Table I. Major Metastable Transitions Determined in the MIKES/DADI Spectra of the Molecular Ions of Cholestan-6-one and Labeled Analogs

| Compd | Isotopic purity | Molecular ion | Transition[a] | | | |
			M − 15	M − 18	Side chain loss	Ring D loss
Cholestan-6-one		386	371 (100)	368 (14)	273 (22)	231 (36)
Cholestan-6-one-3β-d_1	d_1 98%	387	372 (100)	369 (13)	274 (18)	232 (38)
	d_0 2%					
Cholestan-6-one-3α-d_1	d_1 96%	387	372 (100)	369 (12)	274 (17)	232 (36)
	d_0 4%					
Cholestan-6-one-2,2,4,4-d_4	d_4 8%					
	d_3 23%	389	374 (100)	371 (11)	276 (16)	234 (35)
	d_2 50%	388	373 (100)	370 (14)	275 (17)	233 (33)
	d_1 16%					
	d_0 3%					

[a] Relative abundances (in parentheses) are uncorrected for ^{13}C contributions and are expressed in percentages.

tially quantitative. The results of the 3α- and 3β-d_1 analogs are presented to indicate that the patterns of the DADI spectra shift in mass for these transitions, but not in relative abundance. The sample of cholestan-6-one-2,2,4,4-d_4 chosen for this investigation was of relatively low isotopic purity (Table I). Yet MIKES/DADI spectra of m/e 389 (d_3) and m/e 388 (d_2) display the same pattern of metastable ion abundances. Each component has, in effect, been analyzed independently of the other contributors.

Investigations of transitions involving loss of all or part of a deuterium label should be facilitated by employing the MIKES/DADI technique rather than the Barber–Elliott technique utilized previously.[21]

This technique should also be applicable to other mixtures of isotopes. Beynon, et al., have described the MIKE spectra of ions containing one ^{13}C atom of natural abundance.[12c] Isolation of one molecular ion

(21) D. H. Smith, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrom.*, 7, 367 (1973).

of a compound containing a polyisotopic element (*e.g.*, chlorine, germanium) should assist in interpretation of the decomposition of this ion when the fragmentation pattern is complicated by losses of a hydrogen atom or molecule superimposed on the already complex isotopic distribution.

Conclusion

The distributions of daughter ions arising from unimolecular decomposition of metastable molecular ions have been used in the analysis of several types of mixtures of compounds. The examples presented indicate that this technique may be widely applicable to mixtures and related problems involving studies of metastable ion decompositions. The ability in many cases to obtain metastable ion spectra of each component independent of other contributors to a mixture is a powerful asset of the technique whether applied to characterization of the mixture or to studies of metastable ion decompositions of selected components.

Surface Crossings and Surface Touchings in Photochemistry

Lionel Salem

Contribution from the Laboratoire de Chimie Théorique,[1] Université de Paris-Sud, Centre d'Orsay, 91405 Orsay, France. Received August 27, 1973

Abstract: Eight major photochemical reactions [(1) hydrogen abstraction by ketones; (2) photoreduction of aza aromatics; (3) hydrogen abstraction by carbenes; (4) addition of ketones to electron-rich olefins; (5) α cleavage of alkanones; (6) α cleavage of dienones; (7) isomerization of furans to cyclopropenyl ketones; (8) ring opening of azirines] are interpreted in terms of surface crossings or surface touchings between ground singlet state and excited n,π^* singlet and triplet states. State correlation diagrams are drawn for each reaction and are confirmed by detailed *ab initio* calculations. In several cases these diagrams throw additional light on the reaction mechanism. Typical state correlation diagrams are given for the two coplanar reaction types described in the article: σ,π *bitopic* reactions and $\sigma(\sigma,\pi)$ *tritopic* reactions. Finally, an attempt is made to relate the nature of diradical product and multiplicity of the photoreactive state: two general proposals are made.

Photochemistry, more than any other field, brings man in close touch with the realm of multidimensionality. The freedom enjoyed by an excited molecule is associated with the many directions along which

(1) Also part of the Laboratoire de Physico-Chimie des Rayonnements associated with the CNRS.

it can explore the potential energy surface of the excited state. It has been widely assumed that at some point the molecule must leave this excited surface and decay, *via* a radiationless transition, possibly through a wide energy gap, to the ground surface. We show here that, for a large number of photochemical reactions, surface

crossings ensure that the excited molecule, while moving on a *single* potential energy sheet converts directly into ground-state primary photoproduct. In another family of reactions a near *touching* of potential surfaces allows the excited molecule to reach a point energetically very close to the ground surface of the product.

The crossing of surfaces of different electronic spatial symmetry in small polyatomic molecules has been known for many decades. Among the most famous cases are: (a) the crossing of the $^2B_2$ ionic state and $^2A_1$ covalent state at large distances in the isosceles triangle approach of X_2 (X, halogen) and M (M, metal);[2] (b) the intersection between the $^1A_1'$ (near-equilibrium ground state) and $^1A_2''$ (equilibrium excited state) of planar ammonia as an NH bond is stretched to infinity;[3] (c) the predissocation of ($^2B_2 \rightarrow$) $^2A'$ water molecule ions OH_2^+ by a $^2A''$ state leading to $H^+(^1S)$ and $OH(^2\Pi)$.[4] As early as 1957 Brand and Reed attempted to prove the existence of a surface crossing in the coplanar dissociation of formaldehyde CH_2O to formyl radical HCO and hydrogen H. They correlated the ground state of formaldehyde with an excited state of formyl and the excited (n,π^*) state of formaldehyde with the ground state of formyl.[5] Unfortunately, the correlations and crossing were based on an incorrect assumption for the symmetry ($^2A''$ instead of the correct symmetry $^2A'$)[6] of ground-state formyl.

In the early 1960's, Zimmerman used sequences of classical resonance structures, with "continuous electron redistribution," to follow the fate of photochemical reactions.[7] He found that "in certain photochemical reactions the excited state proceeds directly to afford the initially observed product species,"[7d] without electron demotion, *i.e.*, without a step involving an electronic transition. This was particularly true of hydrogen abstraction by and of α cleavage in ketones, in which diradical primary product is obtained in a single step. However, the nature (excited or ground state) of this diradical was not specified, so that conclusions for the potential energy surfaces could not be drawn.

