12

Photochemistry

Introduction

The photochemical reactions of organic compounds attracted great interest beginning in the 1960s. As a result, many useful and fascinating reactions were uncovered and photochemistry is now an important synthetic tool in organic chemistry. A firm basis for mechanistic descriptions of many photochemical reactions has been developed. Some of the more general types of photochemical reactions are discussed in the present chapter. In Section 12.2, the photochemistry of alkenes, dienes, and polyenes is considered, including the relationship of photochemical reactions to orbital symmetry principles. Important reaction types include *cis-trans* isomerization, electrocyclic reactions, photocycloadditions, and rearrangements. In subsequent sections, characteristic photochemical reactions of carbonyl compounds and aromatic rings are introduced.

12.1. General Principles

We begin by summarizing the basic elements of photochemical reactions. The first condition that must be met is that the reactant absorb light emitted by the source. For light to be absorbed, the compound must have an energy level that corresponds to the energy of the radiation. Organic photochemical reactions usually involve excited electronic states. Depending on functionality, organic compounds can have electronic absorption bands in the ultraviolet and/or the visible region of the spectrum. Most of the photochemistry we discuss involves unsaturated groups, mainly alkenes, carbonyl compounds, and arenes, in which an electron is promoted to an antibonding π^* orbital. These excited states involve promotion of electrons in valence shell orbitals. The excited states can be singlets or triplets. In a *singlet excited state* the excited electrons retain opposite spins, whereas in *triplet excited states* they have parallel spins. The photoexcitation of organic molecules can also involve *Rydberg states*, which involve excitation of an electron from the valence level to a higher shell, typically $3s$ and $3p$ for organic molecules. The Rydberg states are similar to a radical cation in the valence shell but with an additional diffuse distribution of the excited electron. In many molecules, there is mixing of character of valence shell excited states with Rydberg states, and the latter can decay to valence shell excited states.

Table 12.1 lists the general regions of absorption for the classes of organic molecules that are discussed in this chapter. A number of light sources can be used, the most common for preparative scale work being mercury vapor lamps, which emit mainly at 214, 254, 313, and 366 nm. The composition of the radiation reaching the sample can be controlled by filters. For example, if the system is constructed so that light passes through standard glass, only wavelengths longer than 300–310 nm reach the sample because the glass absorbs below this wavelength. Pure fused quartz, which transmits down to 200 nm, must be used if the 254-nm radiation is desired. Other glasses have cutoff points between those of quartz and standard glass. Filter solutions that absorb in specific wavelength ranges can also be used to control the energy of the light reaching the sample.[1] Mechanistic studies are frequently done using lasers, which permits intense radiation at specific wavelengths and for brief periods of time.

The energy supplied by a particular wavelength of light can be calculated from the fundamental equation

$$E = h\nu \qquad (12.1)$$

The energy in kcal/mole is

$$E = 2.86 \times 10^4/\lambda$$

where λ is wavelength in nm. Thus, light of $\lambda = 254$ nm equals 112.6 kcal/mol, an energy sufficient to rupture most single bonds. The energy is also often expressed in terms of the frequency of the light:

$$E(\text{cm}^{-1}) = 349.8\,\text{cm}^{-1}/\text{kcal/mol}$$

Energy is also some times expressed in eV, where $1\,\text{eV} = 23.14\,\text{kcal/mol}$.

When a quantum of light is absorbed, the electronic configuration changes to correspond to an excited state. Three general points about this process should be emphasized:

Table 12.1. Approximate Wavelength Ranges for Lowest-Energy Absorption Band of Representative Organic Compounds

Reactant	Absorption maxima (nm)
Monoalkenes	190–200
Acyclic dienes	220–250
Cyclic dienes	250–270
Aryl-substituted alkenes	270–300
Saturated ketones	270–280
α,β-Unsaturated ketones	310–330
Benzene derivatives	250–280
Aromatic ketones and aldehydes	280–300

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[1] Detailed information on the emission characteristics of various sources and the transmission properties of glasses and filter solutions can be found in A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley-Interscience, New York, 1972, pp. 348–368 and in S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry*, 2nd Edition, Marcel Dekker, New York, 1993.

1. The excitation promotes an electron from a filled orbital to an empty one. In many cases, the promotion is from the HOMO to the LUMO, which is usually an antibonding orbital. Higher excited states, can also be populated. In any case, photoexcitation involves *unpairing of electrons* but at the instant of excitation they still have opposite spins.
2. At the instant of excitation, only electrons are reorganized. The nuclei retain their ground state geometry. The excitation is called a *vertical transition*, and the statement of this condition is referred to as the *Frank-Condon principle*. A consequence is that the initial excited state is in a nonminimal energy geometry. The excited state then attains its minimum energy structure extremely rapidly, with release of excess energy.
3. The electrons do not undergo spin inversion at the instant of excitation. Inversion is forbidden by quantum mechanical selection rules, which require that there be conservation of spin during the excitation process. Although a subsequent spin state change may occur, it is a separate step from excitation. In the initial excited state the unpaired electrons have opposite spins in a *singlet state*.

Thus, in the very short time (10^{-15} s) required for excitation, the molecule does not undergo changes in nuclear position or in the spin state of the promoted electron. After the excitation, however, these changes can occur very rapidly. There may be a minimum, usually shallow, close to the initial Franck-Condon geometry. Such states are attained very rapidly (<50 ps). The ultimate minimum energy geometry associated with the excited state is rapidly achieved by vibrational processes that transfer thermal energy to the solvent. This process, called *internal conversion*, results in formation of the minimum energy structure of the singlet excited state. The rate of transformation between different excited states depends on their similarity in structure and energy.[2] The more similar in structure and energy, the faster the transition. Often, the excited state attains its minimum energy without passing any barrier. Sometimes, chemical reactions of the excited molecule are fast relative to this vibrational relaxation, but this is unusual in solution. When reaction proceeds more rapidly than vibrational relaxation, the reaction is said to involve a *hot excited state*, that is, one with excess vibrational energy. The excited state can also undergo *intersystem crossing*, the inversion of spin of an electron in a half-filled orbital to give a *triplet state*, in which both unpaired electrons have the same spin. The triplet state also adopts a new minimum energy molecular geometry. Photochemical transitions can also be described as *diabatic* and *adiabatic*. A diabatic process involves a shift from one energy surface to another without a geometric change. An adiabatic process occurs on one energy surface by geometric reorganization.

Intersystem crossing must also occur when triplet excited states return to singlet ground states. A prominent factor in the rate of such processes is *spin-orbit coupling*, which depends on the structure of the triplet state and strongly affects the rate of intersystem crossing. The extent of spin-orbit coupling and the rate of intersystem crossing decrease with increasing separation of the orbitals containing the unpaired electrons.[3] There is also a preference for perpendicular orientation of the orbitals.

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[2] L. Landau, *Phys.Z. Sowjet.*, **2**, 46 (1932); L. Zener, *Proc. Royal Soc. London*, **A137**, 696 (1932).

[3] L. Salem and C. Rowland, *Angew. Chem. Int. Ed. Engl.*, **11**, 92 (1972); L. Carlacci, C. Doubleday, Jr., T. R. Furlani, H. F. King, and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **109**, 5323 (1987); C. Doubleday, Jr., N. J. Turro, and J.-F. Wang, *Acc. Chem. Res.*, **22**, 199 (1989); M. Klessinger, *Theor. Org. Chem.*, **5**, 581 (1998).

Spin-orbit coupling also increases with the degree of ionic character of the singlet state. The presence of a heavy element, e.g., bromine, also promotes intersystem crossing.

The overall situation can be represented for a hypothetical molecule using a potential energy diagram. The designations *S* and *T* are used for singlet and triplet states, respectively. The excitation is a vertical transition; that is, it involves no distortion of the molecular geometry. Horizontal displacement on the diagram corresponds to motion of the atoms relative to one another. Since the potential energy surfaces of the excited states are displaced from that of the ground state, the species formed by excitation is excited both electronically and vibrationally. The energy wells corresponding to the triplet states also correspond to a different minimum energy molecular geometry. *Nonradiative decay*, also called *internal conversion*, results in dissipation of the vibrational energy as the molecule moves to the bottom of any particular energy well. One of the central issues in the description of any photochemical reaction is the question of whether a singlet or triplet excited state is involved, and this depends on the rate of intersystem crossing in comparison with the rate of chemical reaction of the singlet excited state. If intersystem crossing is fast relative to reaction, reaction will occur through the triplet excited state. If reaction is faster than intersystem crossing, the reaction will occur from the singlet state. The processes that can occur after photochemical excitation are summarized in Figure 12.1.

Photosensitization is an important alternative to direct excitation of molecules and this method usually results in reaction occurring via a triplet excited state. If a reaction is to be carried out by photosensitization, a substance known as the *sensitizer* is included in the system. Each sensitizer has a characteristic energy, E_T, that it can transfer to a reactant. The sensitizer is chosen to meet the following criteria: (1) It must be excited by the irradiation to be used. (2) It must be present in sufficient concentration and absorb more strongly than the other reactants under the conditions

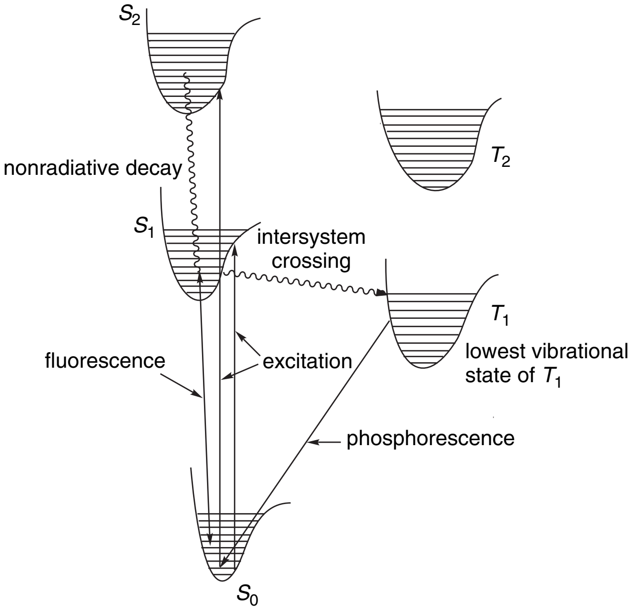

Fig. 12.1. Energy level diagram and summary of photochemical processes.

of the experiment so that it is the major light absorber. (3) Its intersystem crossing rate must be faster than energy transfer to the reactant or solvent from the singlet excited state. (4) The energy of its triplet state must be greater than that of the reactant; if this condition is not met, the energy transfer becomes endothermic and cannot compete with other transformations. (5) The triplet excited sensitizer must be able to transfer energy to the desired reactant.

The transfer of energy proceeds with net conservation of spin. In the usual case, the reactant molecule is a ground state singlet, and its reaction with the triplet excited state of the sensitizer produces a triplet state of the reactant. The mechanism for triplet photosensitization is as follows:

$\text{Sens} \rightarrow {}^1\text{Sens}^*$	Sensitizer singlet formed
${}^1\text{Sens}^* \rightarrow {}^3\text{Sens}^*$	Intersystem crossing of sensitizer
${}^3\text{Sens}^* + \text{Reactant} \rightarrow \text{Sens} + {}^3\text{Reactant}^*$	Energy transfer to reactant molecule

Sensitization can occur from singlet excited states, but for most cases we discuss, triplet sensitization operates.

When an excited state of the reactant has been formed, either by direct or sensitized energy transfer, the stage is set for a photochemical reaction. There are, however, competitive processes that can occur and result in the return of unreacted starting material. The excited state can decay to the ground state by emission of light, a *radiative transition*. The rate of emission can be very fast ($k = 10^5 - 10^9\,\text{s}^{-1}$) for transitions between electronic states of the same multiplicity, but is somewhat slower ($k = 10^3 - 10^5\,\text{s}^{-1}$) between states of different multiplicities. The two processes are known as *fluorescence* and *phosphorescence*, respectively. When energy has been emitted as light, the reactant is no longer excited, of course, and a photochemical reaction does not occur. Excited states can also be *quenched*. Quenching is the same physical process as sensitization, but the term “quenched” is used when a photoexcited state of the reactant is deactivated by transferring its energy to another molecule in solution. This substance is called a *quencher*. Finally, *nonradiative decay* can occur. In this process, the energy of the excited state is transferred to the surrounding molecules as vibrational (thermal) energy without light emission.

Owing to the existence of these competing processes, not every molecule that is excited undergoes a photochemical reaction. The fraction of molecules that react relative to those that are excited is called the *quantum yield*, Φ, which is a measure of the efficiency of the absorption of light in producing reaction product. A quantum yield of 1 means that each molecule excited (which equals the number of quanta of light absorbed) goes to product. If the quantum yield is 0.01, then only 1 out of 100 of the molecules that are excited undergoes photochemical reaction. The quantum yield can vary widely, depending on the structure of the reactants and the reaction conditions. The quantum yield can be greater than 1 in a chain reaction, in which a single photoexcitation initiates a series of repeating reactions leading to many molecules of product per initiation step.

As photochemical processes are very fast, special techniques are required to obtain rate measurements. One method is flash photolysis, in which the excitation is effected by a short pulse of light in an apparatus designed to monitor very fast spectroscopic changes. The rate characteristics of the reactions following radiation can be determined from these spectroscopic changes. Various other techniques have been developed to follow the exceedingly fast changes that occur immediately after excitation. Some of them can detect changes that occur over 10–100 fs (10^{-15} s).

A useful technique for indirectly determining the rates of certain reactions involves measuring the quantum yield as a function of quencher concentration. A plot of the inverse of the quantum yield versus quencher concentration is then made (*Stern-Volmer plot*). As the quantum yield indicates the fraction of excited molecules that go on to product, it is a function of the rates of the processes that result in other fates for the excited molecule. These processes are described by the rate constants k_q (quenching) and k_n (other nonproductive decay to ground state):

$$\Phi = \frac{k_r}{k_r + k_q[Q] + k_n} \tag{12.2}$$

A plot of $1/\Phi$ versus $[Q]$ then gives a line with the slope k_q/k_r. It is often possible to assume that quenching is diffusion controlled, permitting assignment of a value to k_q. The rate of photoreaction, k_r, for the excited intermediate can then be calculated.

In the sections that follow, the discussion centers on the reactions of excited states, rather than on the other routes available for dissipation of excitation energy. The chemical reactions of photoexcited molecules are of interest for several reasons:

1. Excited states have excess energy and can therefore undergo reactions that would be highly endothermic if initiated from the ground state. For example, from the relationship $E = h\nu$ we can calculate that excitation by 350-nm light corresponds to 82 kcal/mol in energy transfer.
2. The population of one or more antibonding orbitals in the excited state allows the occurrence of chemical transformations that are electronically forbidden to ground state species.
3. Both singlet and triplet excited states have unpaired electrons, whereas closed-shell species are involved in most thermal processes (free radical reaction being an exception). This permits the formation of intermediates that are unavailable under thermal conditions.

Another important distinction between ground state and excited state reactions involves the relative rates of conformational interconversion. In thermal reactions, as stated by the Curtin Hammett principle (p. 296) conformers are normally in equilibrium, but the position of the equilibrium does not determine the reaction pathway. Many steps in photochemical reactions occur sufficiently rapidly that various conformers are not in equilibrium. This is the principle of *nonequilibrium of excited rotamers* (NEER).[4] Thus in analyses of photochemical reactions, it is often necessary to consider conformational issues in order to interpret the reaction. *Reaction dynamics* refers to the conformational and other geometrical aspects of the reactions.

As we describe photochemical reactions, we note repeatedly that photochemical reactions involve unpairing and re-pairing of electrons. Frequently, atom and group migrations occur prior to the final electron re-pairing. Although discerning these unpairing/re-pairing schemes is a first step in understanding photochemical mechanisms, we also want to consider the structure of excited states and reaction intermediates. As is the case for transition structures in thermal reactions, computational approaches have provided a new level of insight.

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[4] H. J. C. Jacobs and E. Havinga, *Adv. Photochem.*, **11**, 305 (1979).

The mechanisms of photochemical reactions can be presented at several levels of detail. The most basic level is to recognize the unpairing/re-pairing sequence that is associated with bond breaking and bond forming. These processes can be further described by depicting the orbitals that are involved. Just as in thermal reactions, orbital symmetry and/or stereoelectronic effects can be recognized in this way. Photochemical reactions can also be described by potential energy diagrams, similar to those we have used for thermal reactions. For a photochemical reaction, the diagram represents transitions between the excited structures and aims to trace the path from excitation to photoproduct. As for thermal reactions, the path depicted is the minimum energy path across a potential energy surface. Photochemical reactions, however, can involve several excited states, each with its own potential energy surface, so there are several energy plots representing these surfaces. Two-dimensional representations can depict progress in one structural change, such as a twist about a bond or a bond breaking. Alternatively, the reaction progress may be viewed as a composite of all the structural changes that take place among reactant, excited state, and product. Figure 12.2 is such a diagram, depicting transitions between excited states and, eventually, the ground state surface of the products. The diagram shows excitation to both S_1 and S_2, the first and second singlet excited states. Molecules drop to the S_1 surface at point C. Singlet excited molecules return to the ground state at point A and may return to reactant or proceed to product P_1. Intersystem crossing occurs at points B or D and provides the triplet excited state, which gives product P_2.

Reactions in which structural change is simultaneously occurring in more than one structural parameter can be depicted as interaction between surfaces with coordinates described by the structural parameters. For many photochemical reactions it has been found that transfer from an excited to a ground state involves a *conical intersection* (CI), which can be thought of as a funnel that permits transition from one energy surface (state) to another. The efficiency of the transformation depends on the structural similarity between the excited state and the corresponding ground state molecular ensemble. There can be a number of CIs for the excited states of a typical polyatomic molecule. The transition occurs without luminescence. Conical

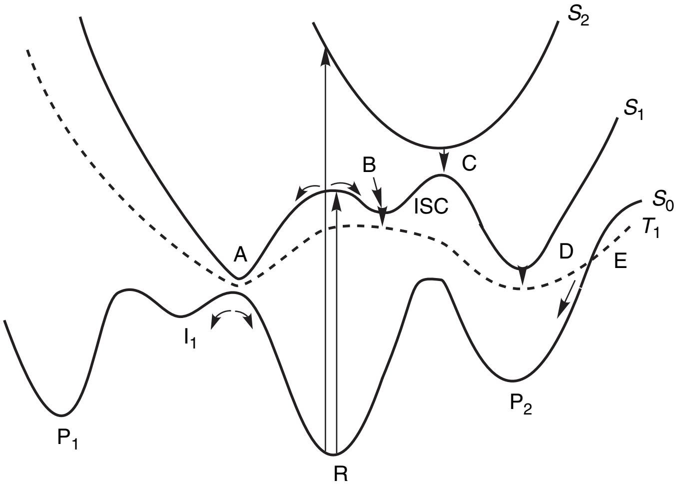

Fig. 12.2. A schematic representation of several transitions between excited states leading to photochemical reaction products.

intersections are analogous to transition states in thermal reactions in that they are points at which the electronic transition from the excited to the ground state is very fast.[5] In a transition structure there is an imaginary vibrational frequency corresponding to the reaction coordinate (Section 3.2.1). Conical intersections can proceed along any direction in a plane and can reach more than one minimum (product). The ultimate outcome of the reaction is influenced by dynamic factors at the CI. Thus motion toward a particular product may be associated with dynamic factors, e.g., direction of rotation at a preceding stage of the reaction. As in the case of thermal TSs, the structure of a CI can be described on the basis of computation.[6] Figure 12.3 is a representation of a conical intersection showing divergent paths to two different products, P_1 and P_2, resulting from different components of motion along the X_1 and X_2 coordinates.

We discuss some prototypical reactions, such as *cis-trans* isomerization, electrocyclic reactions, and cycloadditions in terms of the structures of excited states and conical intersections. For most other reactions, we represent the reaction changes in terms of structures that depict the unpairing and re-pairing events. Such representations identify key structural features that influence the outcome of the reaction, even though they may leave much uncertainty about the detailed structure of the excited states and intermediates. For several reactions, the mechanism is discussed in terms of the structure and reaction paths for CIs. Structures of specific CIs derived from computation are depicted. At this time, it is perhaps too early to fully judge the accuracy of these structural representations. However, just as for depiction of TS structures, visualization of the CI can help understand the course of a photochemical reaction.

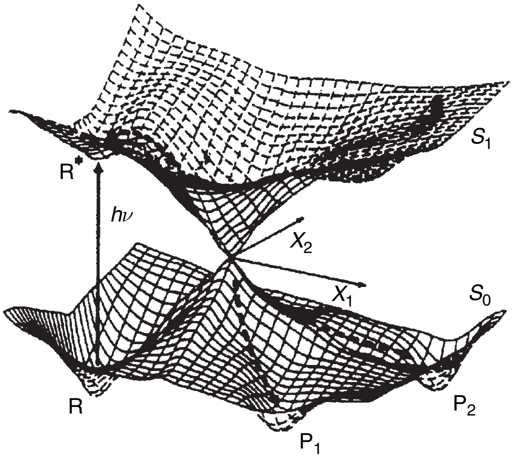

Fig. 12.3. Schematic representation of the potential energy surfaces of the ground (S_0) and excited (S_1) state in a nonadiabatic photochemical reaction. Two reaction channels lead from the conical intersection to products P_1 and P_2. The trajectories entering the conical intersection determine which reaction channel is followed. Reproduced from *Angew. Chem. Int. Ed. Engl*, **34**, 549 (1995), by permission of Wiley-VCH.

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[5] Y. Haas and S. Zilberg, *J. Photochem. Photobiol.*, **144**, 221 (2001); M. Klessinger, *Angew. Chem. Int. Ed. Engl.*, **34**, 549 (1995).

[6] F. Bernardi, M. Olivucci, and M. A. Robb, *J. Photochem. Photobiol. A*, **105**, 365 (1997).

We begin by discussing two fundamental types of photochemical reactions of alkenes and dienes. One is *cis-trans* isomerization and the others fall into the category of pericyclic reactions, including electrocyclic reactions and cycloadditions. As indicated in Chapter 10, there is a broad dichotomy between thermal and photochemical pericyclic reactions. Thermally forbidden processes are typically allowed photochemically and vice versa. Although the interpretation and prediction of the stereoselectivity of pericyclic thermal reactions is generally possible within the framework of the Woodward-Hoffmann rules, we will find several complicating factors when we consider photochemical reactions. We also examine a number of unimolecular photochemical rearrangements of alkenes and polyenes. Cycloadditions are considered further, from a synthetic viewpoint, in Section 6.3.2 of Part B.

12.2.1. *cis-trans* Isomerization

Interconversion of *cis* and *trans* isomers is a characteristic photochemical reaction of alkenes. Usually, the *trans* isomer is thermodynamically more stable, but photolysis can establish a mixture that is richer in the *cis* isomer. Irradiation therefore provides a means of converting a *trans* alkene to the *cis* isomer. The composition of the photostationary state depends on the absorption spectra of the isomeric alkenes. A hypothetical case is illustrated in Figure 12.4. Assume that the vertical line at 265 nm is the lower limit for light reaching the system. This wavelength can be controlled by use of appropriate sources and filters. Because of the shift of its spectrum toward longer wavelengths and higher extinction coefficients, the *trans* isomer absorbs substantially more light than the *cis* isomer. The relative amount of light absorbed at any wavelength is proportional to the extinction

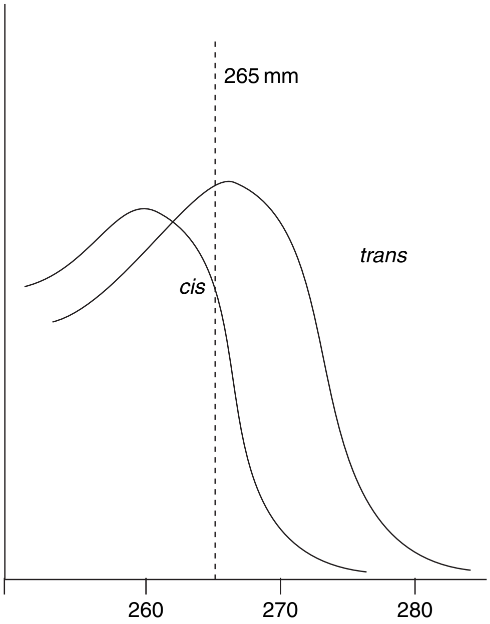

Fig. 12.4. Absorption spectra of a *cis-trans* isomer pair.

coefficients at that wavelength. If we assume that the quantum yield for conversion of *cis*→*trans* is approximately equal to that for *trans*→*cis*, the conversion of *trans* alkene to *cis* will occur faster than the converse process when the two isomers are in equal concentrations. On continued photolysis, a photostationary state will be achieved when the rate of *trans*→*cis* is equal to that of *cis*→*trans*. At this point the concentration of the *cis* isomer will be greater than that of the *trans* isomer. The relationship can be expressed quantitatively for monochromatic light as

$$\frac{[trans]}{[cis]} = \left(\frac{\varepsilon_c}{\varepsilon_t}\right)\left(\frac{\Phi_{c\to t}}{\Phi_{t\to c}}\right) \tag{12.3}$$

The *cis-trans* isomerization of alkenes is believed to take place via an excited state in which the two sp^2 carbons are twisted by about 90° with respect to one another. This twisted geometry is believed to be the minimum energy geometry for both the singlet and triplet excited states. The twisted geometry is an *energy maximum* on the ground state surface. The twisted geometry for the excited state permits the possibility of returning to either the *cis* or *trans* configuration of the ground state. The return from the singlet excited state to the ground state involves re-pairing of the electrons by a nonradiative process. Return from the triplet state requires intersystem crossing.

12.2.1.1. Photoisomerization of Ethene and Styrene We consider the excited states of ethene and styrene in some detail. These molecules do not exist as *cis* and *trans* isomers unless they are isotopically labeled. However, they are prototypes of isolated and conjugated alkenes and have been studied extensively. The excited states of ethene have been studied both by experiment and computation. The S_1 and T_1 excited states have been described by MP4(SDTQ)/6-311G** computations.[7] At this level of computation the energy of T_1 is 2.92 eV and S_1 is 5.68 eV. The T_1 state is calculated to have a perpendicular structure with extension of the C−C bond to 1.455 Å. The S_1 state is also twisted and is very strongly pyramidalized at one carbon. The C−C bond distance is 1.360 Å. This state is believed to have a large degree of zwitterionic character, with the negative charge at the pyramidalized carbon. These structures are depicted in Figure 12.5.

The excited state lifetime of ethene is very short ($<10^{-13}$ s). Both the valence and Rydberg excited states return to the ground state through a conical intersection. The CIs of the S_1 state have been examined using quantum dynamics calculations.[8,9] Return from an excited state to the ground state involves both twisting at the C–C bond and pyramidalization. Another conical intersection, which is similar in structure to the carbene ethylidene, occurs at a similar energy. These structures are shown in Figure 12.6. As we explore alkene photochemistry, we will see that the excited states and CIs depicted in Figures 12.5 and 12.6 are prototypical of the structures that are involved in the photochemistry of alkenes. The triplet T_1 state of alkenes can be represented as a twisted triplet diradical. The S_1 state is often referred to as a zwitterionic state and can be thought of as having cationic character at one carbon and carbanionic character at the other. The S_1 excited state is quite similar to the strongly

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[7] S. El-Taher, P. Hilal, and T. A. Albright, *Int. J. Quantum Chem.*, **82**, 242 (2001); V. Molina, M. Merchan, B. O. Roos, and P.-A. Malmqvist, *Phys. Chem. Chem. Phys.*, **2**, 2211 (2000).

[8] M. Ben-Nun and T. J. Martinez, *Chem. Phys. Lett.*, **298**, 57 (1998); M. Ben-Nun, J. Quenneville, and T. J. Martinez, *J. Chem. Phys. A*, **104**, 5161 (2000); J. Quenneville, M. Ben-Nun, and T. J. Martinez, *J. Photochem. Photobiol.*, **144**, 229 (2001).

[9] M. Ben-Nun and T. J. Martinez, *Chem. Phys.*, **259**, 237 (2000).

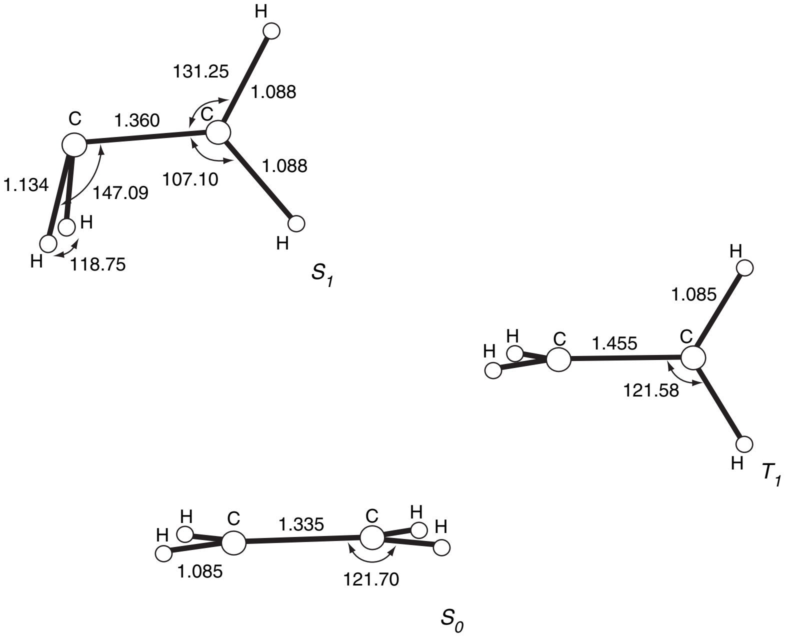
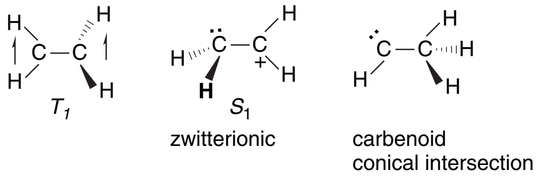


Fig. 12.5. Minimum energy structures (MP2/6-31G*) for S_0, S_1, and T_1 states of ethene. Reproduced from *Int. J. Quantum Chem.*, **82**, 242 (2001), by permission of Wiley-VCH.

pyramidalized CI in Figure 12.6. The CI with carbene character is also a common feature of alkene chemistry and can be considered to form by hydride migration from the zwitterionic excited state. Similar structures involving carbon migration are also found for substituted alkenes.



