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# **Organic Photochemistry**

The study of photochemical reactions provides new information on the excited states of molecules.

George S. Hammond and Nicholas J. Turro

At least one organic photoreaction, photosynthesis, is obviously older than man, and reports of laboratory studies of organic photochemistry are to be found in the very early chemical literature. However, the field has not been numbered among the very active areas of organic chemistry until recently (1-4). Several factors have contributed to a dramatic surge of interest in the subject. First, it has become evident that, potentially, photochemistry provides short routes for the synthesis of systems that are only available otherwise through long and tedious synthetic programs. The promise of the method is due in part to the fact that photochemistry provides a means for selective injection of large "doses" of energy into individual molecules or specific parts of a molecule in any given system. Thus it becomes possible to achieve, in one step, reactions which would have activation energies high enough to lead to general disruption of the system if they were attempted by thermal means. A second important feature of modern photochemistry is the availability of spectroscopic techniques (such as flash photolysis) which make possible the direct study of transient species involved in photoreactions. That the existence of such tools would attract workers interested in reaction mechanisms was alProc. Natl. Acad. Sci. U.S. 47, 270 (1961);
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most inevitable. Many of the concepts which are entering the literature of organic photochemistry have, in fact, been well known to spectroscopists for many years (5, 6), but some kinds of information about excited states which are not readily accessible by spectroscopic techniques are now being discovered.

In a sense, spectroscopists and photochemists are allied in their attempts to answer the following questions:

1) What happens to the excitation pumped into a molecule by absorption of visible or ultraviolet light?

2) What are the energies, electronic distributions, and geometric structures of various excited states?

3) What are the chemical properties of excited states?

### The Manifold of Excited States

Most polyatomic molecules have a number of metastable excited electronic states. Promotion of molecules to these states is accomplished by absorption of visible or ultraviolet light. Virtually all such transitions may be described approximately in terms of the excitation of a single electron from some orbital which is occupied in the ground state to an orbital which is vacant in the ground state. However, the first-formed excited state may undergo radiationless

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transitions to other excited states before it returns to the ground state or undergoes chemical reaction. Furthermore, the excitation may be transferred to other molecules in the system so that the ultimate chemical (or spectroscopic) action does not even involve the molecule which was originally excited.

Most organic molecules have even numbers of electrons which, in the ground state, are all spin-paired-that is, *n*-electrons in n/2 orbitals. Such states possess no net spin angular momentum and are called singlets; the ground singlet is usually labeled S<sub>0</sub>. Absorption of light promotes an electron to a vacant orbital; two electrons become orbitally unpaired. However, unless the electrons remain spinpaired the transition is highly forbidden and can occur only with very low intensity. Nearly all absorption bands observed in ordinary absorption spectroscopy are the result of singlet-singlet transitions—that is,  $S_0 \longrightarrow S_n$ . Since the Pauli principle does not demand that the spins of the electrons remain paired in most excited configurations, spin inversion (intersystem crossing) may take place, forming a second excited state, a triplet  $T_n$ . The latter will have a net spin angular momentum S = 1, and is actually triply degenerate; in a magnetic field separation into three energy levels would occur.



Other processes which can occur are shown in Fig. 1, a modified Jablonski diagram, which shows schematically a typical relationship among the four lowest-lying excited states of a molecule. With rare exceptions, emission of light occurs from only the lowest-lying excited singlet,  $S_1$ , and the lowest-lying triplet,  $T_1$ . The former process is known as fluorescence, and the latter is called phosphorescence. Consequently we know that nonradiative, internal conversion among excited electronic states such as  $S_n \longrightarrow S_1$  and  $T_n \longrightarrow T_1$  are very rapid, requiring no more than  $10^{-11}$  second. After they occur, intersystem crossings must also be rapid in order to compete with deactivation of excited singlets by other means. Since fluorescence lifetimes are of the order of  $10^{-1}$  to  $10^{-8}$  second, no other transformation



Fig. 1. Electronic transitions of a molecule. Straight lines indicate emission or absorption of radiation; wavy lines show nonradiative transitions.

of even the longest-lived excited single, S1, can require more than this amount of time; since most substances do not fluoresce in solution, nonradiative degradation to the ground state must actually shorten the lifetime of excited singlet states well below the values of their fluorescence lifetimes. Phosphorescence lifetimes range upward from 10<sup>-4</sup> second. The slowness of these radiative processes is associated with the fact that spin inversion is involved. The same factor contrives to slow down the nonradiative degradative processes which deactiviate triplets. Consequently, although T<sub>1</sub> is usually the least energetic of the excited states of a molecule, it is frequently the only one that retains electronic excitation long enough to undergo chemical reaction. However, this fact should not lead one to the conclusion that photochemistry is exclusively the chemistry of T1 states. Development of ways of determining which of the various excited states of a molecule are involved in photochemical reactions is one of the important and intriguing problems of theoretical photochemistry.

