING REMARKS

We have already pointed out in the Introduction (see above) that the first review article on radialenes is only a few years old[1]. In this first summary we have enclosed a comprehensive survey and discussion of the structural and spectroscopic properties of the radialenes. Since progress in this latter area has not been very rapid in the last few years, we do not address here again these aspects of the radialenes. Furthermore, nothing new can be added to the statement that all radialenes are nonaromatic and that they have localized endocyclic single bonds and exocyclic double bonds[1] (for recent discussions of $\pi-\pi$ interaction in [5]- and [3]radialene, see elsewhere[90a,109]).

However, the present chapter clearly shows that preparative radialene chemistry is an active and quickly evolving area of synthetic organic chemistry. Many different radialenes are now accessible by various, often surprisingly simple synthetic routes. New substitution patterns and π-system topologies, often emerging in a conceptual approach to new organic materials[1,110], continue to be a challenge for synthetic chemists. If this development remains alive the need will certainly arise in a few years time to present all of radialene chemistry in a (first) monograph on this interesting class of compounds.

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