There are two relatively low-lying singlet states for styrene. S_1 is associated primarily with the benzene ring, whereas S_2 is a singlet quinoid structure. The S_1 state

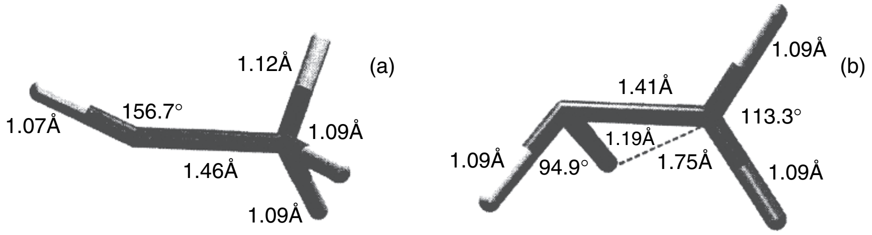
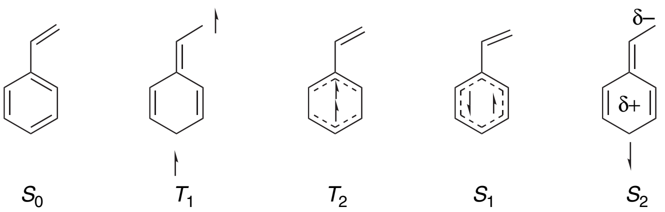


Fig. 12.6. Structures of lowest-energy conical intersections for the singlet excited state of ethene: (a) ethylidene-like structure; (b) twisted and pyramidalized structure. Reproduced from *Chem. Phys.*, **259**, 237 (2000), by permission of Elsevier.

is believed to be planar with a barrier to rotation of the double bond with respect to the ring of at least 3–4 kcal/mol.[10] The decay time for the S_1 styrene is in the nanosecond range, which is considerably longer than for ethene.[11] The S_2 excited state of styrene is a zwitterionic structure similar to the S_1 state for ethene. In this case, as might be expected, the terminal methylene group is pyramidalized, with the cationic character associated with the phenyl-substituted carbon. The T_1 state is quinoid in character with a shortened bond between the benzene ring and the double bond. T_2 involves a triplet configuration of the benzene π electrons. Valence bond representations are shown below.



Valence Bond Representation of Excited States of Styrene

The geometries and energetics of the styrene excited states have been calculated at the CAS-SCF/6-31G* level using all the π orbitals of styrene and are given in Figure 12.7.[12] The changes in bond length relative to the ground state indicate the nature of the excited states. Figure 12.7 shows the computed structures and energies of the excited states and indicates the singlet-singlet and singlet-triplet intersections. The $T_2 \rightarrow T_1$ internal conversion, which involves transfer of triplet character from the benzene ring to the ethylene bond, is efficient. The $T_1 \rightarrow S_0$ intersection, labeled ISC_c, is considered to be inefficient because of small spin-orbit coupling. This conversion is believed to occur in time range 20–100 ns.[13] This appears to be the slowest step in the decay sequence from the triplet excited state. Return to the ground state in the singlet manifold can occur from the ISC_b intersection. The styrene conical intersection appears to be similar to that for ethene and to involve both twisting and pyramidalization.[14] As Figure 12.7 suggests, there is considerable complexity to the styrene excited state surface. The introduction of the second chromophore, the benzene ring, introduces new issues

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[10] J. I. Seeman, V. H. Grassian, and E. R. Bernstein, *J. Am. Chem. Soc.*, **110**, 8542 (1988); V. H. Grassian, E. R. Bernstein, H. V. Secor, and J. I. Seeman, *J. Phys. Chem.*, **93**, 3470 (1989); J. A. Syage, F. Al Adel, and A. H. Zewail, *Chem. Phys. Lett.*, **103**, 15 (1983).

[11] D. A. Condirston and J. D. Laposa, *Chem. Phys. Lett.*, **63**, 313 (1979).

[12] M. J. Bearpack, M. Olivucci, S. Wilsey, F. Bernardi, and M. A. Robb, *J. Am. Chem. Soc.*, **117**, 6944 (1995).

[13] R. Bonneau, *J. Photochem.*, **10**, 439 (1979); R. A. Caldwell, L. D. Jacobs, T. R. Furlani, E. A. Nalley, and J. Laboy, *J. Am. Chem. Soc.*, **114**, 1623 (1992).

[14] V. Molina, M. Merchan, B. O. Roos, and P.-A. Malmqvist, *Phys. Chem. Chem. Phys.*, **2**, 2211 (2000).

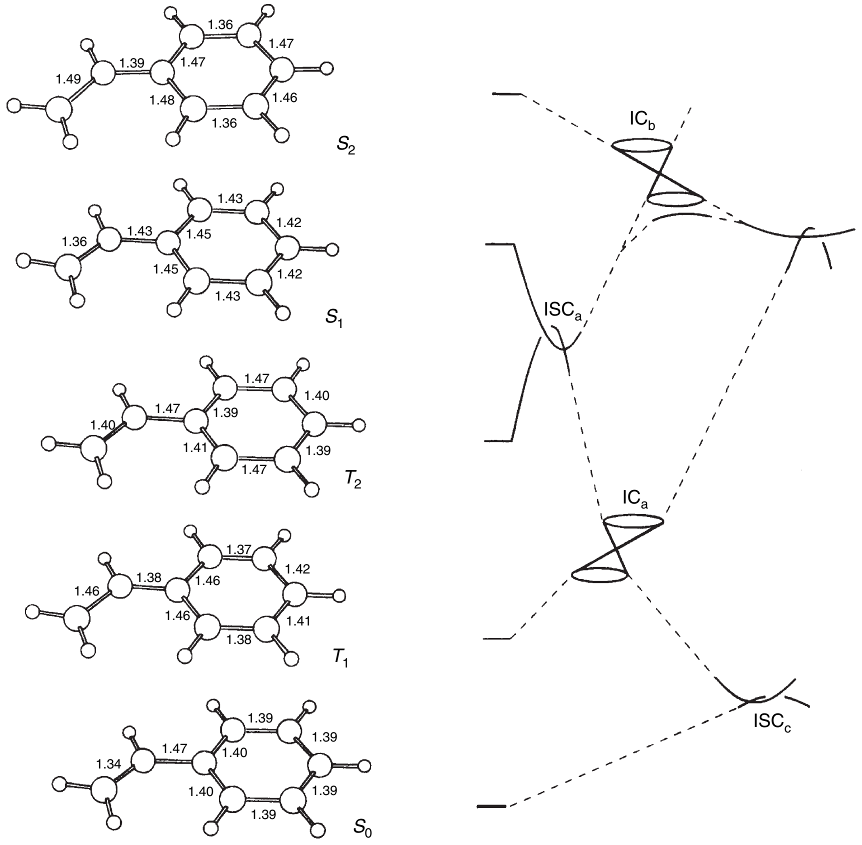

Fig. 12.7. Structures for the excited states T_1, T_2, S_1, and S_2 of styrene. Singlet-singlet conical intersections are labeled IC (internal conversion). Singlet-triplet intersections are labeled ISC (intersystem crossing). Adapted from *J. Am. Chem. Soc.*, **117**, 6944 (1995), by permission of the American Chemical Society.

concerning energy transfer between the chromophores. However, the fundamental aspects of the double-bond rotation seem to be structurally similar to those for ethene.

12.2.1.2. Photoisomerization of Stilbene Especially detailed study of the mechanism of photochemical configurational isomerism has been done on *Z*- and *E*-stilbene.[15] The isomerization involves a twisted singlet state that can be attained from either the *Z*- or the *E*-isomer. Spectroscopic data have established the energies of the singlet and triplet states of both *Z*- and *E*-stilbene and of the twisted excited states that are formed from both isomers. Some features of the potential energy diagram are due to structural

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[15] J. Saltiel, J. T. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriow, *Org. Photochem.*, **3**, 1 (1973); J. Saltiel and J. L. Charlton, in *Rearrangements in Ground and Excited States*, Vol. 3, P. de Mayo, ed., Academic Press, New York, 1980, Chap. 14; D. H. Waldeck, *Chem. Rev.*, **91**, 415 (1991); U. Mazzucato, G. A. Aloisi, G. Bartocci, F. Elisei, G. Galiazzo, and A. Spalletti, *Med. Biol. Environ.*, **23**, 69 (1995); H. Gorner and H. J. Kuhn, *Adv. Photochem.*, **19**, 1 (1995).

differences in the ground state molecules.[16] Although the double bond in *E*-stilbene can be assumed to be planar, the phenyl groups can rotate with respect to the plane of the double bond. In the solid state, the molecule is nearly planar, but in solution or gas phase the molecule is probably somewhat twisted. For the *Z*-isomer, steric interactions between the phenyl rings require their rotation from coplanarity. A rotation of 43° has been found in the gas phase. This steric effect makes the *Z*-isomer somewhat less stable than the *E*-isomer. Computed minimum energy ground state structures are shown in Figure 12.8.[17]

As shown in Figure 12.9, the absorption spectra of *Z*- and *E*-stilbene differ substantially, with the *E*-isomer absorbing more strongly at $\lambda > 260\,\text{nm}$. Thus the

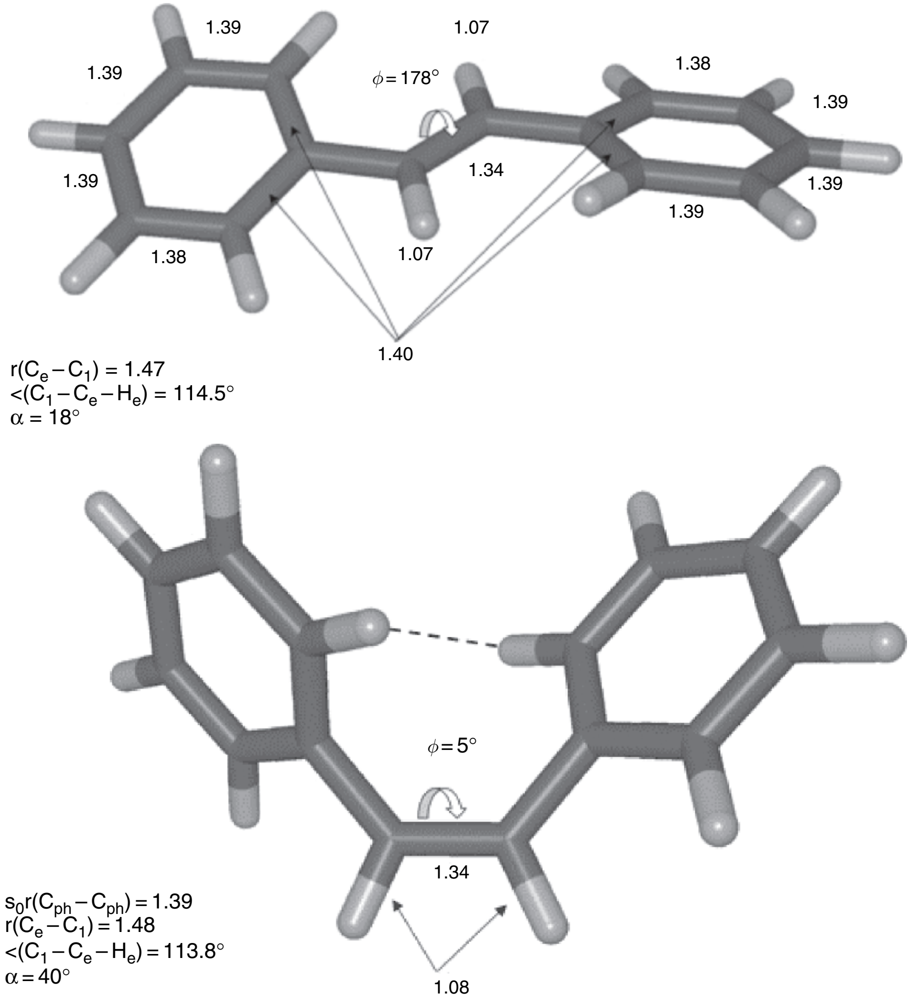

Fig. 12.8. Computed ground state geometries of *E*- and *Z*-stilbene. Reproduced from *J. Phys. Chem. A.*, **107**, 829 (2003), by permission of the American Chemical Society.

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[16] H. Meier, *Angew. Chem. Int. Ed. Engl.*, **31**, 1399 (1992).

[17] J. Quenneville and T. J. Martinez, *J. Phys. Chem. A*, **107**, 829 (2003).

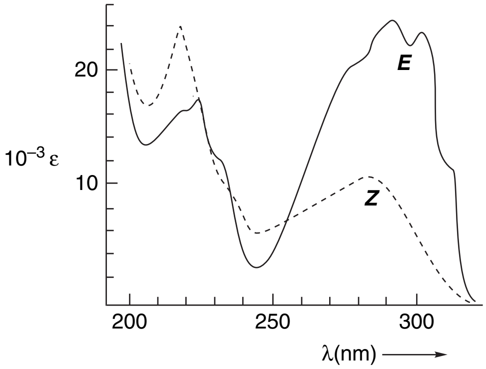

Fig. 12.9. UV spectra of *E*- and *Z*-stilbene in hexane at room temperature. Reproduced from *Angew. Chem. Int. Ed. Engl.*, **31**, 1399 (1992), by permission of Wiley-VCH.

photostationary state composition can be controlled by the wavelength of the irradiation, as indicated by the general examples and Equation (12.3) on p. 1082.[18]

Direct irradiation leads to isomerization via singlet state intermediates.[19] This involves a HOMO→LUMO excitation that involves primarily the ethylenic bond. Among the pieces of evidence indicating that a triplet intermediate is not involved in direct irradiation is the fact that azulene, which is known to intercept stilbene triplets, has only a minor effect on the efficiency of the direct photoisomerization.[20] Some aspects of this process can be described in terms of the two-dimensional energy diagram shown in Figure 12.10, which shows the relative energies and shapes of the S_0, T_1, S_1, and S_2 states with respect to twisting at the double bond. The temperature dependence of the isomerization reveals that the process of formation of the twisted state from S_1 involves a small activation energy. This energy is required for conversion of the initial excited state to the twisted geometry associated with the S_1 state. The energy barrier is greater from the *E*-isomer than from the *Z*-isomer. Note, however, that the large energy gap between the twisted excited and ground states implies a low probability of direct interconversion.

The photoisomerization can also be carried out by photosensitization. Under these conditions, the composition of the photostationary state depends on the triplet energy of the sensitizer. With sensitizers having triplet energies above 60 kcal/mol, $[Z]/[E]$ is slightly more than 1, but a range of sensitizers having triplet energies of 52–58 kcal/mol affords much higher $Z{:}E$ ratios in the photostationary state.[21] The high $Z{:}E$ ratio in this region results from the fact that the energy required for excitation of *E*-stilbene is less than for *Z*-stilbene. Thus sensitizers in the range 52–58 kcal/mol selectively excite the *E*-isomer. Since the rate of conversion of $E \rightarrow Z$ is increased, the composition of the photostationary state is enriched in *Z*-isomer.

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[18] J. Saltiel, A. Marinari, D. W.-L. Chang, J. C. Mitchener, and E. D. Megarity, *J. Am. Chem. Soc.*, **101**, 2982 (1979).

[19] J. Saltiel, *J. Am. Chem. Soc.*, **89**, 1036 (1967); **90**, 6394 (1968).

[20] J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Am. Chem. Soc.*, **88**, 2336 (1966); J. Saltiel and E. D. Megarity, *J. Am. Chem. Soc.*, **91**, 1265 (1969).

[21] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964); S. Yamauchi and T. Azumi, *J. Am. Chem. Soc.*, **95**, 2709 (1973).

Photosensitizer[a]	E_T	$[Z:E]$
Acetophenone	73.6	1.2
Benzophenone	68.5	1.2
2-Acetylnaphthalene	59.3	2.6
1-Naphthyl phenyl ketone	57.5	2.8
Benzil	53.7	4.6
Fluorenone	52.3	8.3
Pyrene	48.7	4.6
3-Acetylpyrene	45	2.8

a. From *J. Am. Chem. Soc.*, **86**, 3197 (1964).

Further insight into the stilbene $E \rightarrow Z$ photoisomerization has been obtained by computational studies. The S_1 state is considered to be a $\pi \rightarrow \pi^*$ state with considerable zwitterionic character. The transfer from the singlet photoexcited state of stilbene to the ground state is observed to be very fast and involves a CI. There have been two computational studies aimed at characterization of the CI. A CAS-SCF(STDQ-CI) study examined five filled and seven vacant π orbitals.[22] The CI was characterized by considering primarily the singlet and doublet HOMO→LUMO excitations. The CI is described as two PhCH fragments that are twisted with respect to one another. The structure of the CI has also been investigated by CAS-SCF-CASPT2 methods,[17] and is shown in Figure 12.11. The qualitative characteristics of the CI are very similar to

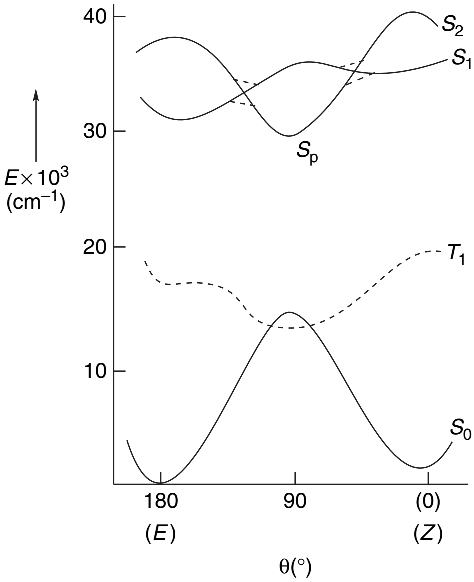

Fig. 12.10. Schematic potential energy profile for the $E \rightarrow Z$ isomerization of stilbene. The reaction coordinate is the torsion angle θ about the double bond. Reproduced from *Angew. Chem. Int. Ed. Engl.*, **31**, 1399 (1992), by permission of Wiley-VCH.

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[22] V. Molina, M. Merchan, and B. O. Roos, *J. Phys. Chem. A*, **101**, 3478 (1997); V. Molina, M. Merchan, and B. O. Roos, *Spectrochim Acta A*, **55**, 433 (1999).

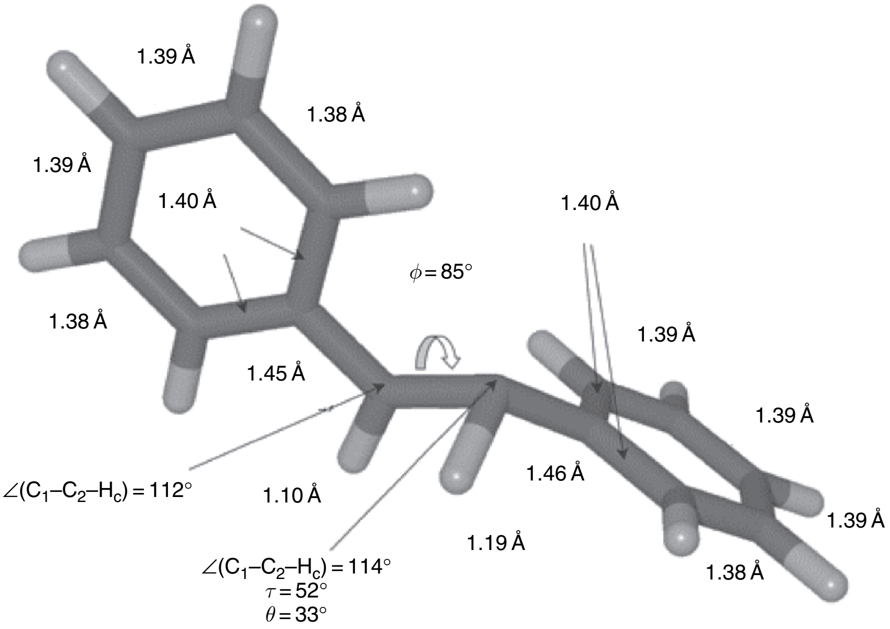


Fig. 12.11. The minimum energy structure for the S_0/S_1 conical intersection for stilbene. The geometrical parameters are from SA-2-CAS(2/2) level computations. Reproduced from *J. Phys. Chem. A*, **107**, 829 (2003), by permission of the American Chemical Society.

those described earlier for ethene and styrene. The structure is both twisted and pyramidalized, and is a mix of zwitterionic and (singlet) diradical character. Figure 12.12 depicts the singlet energy surface for stilbene as a function of both torsion at the ethylenic bond and pyramidalization.

The common feature of the ethene, styrene, and stilbene $S_1 \rightarrow S_0$ transformations is that double-bond isomerization involves not only twisting at the double bond but also pyramidalization. The pyramidalization modifies the energies that are depicted in Figure 12.10, which considers only the bond rotation, and lowers the energy of the S_p state sufficiently to permit rapid internal conversion.

The stilbene *cis-trans* isomerization has also been explored using DFT calculations.[23] The potential energy as a function of rotation of the single bond for the S_0, T_1, S_1, and S_2 states is as shown in Figure 12.13. The S_0 maximum at 90° is characterized as a singlet diradical with the electrons delocalized in the adjacent phenyl ring, *i.e.*, two benzylic radicals. The central bond is essentially a single bond. This structure is 44.9 kcal/mol above the ground state *trans* (180°) minimum. The rotational potential for T_1 is very flat and nearly intersects the S_0 curve near 90°, at an energy of 46.5 kcal/mol. There is essentially no barrier to rotation at the T_1 surface. This structure is a triplet diradical. The vertical energy to the T_1 state is slightly higher for *cis*-stilbene than for *E*-stilbene, and proceeds without a barrier to the twisted minimum. The S_1 state shows a small maximum near 90°. There is a very shallow minimum slightly displaced from the vertical 180° (*trans*) structure. There is also a shallow minimum

[23] W.-G. Han, T. Lovell, T. Liu, and L. Noodleman, *Chem. Phys. Chem.*, **3**, 167 (2002).

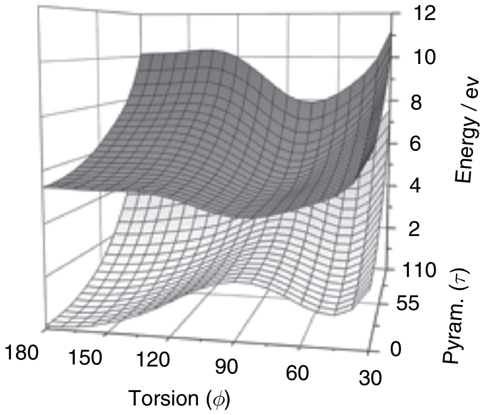


Fig. 12.12. Potential energy surfaces for S_0 and S_1 for stilbene computed at the SA-2-CAS(2/2) level as a function of C=C twist and pyramidalization τ with other dimensions held constant. The S_0 minima correspond to the *E*-isomer (180°) and *Z*- isomer (45°). Reproduced from *J. Phys. Chem. A*, **107**, 829 (2003), by permission of the American Chemical Society.

on S_1 at about 45° beginning from the *Z*-vertical state. At 90°, the S_1 state is about 70 kcal/mol above ground state *E*-stilbene. The twisted structure is a neutral diradical, but in contrast to T_1 and the S_0 maximum, there is nearly equal distribution of each

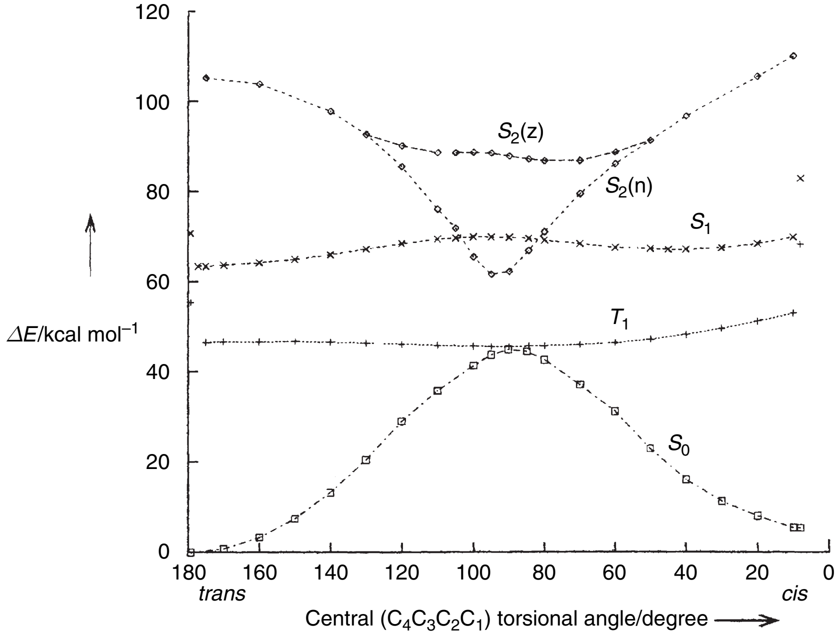
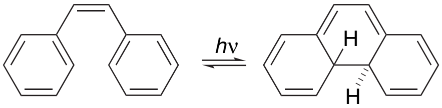


Fig. 12.13. DFT computation of the rotational energy profile of stilbene, beginning at the *trans* (180°) and *cis* (0°) geometries. Both neutral (*n*) and zwitterionic (*z*) versions of S_2 were computed. Reproduced from *Chem. Phys. Chem*, **3**, 167 (2002), by permission of the Royal Society of Chemistry.

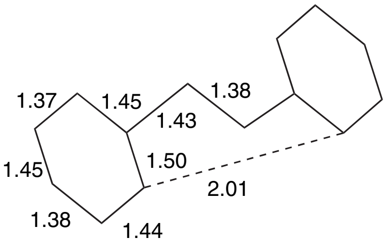
electron over both rings. The S_2 state shows a minimum at 90°, about 18 kcal above T_1 and S_0 at this geometry. The S_2 curve encounters small barriers from the vertical transitions (6.6 kcal/mol for *trans* and 2.2 for *cis*), in agreement with experimental conclusions. The main difference between the DFT and MO calculations is that the DFT computation describes the S_2 minimum as primarily a singlet diradical, rather than a zwitterionic, structure.

In addition to *cis-trans* isomerization, *Z*-stilbene also undergoes photocyclization to 4a,4b-dihydrophenanthrene via an electrocyclization.[24]



The cyclization product is thermally unstable relative to *cis*-stilbene and reverts to starting material unless trapped by an oxidizing agent.[25] The extent of cyclization is solvent dependent, with nonpolar solvents favoring cyclization more than polar ones.[26] The quantum yield for *cis-trans* isomerization is nearly constant at about 0.35, but the cyclization quantum yield is in the range of 0.15–0.18 in hydrocarbons, as compared with 0.05–0.08 in acetonitrile or methanol. The detailed interpretation of the system involves the effect of solvent on the lifetime and dynamics of the excited states.[27] Figure 12.14 incorporates the reaction coordinate for cyclization into the *cis-trans* energy diagram.

The cyclization has been investigated by computation and can be described in terms of a CI involving interaction between the two phenyl rings.[28] The structural features are similar to the CI involved in electrocyclization of *Z*-1,3,5-hexatrienes to cyclohexadienes described on p. 1142.



12.2.2. Photoreactions of Other Alkenes

Direct photochemical excitation of unconjugated alkenes requires light with $\lambda < 220\,\text{nm}$. A study of *Z*- and *E*-2-butene diluted with neopentane demonstrated that *cis-trans* isomerization was competitive with the photochemical $[2\pi + 2\pi]$

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[24] T. Wismonski-Knittel, G. Fischer, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1930 (1974).

[25] L. Liu, B. Yang, T. J. Katz, and M. K. Poindexter, *J. Org. Chem.*, **56**, 3769 (1991).

[26] J.-M. Rodier and A. B. Myers, *J. Am. Chem. Soc.*, **115**, 10791 (1993).

[27] R. J. Sension, S. T. Repinec, A. Z. Szarka, and R. M. Hochstrasser, *J. Phys. Chem.*, **98**, 6291 (1993).

[28] M. J. Bearpark, F. Bernardi, S. Clifford, M. Olivucci, M. A. Robb, and T. Vreven, *J. Phys. Chem. A*, **101**, 3841 (1997).