In recent years several classifications of photochemical reactions have been proposed which include, as a general reaction type, those reactions where excited reactant leads directly to ground-state product. In Förster's class III photoreactions, "an adiabatic transition occurs from the original potential energy surface to that of the ground state at an intermediate configuration. An intersection between both surfaces would

make this especially easy."[8] Dougherty's G-type photochemical reactions "start on an excited surface and proceed directly to a bonding ground-state configuration."[9a] Photochemical pericyclic reactions, in which there is a weakly avoided surface crossing,[9b] are cited as a typical example. In his detailed study of the mechanism of photochemical reactions, Michl underlines the importance of minima in excited-state surfaces.[10] "If this minimum in the (excited singlet) S_1 surface, in which a particular molecule has ended up, is only a little above S_0 (ground singlet), S_0 is reached at a geometry which is determined by the position of the minimum in S_1"; this minimum would correspond to a "funnel," *i.e.*, the region of an avoided crossing. In most of these studies the possibility of an electronically *allowed* crossing is mentioned but its actual occurrence is evoked as a rare event.

Evleth and his collaborators apparently deserve the credit for providing the first example of intersection between ground and excited surface in a large molecular system.[11] In the decomposition of arenediazonium salts, if the N_2 moiety departs in a manner which retains the molecular symmetry plane, the ($^1A''$) ground state of the aryl cation is adiabatically correlated with a high energy σ,π^* or $\pi,\sigma^*(^1A'')$ excited state of the aryldiazonium cation, while the ($^1A'$) ground state of the aryldiazonium cation correlates with a $\pi,\pi^*(^1A')$ excited state of the aryl cation. Other striking examples have since been provided by Evleth; for instance a surface crossing occurs if the OH bond of phenol is broken while maintaining the proton in the benzene ring.[11b]

In 1973, it was shown in a preliminary communication[12] that a surface crossing occurs in the hydrogen abstraction by ketones and that a similar phenomenon should occur in a number of photochemical reactions. Here proof of surface crossings or surface touchings is established for eight major photochemical reactions. Comparison is made between state correlation diagrams derived qualitatively and detailed *ab initio* computations of ground and lowest excited (singlet and triplet) energy surfaces. Finally the general features of excited- and ground-state behavior are assembled in a few highly characteristic energy diagrams, and two general proposals are made.

Method

The method is based on a single assumption or working hypothesis.

Basic Assumption. State Correlation Diagrams. In all the reactions which we shall investigate a molecular plane of symmetry is assumed to be conserved throughout the reaction. This plane of symmetry is not a Woodward–Hoffmann symmetry element;[13] on the contrary it is the *molecular plane* or that plane which

(2) (a) L. Magee, *J. Chem. Phys.*, **8**, 687 (1940). (b) For a detailed study of the F_2 + Li system, see G. G. Balint-Kurti, *Mol. Phys.*, **25**, 393 (1973).

(3) (a) A. E. Douglas, *Discuss. Faraday Soc.*, No. **35**, 158 (1963); (b) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 465.

(4) (a) F. Fiquet-Fayard and P. Guyon, *Mol. Phys.*, **11**, 17 (1969). The main predissociation process occurs *via* a spin-allowed crossing to $^4A''$ state leading to $OH^+(^3\Sigma^-)$ and H(^2S). (b) For many examples of surface crossings in the chemistry of electronically excited atoms, see R. J. Donovan and J. Husain, *Chem. Rev.*, **70**, 489 (1970).

(5) (a) J. C. D. Brand and R. I. Reed, *J. Chem. Soc.*, 2386 (1957) (in particular Figure 2). (b) The correct situation is essentially that of Figure 10 (see further).

(6) (a) J. W. C. Johns, S. H. Priddle, and D. A. Ramsay, *Discuss. Faraday Soc.*, No. **35**, 90 (1963); (b) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

(7) (a) H. E. Zimmerman, Abstracts, 17th National Organic Chemical Symposium, Bloomington, Ind., June 1961, p 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962), in particular p 4533; (d) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); in particular p 198, eq 12, and Chart VII; (e) *Science*, **153**, 837 (1966).

(8) (a) Th. Förster, *Pure Appl. Chem.*, **24**, 443 (1970); (b) *Ber. Bunsenges. Phys. Chem.*, **76**, 9621 (1972); (c) *Pure Appl. Chem.*, **34**, 227 (1973).

(9) (a) R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971); (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(10) J. Michl, *Mol. Photochem.*, **4**, 243 (1972).

(11) (a) R. J. Cox, P. Bushnell, and E. M. Evleth, *Tetrahedron Lett.*, 207 (1970); (b) E. M. Evleth, P. M. Horowitz, and T. S. Lee, *J. Amer. Chem. Soc.*, **95**, 7948 (1973).

(12) L. Salem, W. G. Dauben, and N. J. Turro, *J. Chim. Phys. Physicochim. Biol.*, **70**, 694 (1973).

(13) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

contains the nuclei directly involved in the electronic excitation. In practice along the reaction coordinate the molecular plane may well be destroyed as symmetry element; implications of the deviation from perfect symmetry will be discussed. Relative to the molecular symmetry plane (C_s symmetry) the various electrons have either σ or π symmetry and the corresponding states A′ symmetry (even number of π electrons) or A″ symmetry (odd number of π electrons). The correlation between states of same symmetry then involves a simple electron count.

The electron count is greatly simplified by using *resonance structures* for ground and excited states of reactant and product. Certainly the earliest and probably the most comprehensive effort to date at using resonance structures to follow the fate of a photochemically excited state is that of Zimmerman.[7] After writing out the excitation process of a cyclohexa-2,5-dienone, he follows the electron redistribution accompanying bond formation in the n,π^* excited state, the return ("electron demotion") from a diradical excited state to a zwitterionic ground state, and the ultimate electron redistribution in this product. Zimmerman recognized for this reaction, and emphasized very clearly, the important distinction between resonance structures contributing to the same state (eq 7)[7d] and resonance structures corresponding to different states (eq 9).[7d] In our work *resonance structures are used in conjunction with symmetry*. They allow us to easily count the total number of σ and π electrons, and thereby determine the symmetry of the states. A *state correlation diagram* can then be drawn.

