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Interpretation of Some Organic Photochemistry

Unusual reactions lead to understanding the behavior of electronically excited molecules.

Howard E. Zimmerman

Organic photochemistry is now at an evolutionary stage where almost every species isolated is new and nearly every reaction uncovered is a major advance. Relatively little is known with certainty, and the undiscovered measures immense relative to the discovered. Consider, for each of the multitudinous molecules already described in *Beilstein* and *Chemical Abstracts* that there exists at least one electronically excited state formed by light absorption, and a reasonable fraction of these excited species will undergo new transformations when put to test. Each of these excited states has the gross skeleton of the parent, ground-state molecule but differs in electron distribution and chemical reactivity.

However, research in photochemistry does face impediments, and two of these are of particular consequence. First, the structures of the electronically excited states still can be determined only approximately, and often only by methods not easily accessible to the organic chemist. Second, even when the excited-state structure is known, it is uncertain what criteria control the course of the excited-state reaction.

Controlling Factors in Photochemical Transformations

I have taken the view (*1–4, 5*) that photochemical processes are selective. Bonds are not broken indiscriminately although, frequently, more than enough electronic energy (that is, about 100 kilocalories per mole at 285 millimicrons) is absorbed to break carbon-to-carbon bonds. Rather, photochemical processes seem to be subject to the requirement of "continuous electron redistribution," defined (*1–4*) as a molecular transformation proceeding with minimum electron localization. Such a requirement is implicit in current treatment of the mechanisms of ground-state molecule reactions and is satisfied by mechanisms in which "arrow notation" is used properly. A discontinuous process is exemplified by the type mechanism occasionally unintentionally written by beginning students in organic chemistry when an arrow may be missing or improperly drawn.

This argues that it is fairly certain the excited-state molecules do not climb "energy mountain tops," especially when low-energy routes are available. It is not clear whether the lowest-energy route is invariably followed. A factor, cited by Hammond (*6*), controlling some photochemical reactions is the ease with which an excited-state species, having undergone geometric change, can form its unexcited, ground-state counterpart. Another suggestion occasionally made is that loss of electronic excitation without gross molecular change generates a reactant molecule with excess vibrational energy; and subsequently there is a transformation of the vibrationally excited but electronically unexcited (that is, "hot") species. This would be much like a pyrolysis. Such a mechanism becomes less likely in solution than in the vapor phase because of collisional deactivation. Also, the probability of such a "hot molecule" process occurring diminishes as the molecular size and the number of bonds that can interact with, and absorb, the vibrational energy increases. Except where especially low activation energies are needed for reaction and where the molecule is small, "hot molecule" ground-state processes seem unlikely to compete with solvent deactivation (*7*).

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Nature of Electronically Excited States

The use of the carbonyl group, as in acetone, to illustrate the makeup of excited states is advantageous in that it permits description of the two most important types of excited species, n-π^* and π-π^*, and also allows discussion of two structural representations, resonance and molecular orbital (*1, 3, 4*) (Figs. 1 and 2).

In the atomic orbital version, the carbon p_x and the oxygen p_x, p_y, and *sp* orbitals are shown as occupied. In the molecular orbital counterpart, the p_y and *sp* orbitals remain the same since these are orthogonal to the remaining set and do not mix with these. However, quantum mechanical mixing of the p_x orbitals on carbon and oxygen leads to the π (that is, bonding) and π^* (that is, antibonding) molecular orbitals. Since it is difficult to depict occupation by electrons when there are several lobes, the occupation of these π molecular orbitals is indicated below each drawing. Thus the n-π^* excitation, occurring in ketones on absorption of ultraviolet light at 270 to 390 millimicrons (the precise wavelength effect depends on the compound), can be represented by either the resonance or molecular orbital models, as shown. Here n signifies the nonbonding p_y orbital. However for π-π^* excitation, corresponding to absorption bands obeying Woodward's rules (*8*), the resonance version does not give an adequate indication of the electron redistribution on excitation, and the molecular orbital picture is more useful. Although the singlet state, with no change in electron spin on excitation, is initially formed, the corresponding n-π^* and π-π^* triplet states resulting from a single-spin inversion are especially important. To a first, crude approximation the same representation may be used, although large differences in behavior of the singlet and triplet excited states may arise as a result of quantitative differences in electron distribution, in the paired or unpaired orientation of the spins of the two odd electrons, and in the lifetime of the singlet species as compared to that of the triplet species.

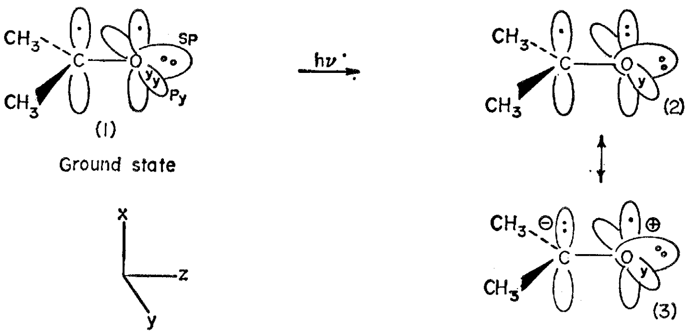


Fig. 1. Resonance picture of n-π^* excitation. The ground state is shown by 1; and 2 and 3 depict two resonance forms of the n-π^* excited state.