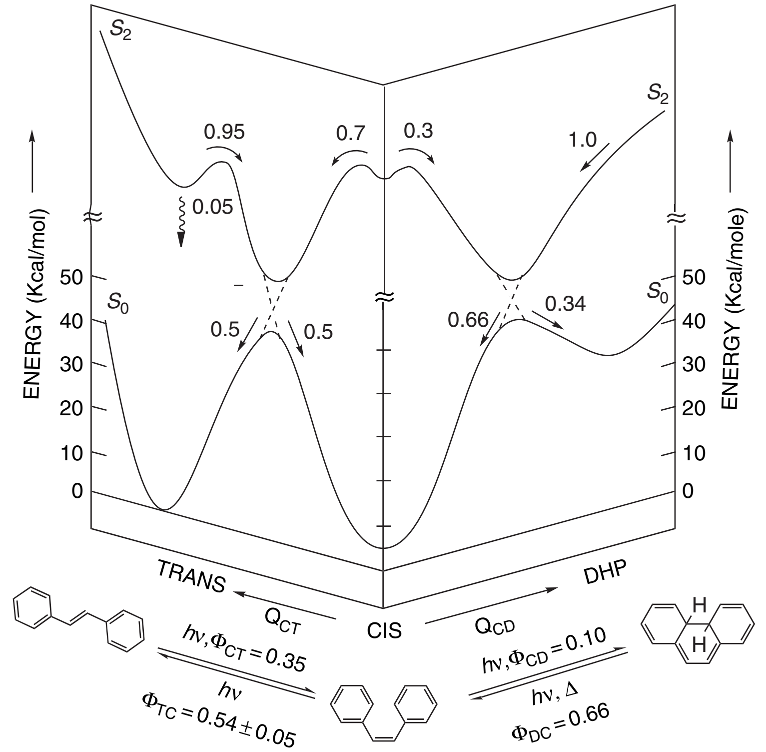

Fig. 12.14. Schematic representation of the potential energy surface for S_2 and S_0 of stilbene including the photocyclization reaction. Approximate branching ratios and quantum yields are indicated. Reproduced from *J. Phys. Chem.*, **98**, 6291 (1993), by permission of the American Chemical Society.

cycloaddition that occurs in pure liquid alkene.[29] We discuss the cycloaddition further in the next section. As the ratio of neopentane to butene increased, the amount of cycloaddition decreased, relative to *cis-trans* isomerization. This effect presumably is the result of the very short lifetime of the intermediate responsible for cycloaddition. When the alkene is diluted by inert hydrocarbon, the rate of encounter of a second alkene molecule is reduced, and the unimolecular isomerization becomes the dominant reaction. Rearrangement reactions are also observed, including 1,2-hydrogen shifts (to carbenes), 1,3-hydrogen and alkyl shifts, and cyclopropane formation. These reactions can occur from CIs that have the character of hydrogen or alkyl groups associated with an allyl or vinyl radical.[30] The vertical excitation energy for unconjugated alkenes is in the range of 150 kcal/mol, and these CIs are at 100 ± 20 kcal/mol. This is similar to the energy required for the dissociation of allylic C−H and C−C bonds, and dissociation is one of the pathways open to excited state alkenes.

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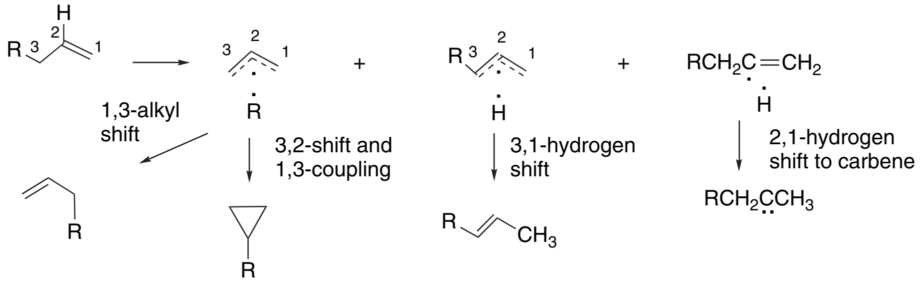
[29] H. Yamazaki and R. J. Cventanovic, *J. Am. Chem. Soc.*, **91**, 520 (1969); H. Yamazaki, R. J. Cventanovic, and R. S. Irwin, *J. Am. Chem. Soc.*, **98**, 2198 (1976).

[30] F. Bernardi, M. Olivucci, M. A. Robb, and G. Tonachini, *J. Am. Chem. Soc.*, **114**, 5805 (1992); S. Wilsey and K. N. Houk, *J. Am. Chem. Soc.*, **122**, 2651 (2000).



Simple alkenes can be isomerized using triplet sensitizers and this often avoids the competing rearrangement reactions. Aromatic compounds such as benzene, toluene, xylene, and phenol can photosensitize *cis-trans* interconversion of simple alkenes.[31] This is a case where the sensitization process must be somewhat endothermic because of the energy relationships between the excited states of the alkene and the sensitizers. The photostationary state obtained under these conditions favors the less strained of the alkene isomers. The explanation for this effect can be summarized with reference to Figure 12.15. Isomerization takes place through a twisted triplet state that is achieved by a combination of energy transfer from the sensitizer and thermal activation. Because the *cis* isomer is somewhat higher in energy, its requirement for activation to the excited state is somewhat less than for the *trans* isomer. If it is also assumed that the excited state forms the *cis* and *trans* isomers with equal ease, the rate of *cis*→*trans* exceeds that for *trans*→*cis* conversion ($k_{c\rightarrow t} > k_{t\rightarrow c}$) at the photostationary state and therefore [*trans*] > [*cis*].[32]

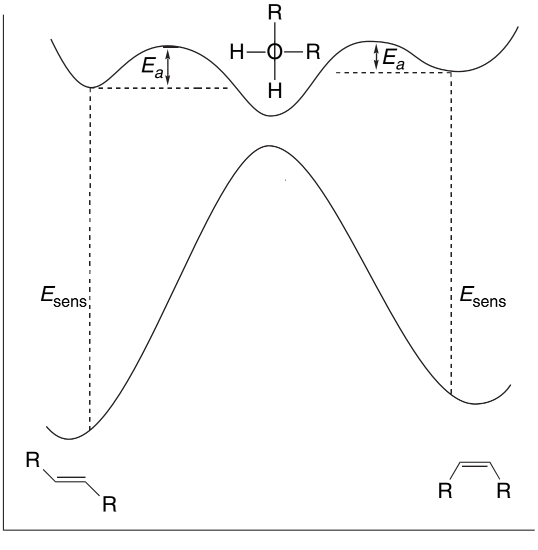


Fig. 12.15. Schematic potential energy diagram illustrating differential in energy required for triplet-sensitized photoisomerization of *cis* and *trans* isomers.

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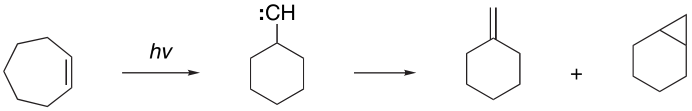
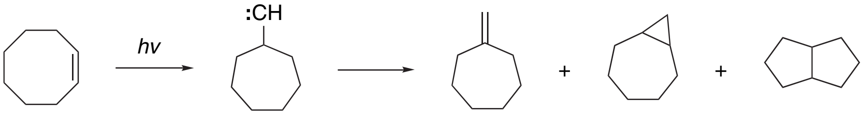
[31] M. Tonaka, T. Terao, and S. Sato, *Bull. Chem. Soc. Jpn.*, **38**, 1645 (1965); G. A. Haninger and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

[32] J. J. Snyder, F. P. Tise, R. D. Davis, and P. J. Kropp, *J. Org. Chem.*, **46**, 3609 (1981).

Photoexcitation of cycloalkenes introduces additional features because the ring limits the extent to which the double bond can twist. Cyclohexene, cycloheptene, and cyclooctene give rise to ring contraction and carbene insertion products.



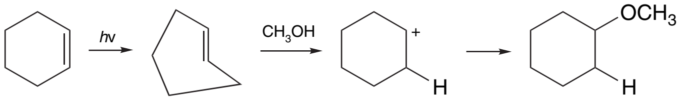
Ref. 33



Ref. 34

It has been possible to observe the processes that occur within 100 fs after excitation of cyclohexene to the π-π^* and π, 3s(R) states (200 nm). This time scale is too short to allow for intermolecular reactions, even in solution. The products are methylenecyclopentane and bicyclo[3.1.0]hexane. The processes are summarized in Figure 12.16.[35] The process designated τ_1 (20 fs) is believed to follow the relaxation of the vertical π-π^* and π,3s(R) states to the equilibrium geometry on the π-π^* surface. The process designated τ_2 represents the start of 1,3-H migration. At τ_3 the isomerization to the carbenoid structure is complete. The C−C bond shift corresponds to τ_4. The carbene can then return to the ground state surface by forming cyclohexene, bicyclo[3.1.0]hexane, or methylenecyclopentane. Some *E*-cyclohexene is formed and can be trapped by hydroxylic solvents.[36]

The reaction course taken by photoexcited cycloalkenes in hydroxylic solvents depends on ring size.[37] Cyclohexene, cycloheptene, cyclooctene, 1-methylcyclohexene, l-methylcycloheptene, and 1-methylcyclooctene all add methanol, but neither 1-methylcyclopentene nor norbornene does so. The key intermediate in the addition reaction is believed to be the highly reactive *E*-isomer of the cycloalkene. The *E*-cycloalkenes can be protonated exceptionally easily because of the enormous relief of strain that accompanies protonation.[36,38]



The *E*-cycloheptene and cyclooctene isomers can be observed and *E*-cyclooctene can be isolated.

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[33] Y. Inoue, S. Takamuka, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 577 (1975).

[34] P. J. Kropp, J. D. Mason, and G. F. H. Smith, *Can. J. Chem.*, **63**, 1845 (1985).

[35] W. Fuss, W. E. Schmid, and S. A. Trushin, *J. Am. Chem. Soc.*, **123**, 7101 (2001).

[36] P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., *J. Am. Chem. Soc.*, **95**, 7058 (1973).

[37] T. Mori and Y. Inoue, *CRC Handbook of Photochemistry and Photobiology*, W. Horspool and F. Lenci, ed., CRC Press, Boca Raton, FL, 2004, Section 16.

[38] J. A. Marshall, *Acc. Chem. Res.*, **2**, 33 (1969).

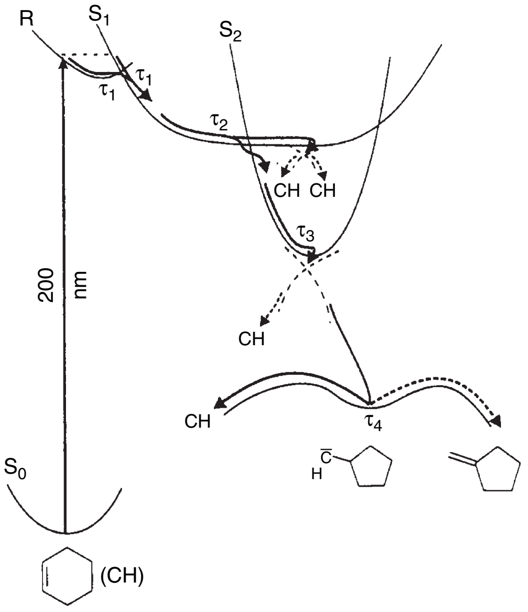
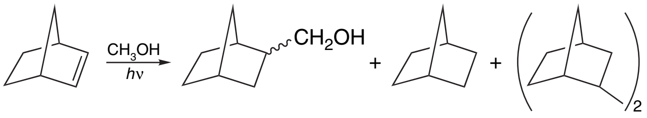
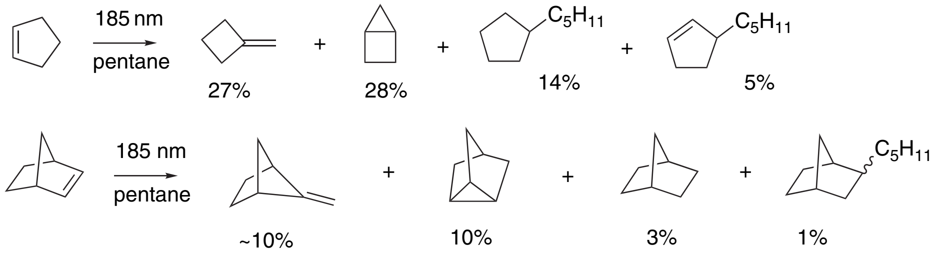


Fig. 12.16. Sequential events in the excitation and return to ground state for cyclohexene. Reproduced from *J. Am. Chem. Soc.*,**123**, 7101 (2001), by permission of the American Chemical Society.

The *trans* isomers of cyclopentene and norbornene are too strained to be formed. Rather, they give products in methanol that result from hydrogen abstraction and other radical-like processes.[39]



Photolysis in hydrocarbon solvents leads to rearranged products similar to those from other cycloalkenes, as well as hydrogen abstraction and coupling products.[40]



The nature of the excited states involved in formation of the carbene intermediates has been explored using CAS-SCF/6-31G* computations including the σ, σ*, π, and

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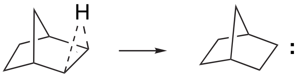
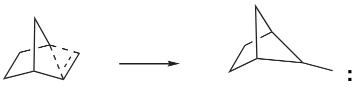
[39] P. J. Kropp, *J. Am. Chem. Soc.*, **91**, 5783 (1969).

[40] R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, **100**, 4602 (1978); Y. Inoue, T. Mukai, and T. Hakushi, *Chem. Lett.*, 1045 (1982).

π* orbitals of the double bond and directly attached atoms.[41] Hydrogen and carbon migration leading to carbene intermediates occurs without any barrier from the excited states. These structures represent CIs corresponding to 1,2-migrations of hydrogen or carbon. The carbenoid structures can account for the rearranged products.



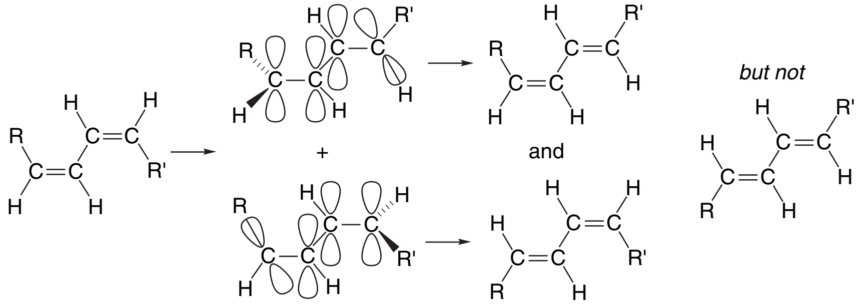
Hydrogen migration



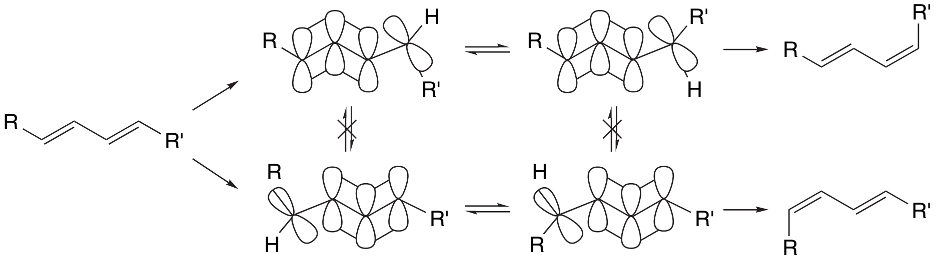
Carbon migration

12.2.3. Photoisomerization of 1,3-Butadiene

The *cis-trans* isomerization reaction of 1,3-dienes can provide insight into the structure of the excited state. If the excited state is an allylmethylene diradical, only one of the two double bonds would be isomerized in any single excitation event.



On the other hand, if the excited state resembles a 1,4-but-2-enyl diradical, isomerization could take place at both double bonds. It is this latter situation that apparently exists in the triplet state. The triplet state has a high bond order between C(2) and C(3) and resists rotation about this bond, but the barrier to rotation at both of the terminal carbons is low.[42] Both double bonds can isomerize through this excited state. In contrast, direct irradiation of 2,4-hexadiene at 257 nm isomerizes only one of the double bonds.[43] The singlet state apparently retains a substantial barrier to rotation about the bonds in the allyl system.



An alternative description of the singlet excited state is a cyclopropylmethyl singlet diradical. Only one of the terminal carbons would be free to rotate in such a structure.

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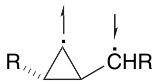
[41] S. Wilsey and K. N. Houk, *J. Am. Chem. Soc.*, **124**, 11182 (2002).

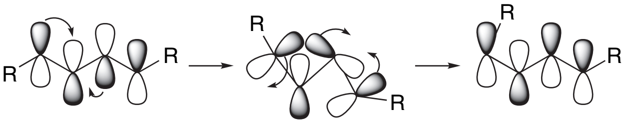
[42] J. Saltiel, L. Metts, and M. Wrighton, *J. Am. Chem. Soc.*, **91**, 5684 (1969).

[43] J. Saltiel, L. Metts, and M. Wrighton, *J. Am. Chem. Soc.*, **92**, 3227 (1970).

(See p. 1138 for a discussion of the role of this structure in the S_2 excited state of 1,3-butadiene.)



Orbital symmetry control of subsequent ring opening could account for isomerization at only one of the double bonds. Taking ψ_3 as the controlling frontier orbital, it can be seen than a concerted return to ψ_2 leads to rotation at only one terminus of the diene.



The conclusion from these studies is that singlet *cis-trans* isomerization of substituted conjugated dienes such as 2,4-hexatriene must proceed through a structure that is free to rotate at only one terminus, whereas sensitized (triplet) isomerization involves a structure that can rotate at both termini.

The discussion of *cis-trans* photoisomerization of alkenes, styrene, stilbene, and dienes has served to introduce some important ideas about the interpretation of photochemical reactions. We see that thermal barriers are usually low, so that reactions are very fast. Because excited states are open-shell species, they present new kinds of structures, such as the twisted and pyramidalized CIs that are associated with both isomerization and rearrangement of alkenes. However, we will also see familiar structural units as we continue our discussion of photochemical reactions. Thus the triplet diradical involved in photosensitized isomerization of dienes is not an unanticipated species, given what we have learned about the stabilization of allylic radicals.

12.2.4. Orbital Symmetry Considerations for Photochemical Reactions of Alkenes and Dienes

The photochemistry of alkenes, dienes, and conjugated polyenes in relation to orbital symmetry relationships has been the subject of extensive experimental and theoretical study.[44] The analysis of concerted pericyclic reactions by the principles of orbital symmetry leads to a complementary relationship between photochemical and thermal reactions. A process that is forbidden thermally is allowed photochemically and vice versa. The complementary relationship between thermal and photochemical reactions can be illustrated by considering some of the reaction types discussed in Chapter 10 and applying orbital symmetry considerations to the photochemical mode of reaction. The case of $[2\pi + 2\pi]$ cycloaddition of two alkenes, which was classified as a forbidden thermal reaction (see Section 10.1), can serve as an example. The correlation diagram (Figure 12.17) shows that the ground state molecules would lead to a doubly excited state of cyclobutane, and would therefore involve a prohibitive thermal activation energy.

How does the situation change when a photochemical reaction involving one ground state alkene and one excited state alkene is considered? If we assume a

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[44] B. H. O. Cook and W. J. Leigh, in *Chemistry of Dienes and Polyenes*, Vol. 2, Z. Rappoport, ed. John Wiley, Chichester, 2000, pp. 197–255.

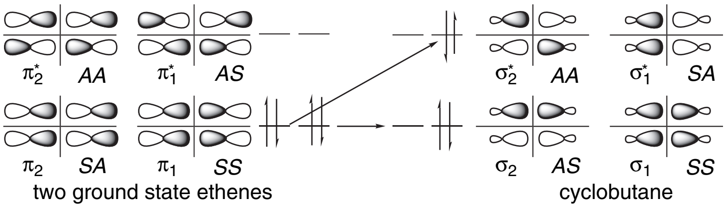
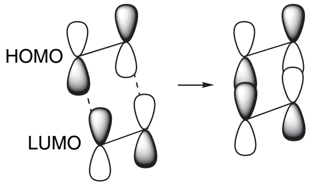


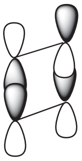
Fig. 12.17. Orbital correlation for two ground state ethenes and cyclobutane. The symmetry designations apply, respectively, to the horizontal and vertical planes for two ethene molecules approaching one another in parallel planes.

symmetrical approach as in the thermal reaction, then the same array of orbitals is involved, but the occupation of the orbitals is different: the π_1 (*SS*) orbital is doubly occupied, but π_2 (*SA*) and $\pi_2{}^*$ (*AA*) are singly occupied. The reaction is therefore allowed in the sense that there is no high-energy barrier. Although the correlation diagram illustrated in Figure 12.18 might suggest that the product would initially be formed in an excited state, this is not necessarily the case. The concerted process can involve a transformation of the reactant excited state to the ground state of product. The nature of this transformation is discussed shortly.

Consideration of the HOMO-LUMO interactions also indicates that the $[2\pi + 2\pi]$ addition is allowed photochemically. The HOMO in this case is the excited alkene π^* orbital. The LUMO is the π^* of the ground state alkene, and a bonding interaction is present between both pairs of carbons where new bonds must be formed. Similarly, the concept of aromatic transition states shows that the reaction has an antiaromatic 4π combination of basis set orbitals, which predicts an *allowed photochemical reaction*. Thus, orbital symmetry considerations indicate that photochemical $[2\pi + 2\pi]$ cycloaddition of alkenes is feasible.



HOMO-LUMO combination for [2 + 2] photocycloaddition.



Aromatic Mobius basis set orbial array for [2 + 2] photocycloaddition

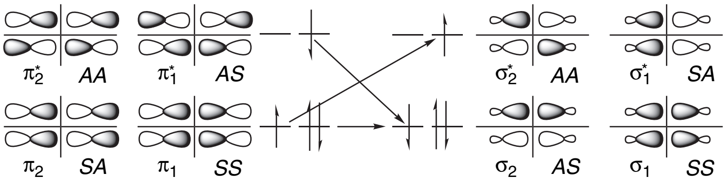
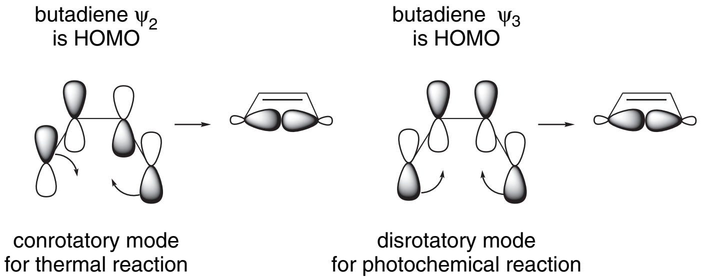


Fig. 12.18. Orbital correlation diagram for one ground state ethene and one ethene in an excited state. The symmetry designations apply, respectively, to the horizontal and vertical planes for two ethene molecules approaching one another in parallel planes.

It is a general result that the Woodward-Hoffmann rules predict that photochemical reactions will be complementary to thermal reactions. What is allowed photochemically is forbidden thermally, and vice versa. *The physical basis for this complementary relationship is that the high barrier associated with forbidden thermal reactions provides a point for strong interaction of the ground state and excited state species.* As the two states are close in energy and of the same symmetry, they "mix" and allow the excited molecule to reach the ground state. This interaction is necessary for efficient photochemical reactions.[45]

Let us now consider photochemical electrocyclic reactions. In Chapter 10, we described the distinction between the conrotatory and disrotatory modes of reaction as a function of the number of electrons in the system. Striking illustrations of the relationship between orbital symmetry considerations and the outcome of photochemical reactions are found in the stereochemistry of electrocyclic reactions. Orbital symmetry predicts that photochemical electrocyclic reactions will show a reversal of stereochemistry relative to thermal reactions.[46] One way of making this prediction is to construct an electronic energy state diagram for the reactant and product molecule and observe the correlation between the states.[47] The reactions in which the reacting state correlates with a state of the product that is not appreciably higher in energy are permitted.[48] The orbitals involved in the photochemical butadiene-to-cyclobutene conversion are ψ_1, ψ_2, and ψ_3 of the first excited state of butadiene and σ, π, and π^* for cyclobutene. The appropriate elements of symmetry are the plane of symmetry for the conrotatory and the axis of symmetry for the disrotatory process. The correlation diagram for this reaction is shown in Figure 12.19. This analysis shows that disrotatory cyclization is allowed, whereas conrotation would lead to a highly excited σ^1, π^2, σ^{*1} configuration of cyclobutene. The same conclusion is reached if it is assumed that the frontier orbital will govern reaction stereochemistry.



Although orbital symmetry provides a starting point for analyses of photochemical reactions of conjugated dienes and polyenes, experimental studies have identified a number of additional facets of the problem, some of which have to do with the fundamental assumptions of the orbital symmetry analysis. One of the underlying

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[45] H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1566 (1966); W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042 (1969); R. C. Dougherty, *J. Am. Chem. Soc.*, **93**, 7187 (1971); J. Michl, *Top. Current Chem.*, **46**, 1 (1974); J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).

[46] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[47] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

[48] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970.

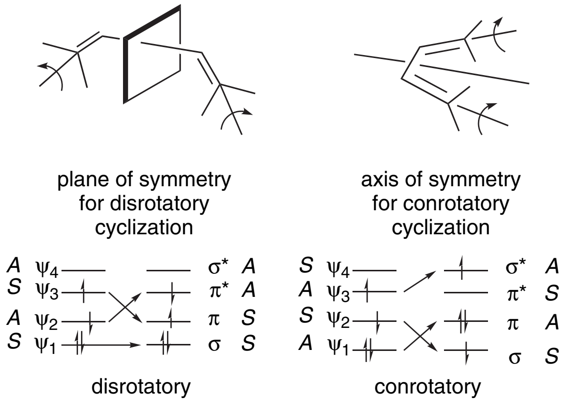


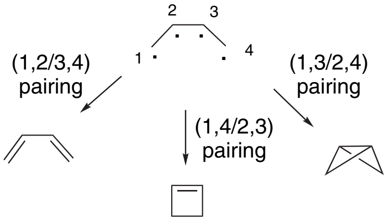
Fig. 12.19. Orbital correlation diagram for the states involved in the photochemical interconversion of butadiene and 1,3-butadiene.

assumptions is that the processes are *concerted.* Although the criteria for concertedness are fairly clear in thermal reactions (the existence or nonexistence of an intermediate), the case for photochemical reactions is not so clear. Several excited state transformations and CIs can appear on the overall reaction path, but there may be no significant barrier. The orbital symmetry analysis also makes assumptions about the *geometry of the interacting molecules*, usually choosing the most symmetrical arrangement. We have to consider whether this assumption is justified. Another difference between the thermal and photochemical reactions is that the *principle of microscopic reversibility applies to the former, but not to the latter*. Concerted thermal pericyclic reactions traverse the same minimum energy pathway in the forward and reverse directions. In photochemical processes, the initial reactant geometries are different, and owing to the NEER principle (see p. 1078) these differences may persist in excited states and influence their reactivity. We first consider some of the experimental observations for dienes and then look at the mechanistic interpretations that have been developed. Computational studies have been applied to the structure of CIs, as was discussed for alkene *cis-trans* isomerization, and these have provided new insights into the photochemical reactions of conjugated dienes and polyenes.

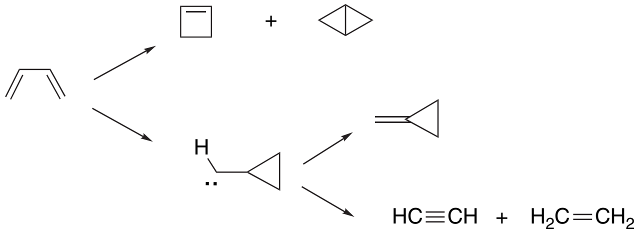
12.2.5. Photochemical Electrocyclic Reactions

The case of butadiene-cyclobutene interconversion, which one might expect to provide a straightforward example illustrating the stereoselectivity of photochemical electrocyclization, is actually quite complex, especially when substituted systems are involved. We first consider experimental outcomes from the photolysis of butadiene and substituted derivatives, as well as the reverse reaction, the photochemical ring-opening reactions of cyclobutenes. We then examine the 1,3,5-hexatriene system in the same way.

In addition to cyclobutene, bicyclo[1.1.0]butane, methylenecyclopropane, and the fragmentation products ethene and ethyne are formed in the direct photolysis of butadiene. These results can be interpreted in terms of CIs related to those described for ethene and other alkenes. Formation of cyclobutene and bicyclobutane can be attributed to different re-pairing schemes that correlate with different motions into and out of the area of a CI that can be described as a tetraradicaloid. (1,2/3,4)-pairing leads to 1,3-butadiene, (1-4/2-3)-pairing leads to cyclobutene, and (1,3/2,4)-pairing leads to bicyclo[1.1.0]butane.

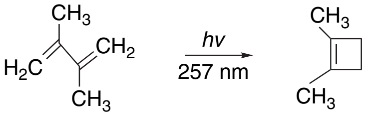


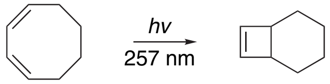
The rearrangement and fragmentation products are thought to arise from a carbene intermediate.



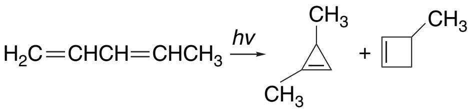
After excitation to the S_2 surface and transition to S_1, the CI leads to partitioning to products and starting material. These processes occur on the femtosecond time scale. Lifetimes have been assigned to several of the transformations, as illustrated in Figure 12.20.[49]

Electrocyclization of conjugated dienes occurs in competition with *cis-trans* isomerization. The cyclization occurs from the *s-cis* conformation of the diene.[50] Cyclobutene formation is favored in cyclic dienes and for other dienes where the *s-cis* diene conformation is dominant.[51] For several dienes, the quantum yield in nonpolar solvents at 257 nm is about 0.1.[52] As the cyclized alkenes do not absorb at this wavelength, the reaction can give substantial preparative yields, despite the competing *cis-trans* isomerization.





On direct irradiation of 1,3-pentadiene, *cis-trans* isomerization is accompanied by cyclization to 1,3-dimethylcyclopropene and 3-methylcyclobutene.[53]



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[49] W. Fuss, W. E. Schmid, and S. A. Trushin, *Chem. Phys. Lett.*, **342**, 91 (2001).

[50] M. E. Squillacote and T. C. Semple, *J. Am. Chem. Soc.*, **112**, 5546 (1990).

[51] W. J. Leigh, K. Zheng, and K. B. Clark, *J. Org. Chem.*, **56**, 1574 (1991); W. H. Laarhoven, *Org. Photochem.*, **9**, 129 (1987).

[52] R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1982).

[53] S. Boué and R. Srinivasan, *J. Am. Chem. Soc.*, **92**, 3226 (1970).