Resonance Structures. It is convenient to represent a molecule in a given electronic state by the predominant classical resonance structure. The method which we adopt here, for drawing these resonance structures, which is essentially equivalent to previous methods, such as Zimmerman's,[7] is as follows: relevant electrons are shown as dots (we are essentially interested in *spatial* symmetry); for localized σ electrons, the larger lobe of the occupied σ orbital is drawn out. For an in-plane-type orbital (such as an n orbital), only a half-lobe is drawn; for π electrons, the orbitals are not drawn out; a double bond formed by the conjugation of two in-plane p orbitals ("σ" double bond) is indicated by a label σ. In this manner the n,π^* excited state of formaldehyde is shown pictorially as

In a similar vein the σ and π radicals formed by the abstraction of the α hydrogen of acrolein are described by

σ Radical   π Radical
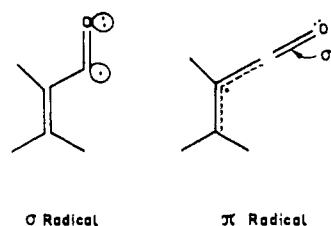
In certain cases there may be two nearly equally appropriate resonance structures. In principle they should both be shown with the appropriate resonance sign.

In practice we will not specify more than one resonance structure unless there is a strict 50:50 resonance mixture, as can be imposed by symmetry. In the latter case it is generally necessary to specify whether the resonance is in-phase (+ sign) or out-of-phase (− sign). For instance, the two zwitterionic excited singlet states[14] of 90°-twisted ethylene can be represented as

($^1B_2$)

($^1A_1$)
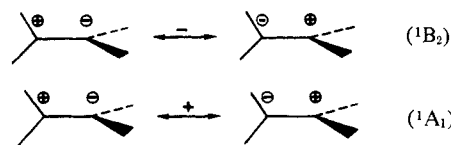
The latter has a slightly higher energy.

Ab Initio **Calculations of Potential Energy Surfaces.** For most of the reactions studied in this article the qualitative state correlation diagrams have been accompanied by more rigorous, computed energy curves. The various calculations of ground- and excited-state surfaces were carried out on a modified version of the self-consistent field GAUSSIAN 70 program of Pople and collaborators using a minimal basis set of Slater-resembling Gaussian orbitals (STO-3G).[15] The modifications, due to Dr. W. J. Hehre, allow for the proper treatment of molecular diradicals[14] in the following manner: in the *closed-shell* program, a 3-by-3 configuration interaction calculation is performed between ground, lowest singly excited, and corresponding doubly excited configurations. This leads to the energies of three singlet states (one diradical state, and two zwitterionic states); concurrently, an *open-shell* calculation is carried out using the restricted Hartree–Fock formalism suggested by Nesbet[16] together with a single Hamiltonian for all the electrons. In eq 1 j

$$F = h + \sum_j^{occ}(2J_j - K_j) + (J_a - \tfrac{1}{2}K_a) + (J_b - \tfrac{1}{2}K_b) \quad (1)$$

represents the doubly occupied orbitals, and a and b the molecular orbitals of the two odd electrons; h, J, and K are the familiar one-electron, two-electron Coulomb, and two-electron exchange operators. The total energy calculated from F in terms of one-electron energies h_i and orbital energies ϵ_i is

$$E_0 = \sum_j^{occ}(\epsilon_j + h_j) + \frac{1}{2}(\epsilon_a + h_a + \epsilon_b + h_b) +$$

nuclear repulsion energy (2)

Equation 2 must be corrected slightly to yield the correct energies of the three singlet configurations ^1ab, $^1a^2$, and $^1b^2$ (as well as ^3ab).[17] Finally configuration inter-

(14) (a) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972); (b) L. Salem, *Pure Appl. Chem.*, 33, 317 (1973).

(15) (a) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.; (b) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).

(16) (a) R. K. Nesbet, *Rev. Mod. Phys.*, 35, 552 (1963). (b) For an interesting alternative method of calculating diradicals, see J. Koutecky and V. Bonacic-Koutecky, *Chem. Phys. Lett.*, 15, 558 (1972), and references therein.

(17) For instance $E(^1ab) = E_0 - 0.25(J_{aa} + J_{bb}) + 1.5K_{ab}$; $E(^1a^2) = E(^1ab) + \epsilon_a - \epsilon_b - J_{ab} - K_{ab} + 0.5(J_{aa} + J_{bb})$; $E(^1b^2) = E(^1a^2) + 2(\epsilon_b - \epsilon_a)$. The method does not give directly, in (2), the energy of any single state and in this sense is not a 100% pure self-consistent field method.

action between these three configurations yields the energy of the three singlet states, while the triplet-state energy is that of ³ab. For a given state, the energy chosen is the *lower* of the appropriate closed-shell and open-shell roots[18] obtained in the two separate calculations. Experience shows that, for excited singlet and triplet n,π* states the open-shell method always gives the lower energy. For the lowest singlet state, there are typical situations (diradical-like or nearly diradical-like molecules) where the open-shell method gives the lower energy. In bonded situations or for zwitterionic states, however, the closed-shell energy is generally lower. The occurrence of a ground triplet state in the open-shell calculation is always a signal that the open-shell result will optimize the energy of the lowest singlet state.

Since we are interested essentially in major features (cols, intersections) of the surfaces, and not in too detailed aspects nor absolute numbers, no calculations were performed with the more reliable,[19] but vastly more expensive, extended basis sets. The bond lengths and bond angles chosen for the model calculations are the standard values indicated originally by Pople and Gordon.[20]

Surface Crossings

We study successively four photochemical reactions: hydrogen abstraction by excited ketones; photoreduction of aza aromatics; hydrogen abstraction by carbenes; addition of excited ketones to electron-rich olefins; in which the same type of surface crossing is shown to occur.