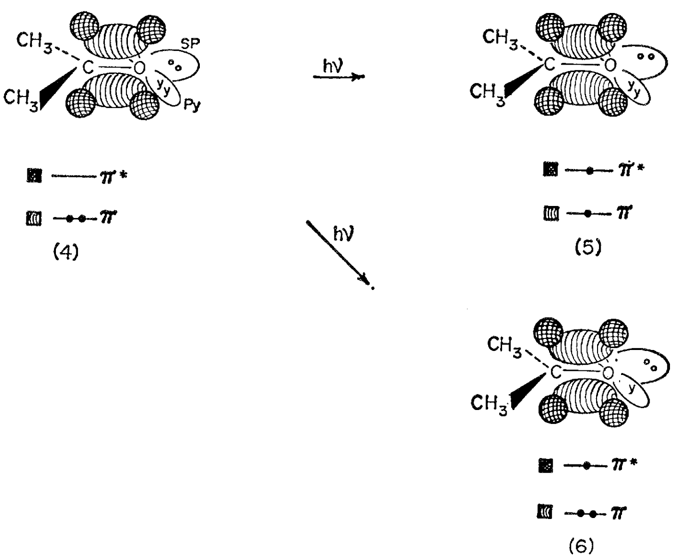
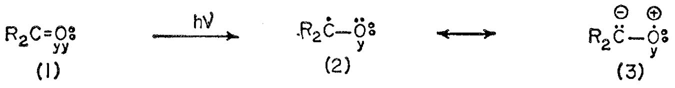


Fig. 2. Molecular orbital versions. The ground state is represented by structure 4, the π-π^* excited state by structure 5, and the n-π^* excited state by structure 6.

For n-π^* reactions, one may simplify matters by writing the three-dimensional excited state in two dimensions and the *sp* hybrid electrons as circles (o), the p_y electrons as *y*'s, and the π system electrons as dots (or lines for two electrons). Where differentiation is unnecessary, one uses dots for all electrons. To the extent that resonance structure 3 for the excited state is important, the dipole $^{\delta+}C = O^{\delta-}$ should be inhibited. Thus it is of interest that Freeman and Klemperer (*9*) have found the dipole moment of singlet-excited formaldehyde to be 1.48 debyes compared with 2.34 debyes for formaldehyde ground state. We must recognize that the dipole moment is the sum of sigma and π components and that the sigma component, normally polarized towards oxygen, will, if anything, become even more polarized in the excited state because of sigma-electron reorganization. Thus the diminution of dipole on excitation must signify considerable π-electron drift towards carbon, as expected.



In the case of ketones, change of spin, or intersystem crossing, is very rapid (*10*) because of spin-orbit interaction. Studies by Wilkinson and Dubois (*11*) have demonstrated that the lifetimes of singlet benzophenone and acetophenone, limited by intersystem crossing, are less than 10^{-10} seconds. Although for most simple ketones the n-π^* singlet configuration is lower in energy than the π-π^* singlet, this will not invariably be the case for the corresponding triplets (*12*). To complicate matters further, the common assumption that the lowest-energy singlet or the lowest triplet will be the reacting species seems to have at least one exception (*13*).

Application of Mechanisms to Photochemistry of Dienones

The chemistry of cyclohexadienones is one of my special interests, and it offers a useful example for explaining the reasoning available (*1–4, 5*) for understanding n-π^* photochemistry. In the example of 4,4-diphenylcyclohexadienone (*2, 3*) (Fig. 3), the n-π^* excited state, structure 8, undergoes sigma bonding between carbon atoms No. 3 and No. 5 to give species 9. This latter, on electron demotion, forms the mesoionic species 10 which rearranges to species 11, which is the first product isolated. The conversion of zwitterion 10 to product 11 has analogy in the well-known cyclopropylcarbinyl carbonium-ion rearrangement. The overall process giving the bicyclic ketone 11 from dienone 7 is conveniently termed a type A rearrangement; it occurs with frequency in the photochemistry of dienones.

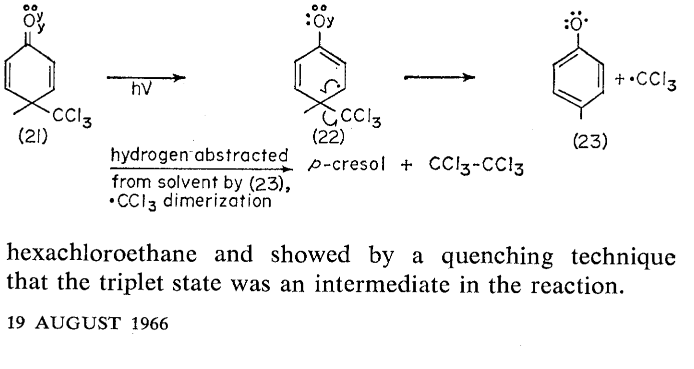
The further irradiation of compound 11 gives a predominance of 2,3-diphenylphenol and 3,4-diphenylphenol in lesser amount *(14)*. This interesting preference for migration to carbon No. 2 occurs in neutral media, while migration to carbon No. 4 becomes increasingly prevalent as the *p*H is decreased. This change is not due to a dark reaction. It is convenient to assign the designations B_2 and B_4 to the processes (Fig. 4) leading from a bicyclic ketone, as structure 11, by fission of the internal three-ring bond and subsequent migration of a group at carbon No. 3 to Nos. 2 and 4, respectively. These processes, too, occur often in photochemistry.

Thus the rather complicated sequence *(15, 16)* in Fig. 5 can be understood as a series of type A, type B_2, and type B_4 rearrangements. Similar reasoning with some variation is applicable to a large number of dienone rearrangements. In the case of rearrangements in acidic media the three-dimensional mechanism (Fig. 6) for the photochemical conversion of santonin, structure 19, to isophotosantonic lactone, structure 20, was originally proposed by me and my co-workers *(1, 3, 4)*. This involves the protonated mesoionic intermediate 19. More recently Kropp *(16)* found further examples of this process (signified by arrows labeled *a* in Fig. 6) and uncovered further support for our intermediate 19 in the form of the process labeled *b*. Kropp has shown that substitution is the major factor determining which mechanism, *a* or *b*, ensues.