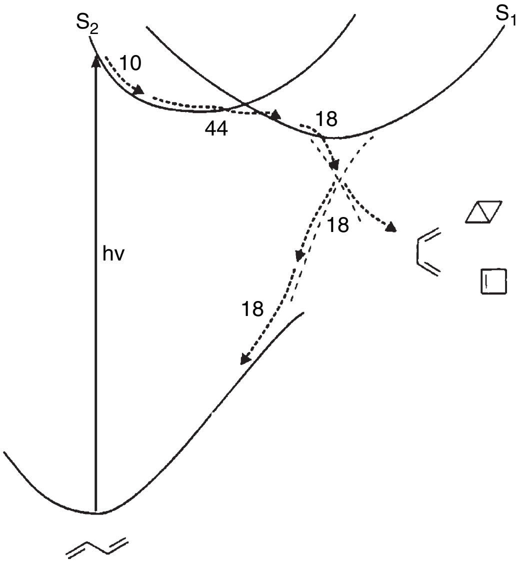
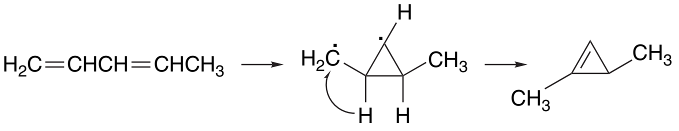
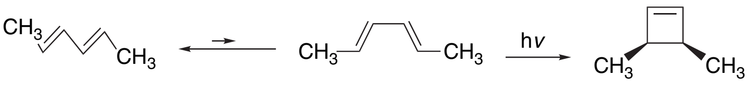


Fig. 12.20. Representation of the 1,3-butadiene potential energy surface based on experimental observations. The broken arrows show the path for return to the ground state reactant and other products. Lifetimes are given in femtoseconds. The dashed lines indicate a conical intersection for partitioning between products. Adapted from *Chem. Phys. Lett.*, **342**, 91 (2001).

The latter product is an example of a photochemically allowed electrocyclic reaction. The cyclopropene arises from (2,4)-pairing and hydrogen migration.



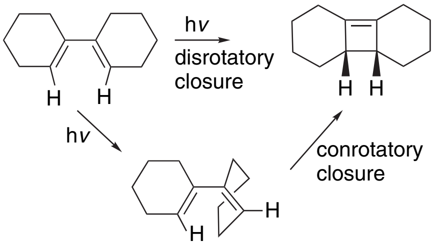
For *E*,*E*-2,4-hexadiene, the cycloaddition reaction is stereospecific and in accord with the Woodward-Hoffmann predictions.[54]



Cyclic dienes can give cyclobutenes by either direct photochemical electrocyclization or by isomerization to the *E*-isomer in one ring, followed by [2 + 2] cycloaddition. The latter process can be intercepted by methanol (see p. 1094).[55]

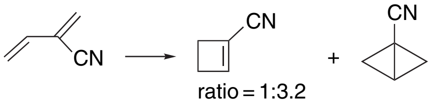
[54] R. Srinivasan, *J. Am. Chem. Soc.*, **90**, 4498 (1968).

[55] Y. Daino, S. Hagiwara, T. Hakushi, Y. Inoue, and A. Tai, *J. Chem. Soc.*, *Perkin Trans. 2*, 275 (1989).

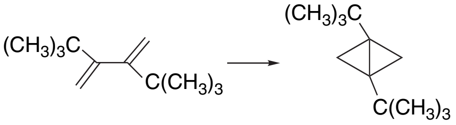


Ref. 56

Substituents can affect the partitioning among the competing reaction paths. The formation of the bicyclo[1.1.0]butane product is favored by radical-stabilizing substituents.[57]

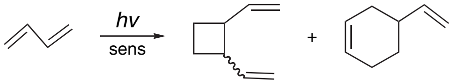


The steric effect of 2,3-di-*t*-butyl groups causes the cyclization to the bicyclo[1.1.0]butane to become the dominant reaction.[58]



Ref. 59

Reactions of conjugated dienes can also occur through the triplet state generated by photosensitization. 1,3-Butadiene gives a mixture of *cis*- and *trans*-1,2-divinylcyclobutane (**1**) and 4-vinylcyclohexene (**2**).



1 **2**

The ratio of divinylcyclobutanes to cyclohexene product depends on the E_T of the sensitizer that is used. With sensitizer $E_T > 60\,\text{kcal/mol}$, either the *s-trans* (dominant) or *s-cis* conformation can be excited. With $E_T \sim 55\,\text{kcal/mol}$, the *s-cis* is preferentially excited (see Figure 12.15). The excited *s-trans* conformer can give only cyclobutanes, whereas the excited*s-cis* structure can also form the cyclohexene product.[60] Isoprene shows a similar effect with cyclohexene formation being at a maximum with E_T at 46–54 kcal/mol.

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[56] J. Saltiel, G. R. Marchand, and R. Bonneau, *J. Photochem.*, **28**, 367 (1987).

[57] D. M. Gale, *J. Org. Chem.*, **35**, 970 (1970); M. Olivucci, F. Bernardi, S. Ottani, and M. A. Robb, *J. Am. Chem. Soc.*, **116**, 2034 (1994).

[58] M. Garavelli, B. Frabboni, M. Fato, P. Celani, F. Bernardi, M. A. Robb, and M. Olivucci, *J. Am. Chem. Soc.*, **121**, 1537 (1999).

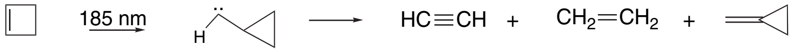
[59] H. Hopf, H. Lipka, and M. Traetteberg, *Angew. Chem. Int. Ed. Engl.*, **33**, 204 (1994).

[60] R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

Sensitizer	E_T	Product composition **1**	**2**
Acetophenone	73.6	97	3
Benzophenone	68.5	92	2
Flavone	62.0	93	7
2-Acetylnaphthalene	59.6	92	8
1-Acetylnaphthalene	56.4	80	20
Benzil	53.7	55	45
Fluorenone	53.3	57	43
Benzanthrone	47	65	35
3-Acetylpyrene	45	55	45
Anthracene	42.5	85	15

Summarizing these experimental results on conjugated dienes, we find that the singlet state electrocyclization to cyclobutenes generally follows the Woodward-Hoffmann expectation and are disrotatory. There are competing reactions, including formation of bicyclo[1.1.0]butanes and rearrangement products. With direct excitation, the *cis-trans* isomerization occurs by rotation at only one double bond. In contrast, for triplet-sensitized reactions, isomerization can occur at both double bonds (see Section 12.1.2.4). Considerable dimerization is observed in the triplet state reactions. The difference in outcomes of the singlet and triplet processes has been ascribed to differences in the structure of the two excited states. In the singlet state, there is a very close interaction among all of the carbons of the diene system. Transformations of the singlet species are also very fast. The T_1 state is more flexible and longer-lived, which allows the triplet to capture ground state butadiene, leading to dimerization.[61]

Let us now turn to the *photochemical ring opening of cyclobutenes to 1,3-dienes.* This reaction requires excitation with light of $\lambda < 200\,\text{nm}$. Interpretation of the resonance Raman spectra of cyclobutene following photoexcitation provides insight into the dynamics of ring opening and is consistent with the predicted disrotatory stereochemistry.[62] Cyclobutene gives ethene, ethyne, and methylenecyclopropane in addition to butadiene.[63] These competing reactions are believed to occur by ring contraction to a carbene, followed by rearrangement or fragmentation.[64] This species is also formed by excitation of butadiene.



Surprisingly, the ring opening of *cis*- and *trans*-3,4-dimethylcyclobutene is not stereospecific.[65] When irradiated with far-UV light, alkyl-substituted cyclobutenes,

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[61] M. Klessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH Publishers, New York, 1995, pp. 339–341.

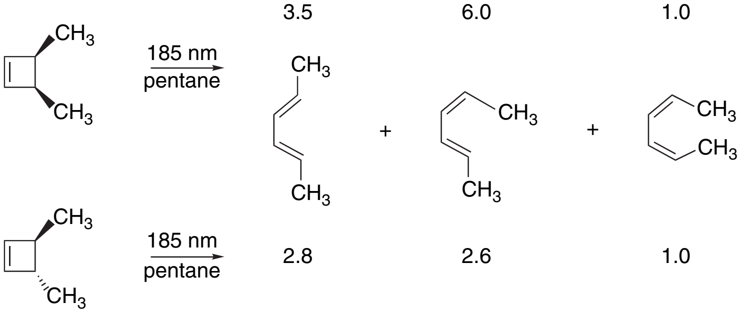
[62] M. K. Lawless, S. D. Wickham, and R. A. Mathies, *J. Am. Chem. Soc.*, **116**, 1593 (1994).

[63] W. Adam, T. Oppenlander, and G. Zang, *J. Am. Chem. Soc.*, **107**, 3921 (1985).

[64] W. J. Leigh, K. Zheng, N. Nguyen, N. H. Werstiuk, and J. Ma, *J. Am. Chem. Soc.*, **113**, 4993 (1993).

[65] K. B. Clark and W. J. Leigh, *J. Am. Chem. Soc.*, **109**, 6086 (1987).

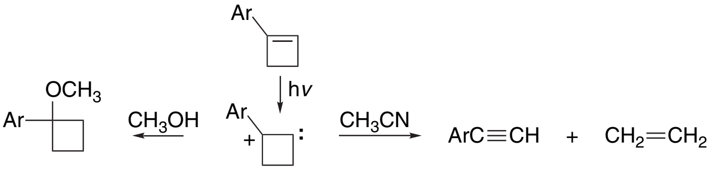
give mixtures of stereoisomers.[66] All of the corresponding butadiene stereoisomers are formed but in different ratios from the stereoisomeric reactants.



A number of other nonstereospecific photolytic ring openings of substituted cyclobutenes have been reported.[67]

These results are not consistent with a concerted disrotatory mechanism for the ring opening and several descriptions of the mechanism have been provided.[64,68] One possibility is that the ring opening proceeds stereospecifically to an *excited state* of the diene, which then decays to the ground state with a stereoselectivity that is independent of the stereochemistry of the original cyclobutene.[69] The transformations are believed to occur via a twisted CI in which all of the π electrons are unpaired, similar to that from singlet excited 1,3-butadiene. Passage through the CI can lead to mixture of stereoisomers.[68] The composition is governed by dynamic and steric factors.

1-Aryl substituted cyclobutenes undergo cycloreversion to arylalkynes but can also give addition products in hydroxylic solvents.[70] These reactions are singlet state processes. The aryl derivatives of cyclobutene do not open to 1,3-butadienes, and based on substituent effects, the excited states appear to have zwitterionic character. These results suggest that the aryl substituent favors the formation of a zwitterionic excited state.



The cyclohexadiene-hexatriene photochemical interconversion is predicted by orbital symmetry considerations to involve conrotatory motion. Cyclohexadiene derivatives undergo photochemical electrocyclic ring opening. The photostationary state

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[66] W. J. Leigh, *Can. J. Chem.*, **71**, 147 (1993); W. J. Leigh, *Chem. Rev.*, **93**, 487 (1993); W. J. Leigh, K. Zheng, and K. B. Clark, *Can. J. Chem.*, **68,** 1988 (1990).

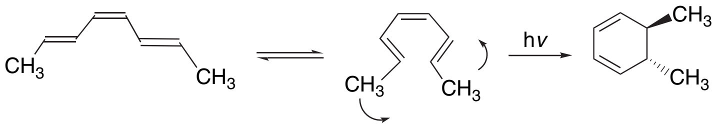
[67] W. G. Dauben and J. E. Haubrich, *J. Org. Chem.*, **53**, 600 (1988); W. J. Leigh and K. Zhang, *J. Am. Chem. Soc.*, **113,** 2163 (1985); G. Maier and A. Bothur, *Eur. J. Org. Chem.*, 2063 (1998).

[68] F. Bernardi, M. Olivucci, and M. A. Robb, *Acc. Chem. Res.*, **23**, 405 (1990); F. Bernardi, M. Olivucci, I. N. Ragazos, and M. A. Robb, *J. Am. Chem. Soc.*, **114**, 2752 (1992).

[69] W. J. Leigh, J. A. Postigo, and K. C. Zheng, *Can. J. Chem.*, **74**, 951 (1996).

[70] W. J. Leigh and J. A. Postigo, *Can. J. Chem.*, **73**, 191 (1995).

favors the triene, and the reaction is highly stereospecific.[71] *E*,*Z*,*E*−Octa-2,4,6-triene gives *trans*-5,6-dimethylcyclohexene.[72]



Ring opening of more highly substituted cyclohexadienes also follows the Woodward-Hoffmann rules.

The conrotatory electrocyclic ring opening of 1,3-cyclohexadiene can be observed by several ultrafast techniques.[73] It is believed that the first step after excitation is attainment of a planar geometry, which occurs within 10^{-11}s.[74] The observations are consistent with an excitation followed by return to the ground state via a CI that permits formation of either reactant or *Z*-1,3,5-hexatriene. The lifetimes of the two excited states are both shorter than 100 fs, and the product is formed within 200 fs.[75] These results are summarized in Figure 12.21.

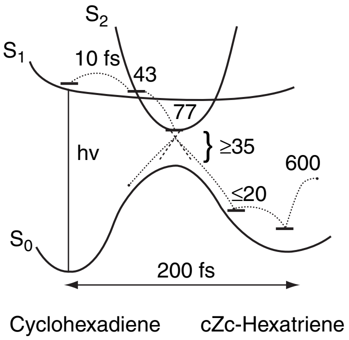


Fig. 12.21. Lifetime in femtoseconds for regions on the potential energy surface for isomerization of 1,3-cyclohexadiene to 1,3,5-hexatriene. Reproduced from *Chem. Phys.*, **232**, 161 (1998) by permission of Elsevier.

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[71] H. J. C. Jacobs and E. Havinga, *Adv. Photochem.*, **11**, 305 (1979); H. J. C. Jacobs and W. H. Laarhoven, in *CRC Press Handbook of Organic Photochemistry and Biology*, W. H. Horspool, ed., CRC Press, Boca Raton, FL, 1995, pp. 155–164.

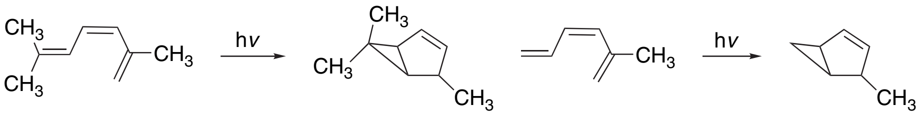
[72] G. J. Fonken, *Tetrahedron Lett.*, 549 (1962).

[73] H. Ihee, V. A. Lebastov, U. M. Gomez, B. M. Goodson, R. Srinivasan, C.-Y. Ruan, and A. H. Zewail, *Science*, **291**, 458 (2001); W. Fuss, W. E. Schmid, and S. A. Trushin, *J. Chem. Phys.*, **112**, 8347 (2000); S. A. Trushin, W. Fuss, T. Schikavski, W. E. Schmid, and K. L. Kompa, *J. Chem. Phys.*, **106**, 9386 (1997); S. H. Pullen, N. A. Anderson, L. A. Walker, II, and R. J. Sension, *J. Chem. Phys.*, **108**, 556 (1998).

[74] P. J. Reid, M. K. Lawless, S. D. Wickham, and R. A. Mathies, *J. Phys. Chem.*, **98**, 5597 (1994); W. Fuss, T. Hoefer, P. Hering, K. L. Kompa, S. Lochbrunner, T. Schikarski, and W. E. Schmid, *J. Phys. Chem.*, **100**, 921 (1996).

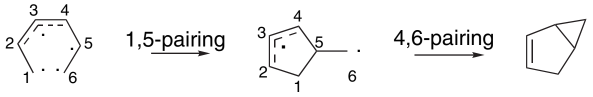
[75] W. Fuss, S. Lochbrunner, A. M. Mueller, T. Schikarski, W. E. Schmid, and S. A. Trushin, *Chem. Phys.*, **232**, 161 (1998).

Particularly interesting photoproducts from hexatrienes are the bicyclo[3.1.0]hex-2-enes.

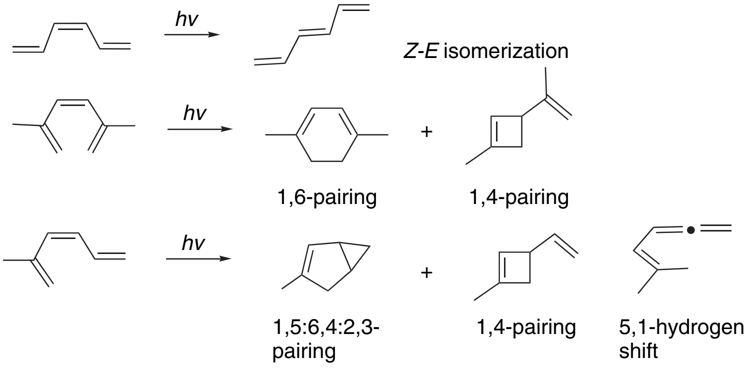


Ref. 76

These products can be formulated as occurring from a tetra-radicaloid CI via a diradical intermediate by (1,5/4,6)-pairing.[77]



The partitioning among *cis-trans* isomerization, closure to cyclohexadiene, and formation of bicyclo[3.1.0]hexenes-2-enes is believed to depend on the conformation of the ground state triene.[78] An extended conformation, as in 1,3,5-hexatriene, is not favorable to cyclization. A conformation that is *s-cis* at both C(2)−C(3) and C(4)−C(5) as well as *Z* at C(3)−C(4) is favorable to electrocyclization. An *s-cis* conformation at C(2)−C(3) and *Z*-configuration at C(3)−C(4) favors formation of the bicyclo[3.1.0]hexene structure.



The stereochemistry of the product from ring opening is also dependent on the ground state conformation of the cyclohexadiene. For example, the composition of

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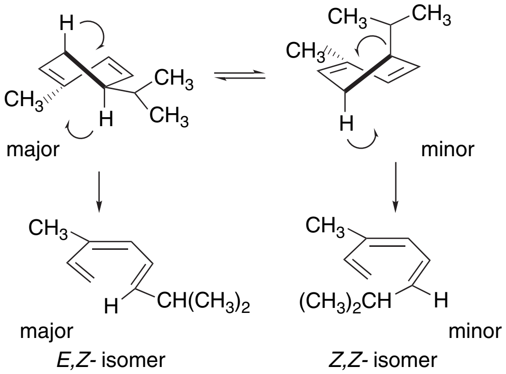
[76] P. Courtot, R. Rumin, and J.-Y. Salaun, *Pure Appl. Chem.*, **49**, 317 (1977); P. Courtot and R. Rumin, *Tetrahedron*, **32**, 441 (1976).

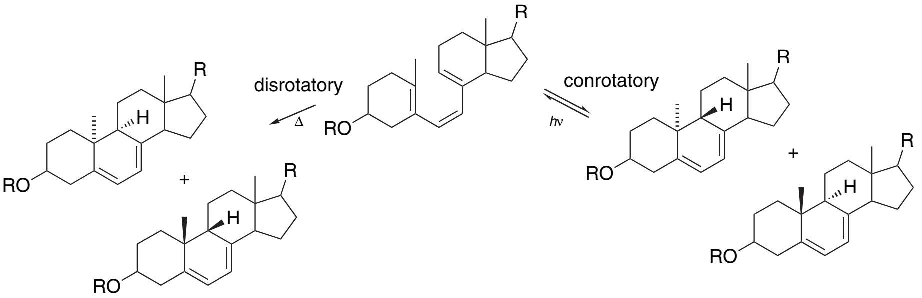
[77] M. Garavelli, R. Celani, M. Fato, M. J. Bearpark, B. R. Smith, M. Olivucci, and M. A. Robb, *J. Phys. Chem. A*, **101**, 2023 (1997).

[78] P. J. Vroegop, J. Lugtenburg, and E. Havinga, *Tetrahedron*, **29**, 1393 (1973); E. Havinga, *Experientia*, **29**, 1181 (1973).

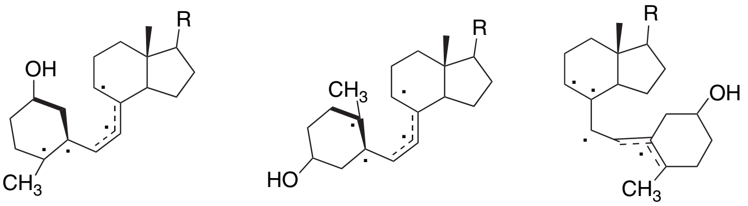
the conrotatory ring-opening products from photolysis of α-phellandrene mirrors the ground state conformational equilibrium.[79]



These results are in accord with orbital symmetry principles. Indeed, examples found in the study of vitamin D provided the initial examples of the dichotomy between thermal and photochemical processes that led to development of the concepts underlying the Woodward-Hoffmann rules for photochemical reaction.[80] It was found that the triene precalciferol gave ergosterol on photocyclization, but the stereoisomer lumisterol on heating.



The vitamin D photochemical system can also be interpreted in terms of CIs with tetraradicaloid character. Three such structures have been identified by computation, and they account for the observed products.[81]



Thus, looking broadly over these results on electrocyclic reactions of conjugated systems, we find that the picture is in general accord with orbital symmetry considerations, *except for the nonstereospecific ring opening of cyclobutenes*. The results also

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[79] J. E. Baldwin and S. M. Krueger, *J. Am. Chem. Soc.*, **91**, 6444 (1969).

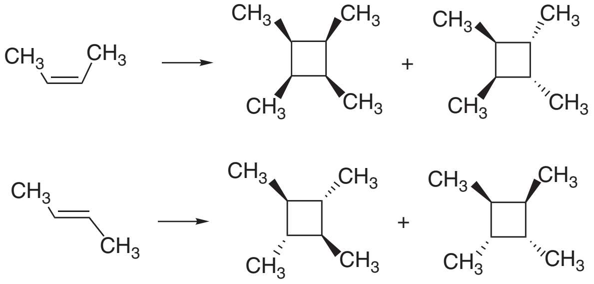
[80] R. B. Woodward, in *Aromaticity*, Chemical Society Special Publication No. 21, 217 (1967); E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); J. A. Berson, *Tetrahedron*, **48**, 3 (1992).

[81] F. Bernardi, M. Olivucci, I. N. Ragazos, and M. A. Robb, *J. Am. Chem. Soc.*, **114**, 8211 (1992).

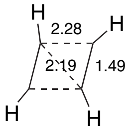
indicate the importance of reactant conformation in influencing the reaction outcome. By contrast, the ring opening of cyclobutenes is more complex. In Topic 12.1 we take a look at the computational interpretation of these results.

12.2.6. Photochemical Cycloaddition Reactions

As described on p. 1098, the original orbital symmetry interpretation of alkene $[2\pi + 2\pi]$ cycloaddition was in terms of a suprafacial transition structure with a rectangular geometry. This arrangement leads to a photochemical process that is allowed by orbital symmetry criteria. Early experimental work also provided examples of stereospecific $[2\pi + 2\pi]$ cycloadditions, lending support to a concerted reaction path. For example, dimerization of *Z*-2-butene gives two products that retain *cis*-methyl groups. The adducts from *E*-2-butene have *trans*-methyl groups.[82] This establishes that the configuration is retained at both alkene double bonds during the formation of the dimers.



The prototypical ethene + ethene cycloaddition has been explored computationally and a somewhat different picture has emerged.[83] The CI for ethene dimerization is calculated to be rhomboid.[84]



These computations lead to an energy surface featuring the rhomboid CI, which can lead to formation of cyclobutane or separation into two ethene molecules, as shown in Figure 12.22. Point *E* is the rhomboid CI that permits rapid return to the ground state surface. The process is expected to be very fast and this is consistent with the observed retention of alkene stereochemistry in substituted cases. In contrast to the pathway through the rhomboid CI, a completely symmetrical rectangular approach does not lead to minima.

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[82] H. Yamazaki and R. J. Cvetanovic, *J. Am. Chem. Soc., Chem. Commun.*, **91**, 520 (1969).

[83] F. Bernardi, S. De, M. Olivucci, and M. A. Robb, *J. Am. Chem. Soc.*, **112**, 1737 (1990); F. Bernardi, A. Bottini, M. Olivucci, A. Venturini, and M. A. Robb, *J. Chem. Soc., Faraday Trans.*, **90**, 1617 (1994).

[84] F. Bernardi, M. Olivucci, and M. A. Robb, *Pure Appl. Chem.*, **67**, 17 (1995).

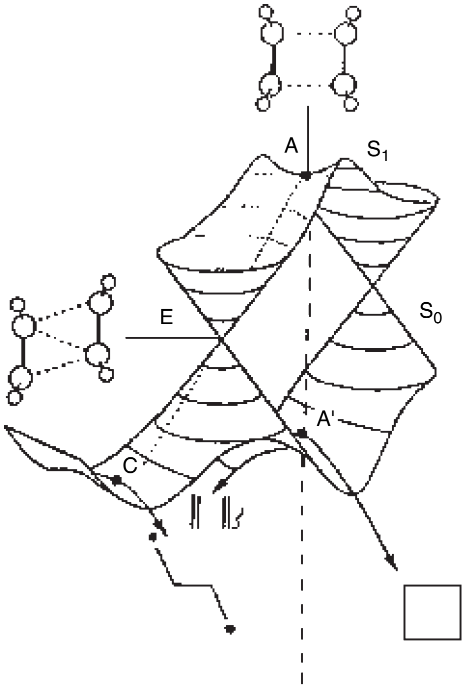
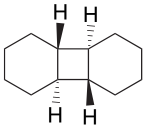
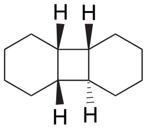


Fig. 12.22. Energy surface depicting the S_1 and S_0 potential energy surfaces for singlet state photodimerization of ethene. Adapted from *J. Photochem. Photobiol.*, **105**, 365 (1997), by permission of Elsevier.

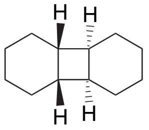
Photodimerization of cyclohexene sensitized by xylene gives a low yield of a mixture of stereoisomers. The reaction was interpreted as a $Z \rightarrow E$ isomerization followed by a nonstereospecific ground state $[2\pi + 2\pi]$ addition.[85]



2%



2.6%



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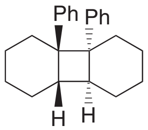
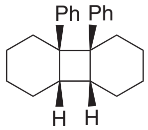
1-Phenylcyclohexene can be photodimerized by irradiation at λ > 280 nm.[86] *E*-2-Phenylcyclohexene is generated under these conditions and can be trapped in methanol. The fact that the tail-to-tail products are formed from both singlet and triplet excited states indicates an intermediate with diradical character.





With high-intensity (laser) irradiation, the reaction also gives stereoisomeric $[2+4]$ dimers. These products are believed to be formed by dimerization of the *E*-isomer.

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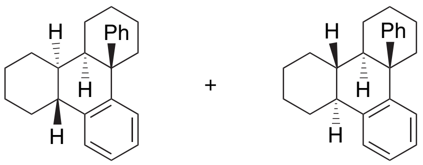
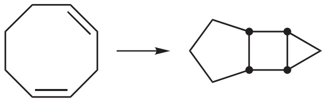
[85] P. J. Kropp, J. J. Snyder, P. C. Rawlings, and H. G. Fravel, Jr., *J. Org. Chem.*, **45**, 4471 (1980).

[86] D. J. Unett, R. A. Caldwell, and D. C. Hrncir, *J. Am. Chem. Soc.*, **118**, 1682 (1996).

Under low intensity, the concentration of the *E*-isomer is too low to permit this reaction.

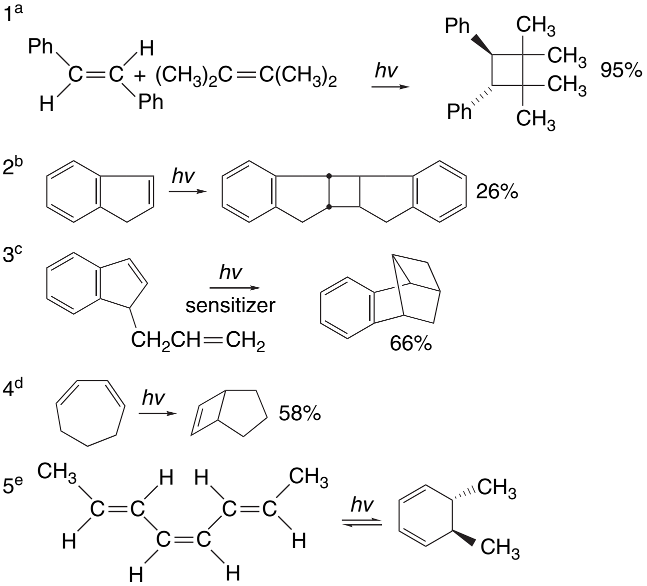


Intramolecular cycloaddition is observed for 1,4-cyclooctadiene.[87]



The most useful intermolecular $[2\pi + 2\pi]$ cycloadditions from a synthetic point of view involve alkenes and cyclic α,ß-unsaturated carbonyl compounds. These reactions are discussed in more detail in Section 6.3.2 of Part B. Scheme 12.1 lists some examples of photochemical cycloaddition and electrocyclic reactions of the type that are consistent with the predictions of orbital symmetry considerations.

Scheme 12.1. Examples of Electrocyclic Reactions and Cycloadditions



a. O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **99**, 2333 (1968).
b. A. G. Anastassiou, F. L. Setliff, and G. W. Griffin, *J. Org. Chem.*, **31**, 2705 (1966).
c. A. Padwa, S. Goldstein, and M. Pulwer, *J. Org. Chem.*, **47**, 3893 (1982).
d. O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).
e. G. J. Fonken, *Tetrahedron Lett.*, 549 (1962).

