7

PHOTOCHEMISTRY

Most reactions carried out in organic chemistry laboratories take place between molecules all of which are in their ground electronic states. In a *photochemical reaction*,[1] however, a reacting molecule has been previously promoted by absorption of light to an electronically excited state. A molecule in an excited state must lose its extra energy in some manner; it cannot remain in the excited condition for long. However, a chemical reaction is not the only possible means of relinquishing the extra energy. In this chapter we first discuss electronically excited states and the processes of promotion to these states. Then we examine the possible pathways open to the excited molecule, first the physical and then the chemical pathways. The subject of electronic spectra is closely related to photochemistry.

Excited States and the Ground State

Electrons can move from the ground-state energy level of a molecule to a higher level (i.e., an unoccupied orbital of higher energy) if outside energy is supplied. In a photochemical process this energy is in the form of light. Light of any wavelength has associated with it an energy value given by $E = h\nu$, where ν is the frequency of the light (ν = velocity of light c divided by the wavelength λ) and h is Planck's constant. Since the energy levels of a molecule are quantized, the amount of energy required to raise an electron in a given molecule from one level to a higher one is a fixed quantity. Only light with exactly the frequency corresponding to this amount of energy will cause the electron to move to the higher level. If light of another frequency (too high or too low) is sent through a sample, it will pass out without a loss in intensity, since the molecules will not absorb it. However, if light of the correct frequency is passed in, the energy will be used by the molecules for electron promotion and hence the light that leaves the sample will be diminished in intensity or altogether gone. A *spectrophotometer* is an instrument that allows light of a given frequency to pass through a sample and that detects (by means of a phototube) the amount of light that has been transmitted, i.e., not absorbed. A spectrophotometer compares the intensity of the transmitted light with that of the incident light. Automatic instruments gradually and continuously change the frequency, and an automatic recorder plots a graph of absorption vs. frequency or wavelength.

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[1]There are many books on photochemistry. Some recent ones are Michl; Bonačić-Koutecký *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990; Scaino *Handbook of Organic Photochemistry*, 2 vols.; CRC Press: Boca Raton, FL, 1989; Coxon; Halton *Organic Photochemistry*, 2nd ed.; Cambridge University Press: Cambridge, 1987; Coyle *Photochemistry in Organic Synthesis*; Royal Society of Chemistry: London, 1986, *Introduction to Organic Photochemistry*; Wiley: New York, 1986; Horspool *Synthetic Organic Photochemistry*; Plenum: New York, 1984; Margaretha *Preparative Organic Photochemistry*, *Top. Curr. Chem.* **1982**, *103*; Turro *Modern Molecular Photochemistry*; W.A. Benjamin: New York, 1978; Rohatgi-Mukherjee *Fundamentals of Photochemistry*; Wiley: New York, 1978; Barltrop; Coyle *Principles of Photochemistry*; Wiley: New York, 1978. For a comprehensive older treatise, see Calvert; Pitts *Photochemistry*; Wiley: New York, 1966. For a review of the photochemistry of radicals and carbenes, see Scaiano; Johnston *Org. Photochem.* **1989**, *10*, 309-355. For a history of photochemistry, see Roth *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1193-1207 [*Angew. Chem. 101*, 1220-1234]. For a glossary of terms used in photochemistry, see Braslavsky; Houk *Pure Appl. Chem.* **1988**, *60*, 1055-1106. See also the series, *Advances in Photochemistry*, *Organic Photochemistry*, and *Excited States*.
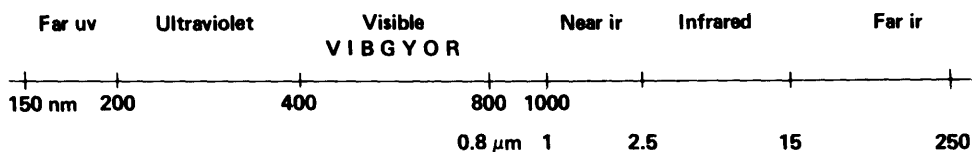
| Far uv | Ultraviolet | Visible | | Near ir | Infrared | | Far ir |
| | | **V I B G Y O R** | | | | | |

150 nm   200   400   800 1000

0.8 μm   1   2.5   15   250

FIGURE 7.1 The uv, visible, and ir portions of the spectrum.

The energy of electronic transitions corresponds to light in the visible, uv, and far-uv regions of the spectrum (Figure 7.1). Absorption positions are normally expressed in wavelength units, usually nanometers (nm).[2] If a compound absorbs in the visible, it is colored, possessing a color complementary to that which is absorbed.[3] Thus a compound absorbing in the violet is yellow. The far-uv region is studied by organic chemists less often than the visible or ordinary uv regions because special vacuum instruments are required owing to the fact that oxygen and nitrogen absorb in these regions.

From these considerations it would seem that an electronic spectrum should consist of one or more sharp peaks, each corresponding to the transfer of an electron from one electronic level to another. Under ordinary conditions the peaks are seldom sharp. In order to understand why, it is necessary to realize that molecules are constantly vibrating and rotating and that these motions are also quantized. A molecule at any time is not only in a given electronic state but also in a given vibrational and rotational state. The difference between two adjacent vibrational levels is much smaller than the difference between adjacent electronic levels, and the difference between adjacent rotational levels is smaller still. A typical situation is shown in Figure 7.2. When an electron moves from one electronic level to another, it moves from a given vibrational and rotational level within that electronic level to some vibrational and rotational level at the next electronic level. A given sample contains a large number of molecules, and even if all of them are in the ground electronic state, they are still distributed among the vibrational and rotational states (though the ground vibrational state V_0 is most heavily populated). This means that not just one wavelength of light will be absorbed but a number of them close together, with the most probable transition causing the most intense peak. But in molecules containing more than a few atoms there are so many possible transitions and these are so close together that what is observed is a relatively broad band. The height of the peak depends on the number of molecules making the transition and is proportional to log ε, where ε is the *extinction coefficient*. The extinction coefficient can be expressed by $\varepsilon = E/cl$, where c is the concentration in moles per liter, l is the cell length in centimeters, and $E = \log I_0/I$, where I_0 is the intensity of the incident light and I of the transmitted light. The wavelength is usually reported as λ_{max}, meaning that this is the top of the peak. Purely vibrational transitions, such as between V_0 and V_1 of E_1, which require much less energy, are found in the ir region and are the basis of ir spectra. Purely rotational transitions are found in the far-ir and microwave (beyond the far-ir) regions.

A uv or visible absorption peak is caused by the promotion of an electron in one orbital (usually a ground-state orbital) to a higher orbital. Normally the amount of energy necessary to make this transition depends mostly on the nature of the two orbitals involved and much less on the rest of the molecule. Therefore, a simple functional group such as the C=C double bond always causes absorption in the same general area. A group that causes absorption is called a *chromophore*.

[2]Formerly, millimicrons (mμ) were frequently used; numerically they are the same as nanometers.
[3]For monographs, see Zollinger *Color Chemistry*; VCH: New York, 1987; Gordon; Gregory *Organic Chemistry in Colour*; Springer: New York, 1983; Griffiths *Colour and Constitution of Organic Molecules*; Academic Press: New York, 1976. See also Fabian; Zahradník *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 677-694 [*Angew. Chem. 101*, 693-710].
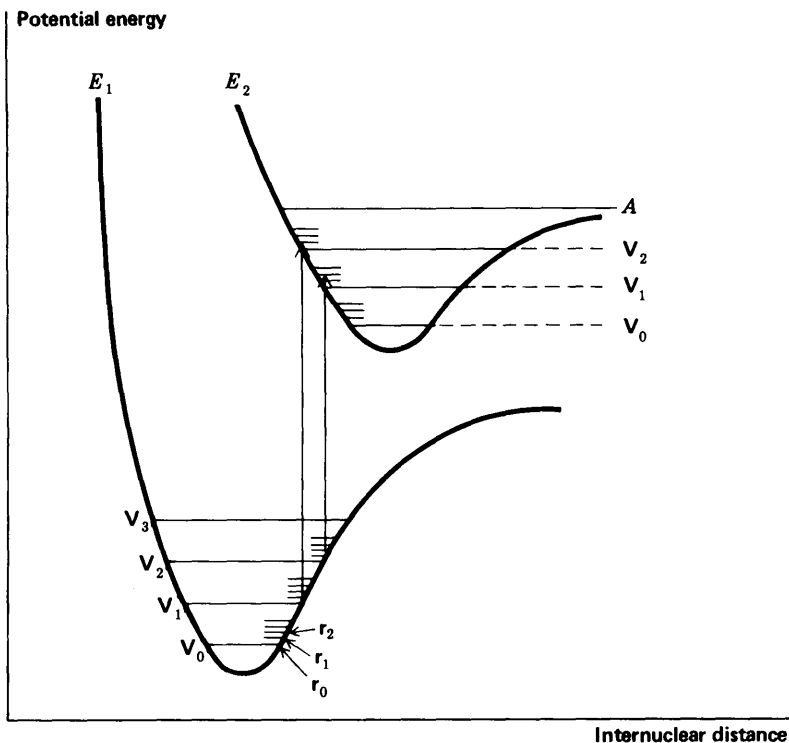
FIGURE 7.2   Energy curves for a diatomic molecule. Two possible transitions are shown. When an electron has been excited to the point marked *A*, the molecule may cleave (p. 236).

Singlet and Triplet States. "Forbidden" Transitions

In most organic molecules, all electrons in the ground state are paired, with each member of a pair possessing opposite spin as demanded by the Pauli principle. When one of a pair of electrons is promoted to an orbital of higher energy, the two electrons no longer share an orbital, and the promoted electron may, in principle, have the same spin as its former partner or the opposite spin. As we saw in Chapter 5, a molecule in which two unpaired electrons have the same spin is called a *triplet*, while one in which all spins are paired is a *singlet*. Thus, at least in principle, for every excited singlet state there is a corresponding triplet state. In most cases, the triplet state has a lower energy than the corresponding singlet because of Hund's rule. Therefore, a different amount of energy and hence a different wavelength is required to promote an electron from the ground state (which is almost always a singlet) to an excited singlet than to the corresponding triplet state.