Subsequent to our original proposal for the mechanism of the type A rearrangement, it was found *(17, 18)* that this type rearrangement proceeds by way of a triplet state; thus extra-spin interconversions need to be superimposed on the chain of events hypothesized.

Molecular-orbital arguments also may be helpful in understanding this chemistry. For example, n-π^* excitation of the dienone system has been shown *(5, 14, 17)* to lead to enhancement of the beta-beta bond order (that is, bonding carbons No. 3 and No. 5 in compound 7, each being in the position beta to the carbonyl) in contrast to π-π^* promotion. The dienone's six molecular orbitals (formed by quantum-mechanical mixing of the six p_x orbitals) and the one p_y (that is, n) orbital were depicted schematically as shown in Fig. 7. The results of the bond-order calculations *(5, 14)* can be seen without resort to numbers *(17)*, for it is clear that n-π^* excitation removes an electron from an orbital (n) having no beta-beta bond-order contribution and places it in π_4, a molecular orbital which has both beta *p*-orbitals with positive signs aimed in the same direction and which therefore contributes to beta-beta bonding.

Schuster and Patel *(19)* have presented some evidence in accord with the view that the reactivity of the beta-carbon atom of 2,5-cyclohexadienones is odd-electron in character. They found that photolysis of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone, 21, yields *p*-cresol and hexachloroethane and showed by a quenching technique that the triplet state was an intermediate in the reaction.



Monoenone Excited State Reactivity

The first clue that reaction mechanisms for monoenones are less than simple was the observation by Eaton *(20)* that cyclopentenone yielded a mixture of dimers consisting of approximately equal quantities of the cyclobutane compounds 24*a* and 24*b*. From molecular-orbital calculations

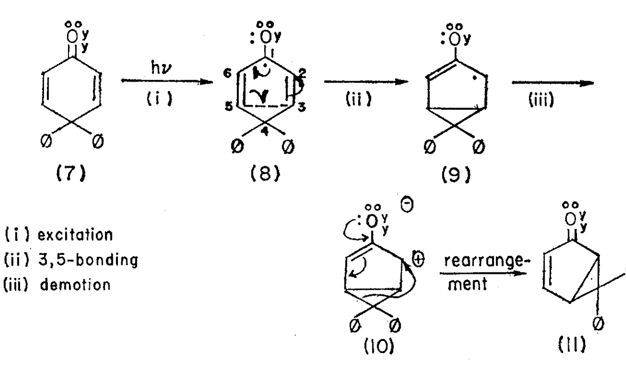


Fig. 3. Type A rearrangement.

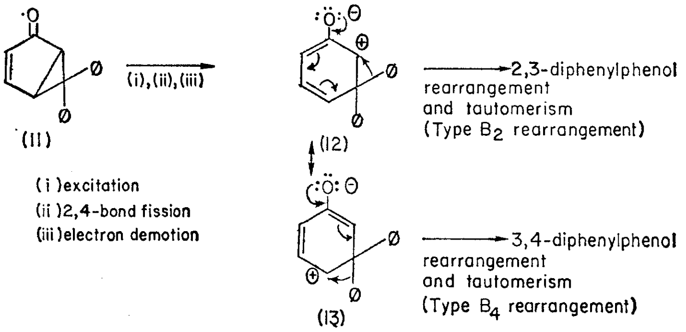


Fig. 4. Type B_2 and type B_4 rearrangements.

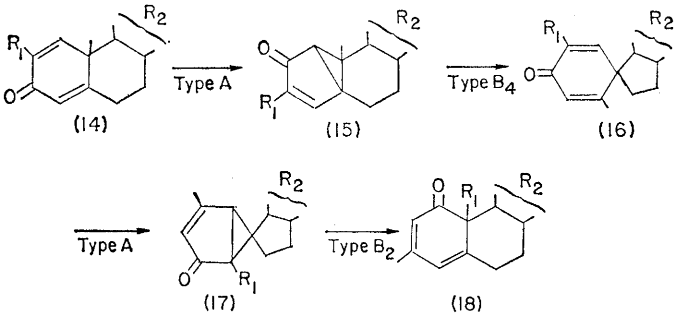


Fig. 5. Rearrangements from refs. *15* and *16*, considered as a series of type A, type B_2, and type B_4 processes. Here $R_1 = CH_3$, R_2 = rings C and D of steroid for ref. *15*; R = H for ref. *16*.

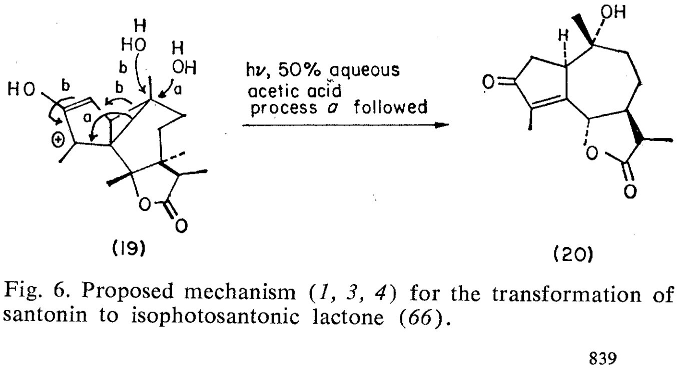


Fig. 6. Proposed mechanism *(1, 3, 4)* for the transformation of santonin to isophotosantonic lactone *(66)*.