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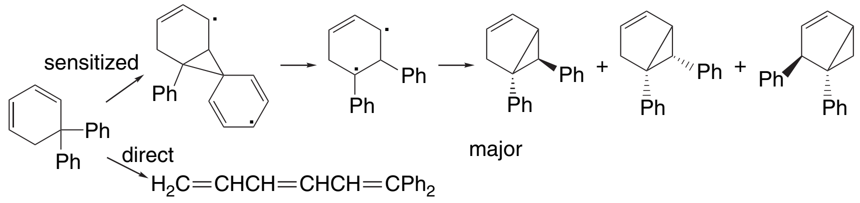
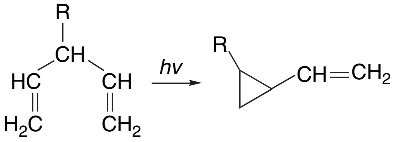
[87] S. Moon and C. R. Ganz, *Tetrahedron Lett.*, 6275 (1968).

12.2.7. Photochemical Rearrangements Reactions of 1,4-Dienes

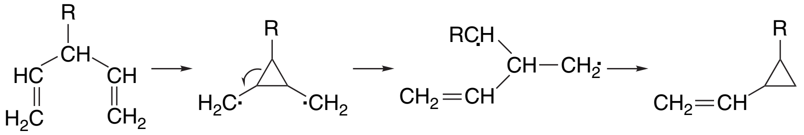
In addition to the electrocyclic and cycloaddition reactions described earlier, certain dienes undergo interesting rearrangements. For example, 5,5-diphenylcyclohexa-1,3-diene shows divergent photochemical behavior, depending on whether the reaction in induced by direct irradiation or by photosensitization. On direct irradiation, the electrocyclic ring opening to 1,1-diphenylhexatriene is dominant, whereas a rearrangement involving migration one of the aromatic rings is the major reaction of the triplet excited state formed by photosensitization.[88]



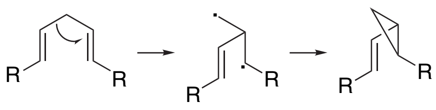
The latter reaction is an example of *the di-π-methane rearrangement*,[89] which is a quite general reaction for 1,4-dienes and other systems that have two π systems separated by an sp^3-carbon atom. The π systems can be a double bond, an aromatic ring, or, as we will see in Section 12.3, a carbonyl group.



The transformation can be formulated in terms of bonding between C(2) and C(4) involving formation of a cyclopropyl diradical intermediate. This diradical can fragment to form a new 1,3-diradical that gives the cyclic product.



An alternative mechanism involves a direct migration of one of the vinyl groups, followed by formation of the ring.[90]



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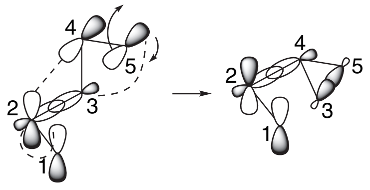
[88] H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972); J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *J. Am. Chem. Soc.*, **93**, 4808 (1971); M.-D. Su, *J. Org. Chem.*, **60**, 6621 (1995).

[89] For reviews of the di-π-methane rearrangement, see S. S. Hixson, P. S. Mariano, and H.E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); H. E. Zimmerman, in *Rearrangements in Ground and Excited States*, Vol. 3, P. de Mayo, ed., Academic Press, New York, 1980, Chap. 16; H. E. Zimmerman, in *Organic Photochemistry and Photobiology*, W. H. Horspool and P.-S. Song, eds., CRC Press, Boca Raton. FL, 1995, pp. 184–193; H. E. Zimmerman and D. Armesto, *Chem. Rev.*, **96**, 3065 (1996).

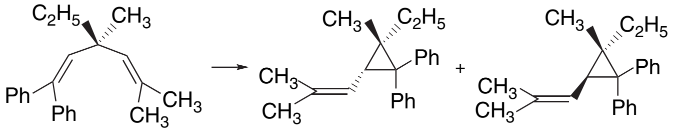
[90] L. A. Paquette and E. Bay, *J. Org. Chem.*,**47**, 4597 (1982).

In some cases, the di-π-methane rearrangement can proceed through either a singlet or a triplet excited state.[91] The singlet reaction can be formulated as a concerted process, and this mechanism is followed in the case of some acyclic dienes and for cyclic systems in which a concerted process is sterically feasible. Note that the orbital array is of the Mobius topology with a phase change depicted between the C(1) and C(2) positions. This corresponds to an allowed photochemical process since there are six electrons involved in bonding changes and this is an antiaromatic system.



orbital array for concerted
di-π-methane rearrangement

The di-π-methane rearrangement is a stereospecific reaction. There are several elements of stereochemistry to be considered. It is known that the double bond that remains uncyclized retains the *E*- or *Z*-configuration present in the starting material. This result excludes any intermediate with a freely rotating terminal radical. The concerted mechanism implies that C(3) would undergo inversion of configuration since the new C(3)−C(5) bond is formed using the back lobe of the C(2)−C(3) σ-bond. This inversion of configuration has been confirmed.[92]



Thus the TS depicted above for the concerted reaction correctly predicts the stereochemical course of the di-π-methane rearrangement, as does the computational analysis discussed below.

The di-π-methane rearrangement of 1,4-pentadiene has been modeled using CAS-SCF/4-31G calculations. The results indicate that a singlet 1,3-diradical is the key intermediate.[93] This species can be reached from the excited state via a CI that involves vinyl migration. It consists of a vinyl group associated with the central carbon of an allylic system and is similar in structure to the CI involved in alkene sigmatropic rearrangements (see p. 1093). The structure of the CI is also consistent with the

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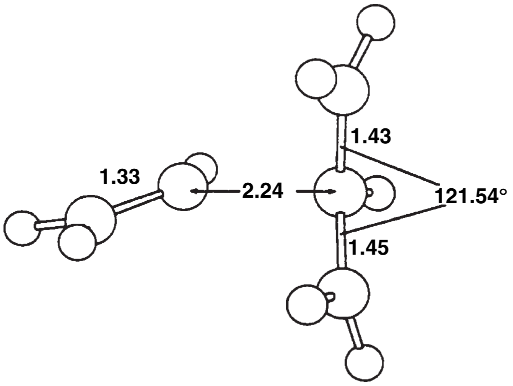
[91] H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969); P. S. Mariano, R. B. Steitle, D. G. Watson, M. J. Peters, and E. Bay, *J. Am. Chem. Soc.*, **98**, 5899 (1976).

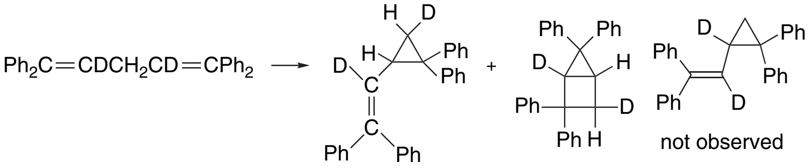
[92] H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Am. Chem. Soc.*, **96**, 1974, 4630 (1974).

[93] M. Reguero, F. Bernardi, H. Jones, M. Olivucci, I. N. Ragazos, and M. A. Robb, *J. Am. Chem. Soc.*, **115**, 2073 (1993).

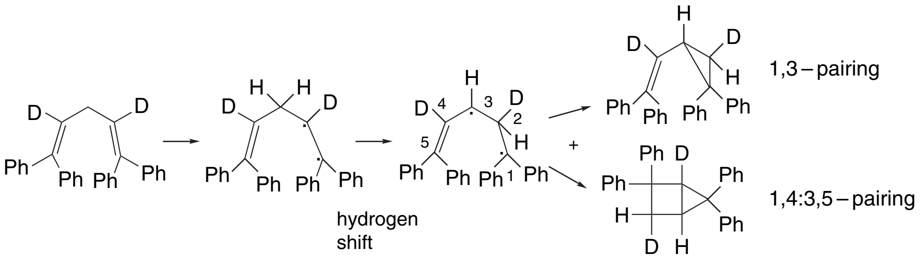
observed stereochemistry of the reaction. It remains to be seen if this mechanism applies to the more highly substituted systems that have been studied experimentally.



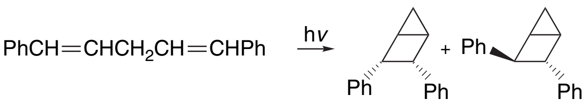
The di-π-methane rearrangement has been studied in a sufficient number of cases to recognize some of the substituent effects. When the central sp^3-carbon is unsubstituted, the di-π-methane path becomes less favorable. The case of 1,1,5,5-tetraphenyl-1,4-pentadiene is illustrative. Although one of the products has the expected structure for di-π-methane rearrangement, labeling with deuterium proves that an alternative mechanism operates.



The cyclopropane ring is formed only after hydrogen atom migration. The driving force for this migration may be the fact that it produces a more stable allylic radical. The resulting 1,3-diradical can re-pair to give the observed products.



Photolysis of 1,5-diphenyl-1,4-pentadiene is another example where a compound undergoes cycloaddition in preference to di-π-methane rearrangement.[94]



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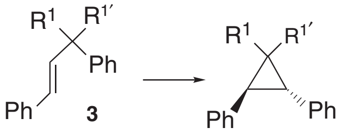
[94] E. Block and H. W. Orf, *J. Am. Chem. Soc.*, **94**, 8438 (1972).

The resistance of the 3-unsubstituted system to the di-π-methane rearrangement probably occurs at the stage of the vinyl rearrangement.[95] If the central carbon is unsubstituted this step results in the formation of a primary radical and would be energetically unfavorable.

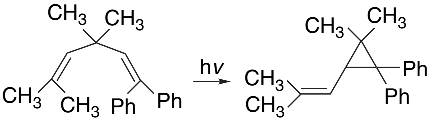
Kinetic studies of **3a**, **3b**, and **3c** have provided experimental evidence that a cyclopropyl diradical is an intermediate.[96] The product composition reveals a temperature dependence that implicates an intermediate. These compounds undergo both *cis-trans* isomerization and di-π-methane rearrangement on direct irradiation and mainly *cis-trans* isomerization when photosensitized (triplet) by benzophenone. The quantum yield of the di-π-methane rearrangement increases dramatically with substitution at the allylic position.



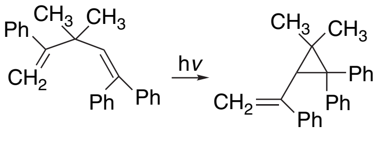
3

	$R^1,R^{1'}$	Φ $E-Z$	Φ di−π−methane
a	H,H	.30	.005
b	H,CH_3	.11	.21
c	CH_3,CH_3	.074	.42

The groups at the termini of the 1,4-pentadiene system also affect the efficiency and direction of the di-π-methane reaction. The general trend is that cyclization occurs at the diene terminus that best stabilizes radical character. Thus, a terminus substituted with aryl groups will cyclize in preference to an unsubstituted or alkyl-substituted terminus.



Ref. 97



Ref. 98

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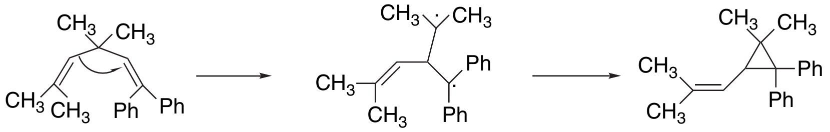
[95] H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **95**, 2957 (1973).

[96] F. D. Lewis, X. Zuo, R. S. Kalgutkar, M. A. Miranda, E. Font-Sanchis, and J. Perez-Prieto, *J. Am. Chem. Soc.*, **122**, 8571 (2000); F. D. Lewis, X. Zuo, R. S. Kalgutkar, J. M. Wagner-Brennan, M. A. Miranda, E. Font-Sanchis, and J. Perez-Prieto, *J. Am. Chem. Soc.*, **123**, 11883 (2001).

[97] H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, **92**, 1409 (1970).

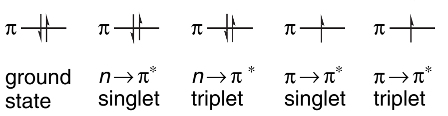
[98] H. E. Zimmerman and A. A. Baum, *J. Am. Chem. Soc.*, **93**, 3646 (1971).

This result can be rationalized in terms of the vinyl migration mechanism by noting that rearrangement will occur to give the more stable of the two possible 1,3-diradicals.[99] The cyclopropane ring in the final product will then incorporate this terminus.



12.3. Photochemistry of Carbonyl Compounds

The photochemistry of carbonyl compounds has been extensively studied, both in solution and in the gas phase. There are major differences between the two phases. In the gas phase, the energy transferred by excitation is not lost rapidly by collision, whereas in the liquid phase the excess vibrational energy is rapidly transferred to the solution. We emphasize solution photochemistry here because both mechanistic study and preparative applications of organic reactions usually involve solution processes. The reactive excited state of alkyl ketones is usually the n-π^* state. On excitation, an electron from an oxygen nonbonding orbital is transferred to the π-antibonding orbital of the carbonyl group. The singlet excited state is formed initially, but intersystem crossing to the triplet can occur. For saturated ketones, the singlet and the triplet lie, respectively, about 80–85 and 75–80 kcal/mol above the ground state. The first excited singlet (S_1) and triplet (T_1) can be described structurally from spectroscopic data available for formaldehyde, which is the simplest analog. In both excited states, the molecule is pyramidal, the C−O bond is lengthened, and the dipole moment is reduced.[100] The reduction of the dipole moment results from the transfer of electron density from an orbital localized on oxygen to one that also encompasses the carbon atom. An alternative excited state involves promotion of a bonding π electron to the antibonding π^* orbital. This is called the π-π^* excited state and is most likely to be involved when the carbonyl group is conjugated with an extended π-bonding system, as is the case for aryl ketones. The excited carbonyl groups have radical character at both carbon and oxygen, and the oxygen is rather similar in its reactivity to alkoxyl radicals. The MO diagrams for the n-π^* and π-π^* states are depicted below.



MP2/6-311G calculations have described the geometric and charge distribution of the excited state of formaldehyde as summarized below.[101] Three valence shell

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[99] H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, **92**, 6259, 6267 (1970).

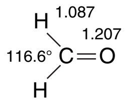
[100] J. C. D. Brand and D. G. Williamson, *Adv. Phys. Org. Chem.*, **1**, 365 (1963); D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966).

[101] C. M. Hadad, J. B. Foresman, and K. B. Wiberg, *J. Phys. Chem.*, **97**, 4293 (1993).

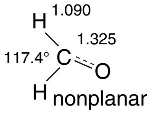
excited states corresponding to $n_y \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n_z \rightarrow \pi^*$ have been described, and there are several Rydberg states as well. The atomic populations and bond orders were calculated using the AIM method.

		Atomic population						Bond order			
		C		O		H		C–O		C–H	
State	E (eV)	π	Total	π	Total	π	Total	π	Total	π	Total
S_0	0.00	0.431	4.833	1.541	9.207	0.014	0.980	0.664	1.43	0.006	0.958
$n_y \rightarrow \pi^*$	4.58	1.025	5.438	1.890	8.821	0.043	0.871	0.094	0.871	0.000	0.886
$\pi \rightarrow \pi^*$	9.19	0.521	5.170	1.425	9.063	0.028	0.883	0.171	0.957	0.011	0.867
$n_z \rightarrow \pi^*$	9.97	1.069	5.467	1.844	8.674	0.043	0.930	0.263	0.797	0.041	0.943

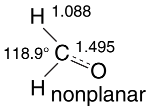
According to these results the $n_y \rightarrow \pi^*$ shows $0.39e$ and $0.11e$ lost from O and H, respectively, whereas C gains $0.61e$ compared to the ground state. The $\pi \rightarrow \pi^*$ state shows a smaller loss from both O ($0.140\,e$) and from H (0.10). The π bond order in all the excited states is decreased by the population of an antibonding π^* orbital. The charge shifts in the σ and π systems are in opposite senses, but the overall effect is that the O becomes less electron rich and takes on the character of an electrophilic radical. The excited states are nonplanar. Some of the computed bond distances and angles are shown below.[102]



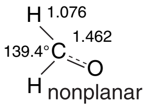
S_0



$n_y \rightarrow \pi^*$

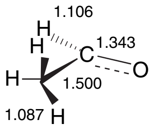


$\pi \longrightarrow \pi^*$



$n_z \longrightarrow \pi^*$

The excited states of other saturated carbonyl compounds are similar. Alkyl groups somewhat stabilize the excited state and reduce the excitation energy. In acetaldehyde, the conformation of the $n \rightarrow \pi^*$ state changes from the H–O eclipsed structure in the ground state (see p. 148) to an H–O staggered conformation.[103]



For conjugated carbonyl compounds, such as α,ß-enones, the orbital diagram is similar, except that the HOMO of the ground state is ψ_2 of the enone system, rather than an oxygen unshared pair orbital. In the π-π^* state, the C=O and C=C bonds lengthen and the C(1)–C(2) bond shortens.[104] Population of the π^* orbital shifts

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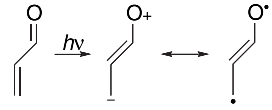
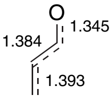
[102] M. Dallos, T. Muller, H. Lischka, and R. Shepard, *J. Chem. Phys.*, **114**, 746 (2001).

[103] J. M. Price, J. A. Mack, G. v. Helden, X. Yang, and A. M. Wodtke, *J. Phys. Chem.*, **98**, 1791 (1994).

[104] C. S. Page and M. Olivucci, *J. Comput. Chem.*, **24**, 298 (2003).

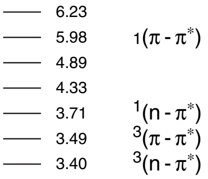
electron density from oxygen to carbon. The excited state can be represented as a hybrid with dipolar and diradical structures.





Although Lewis structures of this type are not entirely adequate descriptions of the excited states, they do correspond to the MO picture by indicating polarization of charge and the presence of polar radical-like centers. In addition to the increased energy content, the high reactivity of the excited states is associated with the presence of half-filled orbitals. The two SOMO orbitals in the excited states have enhanced radical, cationic, or anionic character.

For aromatic carbonyl compounds, as for styrene (see p. 1084), there are excited states associated with the aromatic ring. The absorption spectrum of benzaldehyde, for example, is believed to include two triplet levels and at least five singlet bands.[105]

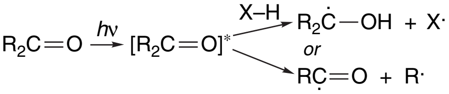


Computed absorption
levels in eV for benzaldehyde

For acetophenone, the S_1 state, like acetaldehyde adopts a H–C–C–O staggered conformation, whereas T_1 retains the eclipsed conformation found in the ground state.[106]

12.3.1. Hydrogen Abstraction and Fragmentation Reactions

One of the most common reactions of photoexcited carbonyl groups is hydrogen atom abstraction from solvent or some other hydrogen donor. A second common reaction is cleavage of the carbon-carbon bond adjacent to the carbonyl group, which is called *α-cleavage*.



The hydrogen atom abstraction can be either intramolecular or intermolecular. The intermediates that are generated are free radicals. If these radicals come to thermal equilibrium, they have the same structure and reactivity as radicals generated by

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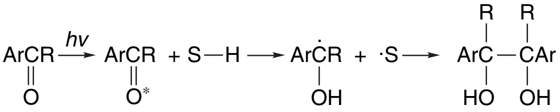
[105] V. Molina and M. Merchan, *J. Phys. Chem. A*, **105**, 3745 (2001).
[106] J. L. Tomer, L. H. Spanler, and D. W. Pratt, *J. Am. Chem. Soc.*, **110,** 1615 (1988).

thermal processes. Many aromatic ketones react by hydrogen atom abstraction and the stable products are diols formed by coupling of the resulting α-hydroxybenzyl radicals.



These reactions usually occur via the triplet excited state T_1. The intersystem crossing of the initially formed singlet excited state is so fast ($k \sim l0^{10}\ \mathrm{s}^{-1}$) that reactions of the S_1 state are usually not observed. The reaction of the benzophenone T_1 state has been particularly closely studied. Some of the facts that have been established in support of the general mechanism outlined above are as follows:

1. For a given hydrogen donor S—H, replacement by S—D leads to a decreased rate of reduction, relative to nonproductive decay to the ground state.[107] This decreased rate is consistent with a primary isotope effect in the hydrogen abstraction step.
2. The photoreduction can be quenched by known triplet quenchers. The effective quenchers are those that have T_1 states less than 69 kcal/mol above S_0. Quenchers with higher triplet energies are ineffective because the benzophenone π-π* triplet is not sufficiently energetic to effect energy transfer.
3. The intermediate diphenylhydroxymethyl radical has been detected after generation by flash photolysis.[108] Photolysis of benzophenone in benzene solution containing potential hydrogen donors results in the formation of two intermediates that are detectable, and their rates of decay have been measured. One intermediate is the $\mathrm{Ph_2\dot{C}OH}$ radical, which disappears by dimerization in a second-order process. A much shorter-lived species disappears with first-order kinetics in the presence of excess amounts of various hydrogen donors. The pseudo-first-order rate constants vary with the structure of the donor; with 2,2-diphenylethanol, for example, $k = 2 \times 10^6\ \mathrm{s}^{-1}$. The rate is much less with poorer hydrogen atom donors. The rapidly reacting intermediate is the triplet excited state of benzophenone.
4. In 2-propanol, the quantum yield for dimeric conversion of benzophenone to the dimeric reduction product is 2.0.[109] The reason is that the radical remaining after abstraction of a hydrogen atom from 2-propanol transfers a hydrogen atom to ground state benzophenone in a nonphotochemical reaction. Because of this process, two molecules of benzophenone are reduced for each one that is photoexcited. These results suggest the following mechanism:

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[107] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

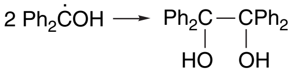
[108] J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

[109] N. J. Turro, *Molecular Photochemistry*, W. A. Benjamin, New York, 1965, pp. 143, 144.

$$\mathrm{Ph_2C{=}O} \xrightarrow{h\nu} \mathrm{[Ph_2C{=}O]^*}$$

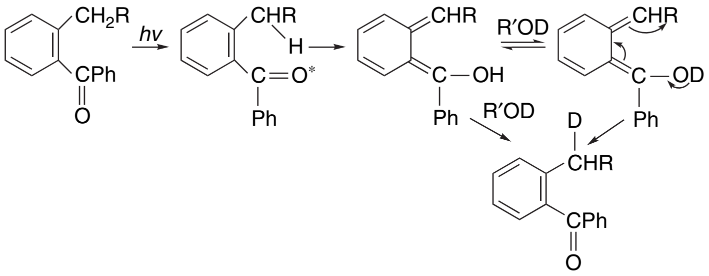
$$\mathrm{[Ph_2C{=}O]^* + (CH_3)_2CHOH \longrightarrow Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH}$$

$$\mathrm{(CH_3)_2\dot{C}OH + Ph_2C{=}O \longrightarrow Ph_2\dot{C}OH + (CH_3)_2C{=}O}$$

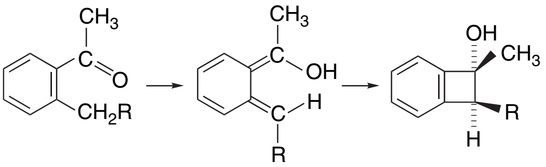


$$\mathrm{2\,Ph_2\dot{C}OH \longrightarrow Ph_2\underset{HO}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}Ph_2}$$

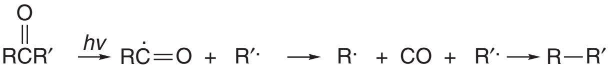
The efficiency of photoreduction of benzophenone derivatives is greatly diminished when an *ortho* alkyl substituent is present because a new photoreaction, intramolecular hydrogen atom transfer, becomes the dominant process. Hydrogen abstraction takes place from the benzylic position on the adjacent alkyl chain, giving an unstable enol that can revert to the original benzophenone without photoreduction. This process, known as *photoenolization*,[110] can be detected by photolysis in deuterated hydroxylic solvents even though there is no net transformation of the reactant. The proton of the enolic hydroxyl is rapidly exchanged with solvent, so deuterium is introduced at the benzylic position. Deuterium is also introduced if the enol is protonated at the benzylic carbon by solvent.



The reactive dienols can also undergo thermal electrocyclization to cyclobutenols.[111]



The dominant photochemical reaction of ketones in the gas phase is cleavage of one of the carbonyl substituents, which is followed by decarbonylation and subsequent reactions of the free radicals that are formed. The initial cleavage occurs within 100 fs of excitation. There is an activation barrier for decarbonylation (see Table 11.2), so decarbonylation can be relatively slow with excitation at 270 nm.[112] At shorter wavelengths, there may be sufficient excess energy for rapid decarbonylation. This reaction is referred to as the *Type-I or α-cleavage* reaction of carbonyl compounds.



$$\mathrm{R\overset{O}{\overset{\|}{C}}R' \xrightarrow{h\nu} R\dot{C}{=}O + R'\cdot \longrightarrow R\cdot + CO + R'\cdot \longrightarrow R{-}R'}$$

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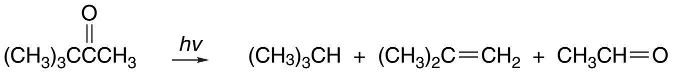
[110] P. G. Sammes, *Tetrahedron*, **32**, 405 (1976).

[111] P. J. Wagner, D. Subrahmayam, and B.-S. Park, *J. Am. Chem. Soc.*, **113**, 709 (1991).

[112] S. K. Kim and A. H. Zewail, *Chem. Phys. Lett.*, **250**, 279 (1996); E. W. G. Diau, C. Kotting, T. I Solling, and A. H. Zewail, *Chem. Phys. Chem.*, **3**, 57 (2000); A. P. Baronavski and J. C. Owrutsky, *Chem. Phys. Lett.*, **33**, 36 (2001).

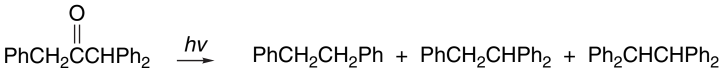
The energetics of α-cleavage and decarbonylation depend on the structure of the ketone. For acetone, the S_1 and T_1 states are 88 and 80 kcal/mol above the ground state, respectively. For acetone, both α-cleavage and decarbonylation are slightly endothermic, owing to the low stability of the methyl radical.[113] However, the reaction is exothermic with radical-stabilizing substituents, as illustrated in Figure 12.23.

Dibenzyl ketone, for example, is readily cleaved photolytically.[114] Similarly, *t*-butyl ketones undergo α-cleavage quite readily on photolysis in solution.[115] The radicals generated undergo coupling, disproportionation, and hydrogen abstraction reactions.



$$(CH_3)_3C\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{h\nu} (CH_3)_3CH + (CH_3)_2C{=}CH_2 + CH_3CH{=}O$$

Ref. 115



$$PhCH_2\overset{\overset{O}{\|}}{C}CHPh_2 \xrightarrow{h\nu} PhCH_2CH_2Ph + PhCH_2CHPh_2 + Ph_2CHCHPh_2$$

Ref. 114

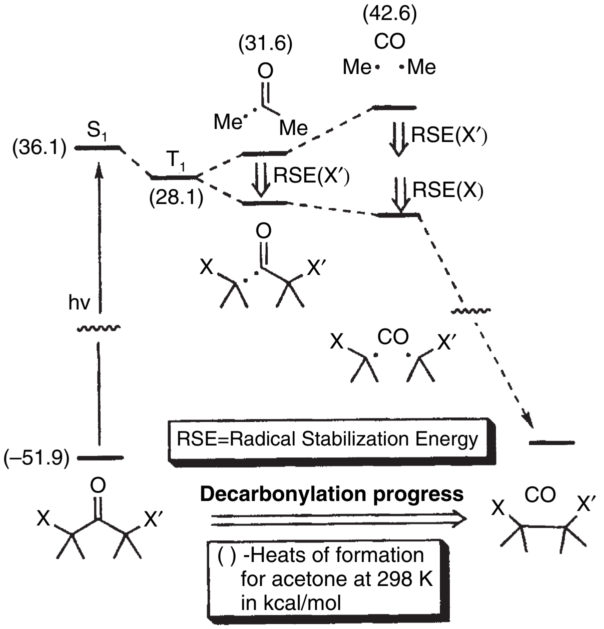


Fig. 12.23. Energetics for α-cleavage and decarbonylation of acetone showing the effect of radical stabilization. Reproduced from *J. Org. Chem.*, **67**, 3749 (2002), by permission of the American Chemical Society.

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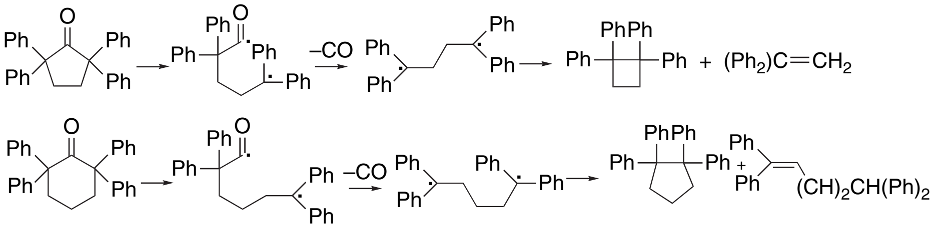
[113] L. M. Campos, H. Dang, D. Ng, Z. Yang, H. L. Martinez, and M. A. Garcia-Garibay, *J. Org. Chem.*, **67**, 3749 (2002).

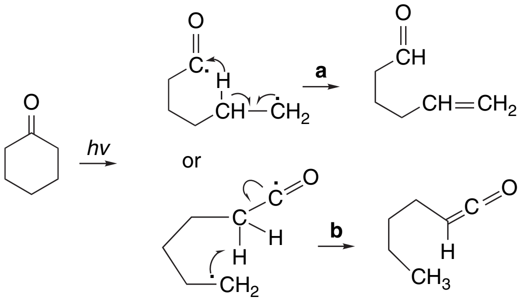
[114] G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).

[115] N. C. Yang and E. D. Feit, *J. Am. Chem. Soc.*, **90**, 504 (1968).