It would thus seem that promotion of a given electron in a molecule could result either in a singlet or a triplet excited state depending on the amount of energy added. However, this is often not the case because transitions between energy levels are governed by selection rules, which state that certain transitions are "forbidden." There are several types of "forbidden" transitions, two of which are more important than the others.

1. *Spin-forbidden transitions.*   Transitions in which the spin of an electron changes are not allowed, because a change from one spin to the opposite involves a change in angular momentum and such a change would violate the law of conservation of angular momentum.

Therefore, singlet–triplet and triplet–singlet transitions are forbidden, whereas singlet–singlet and triplet–triplet transitions are allowed.

2. *Symmetry-forbidden transitions.*   Among the transitions in this class are those in which a molecule has a center of symmetry. In such cases, a $g \rightarrow g$ or $u \rightarrow u$ transition (see p. 5) is "forbidden," while a $g \rightarrow u$ or $u \rightarrow g$ transition is allowed.

We have put the word "forbidden" into quotation marks because these transitions are not actually forbidden but only highly improbable. In most cases promotions from a singlet ground state to a triplet excited state are so improbable that they cannot be observed, and it is safe to state that in most molecules only singlet–singlet promotions take place. However, this rule does break down in certain cases, most often when a heavy atom (such as iodine) is present in the molecule, in which cases it can be shown from spectra that singlet–triplet promotions are occurring.[4] Symmetry-forbidden transitions can frequently be observed, though usually with low intensity.

Types of Excitation

When an electron in a molecule is promoted (normally only one electron in any molecule), it usually goes into the lowest available vacant orbital, though promotion to higher orbitals is also possible. For most organic molecules there are consequently four types of electronic excitation:

1. $\sigma \rightarrow \sigma^*$. Alkanes, which have no n or π electrons, can be excited only in this way.[5]

2. $n \rightarrow \sigma^*$. Alcohols, amines,[6] ethers, etc. can also be excited in this manner.

3. $\pi \rightarrow \pi^*$. This pathway is open to alkenes as well as to aldehydes, carboxylic esters, etc.

4. $n \rightarrow \pi^*$. Aldehydes, ketones, carboxylic esters, etc. can undergo this promotion as well as the other three.

The four excitation types above are listed in what is normally the order of decreasing energy. Thus light of the highest energy (in the far uv) is necessary for $\sigma \rightarrow \sigma^*$ excitation, while $n \rightarrow \pi^*$ promotions are caused by ordinary uv light. However, the order may sometimes be altered in some solvents.

In 1,3-butadiene (and other compounds with two conjugated double bonds) there are two π and two π^* orbitals (p. 31). The energy difference between the higher π (χ_2) and the lower π^* (χ_3) orbital is less than the difference between the π and π^* orbitals of ethylene. Therefore 1,3-butadiene requires less energy than ethylene, and thus light of a higher wavelength, to promote an electron. This is a general phenomenon, and it may be stated that, in general, *the more conjugation in a molecule, the more the absorption is displaced toward higher wavelengths* (see Table 7.1).[7] When a chromophore absorbs at a certain wavelength and the substitution of one group for another causes absorption at a longer wavelength, a *bathochromic shift* is said to have occurred. The opposite kind of shift is called *hypsochromic*.

Of the four excitation types listed above, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ are far more important in organic photochemistry than the other two. Compounds containing C=O groups can be excited in both ways, giving rise to at least two peaks in the uv.

[4]For a review of photochemical heavy-atom effects, see Koziar; Cowan *Acc. Chem. Res.* **1978**, *11*, 334-341.

[5]An *n* electron is one in an unshared pair.

[6]For a review of the photochemistry of amines, see Malkin; Kuz'min *Russ. Chem. Rev.* **1985**, *54*, 1041-1057.

[7]Bohlmann; Mannhardt *Chem. Ber.* **1956**, *89*, 1307.

TABLE 7.1   Ultraviolet absorption[7]
of CH_3—$(CH{=}CH)_n$—CH_3 for some
values of n

n	nm
2	227
3	263
6	352
9	413

As we have seen, a chromophore is a group that causes a molecule to absorb light. Examples of chromophores in the visible or uv are $C{=}O$, $N{=}N$,[8] Ph, and NO_2. Some chromophores in the far uv (beyond 200 nm) are $C{=}C$, $C{\equiv}C$, Cl, and OH. An *auxochrome* is a group that displaces (through resonance) and usually intensifies the absorption of a chromophore present in the same molecule. Groups such as Cl, OH, and NH_2 are generally regarded as auxochromes since they shift (usually bathochromically) the uv and visible bands of chromophores such as Ph or $C{=}O$ (see Table 7.2).[9] Since auxochromes are themselves chromophores (to be sure, generally in the far-uv), it is sometimes difficult to decide which group in a molecule is an auxochrome and which a chromophore. For example, in aceto-phenone (PhCOMe) is the chromophore Ph or $C{=}O$? In such cases the distinction becomes practically meaningless.

TABLE 7.2   Some uv peaks of substituted benzenes in water, or water with a
trace of methanol (for solubility)
Note how auxochromes shift and usually intensify the peaks[9]

|	Primary band		Secondary band	
	λ_{max}, nm	ϵ_{max}	λ_{max}, nm	ϵ_{max}
PhH	203.5	7,400	254	204
PhCl	209.5	7,400	263.5	190
PhOH	210.5	6,200	270	1,450
PhOMe	217	6,400	269	1,480
PhCN	224	13,000	271	1,000
PhCOOH	230	11,600	273	970
PhNH$_2$	230	8,600	280	1,430
PhO$^-$	235	9,400	287	2,600
PhAc	245.5	9,800		
PhCHO	249.5	11,400		
PhNO$_2$	268.5	7,800		

[8]For a review of the azo group as a chromophore, see Rau *Angew. Chem. Int. Ed. Engl.* **1973**, 224-235 [*Angew. Chem.* **85**, 248-258].
[9]These values are from Jaffé; Orchin *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962, p. 257.

Nomenclature and Properties of Excited States

An excited state of a molecule can be regarded as a distinct chemical species, different from the ground state of the same molecule and from other excited states. It is obvious that we need some method of naming excited states. Unfortunately, there are several methods in use, depending on whether one is primarily interested in photochemistry, spectroscopy, or molecular-orbital theory.[10] One of the most common methods simply designates the original and newly occupied orbitals, with or without a superscript to indicate singlet or triplet. Thus the singlet state arising from promotion of a π to a π^* orbital in ethylene would be the $^1(\pi,\pi^*)$ state or the π,π^* singlet state. Another very common method can be used even in cases where one is not certain which orbitals are involved. The lowest-energy excited state is called S_1, the next S_2, etc., and triplet states are similarly labeled T_1, T_2, T_3, etc. In this notation the ground state is S_0. Other notational systems exist, but in this book we shall confine ourselves to the two types just mentioned.

The properties of excited states are not easy to measure because of their generally short lifetimes and low concentrations, but enough work has been done for us to know that they often differ from the ground state in geometry, dipole moment and acid or base strength.[11] For example, acetylene, which is linear in the ground state, has a trans geometry

$$\underset{H}{\overset{}{\diagup}}C\equiv C\underset{}{\overset{H}{\diagup}}$$
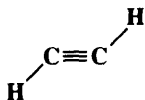
with approximately sp^2 carbons in the $^1(\pi,\pi^*)$ state.[12] Similarly, the $^1(\pi,\pi^*)$ and the $^3(\pi,\pi^*)$ states of ethylene have a perpendicular and not a planar geometry,[13] and the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states of formaldehyde are both pyramidal.[14] Triplet species tend to stabilize themselves by distortion, which relieves interaction between the unpaired electrons. Obviously, if the geometry is different, the dipole moment will probably differ also and the change in geometry and electron distribution often results in a change in acid or base strength.[15] For example, the S_1 state of 2-naphthol is a much stronger acid ($pK = 3.1$) than the ground state (S_0) of the same molecule ($pK = 9.5$).[16]

Photolytic Cleavage

We have said that when a molecule absorbs a quantum of light, it is promoted to an excited state. Actually, that is not the only possible outcome. Because the energy of visible and uv light is of the same order of magnitude as that of covalent bonds (Table 7.3), another

[10]For discussions of excited-state notation and other terms in photochemistry, see Pitts; Wilkinson; Hammond *Adv. Photochem.* **1963**, *1*, 1-21; Porter; Balzani; Moggi *Adv. Photochem.* **1974**, *9*, 147-196. See also Braslavsky; Houk, Ref. 1.

[11]For reviews of the structures of excited states, see Zink; Shin *Adv. Photochem.* **1991**, *16*, 119-214; Innes *Excited States* **1975**, *2*, 1-32; Hirakawa; Masamichi *Vib. Spectra Struct.* **1983**, *12*, 145-204.

[12]Ingold; King *J. Chem. Soc.* **1953**, 2702, 2704, 2708, 2725, 2745. For a review of acetylene photochemistry, see Coyle *Org. Photochem.* **1985**, *7*, 1-73.

[13]Mercr; Mulliken *Chem. Rev.* **1969**, 69, 639-656.

[14]Robinson; Di Giorgio *Can. J. Chem.* **1958**, *36*, 31; Buenker; Peyerimhoff *J. Chem. Phys.* **1970**, *53*, 1368; Garrison; Schaefer; Lester *J. Chem. Phys.* **1974**, *61*, 3039; Streitwieser; Kohler *J. Am. Chem. Soc.* **1988**, *110*, 3769. For reviews of excited states of formaldehyde, see Buck *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 193-198, 225-233; Moule; Walsh *Chem. Rev.* **1975**, *75*, 67-84.