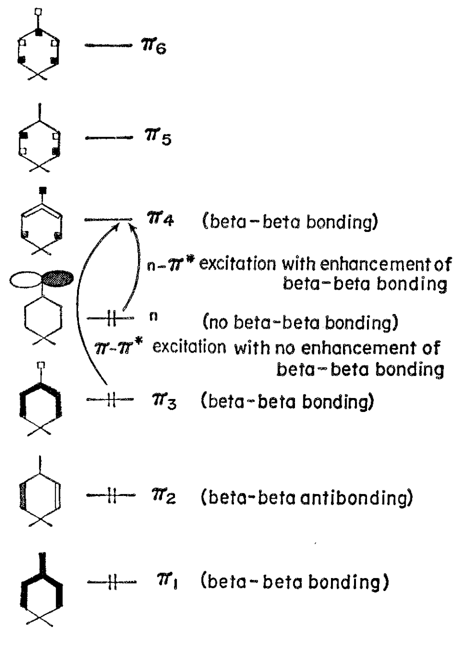
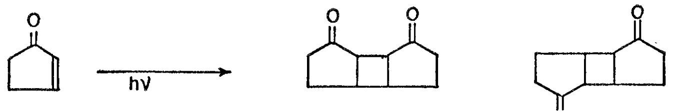


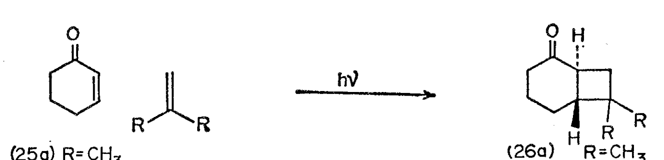
Fig. 7. Molecular orbital representation of n-π^* and π-π^* excitation processes for cyclohexadienones. ■, wavefunction positive. □ indicates wavefunction negative.

(*21*, also *5* and *17*) and resonance considerations one would predict that the *beta* carbon in the n-π^* excited state should be electron-rich and that there would be an odd electron available. Such an excited state should lead to a predominance of adduct 24*a*. In this connection, simple Hückel calculations based on a model with all bonds equal do not afford reasonable results and are incorrect, although occasionally quoted. Unless the bond separating the carbonyl and olefinic moieties is assumed to be longer, one erroneously predicts that the carbonyl group donates electrons to the double bond in the π-π^* excited state, a prediction in direct conflict with known effects of solvent and substituents on the π-π^* spectra.



(24a) (24b)

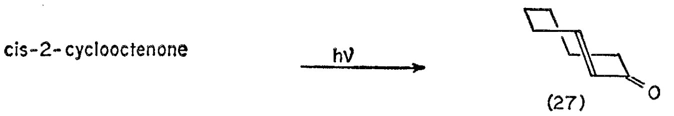
Corey *et al.* (*22, 23*) have shown that cyclohexenone reacts with isobutylene and 1,1-dimethoxyethylene to form preferentially the structural isomer with the methylene group of the olefin bonded to the alpha carbon of cyclohexenone. Furthermore, *trans* adducts are formed in excess. Corey *et al.* suggest as a possibility that the orientation is determined in a step preceding bonding, one in which a complex is formed between the n-π^* excited state and the olefin and that a high *beta* electron density in the enone moiety accounts for the orientation. As pointed out by Corey this does not account for the behavior of cyclopentenone on dimerization. Eaton (*24*) has observed similar orientation with allene as the adduct.



(25a) R=CH_3
(25b) R=OCH_3
(26a) R=CH_3
(26b) R=OCH_3

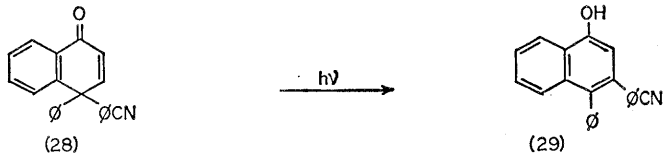
Molecular orbital calculations, both of the one-electron variety and the configuration-interaction type, lead to predictions that the π-π^* excited state of enones is particularly electron-deficient at the alpha carbon atom. Furthermore, regardless of whether the lower-energy excited state of the enone itself is n-π^* or π-π^*, it is likely that, as bonding between the excited enone and olefinic addend proceeds, the π-π^* excited state will decrease in energy selectively as a result of increased conjugation. Thus there is the possibility that it is an electrophilic attack, predominantly by the alpha carbon, of the π-π^* excited state on the olefin; this would explain the orientation and the relative reactivity sequence (*23*) in which 1,1-dimethoxyethylene is more reactive than isobutylene.

Eaton and Lin (*25*) have found that irradiation of *cis*-cyclooctenone yields the strained *trans*-cyclooctenone, 27. The even more strained *trans*-2-cycloheptenone is formed on irradiation of the *cis*-isomer at low temperature (*26, 27*). Although the *trans* isomer shows high reactivity in the dark, its behavior seems different from that observed from the smaller ring enones photochemically. Thus, for example, no adduct was obtained from *trans*-2-cycloheptenone and dimethoxyethylene; dimerization occurred in preference. Whether these strained species are related to the simple enone reactions remains to be seen.



(27)

As a final point bearing on monoenone photochemistry we may note that irradiation of 4-phenyl-4-(*p*-cyanophenyl)-1(4*H*)-naphthalenone, structure 27, proceeds with simple aryl migration and with *p*-cyanophenyl migration being preferred (3 to 2 preference in methanol, 2.2 to 1 in benzene) (*28*). This result strongly suggests that the beta carbon of the excited state possesses odd-electron capabilities.