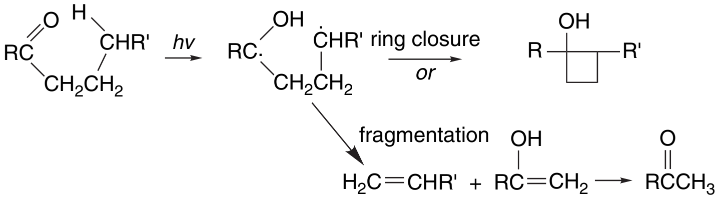
Ketones such as 2,2,5,5-tetraphenylcyclopentanone and 2,2,6,6-tetraphenylcyclohexanone decarbonylate readily because of the stabilization afforded by the phenyl groups. The products result from recombination, disproportionation, or fragmentation of the diradical intermediate.[116]



With some cyclic ketones, the α-cleavage can also be followed by intramolecular hydrogen abstraction that eventually leads to an unsaturated ring-opened aldehyde.[117] An alternative reaction path involves formation of a ketene. The competition between these two reactions is determined by the effect of substituents on the conformation and reactivity of the diradical intermediate.[118]



For ketones having propyl or longer alkyl groups as a carbonyl substituent, intramolecular hydrogen abstraction can be followed by either cleavage of the bond between the α- and ß-carbon atoms or by formation of a cyclobutanol.



Cleavage between C_α and $C_ß$ is referred to as *Type-II photoelimination* to distinguish it from α-cleavage. Type-II photoeliminations are observed for both aryl and allyl ketones.[119] Studies aimed at establishing the identity of the reactive excited state

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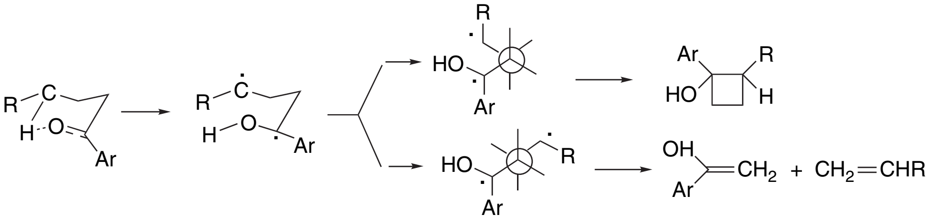
[116] D. H. R. Barton, B. Charpiot, K. U. Ingold, L. J. Johnston, W. B. Motherwell, J. C. Scaiano, and S. Stanforth, *J. Am. Chem. Soc.*, **107**, 3607 (1985).

[117] W. C. Agosta and W. L. Schreiber, *J. Am. Chem. Soc.*, **93**, 3947 (1971); P. J. Wagner and R. W. Spoerke, *J. Am. Chem. Soc.*, **91**, 4437 (1969).

[118] P. J. Wagner, *Top. Curr. Chem.*, **61**, 1 (1976).

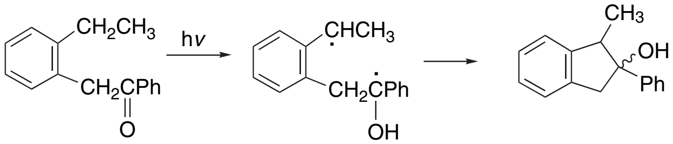
[119] P. J. Wagner and P. Klan, in *CRC Handbook of Photochemistry and Photobiology*, W. Horspod and F. Lenci, eds., CRC Press, Boca Raton, FL, 2004, Chap 52.

indicate that both S_1 and T_1 are involved for allyl ketones, but when one of the carbonyl substituents is aryl, intersystem crossing is very fast and T_1 is the reactive state. Theoretical analysis indicates that the hydrogen abstraction involves an in-plane (*n*) orbital on oxygen, rather than a π orbital. Usually, cleavage is the dominant reaction, with cyclobutanol yields being rather low, but there are exceptions. Activation energies for the hydrogen abstraction process from a methylene group are about 4 kcal, whereas the activation energy for carbon-carbon bond cleavage is 8–12 kcal. The competition between these two processes can be understood in terms of the structure and conformation of the diradical intermediates.[120] The hydrogen abstraction reaction is believed to occur through a chairlike conformation. The diradical can give cyclobutanol from the *gauche* conformation or fragment through the *anti* conformation.

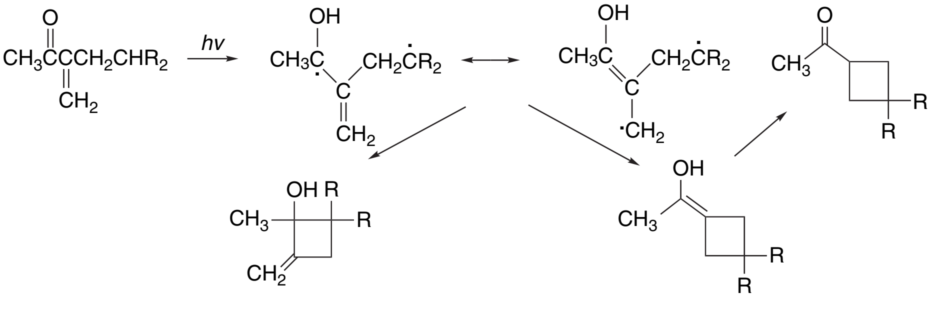


The nature of substituents on the aryl ring can affect the balance between the competing reactions.[121]

With aryl benzyl ketones, indanols can be formed.[122] This is a particularly favorable case because of the benzylic stabilization of both radical sites.



Intramolecular hydrogen atom abstraction is also an important process for acyclic α,ß-unsaturated ketones.[123] The intermediate diradical then cyclizes to give the enol of a cyclobutyl ketone. Among the by-products of such photolyses are methylenecyclobutanols resulting from alternative modes of cyclization of the diradical intermediate.



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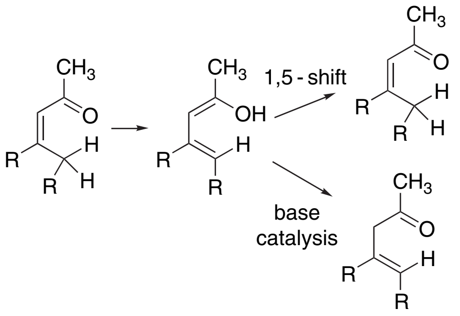
[120] P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

[121] M. V. Encina, E. A. Lissi, E. Lemp, A. Zanocco, and J. C. Scaiano, *J. Am. Chem. Soc.*, **105**, 1856 (1983).

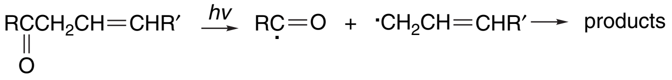
[122] P. J. Wagner, A. Zand, and B.-S. Park, *J. Am. Chem. Soc.*, **118**, 12856 (1996).

[123] R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 4873 (1973); R. A. Cormier and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 618 (1974).

α,ß-Unsaturated ketones with γ-hydrogens can undergo hydrogen atom transfer resulting in formation of a dienol. Because the hydrogen atom transfer occurs through a cyclic TS, the originally formed dienol has *Z*-stereochemistry. The dienol is unstable and two separate processes have been identified for ketonization: a [1,5]-sigmatropic shift of hydrogen leading back to the conjugated enone and a base-catalyzed proton transfer that leads to the ß,γ-enone.[124] The deconjugated enone is formed because of a kinetic preference for reprotonation of the dienolate at the α-carbon. Photochemical deconjugation is a synthetically useful way of effecting isomerization of α,ß-unsaturated ketones and esters to the ß,γ-isomers.

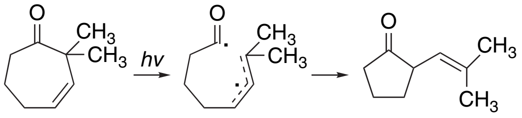


Ketones in which the double bond is located in the ß,γ-position are likely candidates for α-cleavage because of the stability of the allyl radical that is formed. This is an important process in direct irradiation. Products then arise by recombination of the radicals before or after decarbonylation.

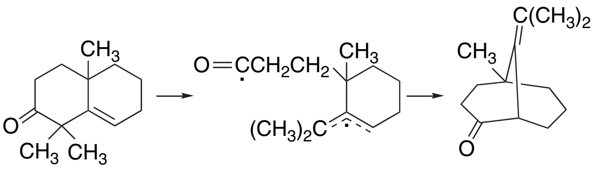


$$\underset{\underset{O}{\|}}{RC}CH_2CH{=}CHR' \xrightarrow{hv} R\underset{\cdot}{C}{=}O + {}^{\cdot}CH_2CH{=}CHR' \longrightarrow \text{products}$$

For cyclic ketones, the diradical intermediates can recombine, leading to isomerized ketones.



Ref. 125



Ref. 126

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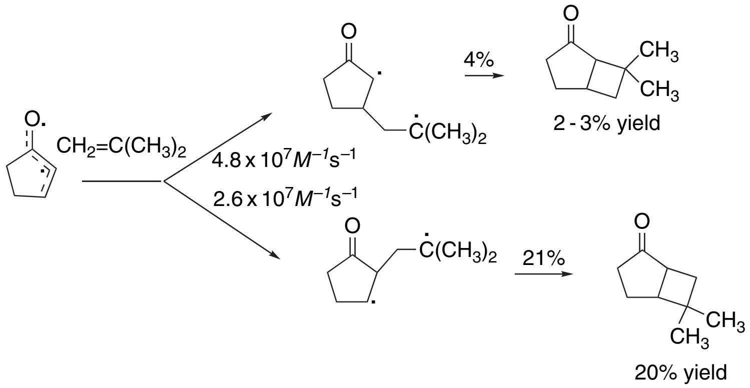
[124] R. Ricard, P. Sauvage, C. S. K. Wan, A. C. Weedon, and D. F. Wong, *J. Org. Chem.*, **51**, 62 (1986).

[125] H. Sato, N. Furutachi, and K. Nakanishi, *J. Am. Chem. Soc.*, **94**, 2150 (1972); L. A. Paquette, R. F. Eizember, and O. Cox, *J. Am. Chem. Soc.*, **90**, 5153 (1968).

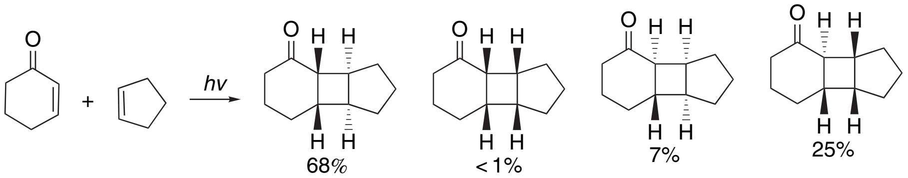
[126] P. S. Engel and M. A. Schnexnayder, *J. Am. Chem. Soc.*, **97**, 145 (1975).

12.3.2. Cycloaddition and Rearrangement Reactions of Cyclic Unsaturated Ketones

Cyclic α,β-unsaturated ketones present a rich array of photochemical reactions, some of which are of considerable synthetic value (see Part B, Section 6.3.2.2). Generally, noncyclic enones relax rapidly by *cis-trans* interconversion and do not undergo intermolecular photochemicial reactions. One useful reaction of cyclic enones is photochemical addition of alkenes.[127] The reaction involves the π-π* triplet excited state and 1,4-diradical intermediates.[128] Both the regiochemistry and stereochemistry of the reaction are determined by the properties of the diradical intermediate. It appears that initial bonding can occur at either C(2) or C(3) of the excited enone system. The alkene reacts at its less-substituted terminus, generating the more stable radical. The regiochemistry is determined by the relative efficiency of cyclization to product versus fragmentation back to reactants. In the case of cyclopentenone and isobutene, both the relative rates of addition and the fraction proceeding on to product have been determined. The preferred regioisomer results from a larger fraction of cyclization for the intermediate with radical character at the β-carbon.[129]



Significantly, both *cis* and *trans* ring junctures are formed.[130] Cyclohexenone and cyclopentene, for example, give four adducts with about a 2:1 *cis*:*trans* ratio.[131]



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[127] P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971); D. I. Schuster, G. Lem, and N. A. Kaprinidis, *Chem. Rev.*, **93**, 3 (1993).

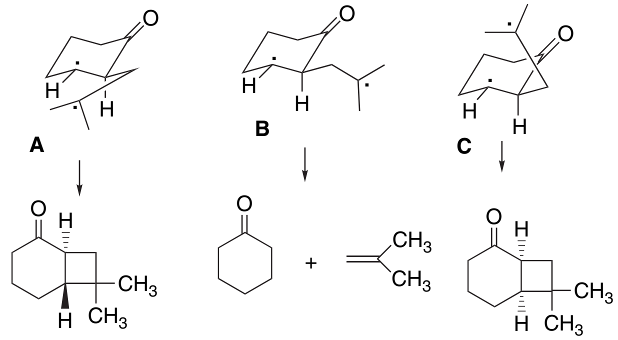
[128] D. I. Schuster, D. A. Dunn, G. E. Heibel, P. B. Brown, J. M. Rao, J. Woning, and R. Bonnneau, *J. Am. Chem. Soc.*, **113**, 6245 (1991).

[129] D. Andrew, D. J. Hastings, D. L. Oldroyd, A. Rudolph, A. C. Weedon, D. F. Wong, and B. Zhang, *Pure Appl. Chem.*, **64**, 1327 (1992); D. Andrew, D. J. Hastings, and A. C. Weedon, *J. Am. Chem. Soc.*, **116**, 10870 (1994); D. Andrew and A. C. Weedon, *J. Am. Chem. Soc.*, **117**, 5647 (1995).

[130] E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

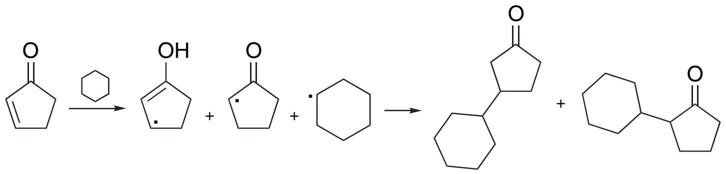
[131] D. I. Schuster, N. Kaprinidis, D. J. Wink, and J. C. Dewan, *J. Org. Chem.*, **56**, 561 (1991).

The *trans* products obviously are more strained. The stereochemistry can be traced to conformational factors in the diradical. For example, the diradical from cyclohexenone and isobutene can be formed in several conformations.

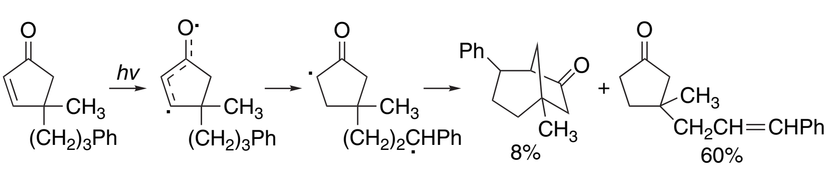


The extended radical **B** is likely to fragment. The *gauche* radicals **A** and **C** lead to *trans* and *cis* ring junctions, respectively. In this particular case, it has been proposed that there is less steric repulsion to cyclization of radical **A**, resulting in a preference for formation of the *trans* ring closure.[132] In general, the competing modes of attack of alkene and the ease of cyclization of the diradical govern the stereochemistry of the ring juncture.

In hydrocarbon solvents, the principal products from cyclopentenones result from hydrogen abstraction processes. Irradiation of cyclopentenone in cyclohexane gives a mixture of 2- and 3-cyclohexylcyclopentanone.[133] These products can be formed by intermolecular hydrogen abstraction, followed by recombination of the resulting radicals. It is interesting that as in the alkene cycloaddition reaction, reactivity is observed at both C(2) and C(3) of the excited enone system.



If a substituent chain is present on the cyclopentenone ring, an intramolecular hydrogen abstraction can take place.



The bicyclic product is formed by coupling of the two radical sites, whereas the unsaturated side chain results from an intramolecular hydrogen atom transfer. These reactions can be sensitized by aromatic ketones and quenched by typical triplet quenchers, and are therefore believed to proceed via triplet excited states.

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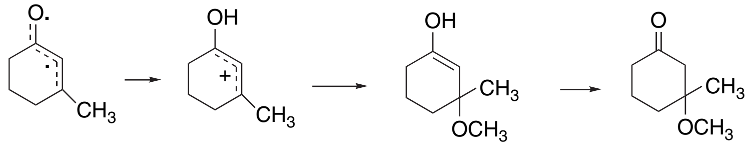
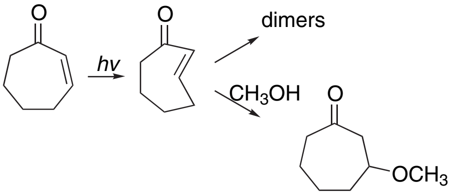
[132] P. G. Bauslaugh, *Synthesis*, 287 (1970).
[133] S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972).

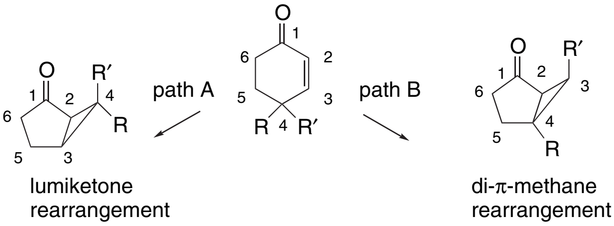
Cyclohexenones can add methanol in an acid-catalyzed reaction. This is thought to involve protonation of the π-π* excited state.[134]



In the case of cycloheptenone and larger rings, the main initial photoproducts are the *trans*-cycloalkenones produced by photoisomerization. In the case of the seven- and eight-membered rings, the *trans*-double bonds are sufficiently strained that rapid reactions follow. In nonnucleophilic solvents dimerization takes place, whereas in nucleophilic solvents addition reactions occur.[135]



There are also important rearrangement reactions for cyclic enones. For cyclohexenones two prominent reactions are the *lumiketone rearrangement* (Path A) and the *di-π-methane rearrangement* (Path B). The di-π-methane rearrangement pathway is restricted to 4-aryl or 4-vinyl cyclohexenones. 4,4-Dialkylcyclohexenones undergo the lumiketone rearrangement, which involves the shift of the C(4)–C(5) bond to C(3) and formation of a new C(2)–C(4) bond.[136]



Both reactions proceed via triplet excited species and to some extent depend on whether the π-π* or n-π* states are involved. At the most basic level of mechanism, the reactions can be depicted as involving the following steps.

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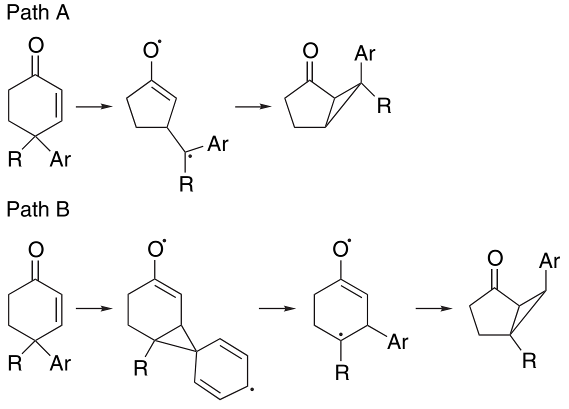
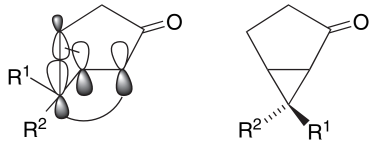
[134] D. I. Schuster, J.-M. Yang, J. Woning, T. A. Rhodes, and A. W. Jensen, *Can. J. Chem.*, **73**, 2004 (1995).

[135] H. Hart, B. Chen, and M. Jeffares, *J. Org. Chem.*, **44**, 2722 (1979).

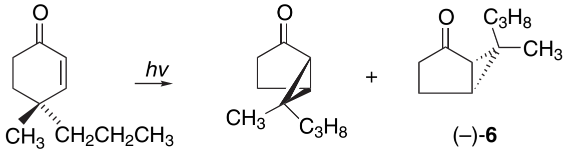
[136] For a review of this reaction, see D. I. Schuster, in *Rearrangements in Ground and Excited States*, Vol. 3, P. de Mayo, ed., Academic Press, New York, 1980, Chap. 17.



The lumiketone rearrangement is stereospecific and can be described as a $[\pi 2_a + \sigma 2_a]$ cycloaddition. This mechanism requires that inversion of configuration occur at C(4) as the new σ bond is formed at the back lobe of the reacting C(4)−C(5) σ bond.



It has been demonstrated in several systems that the reaction is in fact stereospecific with the expected inversion occurring at C(4). The ketone **4** provides a specific example. The stereoisomeric products **5** and **6** are both formed, but in each product inversion has occurred at C(4).



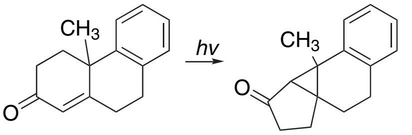
(*R*)-**4**

(+)-**5**

(−)-**6**

Ref. 137

The lumiketone rearrangement also proceeds in the case of some 4-alkyl-4-arylcyclohexenones.



Ref. 138

With 4,4-diarylcyclohexenones, the di-π-methane rearrangement is the preferred reaction. For compounds in which the two aryl groups are substituted differently, it

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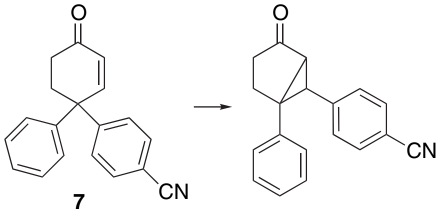
[137] D. I. Schuster and J. M. Rao, *J. Org. Chem.*, **46**, 1515 (1981); D. I. Schuster, R. H. Brown, and B. M. Resnick, *J. Am. Chem. Soc.*, **100**, 4504 (1978).

[138] O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **88**, 161 (1966).

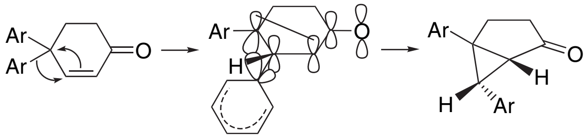
is found that substituents that stabilize radical character favor migration. Thus the *p*-cyanophenyl substituent migrates in preference to the phenyl substituent in **7**.



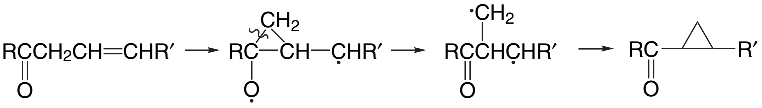
7

Ref. 139

As described on p. 1113, di-π-methane rearrangement can be considered to occur via a TS in which C(2)−C(4) bridging is accompanied by a 4 → 3 aryl migration.[140] Note that the *endo* product is predicted by the concerted mechanism. It is the major product, even though it is sterically more congested than the *exo* isomer. This stereospecificity is characteristic of the reaction.

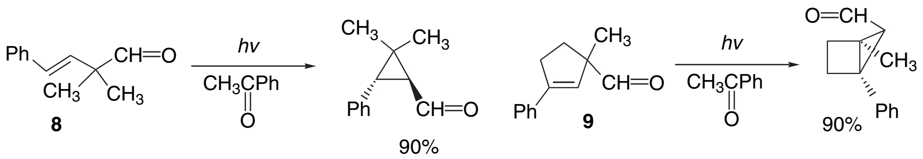


Excitation of acyclic ß,γ-unsaturated ketones by triplet photosensitization can give cyclopropyl ketones.[141] This reaction is known as the *oxadi-π-methane rearrangement*.



$$\mathrm{R\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH{=}CHR'} \longrightarrow \mathrm{R\underset{\underset{\displaystyle \underset{\cdot}{O}}{|}}{C}{-}\overset{CH_2}{CH}{-}\underset{\cdot}{C}HR'} \longrightarrow \mathrm{R\underset{\underset{\displaystyle O}{\|}}{C}\overset{\cdot CH_2}{\overset{|}{C}}H\underset{\cdot}{C}HR'} \longrightarrow \mathrm{R\underset{\underset{\displaystyle O}{\|}}{C}}{-}\triangle{-}\mathrm{R'}$$

Oxadi-π-methane rearrangements have been observed by both direct and triplet-sensitized excitation. The reaction is generally associated with the π-π* excited state, but there are also examples that involve other levels. The most favorable cases for the rearrangement involve conjugation at the γ-carbon (e.g., aryl) and disubstitution or a bulky substituent at the α-carbon. The reaction is also favored by more or less rigid cyclic systems. These features are present in reactants such as **8** and **9**, which give particularly high yields.[142]



8 **9**

As with other reactions involving triplet excited states, the efficiency of intersystem crossing appears to be a major factor in the outcome of the reaction.[143] The

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[139] H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

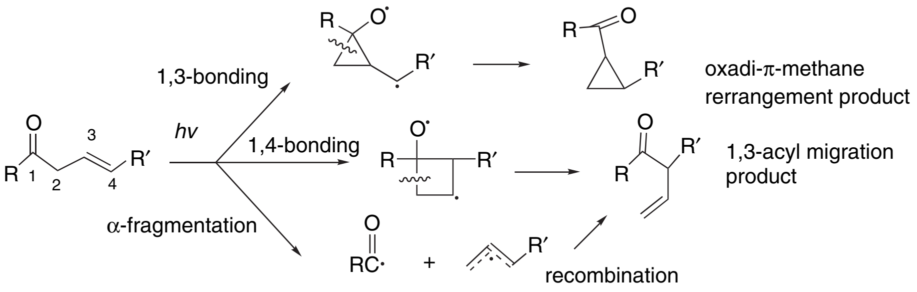
[140] H. E. Zimmerman, *Tetrahedron*, **30**, 1617 (1974).

[141] W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *J. Am. Chem. Soc.*, **92**, 1786 (1970).

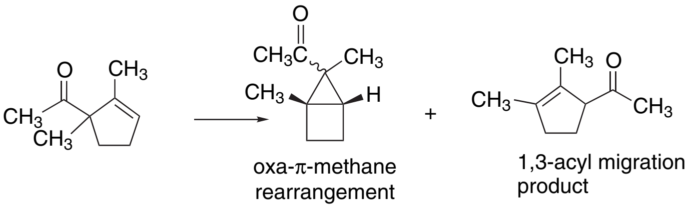
[142] D. Armesto, M. J. Ortiz, and S. Romano, *Tetrahedron Lett.*, **36**, 965 (1995).

[143] B. Reimann, D. E. Sadler, and K. Schaffner, *J. Am. Chem. Soc.*, **108**, 5527 (1986); M.-D. Su, *J. Org. Chem.*, **61**, 3080 (1996).

reaction pathway has been modeled computationally (MC-SCF/6-31G*) using the simplest β,γ-unconjugated carbonyl compound, but-3-en-1-one.[144] The results suggest that two short-lived diradical intermediates are involved, one leading to oxadi-π-methane rearrangement and the other to 1,3-acyl migration. These structures are closely related to CIs that provide efficient crossing to the ground state. The computations suggest that both the singlet and triplet states are energetically comparable. A dissociation-recombination mechanism is also available for the 1,3-shift. It appears that individual structural differences can favor any of the competing reaction paths.



This conclusion is in general agreement with experimental studies that indicate that several excited states can lead to oxadi-π-methane rearrangement and the related reactions.[145] For example, 1,2-dimethylcylopent-2-enyl methyl ketone reacts by all three pathways. In the gas phase about 25% of the 1,3-acyl migration occurs by a dissociation mechanism, as indicated by the ability of NO and O_2 to divert a part but not all of the intermediate.[143]



Other conjugated carbonyl compounds that have received a great deal of attention are the cyclohexadienones.[146] The main photolysis product of 4,4-diphenylcyclohexadienone, for example, is **10.**[147] Quenching and photosensitization

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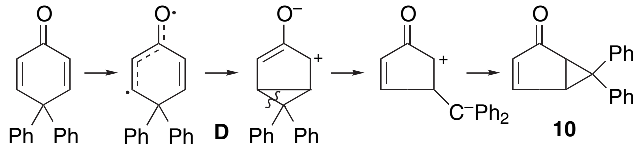
[144] S. Wilsey, M. J. Bearpark, F. Bernardi, M. Olivucci, and M. A. Robb, *J. Am. Chem. Soc.*, **118**, 176 (1996).

[145] T. J. Eckersley, S. D. Parker, and N. A. J. Rogers, *Tetrahedron*, **40**, 3749 (1984); T. J. Eckersley and N. A. J. Rogers, *Tetrahedron*, **40**, 3759 (1984); M. J. C. M. Koppes and H. Cerfontain, *Rec. Trav. Chim. Pays-Bas*, **107**, 549 (1988).

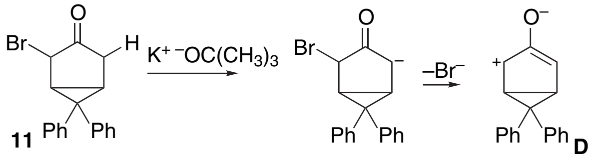
[146] H. E. Zimmerman, *Angew. Chem. Int. Ed. Engl.*, **8**, 1 (1969); K. Schaffner and M. Demuth, in *Rearrangements in Ground and Excited States*, Vol. 3, P. de Mayo, ed., Academic Press, New York, 1980, Chap. 18; D. I. Schuster, *Acc. Chem. Res.*, **11**, 65 (1978).

[147] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

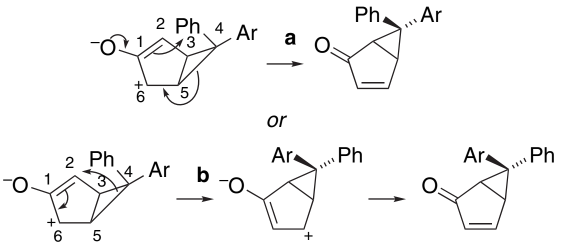
experiments have indicated that the reaction proceeds through a triplet excited state. A scheme that delineates the bonding changes is outlined below.