[15]For a review of acid–base properties of excited states, see Ireland; Wyatt *Adv. Phys. Org. Chem.* **1976**, *12*, 131-221.

[16]Weller *Z. Phys. Chem. (Frankfurt am Main)* **1955**, *3*, 238, *Discuss. Faraday Soc.* **1959**, *27*, 28.

TABLE 7.3 Typical energies for some
covalent single bonds (see Table 1.7) and the
corresponding approximate wavelengths

Bond	*E* kcal/mol	kJ/mol	nm
C—H	95	397	300
C—O	88	368	325
C—C	83	347	345
Cl—Cl	58	243	495
O—O	35	146	820

possibility is that the molecule may cleave into two parts, a process known as *photolysis*.
There are three situations that can lead to cleavage:

1. The promotion may bring the molecule to a vibrational level so high that it lies above
the right-hand portion of the E_2 curve (line *A* in Figure 7.2). In such a case the excited
molecule cleaves at its first vibration.

2. Even where the promotion is to a lower vibrational level, one which lies wholly within
the E_2 curve (such as V_1 or V_2), the molecule may still cleave. As Figure 7.2 shows,
equilibrium distances are greater in excited states than in the ground state. The *Franck–
Condon principle* states that promotion of an electron takes place much faster than a single
vibration (the promotion takes about 10^{-15} sec; a vibration about 10^{-12} sec). Therefore,
when an electron is suddenly promoted, even to a low vibrational level, the distance between
the atoms is essentially unchanged and the bond finds itself in a compressed condition like
a pressed-in spring; this condition may be relieved by an outward surge that is sufficient to
break the bond.

3. In some cases the excited state is entirely dissociative (Figure 7.3), i.e., there is no
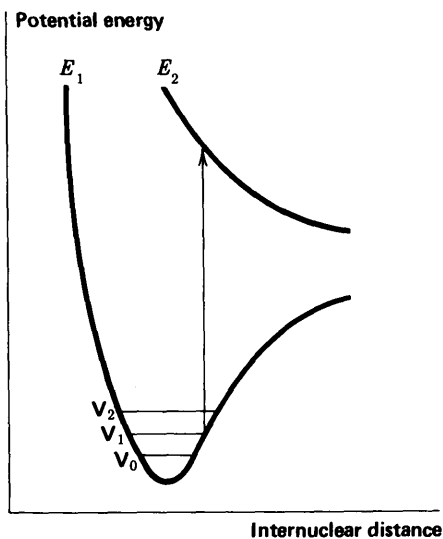

FIGURE 7.3 Promotion to a dissociative state results in bond cleavage.

distance where attraction outweighs repulsion, and the bond must cleave. An example is the hydrogen molecule, where a $\sigma \rightarrow \sigma^*$ promotion always results in cleavage.

A photolytic cleavage can break the molecule into two smaller molecules or into two free radicals (see p. 243). Cleavage into two ions, though known, is much rarer. Once free radicals are produced by a photolysis, they behave like free radicals produced in any other way (Chapter 5) except that they may be in excited states, and this can cause differences in behavior.

The Fate of the Excited Molecule: Physical Processes

When a molecule has been photochemically promoted to an excited state, it does not remain there for long. Most promotions are from the S_0 to the S_1 state. As we have seen, promotions from S_0 to triplet states are "forbidden." Promotions to S_2 and higher singlet states take place, but in liquids and solids these higher states usually drop very rapidly to the S_1 state (about 10^{-13} to 10^{-11} sec). The energy lost when an S_2 or S_3 molecule drops to S_1 is given up in small increments to the environment by collisions with neighboring molecules. Such a process is called an *energy cascade*. In a similar manner, the initial excitation and the decay from higher singlet states initially populate many of the vibrational levels of S_1, but these also cascade, down to the lowest vibrational level of S_1. Therefore, in most cases, the lowest vibrational level of the S_1 state is the only important excited singlet state.[17] This state can undergo various physical and chemical processes. In the following list, we describe the physical pathways open to molecules in the S_1 and excited triplet states. These pathways are also shown in a modified Jablonski diagram (Figure 7.4) and in Table 7.4.

1. A molecule in the S_1 state can cascade down through the vibrational levels of the S_0 state and thus return to the ground state by giving up its energy in small increments to the environment, but this is generally quite slow because the amount of energy is large. The process is called *internal conversion* (IC). Because it is slow, most molecules in the S_1 state adopt other pathways.[18]

2. A molecule in the S_1 state can drop to some low vibrational level of the S_0 state all at once by giving off the energy in the form of light. This process, which generally happens within 10^{-9} sec, is called *fluorescence*. This pathway is not very common either (because it is relatively slow), except for small molecules, e.g., diatomic, and rigid molecules, e.g., aromatic. For most other compounds fluorescence is very weak or undetectable. For compounds that do fluoresce, the fluorescence emission spectra are usually the approximate mirror images of the absorption spectra. This comes about because the fluorescing molecules all drop from the lowest vibrational level of the S_1 state to various vibrational levels of S_0, while excitation is from the lowest vibrational level of S_0 to various levels of S_1 (Figure 7.5). The only peak in common is the one (called the 0–0 peak) that results from transitions between the lowest vibrational levels of the two states. In solution, even the 0–0 peak may be noncoincidental because the two states are solvated differently. Fluorescence nearly always arises from a $S_1 \rightarrow S_0$ transition, though azulene (p. 49) and its simple derivatives are exceptions,[19] emitting fluorescence from $S_2 \rightarrow S_0$ transitions.

[17]For a review of physical and chemical processes undergone by higher states, see Turro; Ramamurthy; Cherry; Farneth *Chem. Rev.* **1978**, *78*, 125-145.
[18]For a monograph on radiationless transitions, see Lin *Radiationless Transitions*; Academic Press: New York, 1980. For reviews, see Kommandeur *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 421-428; Freed *Acc. Chem. Res.* **1978**, *11*, 74-80.
[19]For other exceptions, see Gregory; Hirayama; Lipsky *J. Chem. Phys.* **1973**, *58*, 4697; Sugihara; Wakabayashi; Murata; Jinguji; Nakazawa; Persy; Wirz *J. Am. Chem. Soc.* **1985**, *107*, 5894, and references cited in these papers. See also Ref. 17, pp. 126-129.
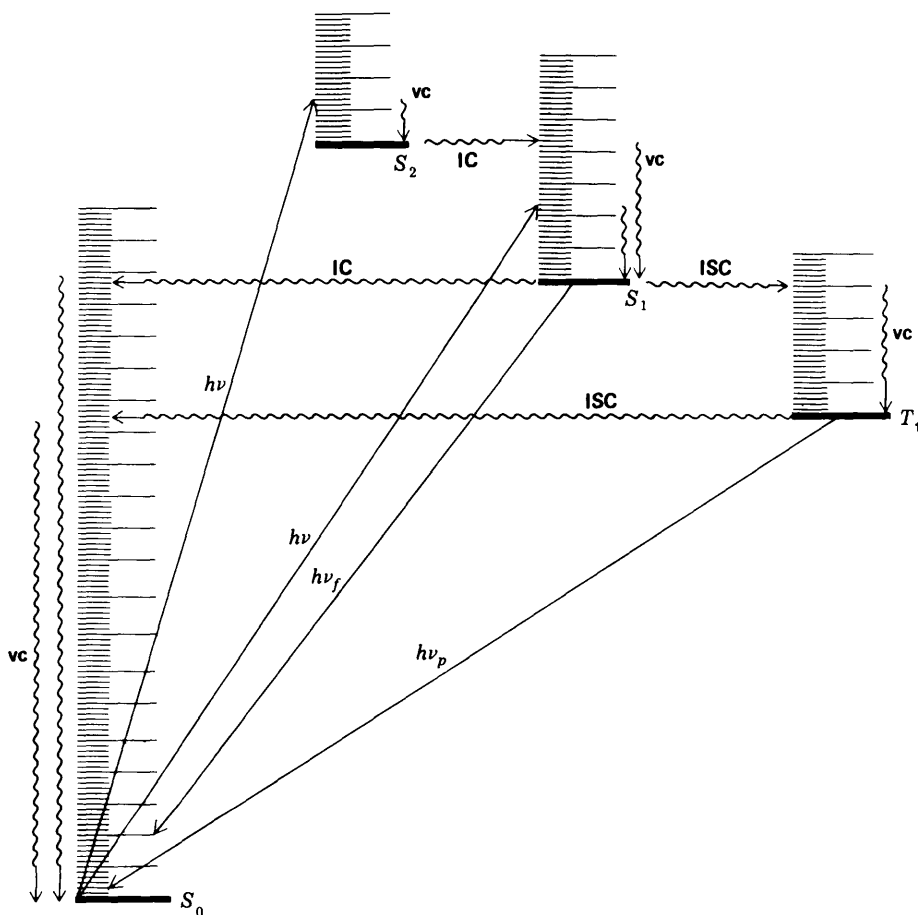
FIGURE 7.4 Modified Jablonski diagram showing transitions between excited states and the ground state. Radiative processes are shown by straight lines, radiationless processes by wavy lines. IC = internal conversion; ISC = intersystem crossing; vc = vibrational cascade; hv_f = fluorescence; hv_p = phosphorescence.

Because of the possibility of fluorescence, any chemical reactions of the S_1 state must take place very fast, or fluorescence will occur before they can happen.