Identification of the particular excited state which is responsible for a given reaction is only a part of the general problem. The ultimate goal is to be able to predict and control photochemistry. We can only hope to do this by developing useful generalizations concerning the structures and reactivities of various excited states. Structural description will necessarily include specification of the electronic distributions in excited molecules and description of their geometries. In connection with this problem we should point out that the information of importance is not given fully by spectroscopy. According to the Franck-Condon principle, the most probable electronic transitions cannot involve change in nuclear positions. Consequently, absorption may produce excited states in configurations which are different from the equilibrium configurations. Vibrational relaxation then produces an excited state with a different equilibrium geometry in electron distribution, and a different energy. The latter relaxed state will normally be involved in chemical reactions.

## **Energy Transfer**

A very important process in organic photochemistry involves transfer of electronic excitation from one molecule to another,

$$A \xrightarrow{h\nu} A^*$$
$$A^* + B \longrightarrow A + B^*$$

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where h is Planck's constant and  $\nu$  is the frequency of the absorbed light. Consequently, a molecule (B) may undergo a photochemical reaction even though it does not originally absorb the exciting light.

Transfer of singlet excitation has been well documented for some time by studies of induced fluorescence and fluorescence depolarization (6, 7). Under suitable circumstances transfer of singlet excitation may occur over long distances (up to 200 angstrom units). Förster has developed a theory of long-range transfer which is based upon coupling of the transition dipoles of the donor and acceptor (8). A requirement for efficient transfer by this mechanism is extensive overlap of the fluorescence spectrum of the donor and an absorption band of the acceptor. In general, the longer a molecule persists in an excited state, the greater

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Fig. 2. Excitation energies of benzophenone and butadiene.

the probability that it will encounter other molecules and transfer its energy to them. Since triplet states have lifetimes longer by several orders of magnitude than excited singlet states, triplets are good candidates for participation in energy transfer.

Transfer of triplet excitation was first reported by Terenin and Ermolaev (9) in 1952, who observed induced phosphorescence at low temperature. Recently, a number of induced photochemical reactions have been shown to involve transfer of triplet excitation as key steps. The energetic separation between the states S<sub>1</sub> and T<sub>1</sub> varies greatly among organic molecules. Consequently, many photosensitized reactions occur despite the fact that activation involves light of a wavelength longer than any absorbed by the reactant. Figure 2, which shows schematically the relationships among the lowest excited states of benzophenone and butadiene, illustrates the point. Given the fact that benzophenone undergoes the intersystem crossing  $S_1 \longrightarrow T_1$  with high efficiency (10, 11), one can understand the fact that absorption of light by benzophenone can ultimately effect photochemical transformation of butadiene.

Both present theory (11) and observation indicate that transfer of triplet excitation must involve molecular contact between donor and acceptor. Most of the work to date indicates that, in solution, transfer occurs on every collision if the process is exothermic—that is, the  $S_0 \leftarrow T_1$  transition of the donor produces more energy than is required for the  $S_0 \longrightarrow T_1$  transition of the acceptor.

# **Organic Photoreactions**

The ultimate objectives of organic photochemistry are those which are traditional in organic chemistry: (i) to discover new general reactions, (ii) to learn to control and exploit known general reactions, and (iii) to use the results of the first two endeavors to synthesize interesting compounds. There is every indication that many new photoreactions will be discovered in the near future, while those already known are sufficient to fire the imaginations of workers in the field. Here we discuss selected types of reactions which illustrate the kinds of problems that are encountered in understanding the photochemistry of small organic molecules. Application of these notions to the synthesis of specific compounds we relegate to the role of exercises left to the reader, despite the fact that these exercises may involve the most difficult intellectual problems in the entire program.

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#### **Molecular Rearrangements**

A system can often be "pumped" by photoexcitation so that a stationary state is established in the interconversion of a pair of isomers, such that the composition is markedly different from that established by equilibration of the system by thermal means.

$$\mathbf{A} \xrightarrow[\Delta]{\mathbf{h}\boldsymbol{\nu}} \mathbf{A'}$$

If the exciting light is absorbed much more strongly by A than by A', and if the quantum yield (defined as moles reacted per einstein of light absorbed) for interconversion is appreciable, the steady-state concentration ratio, [A']/[A], may exceed the ratio observed in thermally equilibrated systems by a large amount.

cis-trans *Isomerization*. Irradiation of many compounds containing olefinic linkages results in isomerization, as in reaction 1 (12). In simple systems it frequently occurs that the *trans* isomer absorbs light of long wavelength more intensely than the *cis* isomer; consequently, the mixture usually reaches a photostationary state in which the less stable, *cis* isomer predominates at equilibrium. Isomerization of the stilbenes has been studied fairly extensively and discussed at even greater length (13). The quantum yields in the *cis* — *trans* and *trans* — *cis* processes are temperature dependent, indicating that the excited states must undergo some activated process in the course of isomerization.