(28) (29)

Other Types of Ketone Reactivity

Much of the photochemistry of n-π^* excited species derives from the partially vacant p_y orbital rather than from the π system. Kasha (*10*) and Zimmerman (*1*) noted that the p_y orbital at oxygen of an n-π^* excited state should exhibit reactivity in the form of hydrogen abstraction. Walling and Gibian (*29*) and Padwa (*30*) have shown that the selectivity of benzophenone triplet in hydrogen abstraction from different substrates parallels that of the *t*-butoxyl radical, a result tending to confirm the picture of the n-π^* excited state presented earlier. Triplet hydrogen abstraction should not be discussed without citing the elegant work of Hammond and co-workers (*31* and their later papers) who clearly demonstrated the role of benzophenone triplet in the hydrogen-abstraction-dimerization reaction giving benzopinacol. Independent important contributions to an understanding of the role of the triplet state have been made by many investigators (*12, 32*).

Also important is the Yang reaction in which cyclobutanols are formed (*33*). The precise timing is now a matter of controversy (*34*). In the original mechanism suggested by Yang as modified here to fit an explicit n-π^* abstraction (*1*), a two-step reaction of hydrogen abstraction followed by ring closure was postulated (Fig. 8). Related to the Yang reaction is the "type II" process in which the same type of reaction leads to chain fission, with generation of an olefin and a ketone (*35*). The reaction is pictured in Fig. 8 as proceeding via a discrete biradical, 31, as was suggested by Zimmerman (*1*), although the reaction may well be concerted (synchronous) in cases. There has been differing evidence on whether the reaction proceeds by way of the singlet excited state (*36*) or the triplet (*37*). Wagner and Hammond (*38*) and Dougherty (*39*) have shown that both excited species may undergo the "type II" reaction.

Not only hydrogen but also π systems are subject to attack by the electron-deficient p_y orbital of the n-π^* excited state. Examples are the phenyl migration reaction of dibenzoylethylenes described by Griffin (*40*) and Zimmerman (*41*), and also the Paterno-Büchi reaction of olefins with ketones or aldehydes (Fig. 9) to give oxetanes (*13, 42–44*). In each case the reaction may be pictured as occurring by attack of the electrophilic p_y orbital on a π system. The preference for formation of the more stable diradical intermediate (not shown) would account for the orientation in the second reaction. In the first reaction, although either of the two benzoyl phenyl groups could have migrated, only in the reaction course followed does the intermediate 34 have odd-electron delocalization by the styryl phenyl group.

In the case of oxetane formation, evidence has been presented (*13, 44*) that it is indeed the n-π^* triplet which is reacting with olefin. Most intriguing, Yang and co-workers (*13*) have found that the reaction of 9-anthraldehyde with 2-methyl-2-butene is dependent on wavelength, with oxetane being formed only at the shorter wavelengths. This suggests that the reaction is faster than internal conversion of the n-π^* triplet (formed by intersystem crossing) to the π-π^* triplet, which is of lower energy in this molecule.

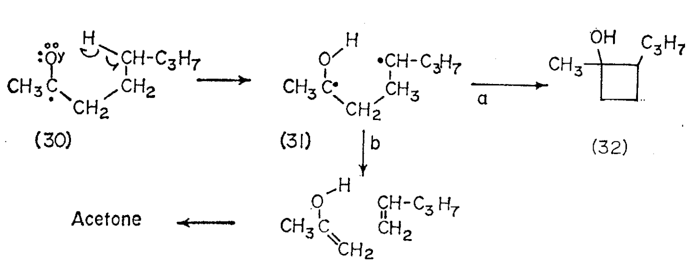


Fig. 8. The Yang reaction of 2-octanone to form 1-methyl-2-propylcyclobutanol (route *a*) and the Norrish type II reaction to form acetone and 1-pentene (route *b*).

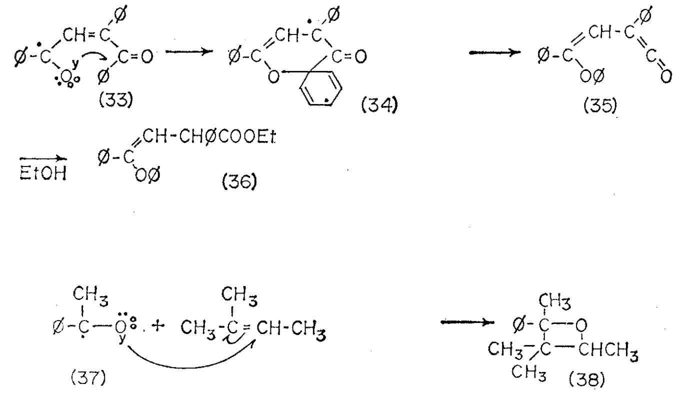


Fig. 9. The dibenzoylstyrene reaction (top equation) (*41*) and the Paterno-Büchi reaction (bottom equation) (*13*).

Pi-Pi* Organic Photochemistry

With respect to the several possible factors controlling the course of photochemical reactions I have emphasized the tendency of the excited-state species to minimize its energy. While this may not be the case invariably, it is of interest to pursue this view further. For example, in the molecular orbital treatment of the beta-beta–bonding step of 4,4-diphenylcyclohexadienone, it was stated that on excitation an increase in the beta-beta bond order results; and it has been shown (*5*) that this bond order is positive. This is equivalent to saying that the molecule will lower its energy by increased beta-beta overlap and bonding. The use of bond order between different atoms in a π system, although the original molecular orbital calculations may not have included the assumption of any such bonding, often may prove helpful in indicating the energy change. In a molecular orbital (MO) of the linear combination of atomic orbitals (LCAO) form

$$\psi = C_1\chi_1 + C_2\chi_2 + C_3\chi_3 \ldots\ldots,$$

where ψ represents the MO, the χ's are the atomic orbitals and the C's are (LCAO MO) weighting coefficients. The bond order between atoms r and s per electron in the MO is given by C_rC_s. The energy which can be ascribed to such bonding is $-2\epsilon C_rC_s$ in the positive units of the absolute value of *beta. Beta* for use in the simplest approximation is about -18 kcal/mole and ϵ is a measure of the overlap between orbitals χ_r and χ_s; ϵ is unity for standard parallel overlap, as in ethylene.