3. Most molecules (though by no means all) in the S_1 state can undergo an *intersystem crossing* (ISC) to the lowest triplet state T_1.[20] An important example is benzophenone, of which approximately 100% of the molecules that are excited to the S_1 state cross over to the T_1.[21] Intersystem crossing from singlet to triplet is of course a "forbidden" pathway, since the angular-momentum problem (p. 233) must be taken care of, but this often takes place by compensations elsewhere in the system. Intersystem crossings take place without loss of energy. Since a singlet state usually has a higher energy than the corresponding

[20]Intersystem crossing from S_1 to T_2 and higher triplet states has also been reported in some aromatic molecules: Li; Lim *Chem. Phys.* **1972**, *57*, 605; Sharf; Silbey *Chem. Phys. Lett.* **1970**, *5*, 314. See also Schlag; Schneider; Fischer *Annu. Rev. Phys. Chem.* **1971**, *22*, 465-526, pp. 490-494. There is evidence that ISC can also occur from the S_2 state of some molecules: Samanta *J. Am. Chem. Soc.* **1991**, *113*, 7427.
[21]Moore; Hammond; Foss *J. Am. Chem. Soc.* **1961**, *83*, 2789.

TABLE 7.4   Physical processes undergone by excited molecules

The superscript v indicates vibrationally excited state: excited states higher than S_1 or T_1 are omitted

|	
$S_0 + h\nu \rightarrow S_1{}^v$	Excitation
$S_1{}^v \rightsquigarrow S_1 +$ heat	Vibrational relaxation
$S_1 \rightarrow S_0 + h\nu$	Fluorescence
$S_1 \rightsquigarrow S_0 +$ heat	Internal conversion
$S_1 \rightsquigarrow T_1{}^v$	Intersystem crossing
$T_1{}^v \rightsquigarrow T_1 +$ heat	Vibrational relaxation
$T_1 \rightarrow S_0 + h\nu$	Phosphorescence
$T_1 \rightsquigarrow S_0 +$ heat	Intersystem crossing
$S_1 + A_{(S_0)} \rightarrow S_0 + A_{(S_1)}$	Singlet–singlet transfer (photosensitization)
$T_1 + A_{(S_0)} \rightarrow S_0 + A_{(T_1)}$	Triplet–triplet transfer (photosensitization)

triplet, this means that energy must be given up. One way for this to happen is for the S_1 molecule to cross to a T_1 state at a high vibrational level and then for the T_1 to cascade down to its lowest vibrational level (see Figure 7.4). This cascade is very rapid (10^{-12} sec). When T_2 or higher states are populated, they too rapidly cascade to the lowest vibrational level of the T_1 state.

4. A molecule in the T_1 state may return to the S_0 state by giving up heat (intersystem crossing) or light (this is called *phosphorescence*).[22] Of course, the angular-momentum difficulty exists here, so that both intersystem crossing and phosphorescence are very slow ($\sim 10^{-3}$ to 10^1 sec). This means that T_1 states generally have much longer lifetimes than S_1 states. When they occur in the same molecule, phosphorescence is found at lower frequencies than fluorescence (because of the higher difference in energy between S_1 and S_0 than between T_1 and S_0) and is longer-lived (because of the longer lifetime of the T_1 state).
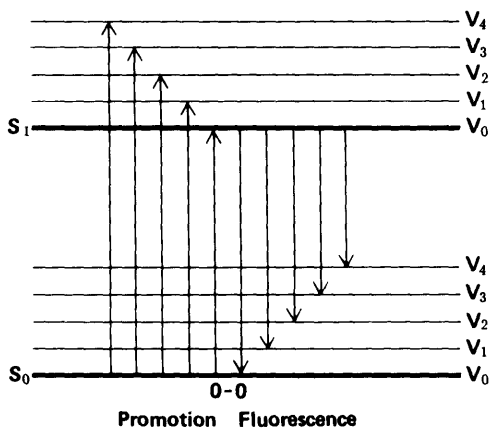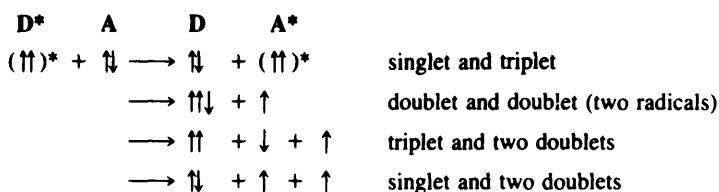

FIGURE 7.5   Promotion and fluorescence between S_1 and S_0 states.

[22]For a review of physical processes of triplet states, see Lower; El-Sayed *Chem. Rev.* **1966**, 66, 199-241. For a review of physical and chemical processes of triplet states see Wagner; Hammond *Adv. Photochem.* **1968**, 5, 21-156.

5. If nothing else happens to it first, a molecule in an excited state (S_1 or T_1) may transfer its excess energy all at once to another molecule in the environment, in a process called *photosensitization*.[23] The excited molecule (which we shall call D for donor) thus drops to S_0 while the other molecule (A for acceptor) becomes excited:

$$D^* + A \longrightarrow A^* + D$$
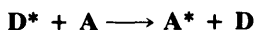
Thus there are *two* ways for a molecule to reach an excited state—by absorption of a quantum of light or by transfer from a previously excited molecule.[24] The donor D is also called a *photosensitizer*. This energy transfer is subject to the *Wigner spin-conservation rule*, which is actually a special case of the law of conservation of momentum we encountered previously. According to the Wigner rule, the total electron spin does not change after the energy transfer. For example, when a triplet species interacts with a singlet these are some allowed possibilities:[25]

$$
\begin{array}{cccc}
\mathbf{D^*} & \mathbf{A} & \mathbf{D} & \mathbf{A^*} \\
(\uparrow\uparrow)^* + \uparrow\downarrow & \longrightarrow & \uparrow\downarrow & + (\uparrow\uparrow)^* & \text{singlet and triplet} \\
& \longrightarrow & \uparrow\uparrow\downarrow & + \uparrow & \text{doublet and doublet (two radicals)} \\
& \longrightarrow & \uparrow\uparrow & + \downarrow + \uparrow & \text{triplet and two doublets} \\
& \longrightarrow & \uparrow\downarrow & + \uparrow + \uparrow & \text{singlet and two doublets}
\end{array}
$$

In all these cases the products have three electrons spinning "up" and the fourth "down" (as do the starting molecules). However, formation of, say, two triplets ($\uparrow\uparrow + \downarrow\downarrow$) or two singlets ($\uparrow\downarrow + \uparrow\downarrow$), whether ground states or excited, would violate the rule.

In the two most important types of photosensitization, both of which are in accord with the Wigner rule, a triplet excited state generates another triplet and a singlet generates a singlet:

$$\mathbf{D}_{T_1} + \mathbf{A}_{S_0} \longrightarrow \mathbf{A}_{T_1} + \mathbf{D}_{S_0} \qquad \text{triplet–triplet transfer}$$

$$\mathbf{D}_{S_1} + \mathbf{A}_{S_0} \longrightarrow \mathbf{A}_{S_1} + \mathbf{D}_{S_0} \qquad \text{singlet–singlet transfer}$$

Singlet–singlet transfer can take place over relatively long distances, e.g., 40 Å, but triplet transfer normally requires a collision between the molecules.[26] Both types of photosensitization can be useful for creating excited states when they are difficult to achieve by direct irradiation. Photosensitization is therefore an important method for carrying out photochemical reactions when a molecule cannot be brought to the desired excited state by direct absorption of light. Triplet–triplet transfer is especially important because triplet states are usually much more difficult to prepare by direct irradiation than singlet states (often impossible) and because triplet states, having longer lifetimes, are much more likely than singlets to transfer energy by photosensitization. Photosensitization can also be accomplished by electron transfer.[27]

[23]For reviews, see Albini *Synthesis* **1981**, 249-264; Turro; Dalton; Weiss *Org. Photochem.* **1969**, *2*, 1-62.

[24]There is also a third way: in certain cases excited states can be produced directly in ordinary reactions. For a review, see White; Miano; Watkins; Breaux *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 229-243 [*Angew. Chem.* **86**, 292-307].

[25]For another table of this kind, see Calvert; Pitts, Ref. 1, p. 89.

[26]Long-range triplet–triplet transfer has been observed in a few cases: Bennett; Schwenker; Kellogg *J. Chem. Phys.* **1964**, *41*, 3040; Ermolaev; Sveshnikova *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1962**, *26*, 29 [*C. A.* **1962**, *57*, 1688], *Opt. Spectrosc. (USSR)* **1964**, *16*, 320.

[27]For a review, see Kavarnos; Turro *Chem. Rev.* **1986**, *86*, 401-449. See also Mariano, Ref. 35.

In choosing a photosensitizer one should avoid a compound that absorbs in the same region as the acceptor because the latter will then compete for the light.[28] For examples of the use of photosensitization to accomplish reactions, see **5-37, 5-49.**

The Fate of the Excited Molecule: Chemical Processes

Although both excited singlet and triplet species can undergo chemical reactions, they are much more common for triplets, simply because these generally have much longer lifetimes. Excited singlet species, in most cases, have a lifetime of less than 10^{-10} sec and undergo one of the physical processes already discussed before they have a chance to react chemically. Therefore, photochemistry is largely the chemistry of triplet states.[29] Table 7.5[30] lists many of the possible chemical pathways that can be taken by an excited molecule.[31] The first four of these are unimolecular reactions; the others are bimolecular. In the case of bimolecular reactions it is rare for two excited molecules to react with each other (because the concentration of excited molecules at any one time is generally low); reactions are between an excited molecule and an unexcited molecule of either the same or another species. The reactions listed in Table 7.5 are primary processes. Secondary reactions often follow, since the primary products are frequently radicals or carbenes; even if they are ordinary molecules, they are often in upper vibrational levels and so have excess energy. In almost all cases the primary products of photochemical reactions are in their ground states, though exceptions are known.[32] Of the reactions listed in Table 7.5, the most common are cleavage into radicals (1), decomposition into molecules (2), and (in the presence of a suitable acceptor molecule) photosensitization (7), which we have already discussed. The following are some specific examples of reaction categories (1) to (6). Other examples are discussed in Part 2 of this book.[33]

TABLE 7.5   Primary photochemical reactions of an excited molecule **A—B—C**[30]
Examples are given in the text; the most common are (1), (2), and, in the presence of a suitable acceptor molecule, (7)

$(A—B—C) \longrightarrow A—B· + C·$	Simple cleavage into radicals	(1)
$(A—B—C) \longrightarrow E + F$	Decomposition into molecules	(2)
$(A—B—C) \longrightarrow A—C—B$	Intramolecular rearrangement	(3)
$(A—B—C) \longrightarrow A—B—C'$	Photoisomerization	(4)
$(A—B—C) \xrightarrow{RH} A—B—C—H + R·$	Hydrogen-atom abstraction	(5)
$(A—B—C) \longrightarrow (ABC)_2$	Photodimerization	(6)
$(A—B—C) \xrightarrow{A} ABC + A^*$	Photosensitization	(7)

[28]For a review of other complications that can take place in photosensitized reactions, see Engel; Monroe *Adv. Photochem.* **1971,** *8,* 245-313.