It has been suggested that the activated process is conversion of singlets to a common, twisted triplet or, alternatively, that the activated step is interconversion of cis and trans triplets. The fact that isomerization of the stilbenes can be effected by means of sensitizers which are known to decay by way of triplets shows at least that the reaction can proceed by way of triplet intermediates (13). Those sensitizers which have  $S_1 \longrightarrow T_1$  transition energies higher than the corresponding transitions of either the cis or trans isomers give the same cis-to-trans ratio in the stationary state. This implies that transfer occurs on every collision of either isomer of stilbene with a sensitizer triplet and that the stationary-state composition is determined only by the relative amounts of cis and trans isomers formed in the decay of the stilbene triplet (or triplets). S\* is the sensitizer in the excited state, T refers to stilbene triplets having unspecified configurations, and subscript s indicates steady-state concentration.

$$\mathbf{S}^* + cis - \mathbf{C}_{14}\mathbf{H}_{14} \xrightarrow{k_1} \mathbf{C}_{14}\mathbf{H}_{14(\mathbf{T}_1)} + \mathbf{S}$$
(2)

$$\mathbf{S}^* + trans - \mathbf{C}_{14} \mathbf{H}_{14} \xrightarrow{k_2} \mathbf{C}_{14} \mathbf{H}_{14(\mathbf{T}_1)} + \mathbf{S}$$
(3)

$$C_{14}H_{14(T_1)} \xrightarrow{k_3} cis - C_{14}H_{14}$$
(4)

$$C_{14}H_{14(T_1)} \xrightarrow{k_4} trans-C_{14}H_{14}$$
(5)

$$\frac{[cis]_s}{[trans]_s} = \frac{k_2 k_3}{k_1 k_4}$$
(6)

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Much more complicated results are obtained with sensitizers having lower triplet excitation energies. From a practical point of view the results show that a wide variation in the steady-state compositions is obtainable by variation in the photosensitizer. At present, theory must rest on the observation that energy transfer becomes a complex process when the excitation energy of a donor is close to that of an acceptor.

Theoretical considerations indicate that the equilibrium configuration of the triplet state of ethylene should have the perpendicular configuration (14). While one is tempted to assign nonplanar configurations to the triplet states of all olefinic compounds, there is no clearcut argument to support this.

There is another interesting suggestion that may account for the isomerization reaction. The nonradiative decay of any excited state to the ground singlet may produce the latter instantaneously with a large amount of vibrational energy. For example, the triplet formed by  $S_0 \longrightarrow T_1$  absorption (15) of trans-stilbene has an energy 49 kilocalories above that of the ground state. If this state should undergo intersystem crossing without transfer of any energy to the environment, the  $S_0$  state would be produced with 49 kcal of excitation energy per mole. The activation energy for thermal,  $cis \longrightarrow trans$  isomerization of stilbene is about 43 kcal per mole, and the frequency factor is  $6 \times 10^{12}$  (that is, close to kT/h). The "normal" frequency factor for the thermal process implies that in a singlet cis-molecule possessing 43 kcal of excitation energy, the excess energy will be effectively partitioned among the various degrees of freedom, including rotation about the central bond, at a rate which is high in comparison with the rate of transfer of the excess energy to the environment. If this is true, the S<sub>0</sub> state produced by intersystem crossing from trans-T1 should go through a freely rotating condition before it cascades back to the thermally equilibrated state of  $S_0$ .

Isomerization of 4-methoxy-4'-nitrostilbene by direct irradiation has been studied in some detail (16).



The quantum yield for the *trans*  $\longrightarrow$  *cis* process is dramatically dependent on both temperature and solvent, whereas the quantum yield for the reverse process is independent of these factors. These facts have been interpreted as meaning that there is an energy barrier between the S<sub>1</sub> state of the *trans* system and another state (perhaps the triplet) in which rotation can occur. The solvent effect is attributed to selective stabilization of the very polar S<sub>1</sub> state by polar solvents. To complete this argument it is assumed that, because of steric hindrance, the *cis* excited state is converted to the freely rotating state with no activation energy.

A very careful study has shown that in the isomerization of the azobenzenes the quantum yield for the *trans-cis* process is temperature dependent, whereas that for the  $cis \longrightarrow trans$  conversion is not (17). The results were interpreted in terms of the existence of a barrier to rotation in the *trans*-S<sub>1</sub> state that is absent in the *cis*-S<sub>1</sub> state.

Obviously, even a comparatively "simple" reaction such as *cis-trans* isomerization is not yet completely understood, but this particular problem will probably be completely solved in the near future. However, the fact that the solution has not been found easily indicates that detailed mechanistic description of other problems may come slowly.

Valence isomerization. A large number of polyunsaturated systems undergo ring closure or ring-opening reactions. Reactions 8 to 15 are typical examples of ring closure (20).



(See respectively, references 18; 19 and 20; 21; 22 and 23; 24; 25–27; and 28). Each of these reactions, except for reaction 15, was carried out by direct irradiation. In addition, reactions 8, 11, and 14 were effected with benzophenone or acetone as photosensitizers (23, 25). This implies that triplet states of the starting materials undergo ring closure, but it does not exclude the possibility that direct irradiation results in ring closure by way of excited singlets.