Hydrogen Abstraction by Ketones.[21,22] We study this reaction in some detail; analogous features in further reactions will be dealt with more rapidly. The general reaction can be summarized crudely as
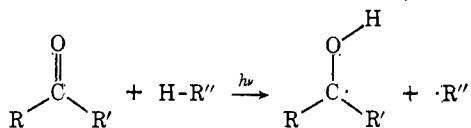
The primary photochemical product is therefore a diradical (intramolecular abstraction) or a pair of radicals (intermolecular abstraction). The electronic states of the radical pair can be considered as diradical states of the supermolecule, so that in both cases we are dealing with a diradical as primary product. Now normally such a diradical lies already on the *ground-state* surface of the products, just as (H· + H·) lies on the ground surface of H₂.[14] For example, the 1,4

(18) This technique is allowable because in our model calculations ground and excited singlet states have different symmetries (when this is not the case, see further footnote 47). A special algorithm allows the operator to force the system into an open-shell configuration ¹ab of chosen symmetry, when necessary.
(19) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).
(20) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).
(21) Hydrogen abstraction is the first step of Norrish "type II photoprocesses:" (a) R. G. W. Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937); (b) N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958); (c) N. C. Yang in "Reactivity of the Photoexcited Molecule," Wiley-Interscience, London, 1967, p 145. (d) For a review see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).
(22) For pertinent reviews of ketone photochemistry, see (a) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972); (b) J. D. Coyle and H. A. J. Carless, *Chem. Soc. Revs.*, **11**, 465 (1972); (c) J. Kossanyi and B. Furth, *L'Actualité Chim.*, **No. 2**, 7, and **No. 3**, 3 (1974).

diradical obtained *via* intramolecular γ-hydrogen abstraction of ketones[23] can in principle be obtained
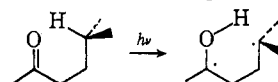
equally well by thermal cleavage of a CC bond in cyclobutanol.[24] Yet the sign *hv* implies electronic *excitation*. Thus all the useful information on the excited state which is reached, and on the manner in which the excited molecule returns to the ground state, is hidden within the single arrow.

Let us try and elucidate the intimate details of the process by considering as a model case the abstraction of a paraffinic hydrogen atom by the carbonyl group of a ketone. We assume, as stated before, that the abstraction occurs in the plane of the keto double bond, which remains a plane of symmetry for the entire system throughout the reaction. The excited state responsible for the reaction can be either the singlet or the triplet n,π* excited state of ketone.[25] We now draw out the resonance structures for ground and lowest excited states of both reactant and primary product. For the resonance structure appropriate to each state we count the number of electrons with σ and π symmetry relative to the symmetry plane. The relevant electrons are (a) the two electrons initially in the oxygen n orbital; (b) the two electrons initially forming the π bond from carbon to oxygen (in the primary product the π electron count then includes a lone pair on oxygen); (c) the two electrons which initially make up the C–H σ bond. A simple count then gives, for the lowest states of reactant and primary product
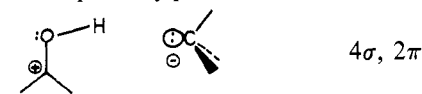
reactant ground state

4σ, 2π

reactant (n,π*) excited state

3σ, 3π

ground state of primary product

3σ, 3π
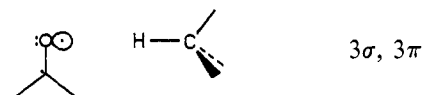
excited state of primary product

4σ, 2π

(23) For recent interesting work in this area, see (a) C. P. Casey and R. A. Boggs, *J. Amer. Chem. Soc.*, **94**, 6457 (1972); (b) R. A. Garnier, W. L. Schreiber, and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 729 (1972); (c) P. J. Wagner, P. A. Kelso, A. E. Kempainnen, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7500 (1972).
(24) For thermally reversible photochemical reactions, see (a) G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **11**, 1072 (1972); (b) N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, **83**, 2213 (1961).
(25) (a) M. Kasha, *Radiat. Res., Suppl.*, **No. 2**, 243 (1960); in "Light and Life," W. D. McElroy and B. Glass, Ed., John Hopkins University Press, Baltimore, Md., 1961, p 31; (b) H. E. Zimmerman, Abstracts, 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961, p 31; (c) J. L. Michaels and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **85**, 1027 (1963); (d) P. Ausloos and R. E. Rebbert, *ibid.*, **86**, 4512 (1964); (e) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4010 (1965); (f) T. Dougherty, *ibid.*, **87**, 4011 (1965); (g) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

Figure 1. State correlation diagram for hydrogen abstraction by ketones.

Figure 2. Energy surfaces for the formaldehyde plus methane hydrogen abstraction reaction: (- - -) triplet energies.

The ground state of primary product is a diradical state; as has been shown[10,14,26] this state is accompanied by two excited zwitterionic states, the lowest one of which is appropriately represented by the last resonance structure.

It is now a simple matter to correlate the singlet states of the reactant with those of the intermediate. This *correlation diagram for states* is shown in Figure 1. The excited-state surface of the reactant correlates with the ground-state surface of product while the ground reactant correlates with the high-energy ionic excited state of product. The surface crossing thus revealed is *rigorously allowed* because the electronic state symmetries are different: $A'(4\sigma, 2\pi)$ and $A''(3\sigma, 3\pi)$. *We encounter here an example of a reaction which occurs in a perfectly adiabatic manner, the excited state of reactant and ground state of product lying on a single energy sheet.*

In practice the crossing may be weakly avoided along the reaction coordinate because the reactants may not have the keto plane as rigorous plane of symmetry, and because H-abstraction need not occur in a coplanar fashion.[23c] It is true that in the full hyperspace spanned by the molecular degrees of freedom and by the energy coordinate, the points corresponding to the intersecting surfaces are extremely rare.[27] However, unless the reacting system is far removed from coplanarity, its chemical behavior should be determined by its "memory" of the intended crossing, a phenomenon which lies at the heart of the reaction mechanism.

We have just drawn a correlation diagram for the two lowest singlet states. The lowest triplet state (n,π^*) follows closely the behavior of the excited (n,π^*) singlet, since they have the same electronic distribution and same spatial symmetry. It correlates with the triplet state of the diradical photoproduct.

Several *ab initio* calculations were carried out on the colinear abstraction of a hydrogen atom of CH_4 by H_2CO. In all of the runs the distance R_{OH} was the major variable. The O_1C_5 bond was held fixed at 2.64

Å, corresponding to a starting O_1H_6 distance of 1.56 Å. In a typical run the carbonyl bond length was restricted to its value in the starting system $(C_2O_1 = 1.22$ Å$)$ and the abstraction carried out for $\alpha = 120°$. In another run the carbonyl bond length was given its value in the product system $(C_2O_1 = 1.43$ Å$)$ and the abstraction carried out for $\alpha = 109.5°$. In a third run the carbonyl bond length and α angle were allowed to vary smoothly by small increments from their initial values $(1.22$ Å, $120°)$ to their final values $(1.43$ Å, $109.5°)$.[28] In all cases the crossing of singlet n,π^* state with ground state is confirmed. It occurs near the end of the abstraction process, when the hydrogen atom is approximately 1.16 Å away from oxygen (equilibrium distance OH $= 0.96$ Å).