[29]For a review of the chemical reactions of triplet states, see Wagner; Hammond, Ref. 22. For other reviews of triplet states, see *Top. Curr. Chem.,* **1975,** vols. 54 and 55.
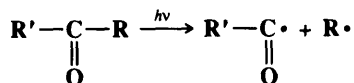
[30]Adapted from Calvert; Pitts, Ref. 1, p. 367.

[31]For a different kind of classification of photochemical reactions, see Dauben; Salem; Turro *Acc. Chem. Res.* **1975,** *8,* 41. For reviews of photochemical reactions where the molecules are geometrically constrained, see Rama-murthy *Tetrahedron* **1986,** *42,* 5753-5839; Ramamurthy; Eaton *Acc. Chem. Res.* **1988,** *21,* 300-306; Turro; Cox; Paczkowski *Top. Curr. Chem.* **1985,** *129,* 57-97.

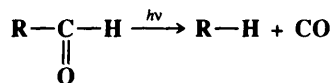[32]Turro; Lechtken; Lyons; Hautala; Carnahan; Katz *J. Am. Chem. Soc.* **1973,** *95,* 2035.

[33]For monographs on the use of photochemistry for synthesis, see Ninomiya; Naito *Photochemical Synthesis;* Academic Press: New York, 1989; Coyle *Photochemistry in Organic Synthesis;* Royal Society of Chemistry: London, 1986; Schönberg *Preparative Organic Photochemistry;* Springer: Berlin, 1968.

Category 1. *Simple cleavage into radicals.*[34]Aldehydes and ketones absorb in the 230 to 330 nm region. This is assumed to result from an $n \rightarrow \pi^*$ singlet–singlet transition. The excited aldehyde or ketone can then cleave.[35]
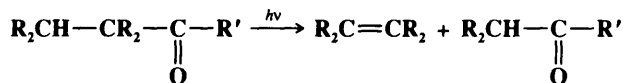
$$R'-\underset{\underset{O}{\|}}{C}-R \xrightarrow{h\nu} R'-\underset{\underset{O}{\|}}{C}\cdot + R\cdot$$

When applied to ketones, this is called *Norrish Type I cleavage* or often just *Type I cleavage*. In a secondary process, the acyl radical R'—CO• can then lose CO to give R'• radicals. Another example of a category 1 process is cleavage of Cl_2 to give two Cl atoms. Other bonds that are easily cleaved by photolysis are the O—O bonds of peroxy compounds and the C—N bonds of aliphatic azo compounds R—N=N—R [36] The latter is an important source of radicals R•, since the other product is the very stable N_2.

Category 2. *Decomposition into molecules.* Aldehydes (though not generally ketones) can also cleave in this manner:

$$R-\underset{\underset{O}{\|}}{C}-H \xrightarrow{h\nu} R-H + CO$$

This is an extrusion reaction (see Chapter 17). In another example of a process in category 2, aldehydes and ketones with a γ hydrogen can cleave in still another way (a β elimination, see Chapter 17):

$$R_2CH-CR_2-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{h\nu} R_2C=CR_2 + R_2CH-\underset{\underset{O}{\|}}{C}-R'$$

This reaction, called *Norrish Type II cleavage*,[37] involves intramolecular abstraction of the γ hydrogen followed by cleavage of the resulting diradical[38] (a secondary reaction) to give an enol that tautomerizes to the aldehyde or ketone product.[39]

[34]For reviews, see Jackson; Okabe *Adv. Photochem.* **1986**, *13*, 1-94; Kresin; Lester *Adv. Photochem.* **1986**, *13*, 95-163.
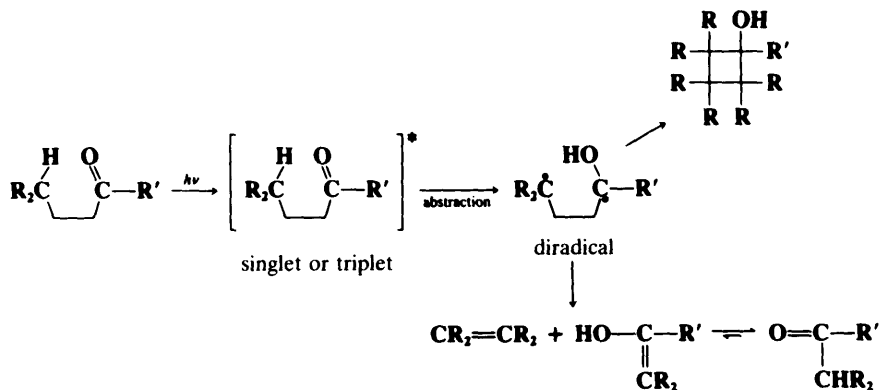
[35]For full discussions of aldehyde and ketone photochemistry, see Formosinho; Arnaut *Adv. Photochem.* **1991**, *16*, 67-117; Newton, in Coyle, Ref. 33, pp. 39-60; Lee; Lewis *Adv. Photochem.* **1980**, *12*, 1-96; Calvert; Pitts, Ref. 1, pp. 368-427; Coyle; Carless *Chem. Soc. Rev.* **1972**, *1*, 465-480; Pitts; Wan, in Patai *The Chemistry of the Carbonyl Group*; Wiley: New York, 1966, pp. 823-916; Dalton; Turro *Annu. Rev. Phys. Chem.* **1970**, *21*, 499-560; Bérces, in Bamford; Tipper *Comprehensive Chemical Kinetics*, vol. 5; Elsevier: New York, 1972, pp. 277-380; Turro; Dalton; Dawes; Farrington; Hautala; Morton; Niemczyk; Shore *Acc. Chem. Res.* **1972**, *5*, 92-101; Wagner *Top. Curr. Chem.* **1976**, *66*, 1-52; Wagner; Hammond, Ref. 22, pp. 87-129. For reviews of the photochemistry of cyclic ketones, see Weiss *Org. Photochem.* **1981**, *5*, 347-420; Chapman; Weiss *Org. Photochem.* **1973**, *3*, 197-288; Morton; Turro *Adv. Photochem.* **1974**, *9*, 197-309. For reviews of the photochemistry of α-diketones, see Rubin *Top. Curr. Chem.* **1985**, *129*, 1-56, **1969**, *13*, 251-306; Monroe *Adv. Photochem.* **1971**, *8*, 77-108. For a review of the photochemistry of protonated unsaturated carbonyl compounds, see Childs *Rev. Chem. Intermed.* **1980**, *3*, 285-314. For reviews of the photochemistry of C=S compounds, see Coyle *Tetrahedron* **1985**, *41*, 5393-5425; Ramamurthy *Org. Photochem.* **1985**, *7*, 231-338. For a review of the chemistry of C=N compounds, see Mariano *Org. Photochem.* **1987**, *9*, 1-128.

[36]For reviews of the photochemistry of azo compounds, see Adam; Oppenländer *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 661-672 [*Angew. Chem. 98*, 659-670]; Dürr; Ruge *Top. Curr. Chem.* **1976**, *66*, 53-87; Drewer, in Patai *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*, pt. 2; Wiley: New York, 1975, pp. 935-1015.
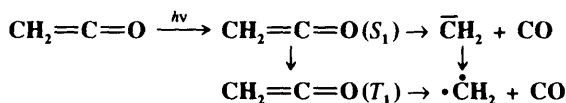
[37]For thorough discussions of the mechanism, see Wagner, in de Mayo *Rearrangements in Ground and Excited States*, vol. 3; Academic Press: New York, 1980, pp. 381-444, *Acc. Chem. Res.* **1971**, *4*, 168-177; Dalton; Turro, Ref. 35, pp. 526-538.

[38]For reviews of the diradicals produced in this reaction, see Wilson *Org. Photochem.* **1985**, *7*, 339-466, pp. 349-373; Scaiano; Lissi; Encina *Rev. Chem. Intermed.* **1978**, *2*, 139-196. For a review of a similar process, where δ hydrogens are abstracted, see Wagner *Acc. Chem. Res.* **1989**, *22*, 83-91.
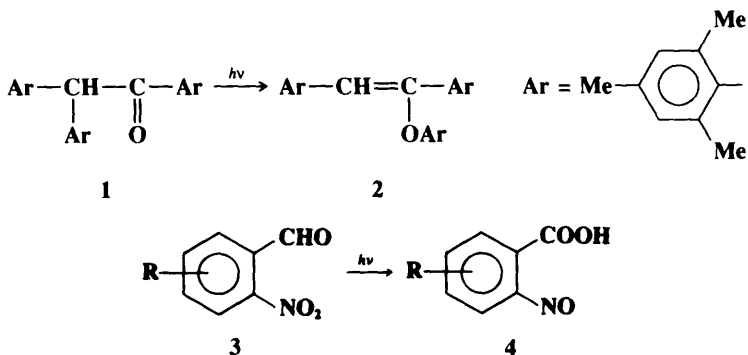
[39]This mechanism was proposed by Yang; Yang *J. Am. Chem. Soc.* **1958**, *80*, 2913. Among the evidence for this mechanism is the fact that the diradical intermediate has been trapped: Wagner; Zepp *J. Am. Chem. Soc.* **1972**, *94*, 287; Wagner; Kelso; Zepp *J. Am. Chem. Soc.* **1972**, *94*, 7480; Adam; Grabowski; Wilson *Chem. Ber.* **1989**, *122*, 561. See also Caldwell; Dhawan; Moore *J. Am. Chem. Soc.* **1985**, *107*, 5163.