Srinivasan has studied the irradiation of cycloheptatriene in the vapor phase (29). Although reaction 8 occurred to the extent of less than 5 percent, the principal course of the reaction was rearrangement to toluene. The fact that quenching by oxygen and nitric oxide did not occur led to the conclusion that triplet states are not involved in the reactions. At low pressures the yield of [3,2,0]-bicycloheptadiene is slightly lower than at high pressures. On the other hand, the yield of toluene is markedly decreased by increasing the total pressure in the system. These results were interpreted as indicating that toluene is formed by rearrangement of the vibrationally excited ground state molecule formed by internal conversion.

$$C_{7}H_{8(S_{1})} \rightarrow C_{7}H_{8(S_{0}^{*})} \rightarrow Toluene$$

$$\downarrow$$

$$C_{7}H_{8(S_{0})} \qquad (16)$$

High pressures cause the  $S_0^*$  state to be rapidly deactivated to cycloheptatriene, before rearrangement to toluene can occur.

Although photochemical opening of the cyclohexadiene ring system in lumisterol (reaction 17) has been known for some time as a step in the photo processes that convert ergosterol to vitamin D, such ring-opening reactions seem on the whole to be less common than ring-forming reactions (20).



Reaction 18 has been carried out in the vapor phase and gives hydrogen and benzene as well as hexatriene (30). Irradiation of 1,3-cylohexadiene in solution with benzophenone as a sensitizer leads to formation of cyclodimers (27). It is virtually certain that the latter reaction involves diene triplets, and comparison of the results from the two types of experiments suggests that triplets are not formed subse-20 DECEMBER 1963 quent to direct irradiation in the vapor phase. The conclusion is not compelling, because the concentration of the diene was much higher in the liquid phase experiments, a factor which would favor dimerization. Absence of characteristic quenching effects led Srinivasan to favor a pure singlet mechanism for the vapor phase reaction.

Irradiation of 5,6-disubstituted 1,3-cyclohexadienes yields a photostationary mixture of the valence isomers (31).

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Dauben and Wiley (32) have recently reported a reaction which seems to be the most extreme instance of molecular knot-tying yet accomplished by photochemistry. Irradiation of  $\Delta^{3,5}$ -cholestadiene, a conjugated diene which is "frozen" in the *s*-trans configuration and cannot readily undergo the reactions described above, produces a saturated isomer which almost certainly contains the highly strained system, bicyclobutane.



#### **Skeletal Rearrangements**

The photochemical rearrangements of dienones have long been known but have only recently begun to receive satisfactory mechanistic treatment. A careful study of reaction 21 has been reported by Zimmerman and Schuster (33).



The many rearrangements of this type have in common a disturbing feature. The reactions are effected by irradiation with light absorbed in the long-wavelength absorption bands of the substrates. The transitions involved are  $n \longrightarrow \pi^*$  processes in which a nonbonding oxygen electron is promoted to an excited  $\pi$ -orbital. Despite the fact that the excitation obviously renders the  $\pi$ -electron system electron rich, the rearrangements which occur seem to be those characteristic of electron-deficient systems. Zimmerman has reasoned that some changes in structure must occur before rearrangement occurs. The suggested scheme is shown in Fig. 3.

In essence, each rearrangement provides a path for the gradual reduction of electronically excited states through



stages which minimize the amounts of energy which must be transferred to the environment in each step. If this principle can be shown to apply to such reactions in general, it may become an important guidepost in photochemistry. However, some caution may be in order. We have rephrased the Zimmerman-Schuster hypothesis in terms of a "principle of maximum awkwardness"; that is, a highly excited molecule will find paths of decay which involve a minimum decrease in energy in each individual step. A different point of view might be that the excited molecules have so much excess energy that reactions characteristic of groundstate molecules may provide no suitable criteria for prediction of chemical reactivity. Consider, for example, the first stage of rearrangement of 4,4-diphenyl-2,5-cyclohexadieneone. If the excited state were to undergo isoenergetic, internal conversion to the ground singlet state, the latter species would be "born" with vibrational energy of more than 60 kcal per mole. The reactions which such a species might undergo before the excess energy is transferred to the medium should be compared with those unimolecular reactions of the system that have activation energies greater than 60 kcal. Such reactions are ordinarily unobservable, because of competition from other processes having lower activation energies. Consequently, ground-state chemistry may not always turn out to provide good criteria for predicting the course of photochemical reactions. Srinivasan (29) argues that since a photoreaction and a known thermal reaction are similar, a particular photoprocess should involve a high vibrational level of a ground state molecule. This criterion will have real meaning only if the particular thermal reaction is the only one, of the system in question, having an activation energy lower than the photoexcitation energy.

Chapman (4) has pointed out that, since simple eneones undergo rearrangements similar to those of dienones, the first rebonding step of the Zimmerman-Schuster formulation, which appears to be uniquely dependent on the presence of two double bonds, cannot be an absolutely necessary feature of these reactions. Reaction 22 is a representative example.