Figure 2 shows the calculated energy surfaces for the third run. The triplet n,π^* state is shown in dotted lines. First, several quantitative aspects of the energy curves are worth mentioning.

(a) The vertical excitation energies for $^3n,\pi^*$ and $^1n,\pi^*$ states are calculated to be respectively 2.53 and 3.16 eV, compared with the experimental values of 3.12 and 3.5 eV for formaldehyde in the gas phase.[29]

(b) Activation energies of 8 and 17.5 kcal/mol are found respectively in the excited singlet and triplet along the reaction pathway.[21c] This can be compared with the experimental activation energy (4.2–7.1 kcal/mol) estimated for γ abstraction in the triplet state.[30]

(26) See also (a) E. M. Evleth, *Chem. Phys. Lett.*, **3**, 122 (1969); (b) D. L. Whilhite and J. L. Whitten, *J. Amer. Chem. Soc.*, **93**, 2858 (1971).

(27) (a) If there are n $(= 3N - 6)$ molecular dimensions, in the $(n + 1)$ dimensional space which includes the energy, the intersections form an $(n - 2)$ dimensional Teller "hyperpoint" (E. Teller, *J. Phys. Chem.*, **41**, 109 (1937); G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, No. **35**, 77 (1963); ref 2b, p 443). However, in the $(n' + 1)$ dimensional subspace $(n' = 2N - 3)$ of *coplanar* reactions, the surfaces form two different sheets which intersect along a $(n' - 1)$ dimensional "hyperline." The author is grateful to Professor Th. Förster for a discussion on this problem. For illuminating discussions of intersecting potential surfaces see also: (b) T. Carrington, *Discuss. Faraday Soc.*, No. **53**, 27 (1972); *Accounts Chem. Res.*, **7**, 20 (1974); (c) R. K. Preston and C. Tully, *J. Chem. Phys.*, **54**, 4297 (1971); S. Chapman and R. K. Preston, *ibid.*, **60**, 650 (1974); (d) K. Morokuma and J. F. George, *ibid.*, **59**, 1959 (1973); (e) C. W. Bauschlicher, S. V. O'Neil, R. K. Preston, H. F. Schaefer, and C. F. Bender, *ibid.*, **59**, 1286 (1973).

(28) (a) This requires the methane moiety to move slightly downwards as the reaction progresses, since O_1, H_6, and C_5 are constrained to be linear. (b) In all the runs the remaining CH_3 group was kept pyramidal. This is proper for the ionic state and not expected to introduce any significant error in the radical state, because of the well-known flat bending potential of $\cdot CH_3$ in *ab initio* calculations. Improved runs would account for depyramidalization at C_5 and thereby increase even more the stability of diradical product relative to its zwitterionic counterpart.

(29) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 612.

(c) The energy difference between singlet diradical product and singlet ground state reactant is 72 kcal/mol, in excellent agreement with the thermochemical prediction of 74 kcal/mol (losses of 85 kcal/mol, CO π bond, and 99 kcal/mol, CH bond, *vs.* a gain of 110 kcal/mol, OH bond).

(d) Net charges calculated for the *excited* product are C_2, +0.18; O_1, −0.14; C_5, −0.46; H_6, +0.28; H_7, H_8, H_9, −0.06. This result is in relatively good agreement with the zwitterionic structure proposed earlier as the major component of this state.

The calculated energy surfaces confirm the fact that a ketone excited to either singlet or triplet n,π^* state can reach diradical photoproduct and yet remain on a single potential energy surface.

Photoreduction (*via* Hydrogen Abstraction) of Aza Aromatics. The photoreduction of aza aromatics such as acridine, quinoline, pyridine, etc., can be summarized[31] in the typical scheme
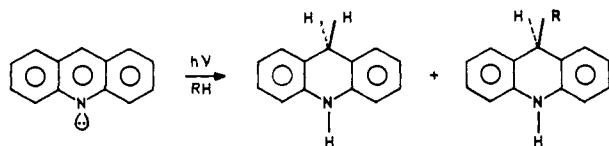
Here RH is an alcoholic or paraffinic hydrogen donor. There is strong evidence, particularly from flash spectroscopic studies, energy-transfer experiments, and electron spin resonance experiments that the primary photoprocess occurs in the n,π^* excited state (triplet or singlet, depending on the particular reaction)[32] and leads to a semiquinone-like radical.[33]
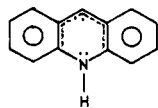
Let us consider as a model reaction the coplanar abstraction of a hydrogen atom by pyridine. An electron count restricted to the n electrons of nitrogen, the π electrons of the ring and the two σ electrons of the R–H bond leads to: 4σ, 6π electrons in the ground state of reactant (Pyr + RH); 3σ, 7π electrons in the n,π^* excited state of reactant (Pyr + RH); 3σ, 7π electrons in the pair of radicals formed by abstraction (diradical ground state of the supermolecule Pyr–H + R·); 4σ, 6π or 2σ, 8π electrons in the higher energy ion pairs which could also conceivably be formed by the abstraction (zwitterionic states of the super molecule: Pyr$^+$–H + R$^-$ and Pyr$^-$–H + R$^+$; both states have the same symmetry).

The singlet-state correlation diagram is then easily

Figure 3. State correlation diagram for hydrogen abstraction by pyridine.

drawn and shown in Figure 3. Thus the pyridinyl radical can be formed in an adiabatic manner directly from the singlet n,π^* state of reactant. In the event that the reaction occurs from the triplet n,π^* state of pyridine, the radical is also formed *via* a surface crossing but the spin of its unpaired electron is parallel to that of ·R.

Hydrogen Abstraction by Singlet Carbenes. Of the three major reactions of carbenes in the presence of hydrocarbons, addition to multiple CC bonds,[34] insertion into alkane CH bonds,[35] and abstraction from CH bonds,[36] the last two appear to be highly spin specific. In the gas phase insertion occurs essentially in the lowest singlet state, while abstraction belongs essentially to the ground triplet state.[37,38] A correlation diagram between initial and final states of the process suffices to yield some insight into the "forbidden" nature of the singlet abstraction reaction.