Of course, any energy-lowering from electronic sources derived as a result of increased overlap between two atomic orbitals must be compared with whatever additional strain energy is incurred. In any event, the consideration of such bond order effects is equivalent to first-order perturbation calculations. Although it is safer to calculate the total change in π system energy as the excited molecule changes toward one product rather than another (*45*), the assumption that a positive bond order favors bond formation can be useful. Nevertheless, one must be careful. For example, finding a zero bond order between two atoms does not mean that energy will not be gained by bonding, and can be misleading.

One reaction found throughout π system photochemistry is the formation of cyclobutenes from butadienes. It was suggested by Zimmerman (*1*) that this derived from the enhanced bond order in the first excited state (Fig. 10). Similarly, Daudel and co-workers (*46*) have found a decreased central bond order in the excited state of stilbene, which can account for the occurrence of *cis-trans* interconversion on excitation. Liu, Turro, and Hammond (*47*) have noted that LCAO MO calculations predict an increased 2,3-bond order for the lowest excited states of butadiene. The reasoning is very similar to that for an enhanced 1,4-bond order and reference may be made to Fig. 10.

Woodward and Hoffmann (*48–50*) and Longuet-Higgins and Abrahamson (*51*) have presented some interesting correlations of theoretical prediction with results in the photochemical literature in addition to applying the same reasoning to some ground-state reactions. The first and last of Woodward and Hoffmann's papers consider the bonding or antibonding interaction of just the highest-energy occupied molecular orbital as a species undergoes transformation. Thus if we use the schematic representation of butadiene molecular orbitals (Fig. 10), one notes that in the ground state the highest occupied molecular orbital is π_2 and that the top lobes of carbon atoms 1 and 4 have the opposite sign; similarly, the bottom lobes have opposite signs. Thus top-top and bottom-bottom interaction between the terminal *p*-orbitals in π_2 is unfavorable, or antibonding.

However, in the first excited state the highest occupied molecular orbital is π_3. Here the top lobes have the same sign; the same is true of the bottom lobes. Hence interaction in this molecular orbital between the top lobes is bonding as is interaction between the bottom lobes. When cyclobutene is formed, a 1,4-sigma bond is formed by rotation at the terminal atoms and by overlap of the orbitals. If rotation occurs with the orbitals and 1,4-attached groups, twisting as in Fig. 11, the 1,4-bonding in π_3 increases and the energy of molecular orbital π_3 decreases. Groups A and D become *cis* to one another.

The reverse (Fig. 12) rotation would lead to a cyclobutene with B and D *cis* to one another, but π_3 becomes increasingly 1,4-antibonding as the rotation proceeds. Woodward and Hoffmann have termed the process in Fig. 11 "disrotatory" and in Fig. 12 "conrotatory"; Doering (*52*) has termed the same processes "antidomino" and "domino," respectively.

One might be concerned about the validity of assuming that the bonding or antibonding trends in the highest occupied molecular orbital will control the energy of the entire species. However, in the cases considered, there are good reasons for the assumption operating, and one-electron (that is, Hückel type) calculations including carbon $2s$, $2p_x$, $2p_y$, $2p_z$ and hydrogen $1s$ orbitals offer additional support (*48*), since the results are in agreement.

Woodward and Hoffmann have extended their treatment to more complex π systems. In the cyclization of hexatriene to cyclohexadiene, the effect is reversed so that the conrotatory (domino) mode is favored in the excited state. Ground state predictions are the reverse.

Longuet-Higgins (*51*) and Hoffmann and Woodward (*49*) utilized another approach; this used symmetry to allow one to draw correlation diagrams. The diagrams are graphs of molecular orbital energies (*49*) or entire molecular state energy (*51*) plotted against the extent of molecular transformation. Space does not permit elaboration here. However, one intriguing result is that reactions favored in the ground state have their bonding molecular orbitals transformed into bonding molecular orbitals of the product while the processes predicted to be photochemically observable have some bonding molecular orbitals that correlate with product antibonding molecular orbitals and vice versa (*49*). Longuet-Higgins and Abrahamson (*51*) very nicely show that when one considers the energy of the entire configuration, the processes predicted by the Woodward-Hoffmann treatment to be "allowed" (that is, here meaning not impeded by unfavorable molecular orbital considerations) do not

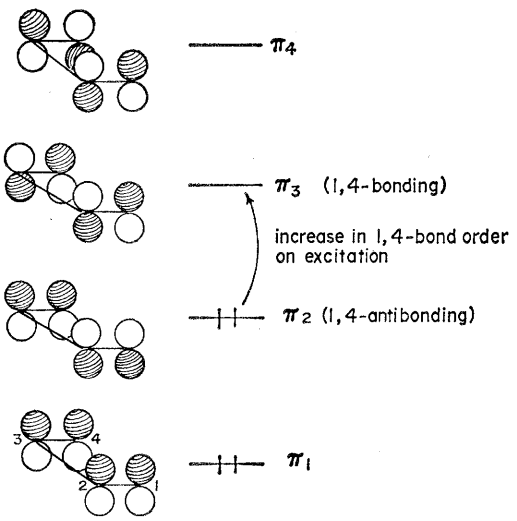


Fig. 10. The four molecular orbitals of butadiene, increasing in energy. Occupation is signified by vertical lines for electrons. (Shaded circle) Wavefunction positive; (open circle) wavefunction negative. Electron excitation indicated by arrow.