Chapman prefers to formulate all rearrangements of  $\alpha,\beta$ -unsaturated ketones as involving electron-deficient  $\pi$  sys-

tems, without specifying the chronology of production of the electron deficiency. He has, furthermore, suggested that excited states may be protonated before rearrangement in some instances. Such a mechanistic device could account for the fact that different products are sometimes produced in protic and aprotic solvents. Clearly a good deal of detailed work is needed to identify the excited states and other transients responsible for these reactions.



A striking dependence of the course of reaction on the nature of the excited state is given by the paths followed by *cis*-dibenzoylethylene, I (34). Upon direct irradiation in alcoholic solution the molecule undergoes  $n \longrightarrow \pi^*$  excitation, forming a singlet state which rearranges, and produces ethyl 3-phenyl-3-phenoxy-propenoate (II in reaction 23).



The photoreaction takes a completely different course in the presence of photosensitizers such as benzophenone. Under these conditions the primary reaction is reduction to 1,2-dibenzoylethane (III in reaction 24). The latter reaction probably involves energy transfer from the triplet state of the sensitizer to (I) forming the triplet of (I), which then proceeds to abstract hydrogen from solvent. The excited species responsible for the formation of (II) must be in an excited singlet state, which is unable to abstract hydrogen atoms efficiently and prefers an alternate course of reaction—that is, rearrangement with 1,5-migration of a phenyl group; the ketene formed by the rearrangement then adds a molecule of solvent, thus forming an ester.

#### **Photochemical Cycloaddition Reactions**

The older photochemical literature is full of examples of reactions in which cyclobutanes are formed by irradiation of molecules containing the  $\alpha,\beta$ -unsaturated carbonyl function (3, 35). Correlation of the course of photodimerization reactions carried out with crystalline solids (the crystal structures having been determined by x-ray diffraction) indicates that cycloaddition occurs if the reactive centers are 4 angstrom units or less apart (36). This interpretation explains the differences noted in the dimers produced by irradiation of the two crystalline forms of *trans*-cinnamic acid.

The course of dimerization in solution sometimes shows a marked dependence upon solvent. Coumarin undergoes photochemical dimerization in ethanol, according to reaction 25, but undergoes no reaction on direct irradiation in benzene (37).



Moreover, the photosensitized dimerization, with benzophenone as sensitizer, proceeds smoothly in ethanol or benzene and produces a dimer of different stereochemistry from that obtained by direct irradiation in ethanol. On the other hand, the photochemical dimerization of cyclopentenone (38) and cyclohexenone (38) goes smoothly in the pure liquid or in a variety of organic solvents, to produce equal amounts of two dimers (reaction 26).



The carbonyl group shows little effect in controlling the course of the dimerization, in contrast to its directive role in thermal cycloadditions (39). In fact, in the presence of 20 DECEMBER 1963

excess of cyclopentene, selfdimerization is completely excluded (40, 41) in favor of cross addition (reaction 27).

These facts, if considered alone, would indicate that the excited state of cyclopentenone which is involved in the reaction is very highly reactive and therefore quite unselective in its action. The contrast between these results and those observed in many other photocyclodimerizations could also mean that cycloaddition reactions of cyclopentenone involve excited singlet states but that many other similar reactions involve triplet states. Photosensitized cycloadditions (42) are believed to involve triplets and do show high selectivity. One might expect an interesting and important difference in the timing of singlet and triplet reactions. Addition of a singlet could give products directly with spin conservation, whereas addition of triplets may normally involve three stages, with spin inversion as a discrete step.



A number of examples of cycloaddition reactions involving the use of carbonyl compounds as photosensitizers have been reported recently (42). Reactions 30 and 31 are typical examples.



There is one striking difference between them: the use of different sensitizers leads to variation in the relative amounts of the three products of reaction 30, but no such variability in amounts is observed in reaction 31. The effect of variation of sensitizers has been studied in detail in the dimerization of isoprene and butadiene. The results indicate that, although seven photodimers are formed from isoprene and three photodimers from butadiene, there are only two independent variables. We believe that variation is due to the existence of noninterconvertible, stereoisomeric triplet states of open chain dienes. These two states would be formed by electronic excitation of the *s*-trans and *s*-cis forms of the dienes which are in dynamic equilibrium in the ground states.



We assume that high energy sensitizers, such as acetophenone or benzophenone, transfer energy to either *s-cis* or *s-trans* forms on every collision. Since *s-trans* forms predominate in butadiene and isoprene at ordinary temperatures, the predominant triplet produced by such sensitizers will be the *trans* isomer. Addition of this species to *trans* diene will give biradicals which are not well disposed to cyclize to cyclohexene derivatives; consequently, cyclobutanes, cyclooctadienes, or both, are formed.



diene molecules to give biradicals which are sterically well suited for cyclization, with formation of six-membered rings.



The analysis shown in reaction 34 is obviously a first approximation since other processes, such as the addition of triplets to *s-cis* diene molecules, are ignored and the cyclization paths shown may not be entirely predominant. As one would expect, the efficiency of production of *cis*-diene triplets is a sensitive function of temperature and the amount of vinyl-cyclohexene produced increases as the temperature is raised.