Let us consider a coplanar abstraction process where the C–H bond remains in the plane of symmetry determined by the abstracting methylene group, and where the displaced hydrogen stays colinear with the two carbon atoms (least motion process). The cor-

relation diagram for hydrogen abstraction by the ground triplet and the *three* lowest singlet states of methylene is easily drawn as soon as one remembers the appropriate electron distribution in each state.[39] In the (CH_3, CH_3) product there are two low-lying radical-pair (triplet, singlet) states and two high-energy ion-
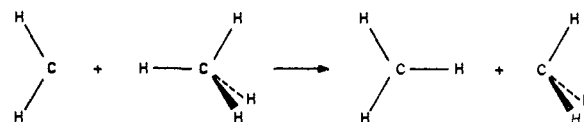
(30) (a) F. D. Lewis, *Mol. Photochem.*, **4**, 501 (1972); (b) J. C. Scaiano, J. Grotewold, and C. M. Previtali, *J. Chem. Soc., Chem. Commun.*, 390 (1972). The comparison is all the more favorable that no geometry optimization has been performed on the excited states. (c) For activation energies in intermolecular hydrogen abstraction, see L. Giering, M. Berger, and C. Steel, *J. Amer. Chem. Soc.*, in press.

(31) For a reivew, see A. Lablache-Combier in "Elements de Photochimie Avancée," P. Courtot, Ed., Hermann Publishers, Paris, 1972, p 289.

(32) (a) A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965); (b) E. Van der Donckt and G. Porter, *ibid.*, **46**, 1173 (1967); (c) D. G. Whitten and Y. J. Lee, *J. Amer. Chem. Soc.*, **93**, 961 (1971); (d) M. Hoshino, S. Niizuma, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **45**, 2988 (1972), and references therein.

(33) V. Zanker and P. Schmid, *Z. Phys. Chem. (Frankfurt am Main)*, **17**, 11 (1958).

(34) (a) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956). (b) W. von E. Doering and P. La Flamme, *ibid.*, **78**, 5447 (1956). (c) G. B. Kistiakowsky and K. Sauer, *ibid.*, **78**, 5699 (1956). (d) For a recent review of carbene chemistry, see W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971. (e) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

(35) (a) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Amer. Chem. Soc.*, **78**, 3224 (1956); (b) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959); (c) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **83**, 1989 (1961); (d) see ref 34d.

(36) (a) H. M. Frey and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **79**, 6373 (1957); (b) H. M. Frey, *Proc. Roy. Soc., Ser. A*, **250**, 409 (1959), in particular p 420; (c) see ref 34d.

(37) (a) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *J. Amer. Chem. Soc.*, **82**, 5001 (1960); **83**, 1934 (1961). (b) H. M. Frey and R. Walsh, *J. Chem. Soc. A*, 2115 (1970). (c) H. D. Roth, *J. Amer. Chem. Soc.*, **94**, 1761 (1972). (d) For a discussion of the difficulty in obtaining unambiguous results on spin state specificity, see M. Jones, W. Ando, M. E. Hendrick, A. Kulczycki, P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Amer. Chem. Soc.*, **94**, 7469 (1972), and the comprehensive literature reviewed therein.

(38) Singlet methylene does, however, abstract halogen atoms: H. D. Roth, *J. Amer. Chem. Soc.*, **93**, 1527, 4935 (1971); F. S. Rowland, P. S. T. Lee, D. C. Montague, and R. L. Russel, *Discuss. Faraday Soc.*, No. 53, 111 (1972).
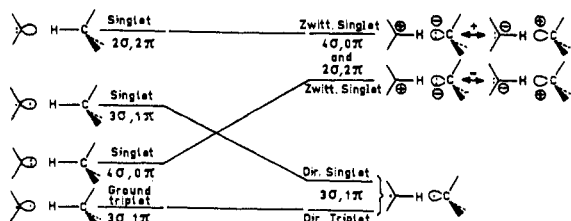
(39) See, for instance, Figure 3 of ref 14b.

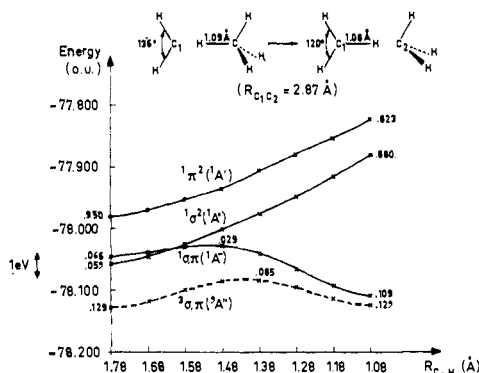**Figure 4.** State correlation diagram for hydrogen abstraction by carbenes.

Figure 5. Energy surfaces for the methylene plus methane hydrogen abstraction reaction: (- - -) triplet energies; (O) unreliable energies.

pair singlet states. These last two states, which are the zwitterionic states of the C_2H_6 supermolecule, are most adequately[40] described by out-of-phase or in-phase resonance between two classical structures, of the type portrayed earlier in this article. These structures carry respectively $(0\pi, 4\sigma)$ and $(2\pi, 2\sigma)$ electrons, corresponding to the same spatial symmetry. Figure 4 shows the schematic state correlation diagram, and Figure 5 the results of an *ab initio* calculation for the methylene-plus-methane abstraction reaction.[41]

Both the schematic correlation diagram and the computed energy surfaces show unambiguously that hydrogen abstraction should be forbidden in the lowest singlet state of methylene. However, hydrogen abstraction should be extremely facile from the *second* singlet of methylene—not surprisingly since the electronic configuration of this state is similar to that of the ground triplet. The activation energy, if any, should be no larger than the calculated value of 11 kcal/mol. In the triplet state the abstraction is feasible with a calculated activation energy of 28 kcal/mol. This is an upper limit,[41] of course, but probably already is not far above the excess energy with which triplet methylene is created in the photolysis of diazomethane (28 kcal/mol excess energy) or ketene (19 kcal/mol excess energy).[42]

(40) This description would be rigorous, with a 50:50 mixture of both resonance structures, only if there were a center of symmetry relating the two product molecules.