$$R_2\overset{\text{H}}{\underset{\smile}{C}}\quad\overset{\text{O}}{\underset{\smile}{C}}{-}R' \xrightarrow{h\nu} \left[R_2\overset{\text{H}}{\underset{\smile}{C}}\quad\overset{\text{O}}{\underset{\smile}{C}}{-}R'\right]^* \xrightarrow{\text{abstraction}} R_2\overset{\text{HO}}{\underset{\smile}{C}}\quad\overset{}{\underset{\smile}{C}}{-}R'$$

singlet or triplet

diradical

$$R\overset{\text{R OH}}{\underset{\text{R}\quad\text{R}}{\overset{|\quad|}{\underset{|\quad|}{+}}}}\overset{}{\underset{}{R'}}$$

$$CR_2{=}CR_2 + HO{-}\underset{CR_2}{\overset{||}{C}}{-}R' \rightleftharpoons O{=}\underset{CHR_2}{\overset{|}{C}}{-}R'$$

Both singlet and triplet n,π^* states undergo the reaction.[40] The intermediate diradical can also cyclize to a cyclobutanol, which is often a side product. Carboxylic esters, anhydrides, and other carbonyl compounds can also give this reaction.[41] The photolysis of ketene to CH_2 (p. 199) is still another example of a reaction in category 2. Both singlet and triplet CH_2 are generated, the latter in two ways:

$$CH_2{=}C{=}O \xrightarrow{h\nu} CH_2{=}C{=}O\,(S_1) \rightarrow \overline{C}H_2 + CO$$
$$CH_2{=}C{=}O\,(T_1) \rightarrow \cdot\overset{\cdot}{C}H_2 + CO$$

Category 3. Intramolecular rearrangement. Two examples are the rearrangement of the trimesityl compound **1** to the enol ether **2**,[42] and irradiation of *o*-nitrobenzaldehydes **3** to give *o*-nitrosobenzoic acids **4**.[43]

$$Ar{-}\underset{Ar}{\overset{|}{C}H}{-}\underset{O}{\overset{||}{C}}{-}Ar \xrightarrow{h\nu} Ar{-}CH{=}\underset{OAr}{\overset{|}{C}}{-}Ar \qquad Ar = Me$$
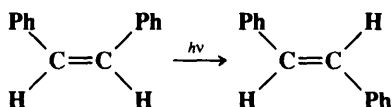
1   **2**

3   **4**

[40]Wagner; Hammond *J. Am. Chem. Soc.* **1965**, *87*, 4009; Dougherty *J. Am. Chem. Soc.* **1965**, *87*, 4011; Ausloos; Rebbert *J. Am. Chem. Soc.* **1964**, *86*, 4512; Casey; Boggs *J. Am. Chem. Soc.* **1972**, *94*, 6457.

[41]For a review of the photochemistry of carboxylic acids and acid derivatives, see Givens; Levi, in Patai *The Chemistry of Acid Derivatives*, pt. 1; Wiley: New York, 1979, pp. 641-753.
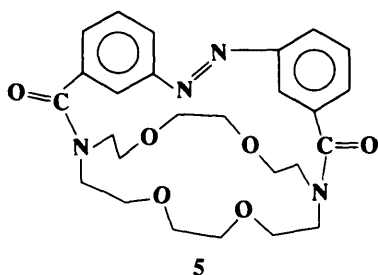
[42]Hart; Lin *Tetrahedron Lett.* **1985**, *26*, 575; Wagner; Zhou *J. Am. Chem. Soc.* **1988**, *110*, 611.

[43]For a review of this and closely related reactions, see Morrison, in Feuer *The Chemistry of the Nitro and Nitroso Groups*, pt. 1; Wiley: New York, 1969, pp. 165-213, 185-191. For a review of photochemical rearrangements of benzene derivatives, see Kaupp *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 243-275 [*Angew. Chem. 92*, 245-276]. See also Yip; Sharma *Res. Chem. Intermed.* **1989**, *11*, 109.
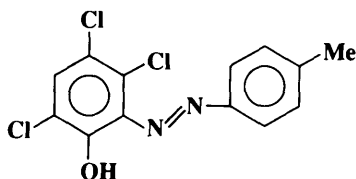
Category 4. *Photoisomerization.* The most common reaction in this category is photo-chemical cis–trans isomerization.[44] For example, *cis*-stilbene can be converted to the trans isomer:

The isomerization takes place because the excited states, both S_1 and T_1, of many olefins have a perpendicular instead of a planar geometry (p. 236), so cis–trans isomerism disappears upon excitation. When the excited molecule drops back to the S_0 state, either isomer can be formed. A useful example is the photochemical conversion of *cis*-cyclooctene to the much less stable trans isomer.[45] Another interesting example of this isomerization involves azo crown ethers. The crown ether **5**, in which the N=N bond is anti, preferentially binds NH_4^+, Li^+, and Na^+, but the syn isomer preferentially binds K^+ and Rb^+ (see p. 83). Thus,

ions can be selectively put in or taken out of solution merely by turning a light source on or off.[46]

In another example, the trans azo compound **6** is converted to its cis isomer when exposed to light. In this case[47] the cis isomer is a stronger acid than the trans. The trans isomer is dissolved in a system containing a base, wherein a liquid membrane separates two sides, one of which is illuminated, the other kept dark. On the illuminated side, the light converts the trans isomer to the cis. The cis isomer, being a stronger acid, donates its proton to the base, converting cis ArOH to cis ArO⁻. This ion migrates to the dark side, where it rapidly reverts to the trans ion, which reacquires a proton. Because each cycle forms one H_3O^+ ion in the illuminated compartment and one OH⁻ ion in the dark compartment, the process

[44]For reviews of cis–trans isomerizations, see Sonnet *Tetrahedron* **1980**, *36*, 557-604; Schulte-Frohlinde; Görner *Pure Appl. Chem.* **1979**, *51*, 279-297; Saltiel; Charlton, in de Mayo, Ref. 37, pp. 25-89; Saltiel; Chang; Megarity; Rousseau; Shannon; Thomas; Uriarte *Pure Appl. Chem.* **1975**, *41*, 559-579; Saltiel; D'Agostino, Megarity, Metts; Neuberger; Wrighton; Zafiriou *Org. Photochem.* **1979**, *3*, 1-113. For reviews of the photochemistry of alkenes, see Leigh; Srinivasan *Acc. Chem. Res.* **1987**, *20*, 107-114; Steinmetz *Org. Photochem.* **1987**, *8*, 67-158; Adam; Oppenländer, Ref. 36; Mattes; Farid *Org. Photochem.* **1984**, *6*, 233-326; Kropp *Org. Photochem.* **1979**, *4*, 1-142; Morrison *Org. Photochem.* **1979**, *4*, 143-190; Kaupp *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 150-168 [*Angew. Chem. 90*, 161-179]. For a review of the photochemistry of allenes and cumulenes, see Johnson *Org. Photochem.* **1985**, *7*, 75-147.
[44a]For a review of the photoisomerization of stilbenes, see Waldeck *Chem. Rev.* **1991**, *91*, 415-436.
[45]Deyrup; Betkouski *J. Org. Chem.* **1972**, *37*, 3561.
[46]Shinkai; Nakaji; Nishida; Ogawa; Manabe *J. Am. Chem. Soc.* **1980**, *102*, 5860. See also Irie; Kato *J. Am. Chem. Soc.* **1985**, *107*, 1024; Shinkai; Miyazaki; Manabe *J. Chem. Soc., Perkin Trans. 1* **1987**, 449; Shinkai; Yoshida; Manabe; Fuchita *J. Chem. Soc., Perkin Trans. 1* **1988**, 1431; Akabori; Kumagai; Habata; Sato *J. Chem. Soc., Perkin Trans. 1* **1989**, 1497; Shinkai; Yoshioka; Nakayama; Manabe *J. Chem. Soc., Perkin Trans. 2* **1990**, 1905. For a review, see Shinkai; Manabe *Top. Curr. Chem.* **1984**, *121*, 67-104.
[47]Haberfield *J. Am. Chem. Soc.* **1987**, *109*, 6177.

In choosing a photosensitizer one should avoid a compound that absorbs in the same region as the acceptor because the latter will then compete for the light.[28] For examples of the use of photosensitization to accomplish reactions, see **5-37, 5-49.**

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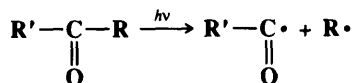[30]Adapted from Calvert; Pitts, Ref. 1, p. 367.
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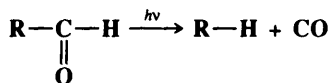[32]Turro; Lechtken; Lyons; Hautala; Carnahan; Katz *J. Am. Chem. Soc.* **1973,** *95,* 2035.
[33]For monographs on the use of photochemistry for synthesis, see Ninomiya; Naito *Photochemical Synthesis;* Academic Press: New York, 1989; Coyle *Photochemistry in Organic Synthesis;* Royal Society of Chemistry: London, 1986; Schönberg *Preparative Organic Photochemistry;* Springer: Berlin, 1968.

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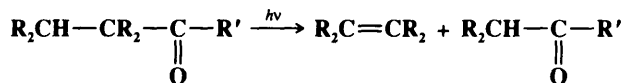
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When applied to ketones, this is called *Norrish Type I cleavage* or often just *Type I cleavage*. In a secondary process, the acyl radical R'—CO• can then lose CO to give R'• radicals. Another example of a category 1 process is cleavage of Cl_2 to give two Cl atoms. Other bonds that are easily cleaved by photolysis are the O—O bonds of peroxy compounds and the C—N bonds of aliphatic azo compounds R—N=N—R [36] The latter is an important source of radicals R•, since the other product is the very stable N_2.