Photochemical addition of maleic anhydride and its derivatives to unsaturated systems can be carried out both by direct irradiation and through the agency of photosensitizers (43).



Cyclohexenone adds, in a remarkably general manner, to carbon-carbon double and triple bonds, to form cyclobutanes (41).



**Carbonyl Additions to Ethylenic Systems** 

The use of sensitizers having lower triplet excitation energies leads to selective excitation of *s*-*cis* diene molecules. (The  $S_0 \longrightarrow T_1$  transition of butadiene occurs at shorter wavelength than does the corresponding transition of 1,3cyclohexadiene.) The *cis* triplets produced add to *trans* 

Only a handful of additions of the carbonyl group to ethylenic systems have been reported. Although the reaction is potentially useful, evaluation of its possibilities and generality await further investigation. Reactions 38 to 42 indicate the results to date (44, 45).





$$(40)$$

 $(C_{6}H_{5})_{2}C = O + \bigcup_{O} \xrightarrow{h_{\nu}} O C_{6}H_{5}$ 

or 
$$C_6H_5$$
 (41)

$$\begin{array}{c} & & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

The usual course of the reaction can be explained by a step-wise mechanism involving addition of the triplet states of the carbonyl compounds to the unsaturated systems.



The biradical derived from the observed product possesses greater stability, due to hyperconjugation, and is therefore formed preferentially (44).

Ultraviolet irradiation of vinylidene fluorides and either a fluoroaldehyde, a fluoroacyl fluoride, or a fluoroketone has been found to result in the cycloadditon of the carbonyl function to the olefin to form polyfluorooxetanes in good yield (46) (reaction 44). Although eight isomeric oxetanes are possible, only two are found (reaction 45). The results are compatible with the diradical mechanism proposed for thermal cycloadditions (39).

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If it is assumed that the intermediate in the addition is the most stable diradical of all those possible, the products are correctly predicted. For example, of the four possible intermediates (IV to VII) in the reaction of trifluoroacetaldehyde with hexafluoropropene, diradical (IV) is predicted to be the most stable.



#### Photolysis

Frequent irradiation leads to dissociation of the absorbing molecule. The species produced may be radicals, ions, carbenes, or small molecules. We do not attempt, here, to review the subject, which has already been studied in great detail (2). We do, however, mention a few examples of interest, with emphasis on solution chemistry, since much has been written about photolysis in the vapor phase.

Formation of free radicals. The best studied of all photochemical reactions is photolysis of aldehydes and ketones in the vapor phase (47). Cleavage to radicals (reaction 46) and, if a  $\gamma$ -hydrogen atom is present, the so-called type II process (reaction 47) are both observed.

$$CH_3COCH_3 \xrightarrow{h_{\nu}} CH_3\dot{CO} + \cdot CH_3$$
 (46)

$$CH_{3}CH_{2}CH_{2}CCH_{3} \xrightarrow{h_{\nu}} \begin{array}{c} \xrightarrow{O} \\ & \xrightarrow{H_{2}=CH_{2} + CH_{2} = CH_{3}} \\ & \xrightarrow{H_{2}=CH_{3} + CH_{2} = CH_{3}} \\ & \xrightarrow{H_{2}=CH_{3} + CH_{3} = CH_{3}} \\ & \xrightarrow{H_{2}=CH_{3} + CH_{3} + C$$

The type II process persists, with low quantum yield, in solution, but cleavage to radicals is usually entirely suppressed in solution. Historically, this observation is responsible for the first statement of the theory of the "cage effect," by Franck and Rabinowitch (48). They pointed out that, in solution, the delay in separation of radical pairs formed by homolytic dissociation might permit the radicals to "cool

$$R_2 CO \xrightarrow{h_{\nu}} R_{\bullet} + RCO^*$$
(48)

$$\mathbf{R} \cdot + \mathbf{R}\dot{\mathbf{C}}\mathbf{O}^* \to \mathbf{R} \cdot + \mathbf{R}\dot{\mathbf{C}}\mathbf{O} + \mathbf{E}$$
 (49)

$$\mathbf{R} \cdot + \mathbf{R}\mathbf{C}\mathbf{O} \to \mathbf{R}\mathbf{C}\mathbf{O}\mathbf{R}$$
 (50)

down" and recombine. Although the cage effect is now well documented, it seems entirely possible that there are other factors primarily responsible for the failure of ketones and aldehydes to undergo photolytic dissociation in solution. In fact, the photolysis of pinacolone to give radicals in solution has recently been observed (49).

$$(CH_3)_3COCH_3 \xrightarrow{h_{\nu}} (CH_3)_3C_{\cdot} + CH_3CO$$
 (51)

Some compounds, such as aliphatic azo compounds and diacyl peroxides, give radicals readily on irradiation in solution (50).

$$CH_3N = NCH_3 \rightarrow 2 \dot{C}H_3 + N_2 \tag{52}$$

Formation of ions. A number of compounds dissociate, with the formation of ions, when irradiated in polar solvents. The best known examples are the leuconitriles of triarylmethanes (51).

$$\operatorname{Ar_3CCN} \xrightarrow{\operatorname{n}\nu} \operatorname{Ar_3C^+} + \operatorname{CN^-}$$
(53)

Having has shown that there is an unexpected substituent effect in the photosolvolysis of m- and p-nitrophenyl phosphates. Irradiation of the *meta* compound results in relatively fast hydrolysis, whereas the *para* substituted compound shows little or no photodissociation (52).