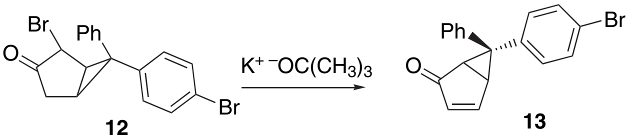
It is believed that a reactive ground state species, the zwitterion **D**, is an intermediate and that it rearranges to the observed product.[148] To test this mechanism, generation of species **D** by nonphotochemical means was undertaken.[149] α-Haloketones, when treated with strong base, ionize to such dipolar intermediates. Thus, the bromoketone **11** is a potential precursor of intermediate **D**.



The zwitterion prepared by this route did indeed lead to **10**, as required if it is an intermediate in the photochemical reaction. Further study of this process established another aspect of the reaction mechanism. The product could be formed by a process involving inversion at C(4) (Path **a**) or by one involving a pivot about the bond C(3)−C(4) (Path **b**).



The two mechanisms predict the formation of stereochemically different products when the aryl groups at C(4) are different. When the experiment was carried out on **12** only **13** the product corresponding to inversion of configuration at C(4) was observed.[150]



The rearrangement step is a ground state thermal process and may be classified as a [1,4]-sigmatropic shift of carbon across the face of a 2-oxybutenyl cation. The Woodward-Hoffmann rules require a sigmatropic shift of this type to proceed with inversion of configuration. The orbitals involved in a [1,4]-sigmatropic shift are shown below.

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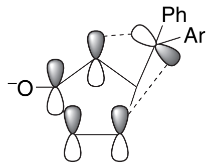
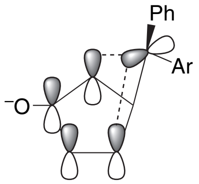
[148] H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967).

[149] H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966).

[150] H. E. Zimmerman and D. S. Crumrine, *J. Am. Chem. Soc.*, **90**, 5612 (1968).



1,4 shift with
inversion
allowed
4 electrons
Mobius system

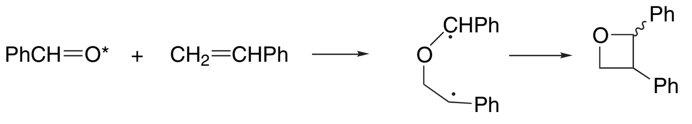


1,4 shift with
retention
forbidden
4 electrons
Hückel system

As is clear from the preceding examples, there are a variety of overall reactions that can be initiated by photolysis of ketones. The course of photochemical reactions of ketones is very dependent on the structure of the reactant. Despite the variety of overall processes that can be observed, the number of individual steps involved is limited. For ketones, the most important are inter- and intramolecular hydrogen abstraction, α-cleavage at the carbonyl group, and substituent migration to the ß-carbon atom of α,ß-unsaturated ketones. Reexamination of the mechanisms illustrated in this section will reveal that most of the reactions of carbonyl compounds that have been described involve combinations of these fundamental processes. The final products usually result from re-bonding of reactive intermediates generated by these steps.

12.3.3. Cycloaddition of Carbonyl Compounds and Alkenes

Ketones and aldehydes can undergo photochemical [2 + 2] cycloaddition reactions with alkenes to give oxetanes. This is called the *Paterno-Buchi reaction*. For alkyl carbonyl compounds both singlet and triplet excited states seem to be involved, but for aromatic compounds the reaction occurs through the triplet state.[151] The regiochemistry can usually be accounted for on the basis of formation of the most stable 2-oxa-1,4-diradical. For example, styrene and benzaldehyde give 2,3- not 2,4-diphenyloxetane.[152]



3:1 *trans:cis*

The same generalization can also account for the reversal of orientation between furan and dihydrofuran.[153]

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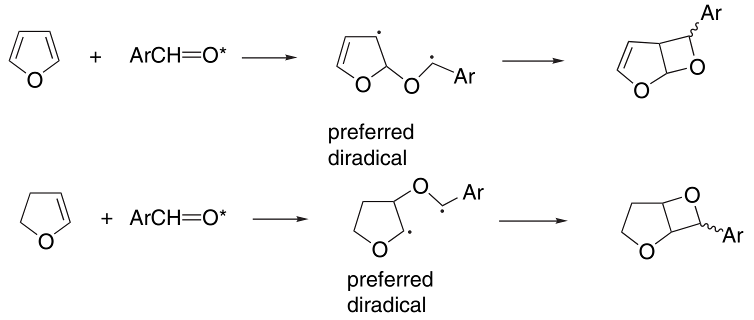
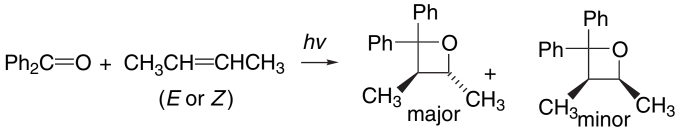
[151] R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973).

[152] S. A. Fleming and J. J. Gao, *Tetrahedron Lett.*, **38**, 5407 (1997).

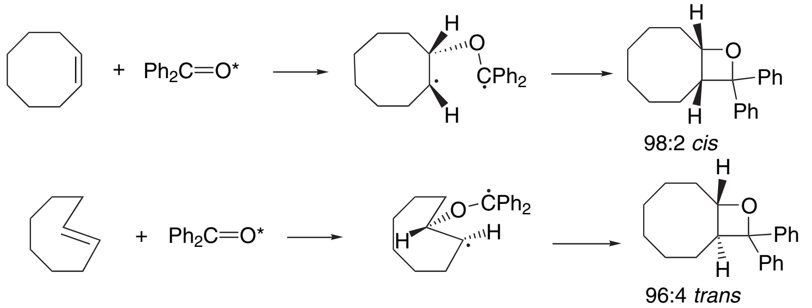
[153] A. G. Griesbeck and S. Stadtmuller, *Chem. Ber.*, **123**, 357 (1990).



The Paterno-Buchi reaction is ordinarily not stereospecific, but instead favors the more stable adduct for either alkene isomer, indicating the involvement of a relatively a long-lived diradical intermediate.[154]



An exception to this generalization has been noted for *E*- and *Z*-cyclooctene.[155] This reaction is nearly stereospecific at low temperature. This result is attributed to conformationally distinct 1,4-diradical intermediates that undergo intersystem crossing and cyclization faster than stereochemical interconversion.



At higher temperature, some stereorandomization occurs as the result of competition between rotational processes and fragmentation of the 1,4-diradical intermediate.

Many of the details of both regio- and stereoselectivity of the Paterno-Buchi reaction can be understood in terms of the conformation and lifetime of the 1,4-diradical intermediates. Griesbeck and co-workers have proposed that the relative lifetime of the radicals, and whether they cyclize or revert to reactants, is governed by the rate of intersystem crossing, which in turn depends on the efficiency of spin-orbit coupling.[156] With cyclic alkenes, for example, the *endo* stereoisomer is often preferred. This can be explained by noting that the conformation leading to *exo* product is not well oriented for the perpendicular orbital interaction that favors intersystem crossing (see p. 1075).

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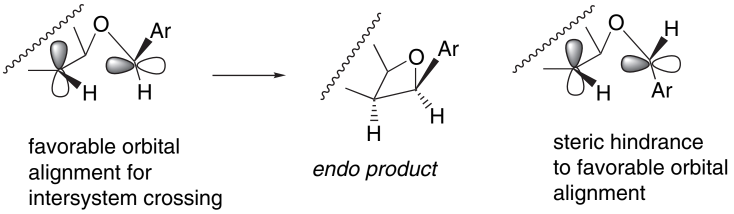
[154] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

[155] W. Adam, V. R. Stegmann, and S. Weinkotz, *J. Am. Chem. Soc.*, **123**, 2452 (2001); W. Adam and V. R. Stegmann, *J. Am. Chem. Soc.*, **124**, 3600 (2002).

[156] A. G. Griesbeck and S. Stadtmueller, *J. Am. Chem. Soc.*, **112**, 1281 (1990); A. G. Griesbeck, H. Mauder, and S. Stadtmuller, *Acc. Chem. Res.*, **27**, 70 (1994).

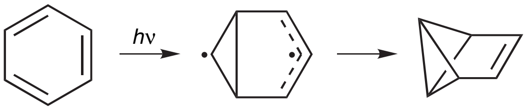
Computational modeling of orbital interactions supports this proposal.[157]



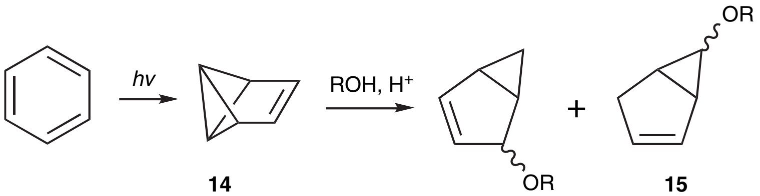
The Paterno-Buchi reaction, particularly its synthetic application,[158] is considered in more detail in Section 6.3.2.3 of Part B.

12.4. Photochemistry of Aromatic Compounds

Irradiation of benzene and certain of its derivatives results in bond reorganization and formation of nonaromatic products.[159] Irradiation of liquid benzene with light $\lambda = 254\,\text{nm}$ wavelength results in the accumulation of fulvene and a very small amount of tricyclo[3.1.0.0^{2,6}]hex-3-ene, also known as benzvalene.[160] The maximum conversion to this product in liquid benzene is about 0.05%. The key intermediate is believed to be a diradical formed by 1,3-bonding.



Because of the low photostationary concentration of benzvalene, photolysis is not an efficient way of accumulating this compound. However, the highly reactive molecule can be trapped if it is generated in the presence of other molecules with which it reacts. Irradiation of benzene in acidic hydroxylic solvents gives products resulting from 1,3-bonding in the benzene ring and addition of a molecule of solvent. The compounds of structure **15** arise by solvolysis of, the initial photoproduct benzvalene.[161]



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15

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[157] A. G. Kutateladze, *J. Am. Chem. Soc.*, **123**, 9279 (2001).

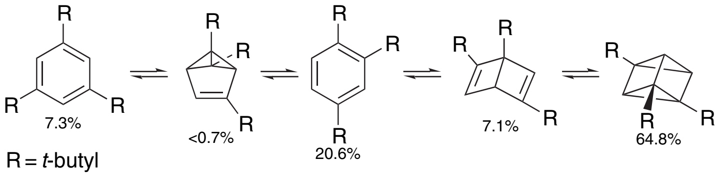
[158] T. Bach, *Synthesis*, 683 (1998).

[159] D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **32**, 1309 (1976); A. Gilbert, in *Organic Photochemistry and Photobiology*, W. M. Horspool and P.-S. Song, eds., CRC Press, Boca Raton, FL, 1995, pp. 229–236.

[160] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967).

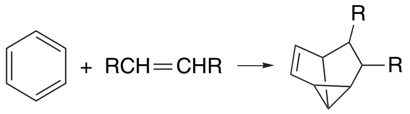
[161] L. Kaplan, D. J. Rausch, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **94**, 8638 (1972).

The photoisomerization of aromatic rings has also been studied using 1,3,5-tri-*t*-butylbenzene. The composition of the photostationary state is shown below.[162]

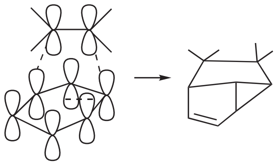


These various photoproducts are all valence isomers of the normal benzenoid structure. The alternative bonding patterns are reached from the excited state, but it is difficult to specify a precise mechanism. The presence of the *t*-butyl groups introduces a steric factor that works in favor of the photochemical cyclization. Although the *t*-butyl groups are coplanar in the aromatic ring, the geometry of the bicyclic products reduces steric interactions between adjacent *t*-butyl groups.

Irradiation of solutions of alkenes in benzene or substituted benzenes gives primarily 1:1 adducts in which the alkene bridges *meta* positions of the aromatic ring.[163]



These reactions are believed to proceed through a complex of the alkene with a singlet excited state of the aromatic compound (an exciplex). The alkene and aromatic ring are presumed to be oriented in such a manner that the alkene π system reacts with *p* orbitals on the 1,3-carbons of the ring. This addition to the aromatic ring is evidently concerted because the relative geometry of the substituents on the alkene is retained in the product. Note that the re-bonding scheme is related to that observed in benzvalene formation. Lesser amounts of products involving addition to 1,2- or 1,4- positions of the aromatic ring are also formed in some cases.[164]



The product distribution of addition of cyclopentene to substituted benzenes has been studied in detail. Three regioisomeric and two stereoisomeric orientations are possible. *Endo* addition is generally preferred.[163f]

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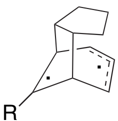
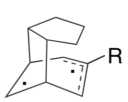
[162] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

[163] (a) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **88**, 2066 (1966); (b) J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Am. Chem. Soc.*, **95**, 6197 (1973); (c) A. Gilbert and P. Yianni, *Tetrahedron*, **37**, 3275 (1981); (d) D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **33,** 2459 (1977);(e) T. Wagner-Jauregg, *Synthesis*, 165, 769 (1980); (f) J. Cornelisse, *Chem. Rev.*, **93**, 615 (1993).

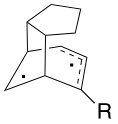
[164] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **93**, 2073 (1971).



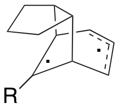
2,6-*endo*



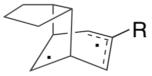
3,5-*endo*



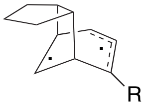
2,4-*endo*



2,6-*exo*

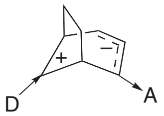


3,5-*exo*

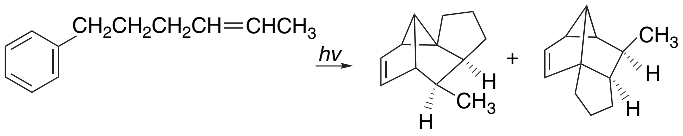


2,4-*exo*

Donor substituents favor the 2,6-regioisomer, whereas EWGs favor the 2,4-orientation.[165] These results suggest that there is considerable polar character to the reaction between the excited aromatic and the alkene. Acceptor substituents at C(3) can stabilize the negative charge at C(3) and C(5), whereas donor substituents can stabilize the positive charge at C(1).[166]



Addition of alkenes and aromatic rings has also been realized intramolecularly when the distance between the alkene and phenyl substituent is sufficient to permit bonding.



The photocycloaddition of ethene and benzene has been studied by CAS-SCF computation using the 6-31G* basis set for energies and 4-31G orbitals for structural minimization.[167] The structure of the CI is shown in Figure 12.24. The *ortho* and *meta* cycloaddition processes proceed through alternate electron-pairing schemes from a single CI without barriers. For unsubstituted alkenes, the *meta* CI is lower in energy than the *ortho*, whereas the *ortho* CI is stabilized by alkenes with ERG and EWG substituents. Product compositions tend to reflect these differences.[168]

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[165] P. de Vaal, E. M. Osselton, E. S. Krijnen, G. Lodder, and J. Cornelisse, *Rec. Trav. Chim. Pays-Bas*, **107**, 407 (1988).

[166] D. Bryce-Smith, B. Foulger, J. Forrester, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *J. Chem. Soc., Perkin Trans. 1*, 55 (1980); G. Weber, J. Runsink, and J. Mattay, *J. Chem. Soc., Perkin Trans.*, **1,** 2333 (1987); V. Y. Merritt, J. Cornelisse, and R. Srinivasan, *J. Am. Chem. Soc.*, **95**, 8250 (1973).

[167] S. Clifford, M. J. Bearpark, F. Bernardi, M. Olivucci, M. A. Robb, and B. R. Smith, *J. Am. Chem. Soc.*, **118**, 7353 (1996).

[168] A. Gilbert and P. Yianni, *Tetrahedron*, **37**, 3275 (1981); J. Mattay, *Tetrahedron*, **41**, 2405 (1985).

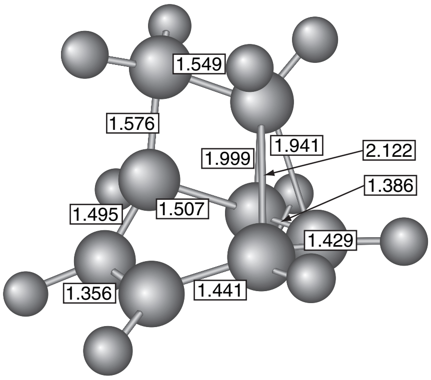
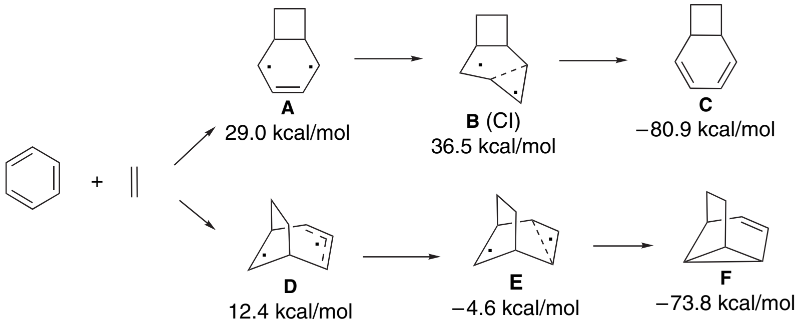


Fig. 12.24. Structure of conical intersection for benzene + ethene addition from *J. Am. Chem. Soc.*, **118**, 7353 (1996), by permission of the American Chemical Society.



Topic 12.1. Computational Interpretation of Diene and Polyene Photochemistry

As a starting point for the mechanistic discussion, it is useful to review the structural features of the excited states. The first singlet excited state of butadiene, S_1, can be approximated as the $\psi_2 \rightarrow \psi_3$/HOMO→LUMO π-π^* transition.[169] The lack of fluorescence from this excited state indicates that a very facile path exists for nonradiative energy transfer. The S_2 state has doubly excited character and relaxes to a structure with ionic character that can rotate at the pyramidal carbon but not at the allyl fragment. The minimum energy of the T_1 state corresponds to the allyl-methylene diradical with a nearly 90° twist and slight pyramidalization at the methylene carbon. In substituted systems, one or the other of the zwitterion structures (e.g., allyl cation versus allyl anion) may be favored.[170]

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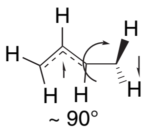
[169] K. B. Wiberg, C. M. Hadad, G. B. Ellison, and J. B. Foresman, *J. Phys. Chem.*, **97**, 13586 (1993).

[170] M. E. Squiallacote and T. C. Semple, *J. Am. Chem. Soc.*, **109**, 892 (1987).

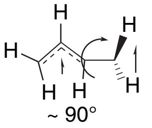
As computational methods for describing excited states have been refined, additional understanding of the structures has developed. Relatively early computational studies provided some indication of the geometries associated with the butadiene excited states.[171] The ground state has a maximum at a twist of 90° about the C(1)−C(2) bond. This structure, which can be approximately described as a singlet methylene-allyl diradical, is found at about 2.3 eV and is more stable than a structure with 90° twist at both terminal groups (3.1 eV). There is no major pyramidalization of the methylene groups in this second structure. The spectroscopic (Franck-Condon) T_1 state is about 3.5 eV above S_0. A *local planar minimum* is found to have a shortened C(2)−C(3) bond and lengthened C(1)−C(2) and C(3)−C(4) bonds The energy of this structure is about 2.7 eV. The C(2)−C(3) bond distance is 1.36 Å, so the bond has considerable double-bond character. This local minimum can be represented as a 1,4-but-2-enyl diradical. The *global minimum* on the T_1 surface is a twisted triplet allyl-methylene diradical that is at about 2.3 eV. This structure is very similar in geometry to the singlet diradical on the ground state surface.

The *initial* S_1 state has all bonds lengthened and both ends are able to rotate. The most stable geometry for this state is twisted and pyramidalized at both ends. The energy is about 5.5 eV, but is slightly higher (5.7 eV) when only one end is twisted 90°. All the C−C bonds are around 1.48 Å, and the structure can be described as a completely unpaired singlet tetraradical. The S_2 state also has a *local planar minimum* and has considerable 3*p* (Rydberg) character in this geometry. The S_2 *global minimum* energy structure has one end twisted 90°; this end is strongly pyramidalized and the structure has considerable zwitterionic character. Approximate representations of these are given below, and this representation of the excited states in terms of energy is given in Figure 12.25.

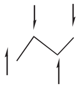


singlet diradical character of twisted ground state

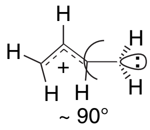
planar local minimum of T_1 state



twisted global minimum of T_1 state

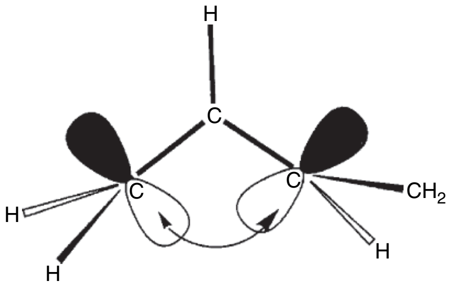


tetraradical structure of S_1 state



zwitterionic character of S_2 state

As we shall see shortly, the singlet state often gives rise to products with 1,3-bridging, which suggests that there is a pronounced C(1)−C(3) interaction.[172]



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[171] M. Aoyagi, Y. Osamura, and S. Iwata, *J. Chem. Phys.*, **83**, 1140 (1985); P. G. Szalay, A. Karpfen, and H. Lischka, *Chem. Phys.*, **130**, 219 (1989).

[172] M. Ito and I. Ohmine, *J. Phys. Chem.*, **106**, 3159 (1997).

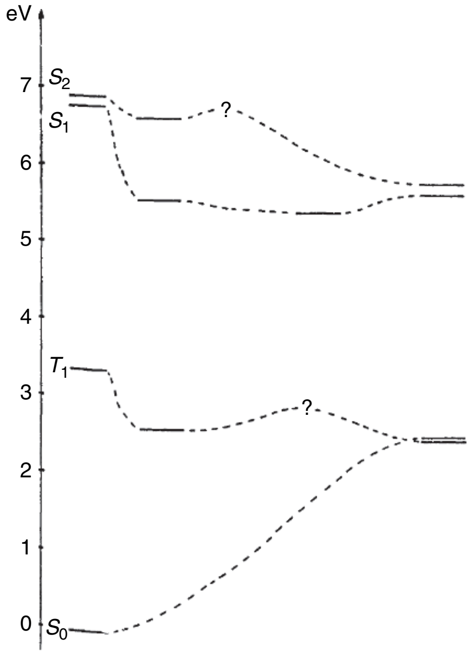

Fig. 12.25. Energy level diagram for the low-lying states of *trans*-1,3-butadiene. The left-hand levels correspond to the vertical excitation energies; the intermediate levels correspond to planar structures resulting from relaxation of bond lengths; and the right-hand levels are the 90° twist structures. Reproduced from *J. Phys. Chem.* **83**, 1140 (1985), by permission of the American Chemical Society.

More recent studies have refined these structural representations. The excited states can be attained by excitation of either the *s-trans* or *s-cis* conformers of 1,3-butadiene, and the excited state structure depends on the original conformation. The structures of the *initial* excited states have been calculated at the MC-SCF/4-31G level.[173] Two slightly different structures were found for each of the conformations. The lower-energy structures are shown in Figure 12.26. Both structures show stretching and twisting about the C=C, indicating loss of electron pairing. These excited state structures can continue to twist at the C(2)−C(3) bond to reach the global minima.[174]

The singlet photochemistry of 1,3-butadiene is believed to be dominated by the S_2 state, which is rapidly reached from the S_1 state by rotation. S_1 and S_2 are, respectively, singly and doubly excited $\pi \rightarrow \pi^*$ states. The return to ground state is believed to involve an S_2-S_0 CI. The S_2 energy surface of butadiene has been modeled by a computation that combines molecular mechanics and a valence bond structural

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[173] (a) M. Olivucci, I. N. Ragazos, F. Bernardi, and M. A. Robb, *J. Am. Chem. Soc.*, **115**, 3710 (1993); (b) M. Olivucci, F. Bernardi, S. Ottani, and M. A. Robb, *J. Am. Chem. Soc.*, **116**, 2034 (1994); (c) F. Bernardi, M. Olivucci, and M. A. Robb, *J. Photochem. Photobiol.*, **105**, 365 (1997); (d) M. Garavelli, F. Bernardi, P. Celani, M. A. Robb, and M. Olivucci, *J. Photochem. Photobiol.*, **114**, 109 (1998).

[174] V. Bonacic-Koutecky, M Persico, D. Dohnert, and A. Sevin, *J. Am. Chem. Soc.*, **104**, 6900 (1982); M. Aoyagi, Y. Osamura, and S. Iwata, *J. Chem. Phys.*, **83**, 1140 (1985).

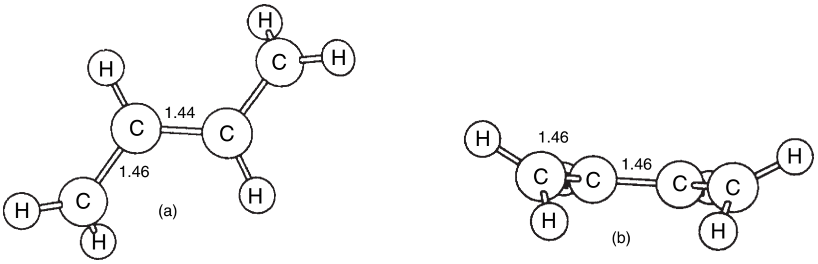

Fig. 12.26. Computed initial excited state structures of butadiene. (a) *s-trans* S_1; (b) *s-cis* S_1. Reproduced from *J. Am. Chem. Soc.*, **115**, 3710 (1993), by permission of the American Chemical Society.

representation.[173a] The structural parameters that were followed were the rotations of the C(1)–C(2) (α), C(2)–C(3) (β), and C(3)–C(4) (α′) bonds. The structures that were located were then refined using MC-SCF/4-31G calculations. The excited state near the CI involves rotation at all three bonds and can be represented as having all four π electrons unpaired.

Comparison of the disrotatory and conrotatory paths for electrocyclization indicates that the disrotatory path can proceed without a barrier. Figure 12.27 is a cross section of the S_2 and S_0 surfaces and depicts the formation of the observed products via transition from S_2 to the ground state surface. Figure 12.28 is a "reaction cube" in which each of the edges represents rotation about one of the bonds. The shaded central area is near 90-90-90 and is the region in which the CIs are located. Figure 12.29 shows the structures of three CIs found in this area.

There are also higher-energy CIs, which resemble the H migration carbenoid structures found for ethene.[175] (See Figure 12.29) These structures have also been located

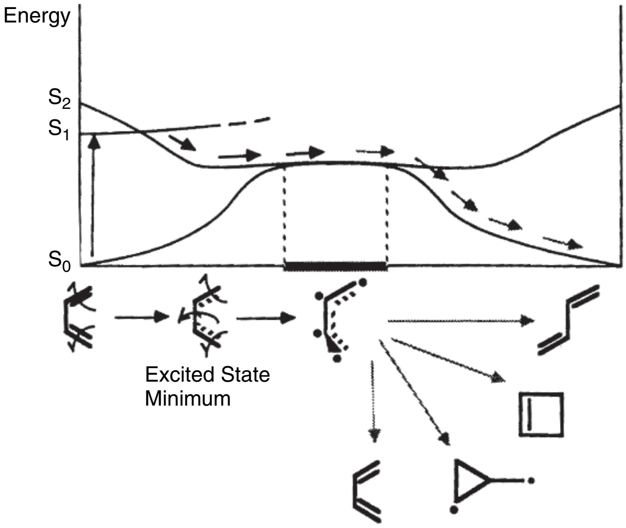

Fig. 12.27. Cross section of energy surface indicating re-pairing of S_2 to reactant and other products. Reproduced from *J. Am. Chem. Soc.*, **115**, 3710 (1993), by permission of the American Chemical Society.

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[175] S. Wilsey and K. N. Houk, *Photochem. Photobiol.*, **76**, 616 (2002).

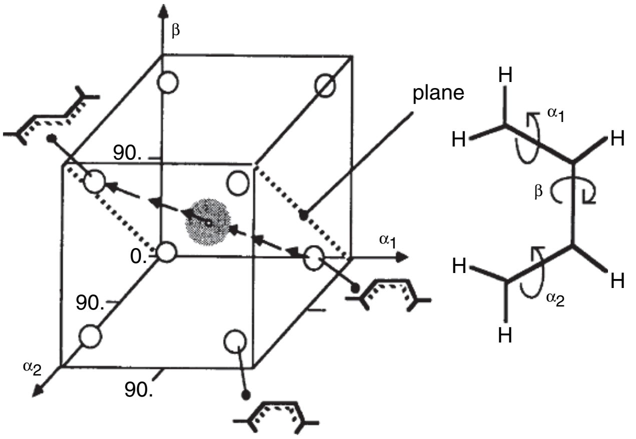

Fig. 12.28. Reaction cube locating the butadiene conical intersection in relation to rotation at each of the bonds. The shaded area in the center represents the location of the conical intersection with all bond rotations near 90°. The open circles represent initial excited states. The energy surface in Figure 12.27 represents the diagonal plane bisecting the cube. Reproduced from *J. Am. Chem. Soc.*, **115**, 3710 (1993), by permission of the American Chemical Society.

at the MC-SCF/4-31G level of computation.[173a] CASPT2 theory, which is appropriate for excited states with large ionic character,[176] gives a similar description of the CI.[177] Other descriptions of the butadiene excited surface have also been developed,[178,179] including explicit consideration of the formation of bicyclo[1.1.0]butane by 1,3-bonding.[180]

The energy profile in Figure 12.30 compares the disrotatory and conrotatory paths for cyclization. There is no barrier on the disrotatory path but the conrotatory path

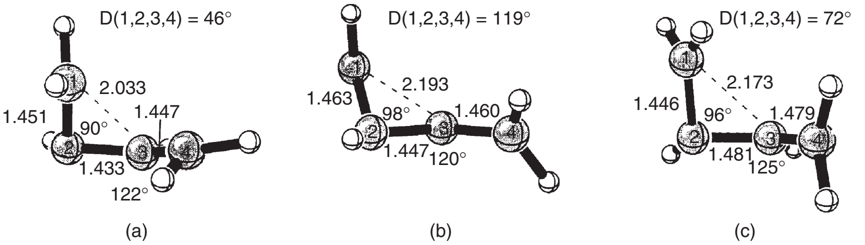

Fig. 12.29. Structure of the 1,3-butadiene conical intersections from CAS(6,6)/6-31G* computations: (a) cisoid, (b) transoid, (c) central. Reproduced from *Photochem. Photobiol.*, **76**, 616 (2002), by permission of Elsevier.