Category 2. *Decomposition into molecules.* Aldehydes (though not generally ketones) can also cleave in this manner:

$$\underset{\substack{\| \\ O}}{R-C-H} \xrightarrow{hv} R-H + CO$$

This is an extrusion reaction (see Chapter 17). In another example of a process in category 2, aldehydes and ketones with a γ hydrogen can cleave in still another way (a β elimination, see Chapter 17):

$$\underset{\substack{\| \\ O}}{R_2CH-CR_2-C-R'} \xrightarrow{hv} R_2C=CR_2 + \underset{\substack{\| \\ O}}{R_2CH-C-R'}$$

This reaction, called *Norrish Type II cleavage*,[37] involves intramolecular abstraction of the γ hydrogen followed by cleavage of the resulting diradical[38] (a secondary reaction) to give an enol that tautomerizes to the aldehyde or ketone product.[39]

[34]For reviews, see Jackson; Okabe *Adv. Photochem.* **1986**, *13*, 1-94; Kresin; Lester *Adv. Photochem.* **1986**, *13*, 95-163.
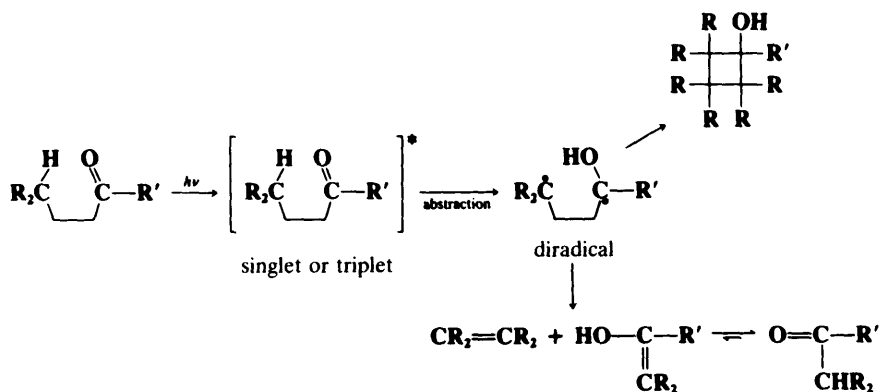
[35]For full discussions of aldehyde and ketone photochemistry, see Formosinho; Arnaut *Adv. Photochem.* **1991**, *16*, 67-117; Newton, in Coyle, Ref. 33, pp. 39-60; Lee; Lewis *Adv. Photochem.* **1980**, *12*, 1-96; Calvert; Pitts, Ref. 1, pp. 368-427; Coyle; Carless *Chem. Soc. Rev.* **1972**, *1*, 465-480; Pitts; Wan, in Patai *The Chemistry of the Carbonyl Group*; Wiley: New York, 1966, pp. 823-916; Dalton; Turro *Annu. Rev. Phys. Chem.* **1970**, *21*, 499-560; Bérces, in Bamford; Tipper *Comprehensive Chemical Kinetics*, vol. 5; Elsevier: New York, 1972, pp. 277-380; Turro; Dalton; Dawes; Farrington; Hautala; Morton; Niemczyk; Shore *Acc. Chem. Res.* **1972**, *5*, 92-101; Wagner *Top. Curr. Chem.* **1976**, *66*, 1-52; Wagner; Hammond, Ref. 22, pp. 87-129. For reviews of the photochemistry of cyclic ketones, see Weiss *Org. Photochem.* **1981**, *5*, 347-420; Chapman; Weiss *Org. Photochem.* **1973**, *3*, 197-288; Morton; Turro *Adv. Photochem.* **1974**, *9*, 197-309. For reviews of the photochemistry of α-diketones, see Rubin *Top. Curr. Chem.* **1985**, *129*, 1-56, **1969**, *13*, 251-306; Monroe *Adv. Photochem.* **1971**, *8*, 77-108. For a review of the photochemistry of protonated unsaturated carbonyl compounds, see Childs *Rev. Chem. Intermed.* **1980**, *3*, 285-314. For reviews of the photochemistry of C=S compounds, see Coyle *Tetrahedron* **1985**, *41*, 5393-5425; Ramamurthy *Org. Photochem.* **1985**, *7*, 231-338. For a review of the chemistry of C=N compounds, see Mariano *Org. Photochem.* **1987**, *9*, 1-128.

[36]For reviews of the photochemistry of azo compounds, see Adam; Oppenländer *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 661-672 [*Angew. Chem. 98*, 659-670]; Dürr; Ruge *Top. Curr. Chem.* **1976**, *66*, 53-87; Drewer, in Patai *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*, pt. 2; Wiley: New York, 1975, pp. 935-1015.
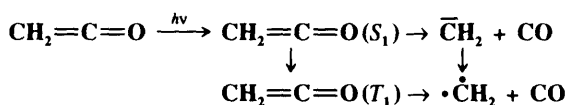
[37]For thorough discussions of the mechanism, see Wagner, in de Mayo *Rearrangements in Ground and Excited States*, vol. 3; Academic Press: New York, 1980, pp. 381-444, *Acc. Chem. Res.* **1971**, *4*, 168-177; Dalton; Turro, Ref. 35, pp. 526-538.

[38]For reviews of the diradicals produced in this reaction, see Wilson *Org. Photochem.* **1985**, *7*, 339-466, pp. 349-373; Scaiano; Lissi; Encina *Rev. Chem. Intermed.* **1978**, *2*, 139-196. For a review of a similar process, where δ hydrogens are abstracted, see Wagner *Acc. Chem. Res.* **1989**, *22*, 83-91.
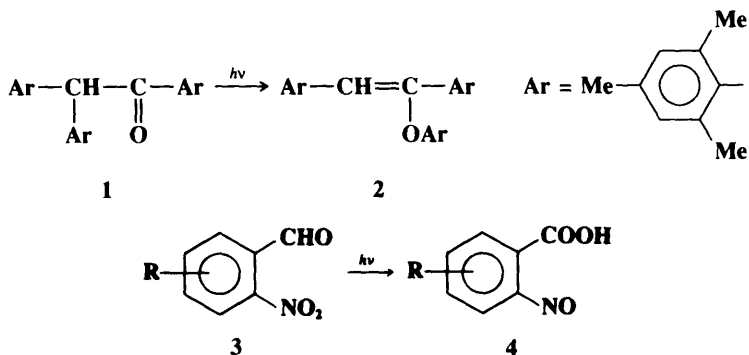
[39]This mechanism was proposed by Yang; Yang *J. Am. Chem. Soc.* **1958**, *80*, 2913. Among the evidence for this mechanism is the fact that the diradical intermediate has been trapped; Wagner; Zepp *J. Am. Chem. Soc.* **1972**, *94*, 287; Wagner; Kelso; Zepp *J. Am. Chem. Soc.* **1972**, *94*, 7480; Adam; Grabowski; Wilson *Chem. Ber.* **1989**, *122*, 561. See also Caldwell; Dhawan; Moore *J. Am. Chem. Soc.* **1985**, *107*, 5163.

Both singlet and triplet n,π^* states undergo the reaction.[40] The intermediate diradical can also cyclize to a cyclobutanol, which is often a side product. Carboxylic esters, anhydrides, and other carbonyl compounds can also give this reaction.[41] The photolysis of ketene to CH_2 (p. 199) is still another example of a reaction in category 2. Both singlet and triplet CH_2 are generated, the latter in two ways:

$$CH_2{=}C{=}O \xrightarrow{h\nu} CH_2{=}C{=}O(S_1) \to \bar{C}H_2 + CO$$

$$CH_2{=}C{=}O(T_1) \to \cdot\dot{C}H_2 + CO$$

Category 3. Intramolecular rearrangement. Two examples are the rearrangement of the trimesityl compound **1** to the enol ether **2**,[42] and irradiation of *o*-nitrobenzaldehydes **3** to give *o*-nitrosobenzoic acids **4**.[43]
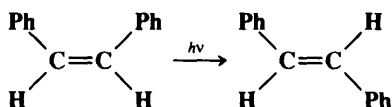

[40]Wagner; Hammond *J. Am. Chem. Soc.* **1965**, *87*, 4009; Dougherty *J. Am. Chem. Soc.* **1965**, *87*, 4011; Ausloos; Rebbert *J. Am. Chem. Soc.* **1964**, *86*, 4512; Casey; Boggs *J. Am. Chem. Soc.* **1972**, *94*, 6457.

[41]For a review of the photochemistry of carboxylic acids and acid derivatives, see Givens; Levi, in Patai *The Chemistry of Acid Derivatives*, pt. 1; Wiley: New York, 1979, pp. 641-753.
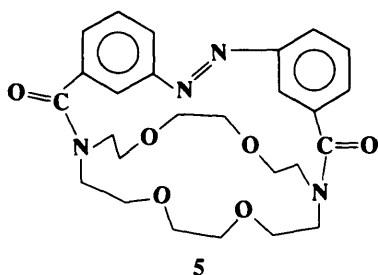
[42]Hart; Lin *Tetrahedron Lett.* **1985**, *26*, 575; Wagner; Zhou *J. Am. Chem. Soc.* **1988**, *110*, 611.