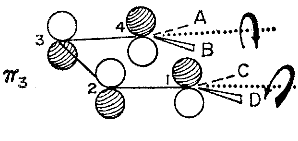


Fig. 11. Molecular orbital π_3 during disrotatory (antidomino) ring closure of butadiene to cyclobutene. Increasingly 1,4-bonding with rotation. Product has A and D *cis*.

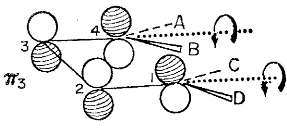


Fig. 12. Molecular orbital π_3 during conrotatory (domino) ring closure; increasingly 1,4-antibonding. Groups B and D becoming *cis*.

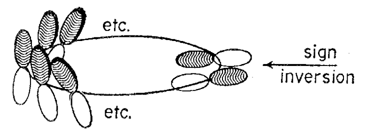


Fig. 13. Heilbronner's large ring Möbius polyene. The basis set of *p*-orbitals is indicated with plus lobes dark and minus lobes light.

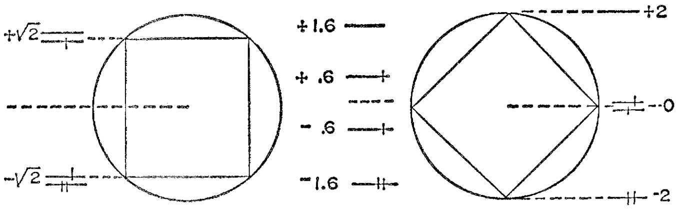


Fig. 14. Frost-Hückel mnemonic device illustrated at right; Zimmerman's device at left; butadiene molecular orbitals in center. The vertical lines represent electrons populating the molecular orbitals. The butadiene molecular orbitals transform themselves either into the Hückel set at the right or the Möbius set at the left as the reaction proceeds.

have an energy maximum along the reaction path while the "forbidden" ones do.

One point should be made clear. This is that the above approaches do require knowledge of the molecular orbital energies and symmetries of reactants and products in a process to be considered. Either these must be known or a calculation is necessary.

There is another perspective which may be of help in predicting the likelihood of photochemical and ground-state reactions. Recently, Heilbronner (*53*) discussed the possibility of existence of large-ring polyenes, twisted once and thus resembling a Möbius strip. In such molecules there would be a contiguous set of *p*-orbitals with like signs adjacent except at one point where, in the basis set, there would have to be a sign inversion (Fig. 13). Heilbronner derived a general algebraic relation for the energies of molecular orbitals of such systems.

Now it is very easy to show (*54*) that this algebraic form justifies use of the following mnemonic device reminiscent of that suggested by Frost and Musulin (*55*) for Hückel systems (that is, cyclic with no sign inversion in the basis set). Both the new mnemonic device (*56*) and that of Frost and Musulin (*55*) require drawing a circle of diameter $2\,|\beta|$ (that is, the positive energy unit of the absolute value of *beta; beta* here represents the resonance integral between two adjacent *p*-orbitals). In this circle there is inscribed a polygon having the same number of sides as the cyclic hydrocarbon of interest has bonds. The center of the circle is taken as the energy zero, namely the energy of an electron isolated in a single *p*-orbital. At every intersection of the polygon and the circle a horizontal line is drawn, the vertical displacement of which gives the energy of one of the molecular orbitals. The Frost-Hückel rule requires that one vertex be placed at the bottom of the circle. My device for Möbius systems requires that one side of the polygon be placed horizontally at the bottom of the circle (*56*). Both mnemonics are illustrated in Fig. 14.

We note that, as the ends of butadiene are brought together with the top lobes of the basis set of atomic orbitals overlapping (disrotatory, antidomino), we have a system roughly approximating the electronics of cyclobutadiene (note Fig. 15 left). The "basis set" of atomic orbitals consists of the set available for molecular orbital mixing and should not be confused with the molecular orbitals (Fig. 10) which result after mixing. Alternatively, during a conrotatory (domino) approach the top lobe at carbon-1 will overlap with the bottom lobe at carbon-4 (Fig. 15, right), and we will have a sign discontinuity in the basis set of atomic orbitals. Thus the conrotatory twisted butadiene will approach Möbius cyclobutadiene electronically. Also illustrated in Fig. 14 (center) is the starting set of molecular orbitals for butadiene prior to twisting. The molecular orbitals then will approach either those of "Hückel cyclobutadiene" or "Möbius cyclobutadiene" as the reaction proceeds with disrotatory or conrotatory 1,4-closure. Assuming no change in molecular orbitals occupied, we note that the total π energy of the Möbius system approached (Fig. 14, left) (−2.8 positive units of energy) is not as low as that of the Hückel system (Fig. 14, right) ($-4.0\,|\beta|$) for the excited state. The situation reverses itself in the ground state closure.

We can use this method generally for symmetrical closures. Hückel closure of hexatriene to cyclohexadiene in the excited state leads to a higher energy than Möbius closure does, and therefore Möbius closure is favored. The ground state situation is again reversed. For hydrogen transfer reactions (see *50*) one can apply the method by merely determining whether the number of sign inversions in the basis set of orbitals is even or odd, and treating the system as a Hückel or Möbius one, respectively. The method does not require explicit calculations and thus would appear to be useful.