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[176] C. S. Page and M. Olivucci, *J. Comput. Chem.*, **24**, 298 (2003).

[177] B. Ostojic and W. Domcke, *Chem. Phys.*, **269**, 1 (2001); R. P. Krawczyk, K. Malsch, G. Hohlneicher, R. C. Gillen, and W. Domcke, *Chem. Phys. Lett.*, **320**, 535 (2000).

[178] S. Saki, *Chem. Phys. Lett.*, **287**, 263 (1998); R. P. Krawczyk, K. Malsch, G. Hohlneicher, R. C. Gillen, and W. Domcke, *Chem. Phys. Lett.*, **320**, 535 (2000).

[179] M. Olivucci, I. N. Ragazos, F. Bernardi, and M. A. Robb, *J. Am. Chem. Soc.*, **115**, 3710 (1993); M. Olivucci, F. Bernardi, S. Ottani, and M. A. Robb, *J. Am. Chem. Soc.*, **116**, 2034 (1994).

[180] S. Sakai, *Chem. Phys. Lett.*, **319**, 687 (2000).

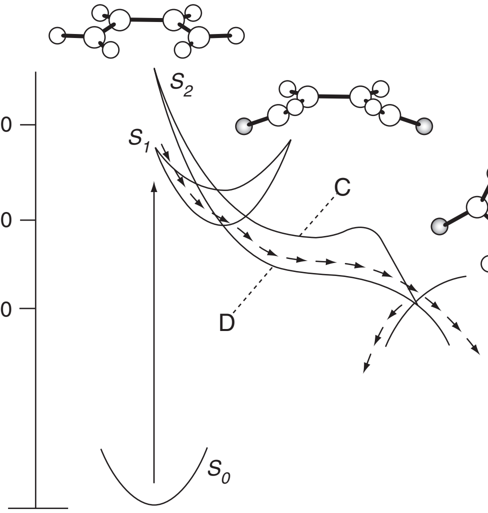
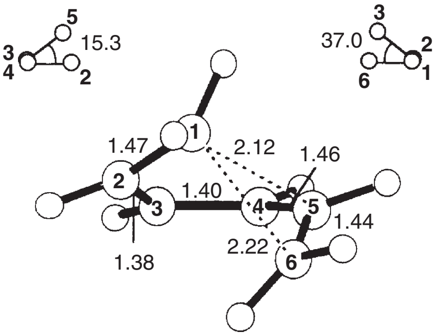


Fig. 12.30. Comparison of disrotatory (D) and conrotatory (C) minimum energy paths for photocyclization of 1,3-butadiene. The disfavored conrotatory motion encounters a barrier. Reproduced from *J. Photochem. Photobiol.*, **105**, 365 (1997), by permission of Elsevier.

encounters a small barrier. The reverse reaction, opening of cyclobutene to butadiene, has also been explored computationally, using CAS-SCF/double ζ calculations. The disrotatory pathway is found to be favored, although the interpretation is somewhat more complex than the simplest Woodward-Hoffmann formulation. Computational quantum dynamics calculations have been used to model the very early stages of the photoreaction of cyclobutene (<50 fs).[181] The C=C bond stretches and the CH_2-CH_2 bond weakens as the CH_2 groups move toward sp^2 hybridization. The motion is in agreement with the predicted (Woodward-Hoffmann) disrotatory motion.[182] It can be shown that a CI exists for the disrotatory but not the conrotatory mode.[183]

The 1,3,5-hexatriene-1,3-cyclohexadiene system has also been studied by computation. A CI connecting the excited state to the ground state has been located. The CI can be described as a tetraradical.[182] The structure is shown below.



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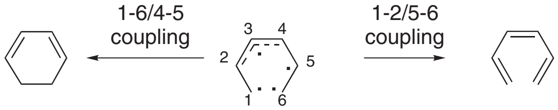
[181] M. Ben-Nun and T. J. Martinez, *J. Am. Chem. Soc.*, **122**, 6299 (2000).

[182] M. Garavelli, F. Bernardi, M. Olivucci, T. Vreven, S. Klein, P. Celani, and M. A. Robb, *Faraday Discussions*, **110**, 51 (1998); P. Celani, S. Offani, M. Olivucci, F. Bernardi, and M. A. Robb, *J. Am. Chem. Soc.*, **116**, 10141 (1994).

[183] Y. Haas and S. Zilberg, *J. Photochem. Photobiol.*, **144**, 221 (2001).

In this structure C(1) is actually a bit closer to C(5) than to C(6). The C(2,3,4) fragment resembles an allyl radical. There are recoupling patterns that can lead either to cyclohexadiene or to *Z*-1,3,5-hexatriene.



The minimum energy reaction path after transit through the CI has also been investigated.[184] Two major reaction channels were identified that lead to the two products. These channels are sufficiently comparable in terms of their topological features that product formation can occur along both routes in approximately equal amounts. It would be expected that substituents that favored one or the other pathway would alter the relative yields of the two types of products. There is also a minor channel that can lead to formation of the bicyclo[3.1.0]hex-2-ene ring system. This situation is represented schematically in Figure 12.31.

Another kind of tetraradicaloid CI has been invoked and computationally characterized for photoisomerization of cyclooctatetraene.[185] Photoexcitation leads to return to reactant, double-bond shift, and formation of semibullvalene. The tetraradicaloid

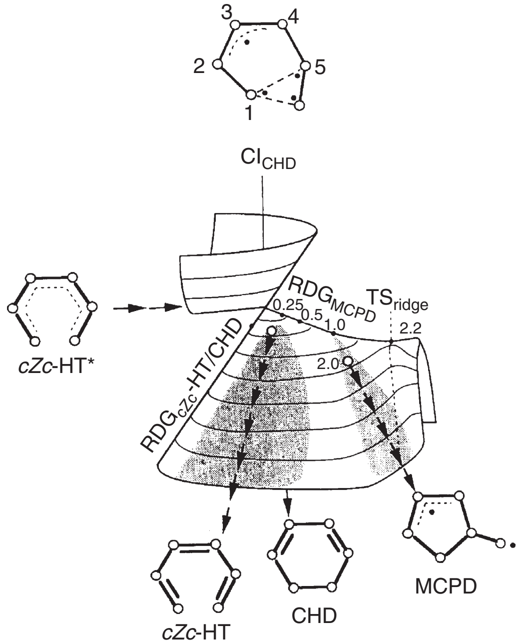


Fig. 12.31. Schematic representation of conical intersection showing partitioning between 1,3,5-hexatriene, 1,3-cyclohexadiene, and bicyclo[3.1.0]hex-2-ene products. Reproduced from *J. Phys. Chem. A*, **101**, 2023 (1997), by permission of the American Chemical Society.

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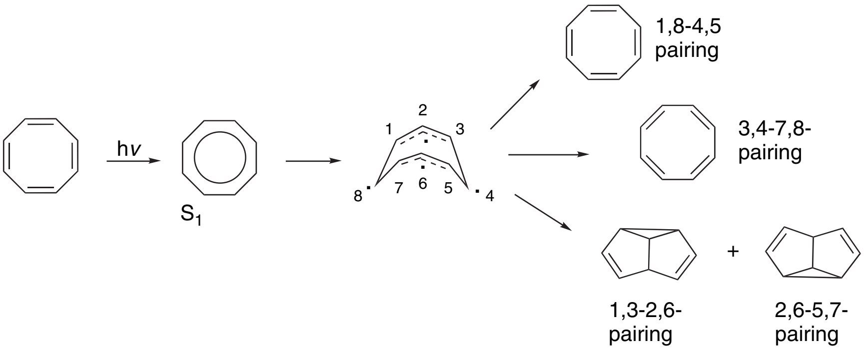
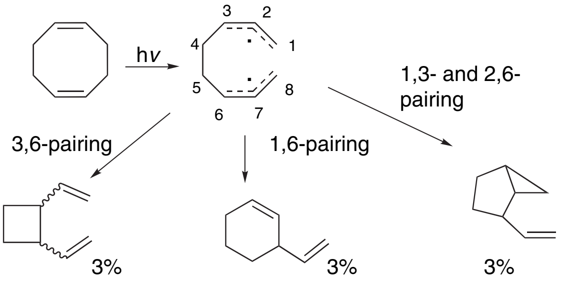
[184] M. Garavelli, P. Celani, M. Fato, M. J. Bearpark, B. R. Smith, M. Olivucci, and M. A. Robb, *J. Phys. Chem. A*, **101**, 2023 (1997).

[185] M. Garavelli, F. Bernardi, V. Molino, and M. Olivucci, *Angew. Chem. Int. Ed. Engl.*, **40**, 1466 (2001).

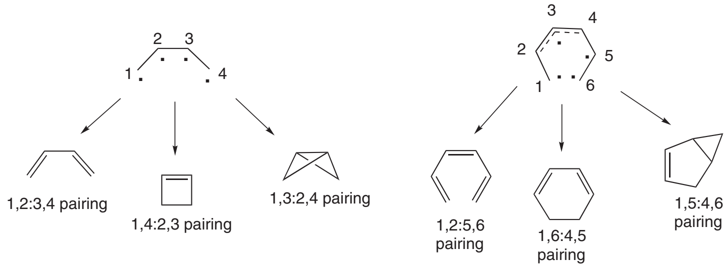
CI consist of two allyl fragments and two localized unpaired electrons. Alternate re-pairing schemes lead to the observed products.



Photolysis of both acyclic and cyclic 1,5-dienes leads to both 1,3-sigmatropic shifts and formation of allylcyclopropanes by 1,2-shift followed by cyclization.[186] The product mixture from 1,5-cyclooctadiene illustrates these reaction patterns.



The pattern that emerges from the experimental and computational studies of the conjugated dienes and trienes is the involvement of CIs having certain features in common. The singlet CI for the dienes appears to be a tetraradicaloid with the potential for several re-bonding schemes. In the absence of steric problems, it is structurally compact. The hexatriene-cyclohexadiene system also appears to involve a tetraradicaloid structure, one component of which is an allylic system. These structures can account for the major product types in both systems.



These results, as well as those from cyclooctatetraene and 1,5-cyclooctadiene, indicate that structures with isolated and allylic unpaired electrons play a key role in diene

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[186] T. D. R. Manning and P. J. Kropp, *J. Am. Chem. Soc.*, **103**, 889 (1981).

and polyene photochemistry. For triplet excited states of dienes, the minimum energy corresponds to a twisted diradical that consists of an allylic radical and a localized radical. The pattern continues for higher polyenes with the excited states consisting of components similar to those recognized for simple alkenes and dienes.

General References

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N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA, 1978.

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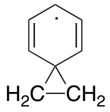
Problems

(*References for these problems will be found on page 1168.*)

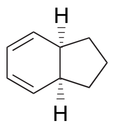
12.1. The bridged radical **1-A** has been suggested as a possible intermediate in the photochemical decarbonylation of 3-phenylpropanal. Suggest an experiment to test this hypothesis.



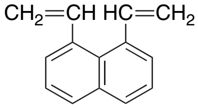
1-A

12.2. Predict the structure, including all aspects of the stereochemistry, based on orbital symmetry principles for the following photochemical electrocyclic and cycloaddition reactions.

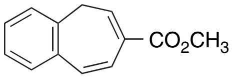
(a)



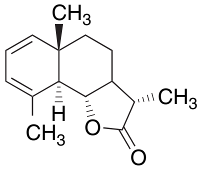
(b)



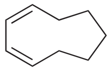
(c)



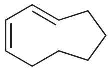
(d)



(e)



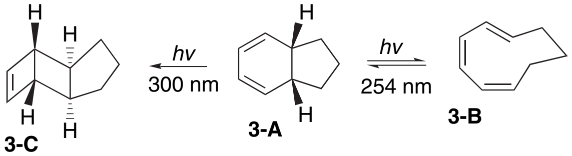
(f)



12.3. Suggest reasonable mechanisms for the following observations:

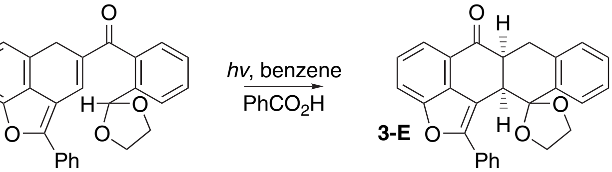
a. The optically active allene, 2,3-pentadiene, is racemized under toluene-sensitized photolysis.

b. Direct photolysis of diene **3-A** at 254 nm produces a photostationary state containing about 30% **3-A** and 70% **3-B**. When photolysis is carried out at 300 nm, photocyclization to **3-C** occurs and little **3-B** is present in the mixture.



3-C **3-A** **3-B**

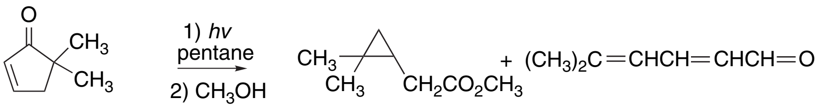
c. Photocyclization of the acetal **3-D** to **3-E** is catalyzed by benzoic acid.



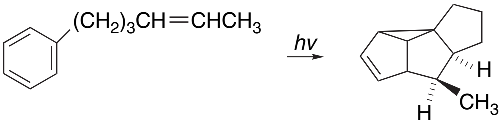
3-D **3-E**

12.4. Provide a mechanistic rationalization for each of the following reactions:

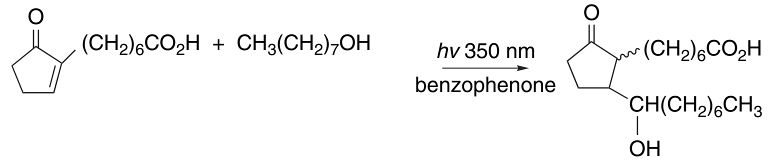
a.



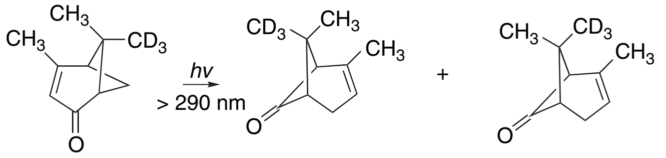
b.



c.

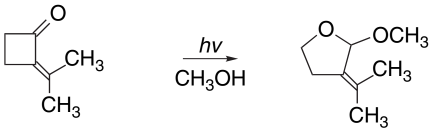


d.

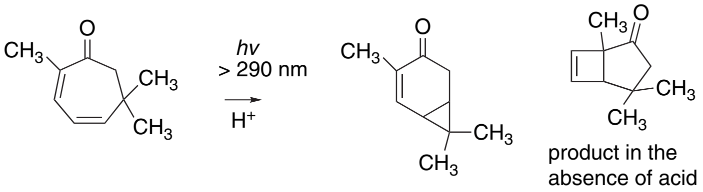


CD$_3$ group is equally distributed between the *exo* and *endo* positions

e.

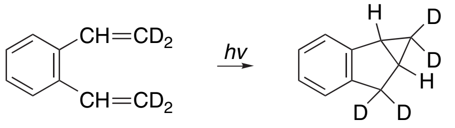


f.

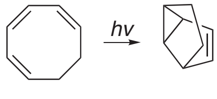


product in the absence of acid

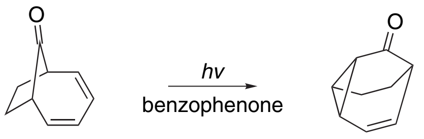
g.



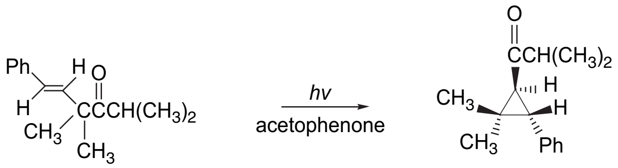
h.



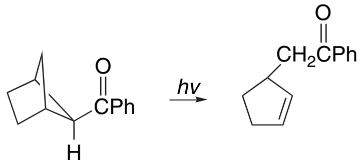
i.



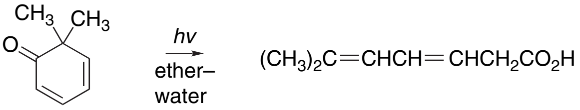
j.



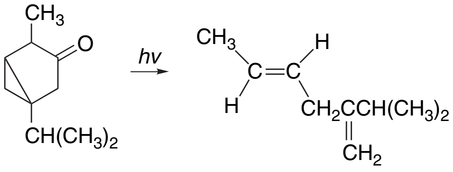
k.



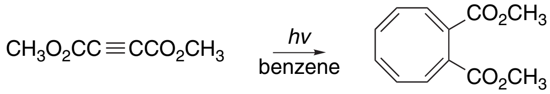
l.



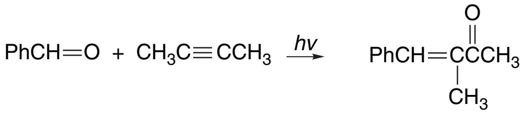
m.



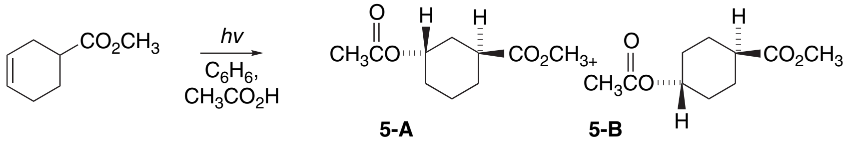
n.



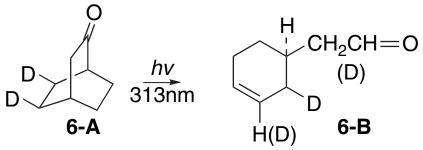
o.



12.5. Benzene-sensitized photolysis of methyl 3-cyclohexene-1-carboxylate in acetic acid leads to addition of acetic to the double bond. Only the *trans* adducts are formed. What factor(s) might be responsible for this stereoselectivity? Which of the two regioisomers do you expect to be the major product?

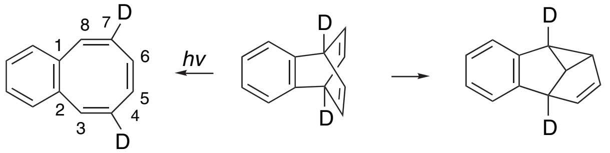


12.6. Photolysis of bicyclo[2.2.2]octan-2-one (**6-A**) gives **6-B** in good yield. When **6-A** is labeled as shown, the aldehyde group carries 48.3% of the deuterium. Write a mechanism to account for the overall transformation. Calculate the isotope effect for the hydrogen abstraction step. What mechanistic conclusion do you draw from the magnitude of the isotope effect?



6-A **6-B**

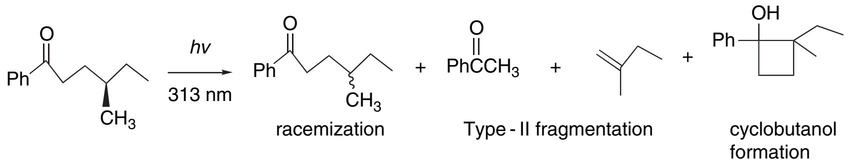
12.7. The photolysis of benzobarrelene **7-A** has been studied in considerable detail. Direct photolysis gives **7-C** (benzocyclooctatetraene), but when acetone is used as a photosensitizer, the di-π-methane rearrangement product **7-B** (benzosemibullvalene) is formed. A deuterium-labeling study gave the results shown. What mechanistic conclusions do you draw from these results? Is there a feasible mechanism that would have resulted in a different isotopic label distribution in **7-B**?



7-C **7-A** **7-B**

(A small amount of D is at C – 3,8.)

12.8. Quantum yield data for three competing processes that occur on photolysis of *S*-methyl-1-phenyl-1-hexanone at 313 nm in benzene have been determined and are tabulated below. When the reaction is run in *t*-butanol, the racemization is entirely suppressed and the Type-II fragmentation is the major reaction. What information do these data provide about the mechanism operating under these conditions?



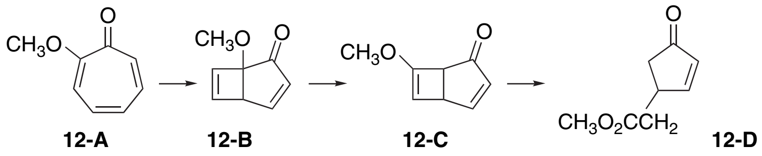
Process	Quantum yield	
	Benzene	*t*-Butanol
Type-II fragmentation	0.23	0.94
Cyclobutanol formation	0.03	0.05
Racemization	0.78	0.0

12.9. Show by means of an energy diagram the reason that the energy of light emitted from an excited electronic state by fluorescence or phosphorescence is of lower energy than the exciting radiation. Would you expect the shift in energy to be more pronounced for fluorescence or phosphorescence? Explain?

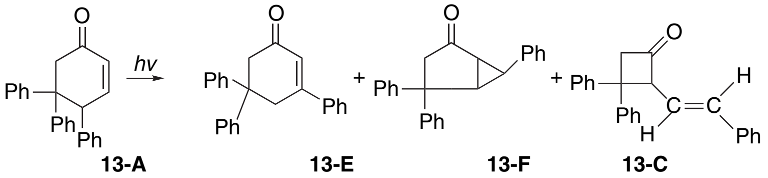
12.10. *cis*-2-Propyl-4-*t*-butylcyclohexanone undergoes cleavage to 4-*t*-butylcyclohexanone on photolysis. The *trans* isomer does not undergo fragmentation directly, but is converted to the *cis* isomer, which then fragments. The *trans* → *cis* isomerization is quenched by 1,3-pentadiene, but the photofragmentation is not. Offer an explanation of this pronounced stereochemical effect.

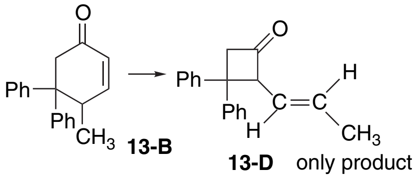
12.11. The quantum yield for formation of 3-methylcyclobutene from *E*-1,3-pentadiene by 254 nm radiation is ten times greater than for cyclization of the *Z*-isomer. 1,3-Dimethylcyclopropene is also formed but the difference in Φ for this reactions is only a factor of two. Offer an explanation for these differences in terms of energy surfaces that are involved.

12.12. The irradiation of 2-methoxytropone (**12-A**) leads to methyl 4-oxo-2-cyclopentenylacetate (**12-D**). The course of the reaction can be followed by gas chromatography and two intermediates are observed, which have structures **12-B** and **12-C**. Indicate a mechanism for the three successive reactions. The first two are photochemical, whereas the third is probably an acid-catalyzed reaction that does not require light.



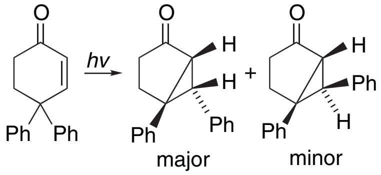
12.13. When an aryl substituent is placed at C(5) of a 4-substituted cyclohexenone, a new product type involving formation of a cyclobutanone ring is formed.



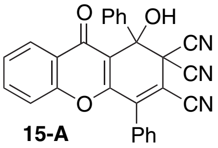


The reaction products are the same for both direct irradiation and acetophenone sensitization. When reactant **13-B** is used in enantiomerically pure form, the product **13-D** is nearly racemic (6% e.e.). Relate the formation of the cyclobutanone to the more normal products of 4-substituted cyclohexenones.

12.14. In the rearrangement of 4,4-diphenylcyclocyclohex-2-enone to 5,6-diphenylbicyclo[3.1.0]hexan-2-one, there is a strong preference for formation of the *endo* phenyl stereoisomer. Offer an explanation for this stereoselectivity.

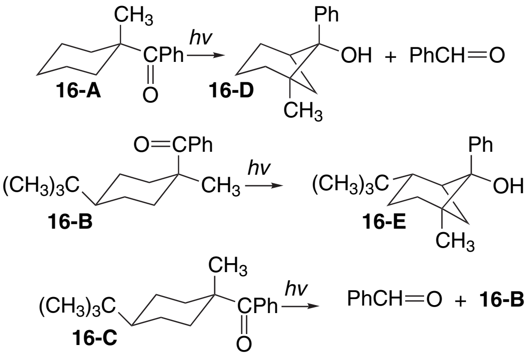


12.15. Compound **15-A** is photochromic; that is, it becomes colored on exposure to light. The process is reversible, giving back the starting material in the dark. Suggest a structure for the colored photoisomer.

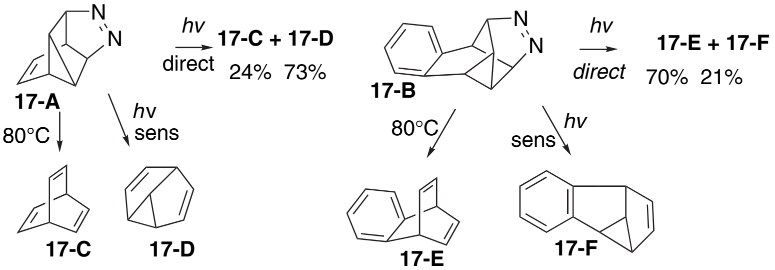


15-A

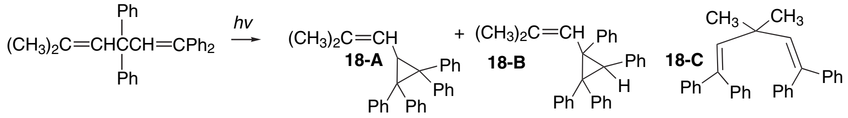
12.16. The photolysis of **16-A**, **16-B**, and **16-C** has been studied. **16-A** gives both **16-D** and the cleavage product benzaldehyde. **16-B** gives only **16-E**. **16-C** gives **16-B** and benzaldehyde. Discuss how the presence of the *t*-butyl group and its stereochemistry can influence the reaction outcome.



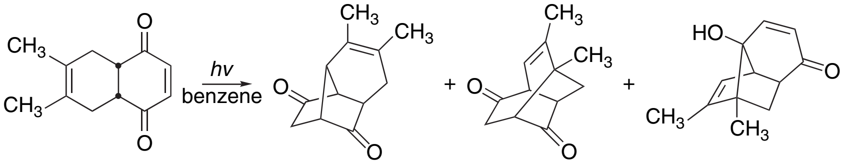
12.17. The azo compounds **17-A** and **17-B** were prepared and the thermal and photochemical behavior of these materials was investigated. The results are summarized in the Formulas below. It is also known that triplet photosensitization converts **17-C** to **17-D** and **17-E** to **17-F**, respectively. Discuss how these results relate to the mechanism of the di-π-methane rearrangement.



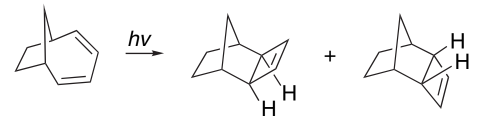
12.18. Direct irradiation of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene gives the products **18-A** and **18-B** shown below. When the reaction is carried out by photosensitization, only **18-A** is formed. Suggest mechanisms for formation of **18-A** and **18-B**. A minor product **18-C** is formed only in the photosensitized reaction. What other products might have been expected? Can you explain the preference for the observed products?



12.19. Suggest a mechanistic pathway for formation of each of the products formed on irradiation of the Diels-Alder adduct of 2,3-dimethylbutadiene and quinone.

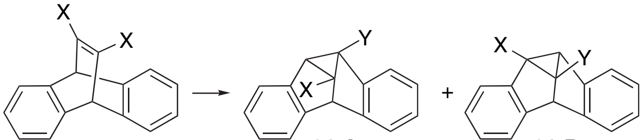


12.20. The direct irradiation of **20-A** gives predominantly **20-B**, but the photosensitized reaction gives more **20-C**. Explain these observations.



20-A	**20-C**	**20-B**
Direct:	28%	72%
Sensitized:	68%	32%:

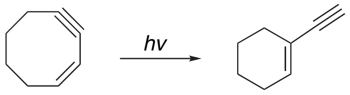
12.21. 9,10-Ethanoanthracenes undergo the di-π-methane rearrangement. Analyze the substituent effects that are observed in this reaction.



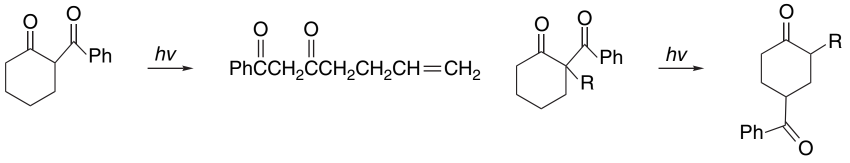
21-A **21-B**

Substituent X	Substituent Y	% **21-A**	% **21-B**
H	CO_2CH_3	0	100
H	$CON(CH_3)_2$	0	100
$CON(CH_3)_2$	CO_2CH_3	3	97
CO_2CH_3	$CSOCH_3$	0	100
CH_3	CO_2CH_3	0	100
Ph	CO_2CH_3	100	0

12.22. Formulate a mechanism for the following reaction.



12.23. The photochemistry of 2-benzoylcyclohexanone and its 2-alkyl derivatives diverges. The unsubstituted compound undergoes ring cleavage, whereas the substituted compounds result in migration of the benzoyl substituent to the 4-position of the ring. Suggest mechanisms for both reactions and account for the effect of the alkyl substituent.



$\mathrm{Ph\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2}$