(41) Again no attempt has been made to minimize the energy of each separate state by optimizing geometries along the reaction coordinate. For instance, the starting ∠HCH angle in methylene is chosen at the equilibrium value (136°) for the triplet ground state, a value intermediate between that (102°) for lowest singlet, and that (180°) for second singlet. The crossing between these two states then occurs at an early stage in the abstraction (Figure 5). For other values of the ∠HCH angle the crossing would occur at different *R* values. All together there will be a full crossing contour in 18-dimensional space.

(42) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).
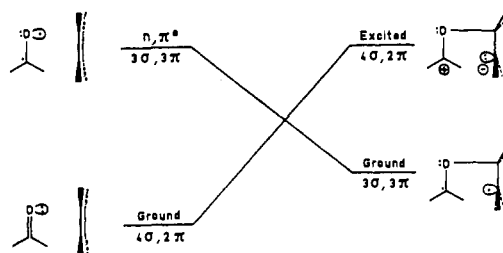
Figure 6. State correlation diagram for (n orbital) addition of ketones to olefins: (- - -) triplet energies.

Hoffmann has made the spirited suggestion[43] that "no carbene in its sane mind would head for a four-electron transition state when it has a (non-least-motion) two-electron process available to it." We will consider Hoffmann's alternative approach, in which the molecular symmetry plane is destroyed, and the corresponding energetic profiles in a further section.

(n Orbital) Addition of Excited Ketones to Electron-Rich Olefins.[22,44] Excited ketones can add to olefins either *via* their π orbital (electron-poor olefins) or *via* their n orbital (electron-rich olefins). The process where addition occurs through the n orbital can be summarized as
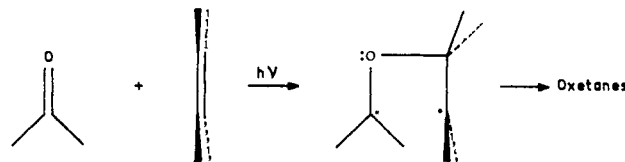
Although recent evidence has accumulated for an excited-state complex prior to formation of the diradical,[45] we restrict our study to the simple process written above as if it were occurring in a single step.

The olefin molecule is assumed to approach the ketone in such a manner that its π orbitals lie in the plane defined by the ketone molecule. For a symmetrically substituted olefin this molecular plane is then a symmetry plane for the entire system. The now familiar electron-counting process yields the correlation diagram shown in Figure 6.[46] The prominent feature of this diagram is again an intersection of the two lowest singlet energy sheets. The ground-state reactants correlate with a zwitterionic state of adduct, while the $(n,\pi^*$ ketone, ground olefin) excited state correlates with the diradical state of adduct, *i.e.*, the assumed primary photoproduct.

Figure 7 shows the results of a computation for the addition of formaldehyde to ethylene. The starting geometry is that of ground-state reactants and progressive relaxation to the geometry of ground product is allowed along the reaction path. The surface crossing is shown to occur at a CO bond distance of approximately 1.9 Å. Two features of the calculated n,π^* excited-state surfaces are worth mentioning. (1) The singlet–triplet separation, 0.7 eV, in the isolated

(43) R. Hoffmann, private communication to the author, 1972.

(44) (a) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909). (b) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954); G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *ibid.*, **78**, 876 (1956). (c) For a review, see D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(45) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Amer. Chem. Soc.*, **95**, 2549 (1973).

(46) We include the n electrons on oxygen (2σ), the carbonyl π electrons (2π), and the olefin π electrons (2σ).
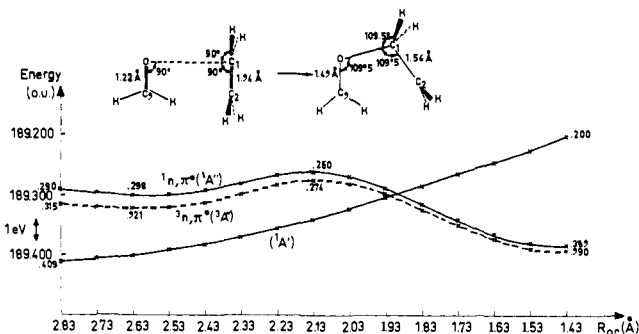
Figure 7. Energy surfaces for (n orbital) addition of formaldehyde to ethylene: (- - -) triplet energies.

ketone, decreases progressively as diradical character increases in the two states. In the product diradical the separation is only 0.2 eV, corresponding to twice the exchange integral between the atomic orbitals (on C_2 and C_3) of the odd electrons. A similar feature is perceptible in the hydrogen abstraction reaction of ketones (Figure 2) and for the $^{1,3}(\sigma,\pi)$ pair of states in the hydrogen abstraction by carbenes (Figure 5). (2) At a distance of 2.6 Å both states show a shallow minimum. Relative to separated ethylene and (n,π^*) excited formaldehyde molecules the depth of this minimum is found to be $\sim$5 kcal/mol in both states. Furthermore activation energies of 24 and 29 kcal/mol are required for excited reactant to leave this well and reach diradical product. However, this minimum does not appear to be related to the observed excited complex.[45] It arises from the stabilization due to the incipient C_3O bond lengthening in the excited formaldehyde—a stabilization not yet overcome by the energy increase due to the oncoming olefin. Similar calculations for fully relaxed excited formaldehyde show no such secondary minimum.

Avoided Crossings. If the molecular plane is not strictly conserved as plane of symmetry during the reaction, the crossing of the two lowest singlet energy surfaces will be avoided. The excited singlet will correlate with the high-energy zwitterionic product; its energy will rise continuously. If the crossing region is "late" in the reaction (Figure 2), a secondary minimum will show up as a "memory" of the intended crossing. If the crossing region occurs "early" along the reaction path (Figure 5) the energy of the excited surface will rise continuously. As to the lowest singlet state surface, it goes through a maximum which may or may not correspond to the avoided-crossing region.