[43]For a review of this and closely related reactions, see Morrison, in Feuer *The Chemistry of the Nitro and Nitroso Groups*, pt. 1; Wiley: New York, 1969, pp. 165-213, 185-191. For a review of photochemical rearrangements of benzene derivatives, see Kaupp *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 243-275 [*Angew. Chem. 92*, 245-276]. See also Yip; Sharma *Res. Chem. Intermed.* **1989**, *11*, 109.
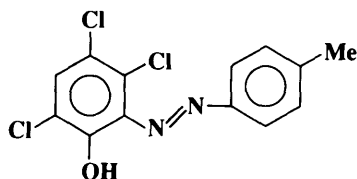
Category 4. *Photoisomerization.* The most common reaction in this category is photo-chemical cis–trans isomerization.[44] For example, *cis*-stilbene can be converted to the trans isomer:

The isomerization takes place because the excited states, both S_1 and T_1, of many olefins have a perpendicular instead of a planar geometry (p. 236), so cis–trans isomerism disappears upon excitation. When the excited molecule drops back to the S_0 state, either isomer can be formed. A useful example is the photochemical conversion of *cis*-cyclooctene to the much less stable trans isomer.[45] Another interesting example of this isomerization involves azo crown ethers. The crown ether **5**, in which the N=N bond is anti, preferentially binds NH_4^+, Li^+, and Na^+, but the syn isomer preferentially binds K^+ and Rb^+ (see p. 83). Thus,

5　　　　　　　　　　　　　　　　　**6**

ions can be selectively put in or taken out of solution merely by turning a light source on or off.[46]

In another example, the trans azo compound **6** is converted to its cis isomer when exposed to light. In this case[47] the cis isomer is a stronger acid than the trans. The trans isomer is dissolved in a system containing a base, wherein a liquid membrane separates two sides, one of which is illuminated, the other kept dark. On the illuminated side, the light converts the trans isomer to the cis. The cis isomer, being a stronger acid, donates its proton to the base, converting cis ArOH to cis ArO^-. This ion migrates to the dark side, where it rapidly reverts to the trans ion, which reacquires a proton. Because each cycle forms one H_3O^+ ion in the illuminated compartment and one OH^- ion in the dark compartment, the process

[44]For reviews of cis–trans isomerizations, see Sonnet *Tetrahedron* **1980**, *36*, 557-604; Schulte-Frohlinde; Görner *Pure Appl. Chem.* **1979**, *51*, 279-297; Saltiel; Charlton, in de Mayo, Ref. 37, pp. 25-89; Saltiel; Chang; Megarity; Rousseau; Shannon; Thomas; Uriarte *Pure Appl. Chem.* **1975**, *41*, 559-579; Saltiel; D'Agostino, Megarity, Metts; Neuberger; Wrighton; Zafiriou *Org. Photochem.* **1979**, *3*, 1-113. For reviews of the photochemistry of alkenes, see Leigh; Srinivasan *Acc. Chem. Res.* **1987**, *20*, 107-114; Steinmetz *Org. Photochem.* **1987**, *8*, 67-158; Adam; Oppenländer, Ref. 36; Mattes; Farid *Org. Photochem.* **1984**, *6*, 233-326; Kropp *Org. Photochem.* **1979**, *4*, 1-142; Morrison *Org. Photochem.* **1979**, *4*, 143-190; Kaupp *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 150-168 [*Angew. Chem. 90*, 161-179]. For a review of the photochemistry of allenes and cumulenes, see Johnson *Org. Photochem.* **1985**, *7*, 75-147.

[44a]For a review of the photoisomerization of stilbenes, see Waldeck *Chem. Rev.* **1991**, *91*, 415-436.

[45]Deyrup; Betkouski *J. Org. Chem.* **1972**, *37*, 3561.

[46]Shinkai; Nakaji; Nishida; Ogawa; Manabe *J. Am. Chem. Soc.* **1980**, *102*, 5860. See also Irie; Kato *J. Am. Chem. Soc.* **1985**, *107*, 1024; Shinkai; Miyazaki; Manabe *J. Chem. Soc., Perkin Trans. 1* **1987**, 449; Shinkai; Yoshida; Manabe; Fuchita *J. Chem. Soc., Perkin Trans. 1* **1988**, 1431; Akabori; Kumagai; Habata; Sato *J. Chem. Soc., Perkin Trans. 1* **1989**, 1497; Shinkai; Yoshioka; Nakayama; Manabe *J. Chem. Soc., Perkin Trans. 2* **1990**, 1905. For a review, see Shinkai; Manabe *Top. Curr. Chem.* **1984**, *121*, 67-104.
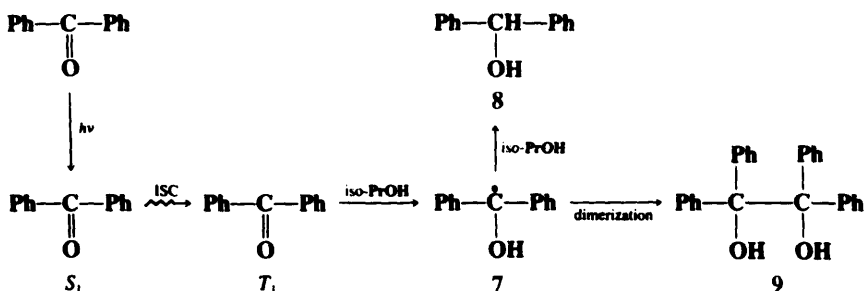
[47]Haberfield *J. Am. Chem. Soc.* **1987**, *109*, 6177.

reverses the normal reaction whereby these ions neutralize each other.[48] Thus the energy of light is used to do chemical work.[49] Two other examples of category 4 reactions are[44]


Cholesta-3, 5-diene
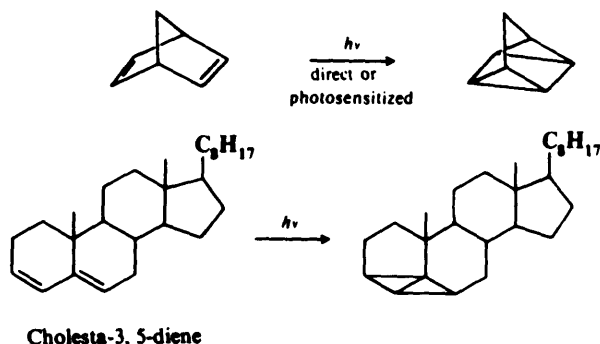
These examples illustrate that the use of photochemical reactions can make it very easy to obtain compounds that would be difficult to get in other ways. Reactions similar to these are discussed at **5-49**.

Category 5. Hydrogen atom abstraction. When benzophenone is irradiated in isopropyl alcohol, the initially formed S_1 state crosses to the T_1 state, which abstracts hydrogen from the solvent to give the radical **7. 7** then abstracts another hydrogen to give benzhydrol (**8**) or dimerizes to benzpinacol (**9**):

An example of intramolecular abstraction has already been given (p. 243).

Category 6. Photodimerization. An example is dimerization of cyclopentenone:[51]
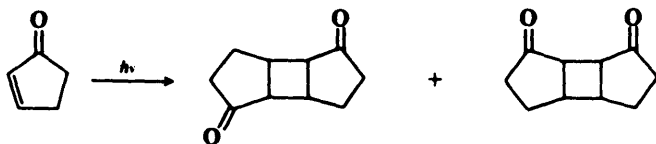
See **5-49** for a discussion of this and similar reactions.

[48]Haberfield *J. Am. Chem. Soc.* **1987**, *109*, 6178.

[49]For a review of instances where macrocycles change in response to changes in light, pH, temperature, etc., see Beer *Chem. Soc. Rev.* **1989**, *18*, 409-450. For an example not involving a macrocycle, see Feringa; Jager; de Lange; Meijer *J. Am. Chem. Soc.* **1991**, *113*, 5468.

[50]Hammond; Turro; Fischer *J. Am. Chem. Soc.* **1961**, *83*, 4674; Dauben; Cargill *Tetrahedron* **1961**, *15*, 197; Dauben; Wipke *Pure Appl. Chem.* **1964**, *9*, 539.

[51]Eaton *J. Am. Chem. Soc.* **1962**, *84*, 2344, 2454, *Acc. Chem. Res.* **1968**, *1*, 50. For a review of the photochemistry of α,β-unsaturated ketones, see Schuster, in Patai; Rappoport *The Chemistry of Enones*, pt. 2; Wiley: New York, 1989, pp. 623-756.

The Determination of Photochemical Mechanisms[52]

The methods used for the determination of photochemical mechanisms are largely the same as those used for organic mechanisms in general (Chapter 6): product identification, isotopic tracing, the detection and trapping of intermediates, and kinetics. There are, however, a few new factors: (1) there are generally many products in a photochemical reaction, as many as 10 or 15; (2) in measuring kinetics, there are more variables, since we can study the effect on the rate of the intensity or the wavelength of light; (3) in the detection of intermediates by spectra we can use the technique of *flash photolysis*, which can detect extremely short-lived intermediates.

In addition to these methods, there are two additional techniques.

1. The use of emission (fluorescence and phosphorescence) as well as absorption spectroscopy. From these spectra the presence of as well as the energy and lifetime of singlet and triplet excited states can often be calculated.

2. The study of quantum yields. The *quantum yield* is the fraction of absorbed light that goes to produce a particular result. There are several types. A *primary quantum yield* for a particular process is the fraction of molecules absorbing light that undergo that particular process. Thus, if 10% of all the molecules that are excited to the S_1 state cross over to the T_1 state, the primary quantum yield for that process is 0.10. However, primary quantum yields are often difficult to measure. A *product quantum yield* (usually designated Φ) for a product P that is formed from a photoreaction of an initially excited molecule A can be expressed as

$$\Phi = \frac{\text{number of molecules of } \mathbf{P} \text{ formed}}{\text{number of quanta absorbed by } \mathbf{A}}$$

Product quantum yields are much easier to measure. The number of quanta absorbed can be determined by an instrument called an *actinometer*, which is actually a standard photochemical system whose quantum yield is known. An example of the information that can be learned from quantum yields is the following. If the quantum yield of a product is finite and invariant with changes in experimental conditions, it is likely that the product is formed in a primary rate-determining process. Another example: in some reactions, the product quantum yields are found to be well over 1 (perhaps as high as 1000). Such a finding indicates a chain reaction (see p. 678 for a discussion of chain reactions).

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[52]For a review, see Calvert; Pitts, Ref. 1, pp. 580-670.