Similar studies of *m*- and *p*-nitrophenyl trityl ethers by Zimmerman and his co-workers (53) show the same selective activation toward photoionization by an *m*-nitrosubstituent. Zimmerman has explained the effect in an interesting manner. He has calculated from simple molecular orbital theory the electron distribution in the excited states produced by  $\pi$ - $\pi$ \* excitation of species of the general structure



in which Z is an electron-deficient center—for example, the nitrogen atom of a nitro group.

In the excited state there is extensive electron transfer from the meta positions to Z. Consequently, the excited states might be expected to ionize much more easily than the ground states. Zimmerman has translated the molecular orbital calculations into resonance formulation, as shown in reaction 55. If this explanation is correct, it has further interesting implications. The  $\pi,\pi^*$  excited state is probably not the lowest excited singlet of nitroaromatics. The fact that the absorption spectra of nitrobenzene and related compounds have long "tails" which extend into the visible spectrum probably shows that the lowest excited singlet states have  $n,\pi^*$  configurations in which an oxygen nonbonding electron has been promoted to a  $\pi^*$  orbital. The Zimmerman hypothesis implies one of two situations: (i) the solvolysis may occur before the system can undergo internal conversion from  $S_2$  to  $S_1$ , or (ii) the solvolysis may take place from a triplet state which has the  $\pi,\pi^*$  configuration (54). This hypothesis is not at all clear-cut, since the dissociation formulated in reaction 55 is predicated upon the formation of spin-paired products.



Formation of carbenes. The best-known examples of a photolytic process which produces carbenes is found in the photochemical dissociation of diazomethane. Direct irradiation produces the unstable singlet state of : $CH_2$  (55, 56). In the presence of a high pressure of inert gas, this species decays to triplet methylene (55).

$$\mathrm{CH}_{2}\mathrm{N}_{2} \xrightarrow{\mathrm{h}_{\nu}} \mathrm{CH}_{2}\mathrm{N}_{2}^{*} \downarrow \uparrow \to \mathrm{N}_{2} + \downarrow \uparrow \mathrm{CH}_{2} \xrightarrow{\mathrm{N}_{2} \text{ or}}_{\mathrm{A}} \uparrow \uparrow \mathrm{CH}_{2}$$
(56)

For the organic chemist, a principal significance of these experiments is the fact that singlet and triplet methylene have quite different chemical properties (56a). Singlet methylene is highly indiscriminate in its action. It reacts with hydrocarbons both by random insertion in C-H bonds and by addition to double bonds.



Triplet methylene, on the other hand, does not insert in nonactivated C—H bonds (55, 56). Furthermore, addition to olefinic linkages is nonstereospecific, in contrast to the addition of singlet methylene.



The products noted by question marks in reaction 59 are observed in vapor-phase reactions but not in solution. It is possible that 2-pentene is produced by a radical chain reaction in the vapor phase. 3-Methyl-1-butene is believed to be produced by a hydrogen transfer reaction.

$$\begin{array}{c} \operatorname{CH}_{3} \\ \operatorname{H} - \stackrel{\downarrow}{\operatorname{C}} \\ \stackrel{\downarrow}{\operatorname{CH}}_{2} \cdot \stackrel{\downarrow}{\operatorname{CH}} \\ \operatorname{CH}_{2} \cdot \downarrow \end{array} (\operatorname{CH}_{3} \to (\operatorname{CH}_{3})_{2} \operatorname{CHCH} = \operatorname{CH}_{2} \tag{60}$$

This product is produced in the vapor phase but apparently not in solution. Another contrast between the vapor-phase and the solution chemistry of triplet methylene is the fact that addition to *cis*- and *trans*-2-butene appears to be nonstereospecific in the vapor phase but shows some stereospecificity in solution—that is, *cis*- and *trans*-dimethylcyclopropane are formed in different ratios from the reaction of *cis*- and *trans*-2-butene with triplet methylene in solution. The two results are compatible with the assumption that the addition occurs in two steps, as shown in reaction 61. The first step is the formation of a triplet biradical.



In the vapor phase the biradical apparently lives long 20 DECEMBER 1963

enough to arrive at rotational equilibrium and to undergo the rearrangement shown in reaction 60 before spin inversion, and consequent ring formation, occur. In solution, spin inversion may occur at a rate comparable to the rate of rotation. Although the basis for this argument is weak, it is at least reasonable, since spin inversion should be much faster in a condensed phase than in the vapor phase.