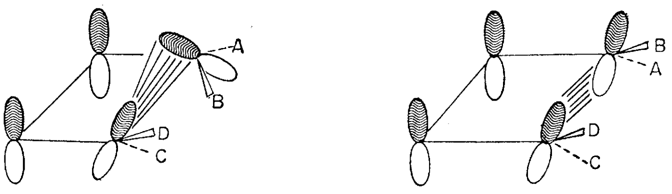
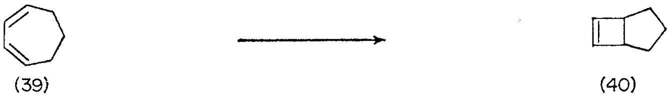


Fig. 15. (Left) An intermediate stage of butadiene disrotatory closure with basis set orbitals shown, a Hückel system; (right) the corresponding conrotatory closure, a Möbius system.

Fukui (*57*) has arrived at conclusions similar to those of Woodward and Hoffmann. The importance of the symmetry in the highest occupied molecular orbital was actually first noted by Oosterhof (in *58*) for the reaction of trienes. Orbital symmetry has been used in ground state reactions to explain the Sommelet and Stevens reactions (*59*) and also the Diels-Alder reaction (*60*).

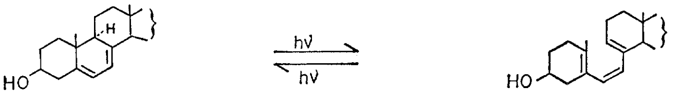
Application of Theory to Photochemical Reactions of Polyenes

Cyclic dienes do tend to rearrange photochemically to products containing the cyclobutene ring, as would be anticipated from the preceding discussion. Where part of a cyclohexadiene system, these cyclic dienes tend to open to trienes, also an expected process. Thus cycloheptadiene



(39) (40)

closes photochemically to the bicyclic compound 40 (*61*), while cyclohexadiene yields hexatriene (*62*). Clearly cycloheptadiene cannot open. Its closure necessarily is of the disrotatory or Hückel type, for Möbius closure would lead to an exceedingly strained system. In any event the electronics favor the Hückel closure. Dauben has discussed (*63*) the subject (see *58* for review) and has noted that in general the steroid 9,19-*anti*-5,7-dienes, as compound 41, tend to open to trienes. The change from ergosterol, 41, to precalciferol, 42, is a typical example. Inspection of this



(41) (42)

system reveals that geometry favors a disrotatory opening of the diene and closure of the triene. Electronic considerations of the type discussed above lead to similar predictions.

In contrast, in the 9,10-*syn* isomers as compound 43 we find the diene system closing to form a cyclobutene derivative, 44, rather than opening as before (*64*). Here

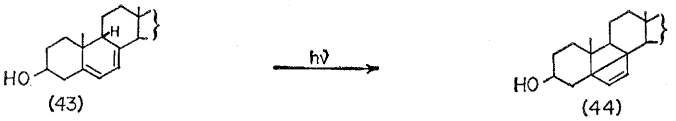
Table 1. Energy change and highest occupied molecular orbital bonding as a function of the type of bonding of hexatriene in ground and excited states. A, antibonding; B, bonding. HOCMO, highest occupied molecular orbital.

Type of bonding*	Ground state		Excited state	
	Energy change†	Overlap of HOCMO	Energy change†	Overlap of HOCMO
1,6-Hückel	−1.01	B	+0.10	A
1,6-Möbius	+ .06	A	− .83	B
1,5-Hückel	− .48	B	− .50	B
1,5-Möbius	− .48	A	− .50	A
1,4-Hückel	+ .39	A	− .50	B
1,4-Möbius	−1.07	B	− .43	A
1,3-Hückel	− .56	A	− .30	A
1,3-Möbius	− .56	B	− .30	B

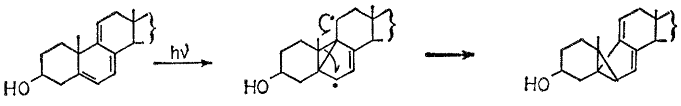
* An arbitrary extent of bonding is assumed, equal to that of adjacent olefinic orbitals. † Energies in absolute value of *beta* units.

geometrical considerations favor a disrotatory opening with formation of the triene, whereas the electronic requirement is for a Möbius or conrotatory opening. In forming the cyclobutene derivative, the molecule faces no such dilemma, for both geometry and electronic factors favor Hückel closure.

In many photochemical experiments on trienes, products have been obtained which seem to have arisen from an initial 1,5-bonding. An excellent example is the reaction described by Barton and Kende (*65*) of 9-dehydroergosterol, 45, which yields the photoisomer, 46.



(43) (44)



(45) (46)

Upon inspection of Table 1, which gives energy changes as different types of bonding occur in the hexatriene system, we find, quite expectedly, that Möbius 1,6-bonding is the lowest energy process for the excited state. Interestingly, we find 1,5-bonding to be favorable and thus in accord with experiment. Since 1,3-bonding is somewhat favorable, and in many reactions of hexatrienes both 1,5- and 4,6-(that is, from 1,3-bonding) bonds appear in the product, it is likely that 4,6-bonding occurs concertedly with 1,5-bonding in many cases. Most important, Table 1 shows that the bonding or antibonding nature of the highest occupied molecular orbital is not a reliable guide to the effect of bonding on the energy of the entire species.

Summary

A general introduction to current organic photochemical research is presented. A limited survey of typical organic photochemical reactions, with an emphasis on recent studies, is given. Reactions of the *n*-π^* and π-π^* type are included. Some new thoughts are included; among these is the relation of Möbius strip geometry to organic photochemistry.

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67. This work was supported by NSF and NIH (grant GM 07487).