In the vapor phase, triplet methylene is produced by direct photolysis, with a high pressure of an inert gas which promotes decay, according to reaction 56, before the methylene species encounters a substrate molecule. In solution the triplet is produced by photosensitized decomposition (56), as shown in reactions 62 to 64.

$$(C_6H_5)_2CO \xrightarrow{h\nu} (C_6H_5)_2CO_{(S_1)} \rightarrow (C_6H_5)_2CO_{(T_1)}$$
(62)

$$(C_6H_5)_2CO_{(T_1)} + CH_2N_2 \rightarrow (C_6H_5)_2CO + CH_2N_{2(T_1)}$$
 (63)

$$\mathrm{CH}_{2}\mathrm{N}_{2(\mathrm{T}_{1})} \to \mathrm{CH}_{2} \downarrow \downarrow + \mathrm{N}_{2} \tag{64}$$

McNesby and Okabo have reported that irradiation of saturated hydrocarbons with far-ultraviolet light leads to fragmentation to carbenes (57).

$$\mathrm{RCH}_3 \xrightarrow{h_{\nu}} \mathrm{RCH}: + \mathrm{H}_2 \tag{65}$$

Nothing is yet known about the spin states of the fragments produced.

#### Photoreduction

Among the well-known photoreactions of carbonyl compounds is the reductive process which occurs in the presence of good hydrogen donors. Fairly extensive studies of benzophenone seem to assure that, at least in the one case, the reactive species is the lowest triplet state of the carbonyl compound (58).

$$(C_6H_5)_2CO \xrightarrow{h_{\nu}} (C_6H_5)_2CO_{(\mathbf{8_x})} \to (C_6H_5)_2CO_{(\mathbf{T_1})}$$
(66)

$$(C_{6}H_{5})_{2}CO_{(T_{1})} + RH \rightarrow (C_{6}H_{5})_{2}COH + R \cdot$$

$$\downarrow OH OH$$

$$(C_{6}H_{5})_{2}C - C(C_{6}H_{5})_{2} +$$

$$OH \qquad (67)$$

$$\downarrow (C_{6}H_{5})_{2}CR + R - R$$

It is entirely possible that reactions such as 67 are the principal radical-producing reactions of carbonyl compounds in condensed phases. The reactivity of hydrogen donors seems to parallel, at least qualitatively, their reactivity in atom abstraction by free radicals. Since the latter type of reactivity is not rigidly fixed but varies with the nature of the attacking radical, we can only consider our knowledge of the reactivity of carbonyl triplets in hydrogen abstraction to be incomplete. One interesting variable has already been discovered. Many aromatic aldehydes and ketones do not undergo the reduction reaction with the usual hydrogen donors. Typical examples are derivatives of naphthalene and anthracene. Hydrogen transfer does, however, occur with very powerful hydrogen donors such as tri-*n*-butylstannane. The low reactivity of triplets, presumably formed from the unreactive compounds, is associated with the fact that in the systems in question the lowest triplet states have  $\pi,\pi^*$ , rather than  $n,\pi^*$ , configurations (59). That  $n,\pi^*$  triplets should be especially reactive in hydrogen abstraction is reasonable, since they have an electron deficiency at the oxygen atom to which the hydrogen atom becomes bonded.

An important variant of photoreduction involves internal hydrogen transfer followed (or accompanied) by cyclization. The process leads to formation of derivatives of cyclobutanol (60).



It should be noted that the process is, in a sense, analogous to the type II cleavage of ketones as well as to intermolecular photoreduction.

### Enolization

A remarkable isomerization of 1-acetylcyclohexene has been claimed recently (61).



It has been surmised that the reaction involves enolization. Although the enol may be involved, the geometry of the cyclic system would seem to preclude the direct transfer of hydrogen from C<sub>3</sub> to the oxygen of the carbonyl group. Possibly a proton is lost from a  $\pi,\pi^*$  excited state in which C<sub>2</sub> has become electron-deficient (reaction 72). Recapture of a proton might conceivably produce 3-acetyl-cyclohexene directly, but, because the rates of proton transfers involving oxygen are ordinarily higher than those involving carbon,





#### **Other Photolytic Reactions**

An interesting photoisomerization of nitrite esters has recently been developed for the selective introduction of functionality at certain saturated centers in complex molecules (62).



The reaction probably involves homolysis of the nitrite, internal hydrogen abstraction by an alkoxy radical, radical coupling, and, finally, isomerization of a nitroso compound to an oxime.





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Other reactions, such as fragmentation of the intermediate alkoxy radicals, may occur even though an abstractable hydrogen atom may be sterically accessible (63) (reaction 75).

The reactions which are observed can all be attributed to known transformations of alkoxy radicals. However, there are instances in which minor variation in the nature of remote substituents alters the course of the reaction significantly (64). Whether the control is exerted in the radical chemistry or in the photochemistry is not known.

Superficially similar transformations are accomplished by irradiation of hypohalites (65) and azides (66).



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(77) H h (78) cyclohexane

The azide photolysis probably involves the intermediacy of nitrenes (R-N:) which undergo insertion reactions with the most available C-H bonds. The few recorded observations suggest that there may be a wide field for activity in the study of nitrenes produced photochemically. These species should, like carbenes, have both low-lying singlet and triplet states (67).

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