After solving for computational uncertainties,[47] we

(47) We mentioned earlier, in the section on potential energy calculations, that the open-shell method deals well with n,π^* excited singlet states and poorly with closed-shell ground states, while the contrary is true for the closed-shell method. To obtain an avoided crossing of two states with same symmetry requires, however, that their energies be calculated by a *single method* as roots of one CI matrix. If both states are calculated with the closed-shell technique the second singlet tends to be too high and the crossing occurs too far along the reaction coordinate. If both states are calculated by the open-shell technique the lower singlet starts off too high and the intended crossing occurs much earlier ($R_{OH} = 1.36$ Å) than in Figure 2. The appropriate method uses a Hamiltonian "intermediate" between the closed-shell Hamiltonian appropriate to the ground state and the open-shell Hamiltonian appropriate to the excited state (K. K. Docken and J. Hinze, *J. Chem. Phys.*, **57**, 4928 (1972); L. Salem, C. Leforestier, G. Segal, and R. Wetmore, *J. Amer. Chem. Soc.*, submitted for publication). This method gives a crossing in the correct region (Figure 8) although the energies of each state are slightly higher than in Figure 2.
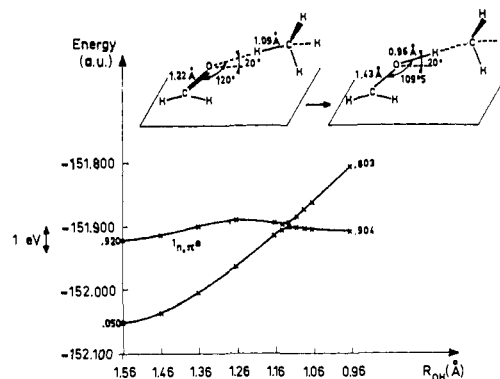
Figure 8. Energy surfaces of two lowest singlets for out-of-plane abstraction reaction of formaldehyde plus methane: (O) unreliable energies; (- - -) intended crossing. Compare with Figure 2.
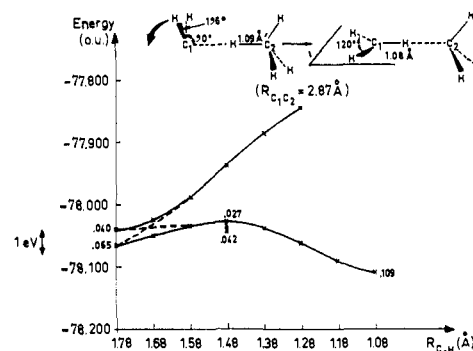
Figure 9. Energy surfaces of two lowest singlets for out-of-plane abstraction reaction of methylene with methane: (- - -) intended crossing. Compare with Figure 5.

have been able to perform two *ab initio* calculations which illustrate, at least qualitatively, these features. First a calculation has been carried out for the colinear abstraction of a hydrogen atom from methane by excited formaldehyde. The dihedral angles $C_5O_1C_2H_4$ and $H_6O_1C_2H_4$ were held at 20° instead of 0°, corresponding to a 20° approach of the hydrogen atom above the plane of the carbonyl group. The avoided crossing shows up clearly (Figure 8) as a maximum in the ground surface and as a secondary minimum in the excited surface. The minimum is of the type predicted by Michl[10] for an avoided crossing region. The energy separation at the avoided crossing is only 0.13 eV (= 3 kcal/mol), *i.e.*, of the order of magnitude of a vibrational spacing. For a 40° approach, the gap increases to 0.87 eV (20 kcal/mol). There is a relatively *strong memory* of the symmetry-allowed crossing.[48]

We also investigated the *non-least motion* approach of methylene to methane (with abstraction of hydrogen) suggested by Hoffmann.[43] The results obtained by an open-shell calculation are shown in Figure 9. As predicted by Hoffmann, the abstraction now occurs in the lowest singlet. The memory of its intended correlation with a high-energy zwitterionic state may be

(48) W. J. Hehre (private communication to the author, 1973) has suggested that the reactants will follow the *least avoided crossing* pathway; *i.e.*, all other things being equal, in-plane abstraction should be preferred to out-of-plane abstraction. Delicate experimental tests, and calculations of internal conversion as a function of avoided-crossing width, are required to test this prediction, which is akin to the minimum energy gap laws and to Dauben's principle of ground-state control (W. G. Dauben, private communication to the author, 1973).
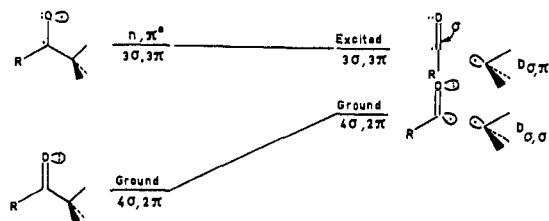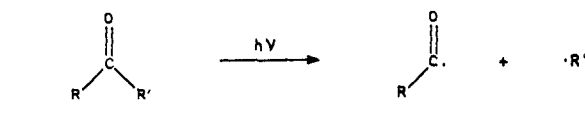
Figure 10. State correlation diagram for α cleavage of alkanones.

reflected, however, in the high activation energy (24 kcal/mol), combined with a smaller available excess energy, for singlet abstraction. Indeed the lowest singlet curve now joints the starting minimum for the $^1\sigma^2$ configuration to the col previously belonging to the higher energy $^1\sigma,\pi$ configuration (see Figure 5). However, this 24 kcal/mol activation energy can be lowered by at least 10 kcal/mol (arrow under the col) by changing the reaction path to one which involves a smaller backwards "balancing" motion of the initially vertical CH_2 group. We have therefore partially answered the question of why singlet methylene does not abstract hydrogen from alkanes: in approaches in which the hydrogen is removed in the plane of the abstracting methylene group, or in encounters which resemble such a least motion, the abstraction is forbidden because it leads to a high-energy ion-pair state. *To the extent* that such approaches weigh heavily in the overall dynamics of the reaction, and to the extent that they have slightly lower activation energies than other trajectories, hydrogen abstraction by the lowest singlet state of methylene should be forbidden.

Surface Touchings

The reactions which we consider in this section all involve cleavage of a single bond between a carbon atom doubly bonded to an atom X carrying an n lone-pair and a carbon atom α to it. This cleavage leads to a σ-radical center on C_α and to an unsaturated radical involving the CX moiety. An important question is the location of the odd electron in the $R\dot{C}{=}X$ radical. This will determine whether we are dealing with a σ radical or a π radical (with the overall system, accordingly, a σ,σ diradical or a σ,π diradical). We can anticipate, therefore, that the two lowest singlet states of reactant correlate, not with a diradical state and a zwitterionic state as in the previous section, but with *two diradical states* of different symmetries.

α **Cleavage of Saturated Ketones.**[7,22,49,50] Let us consider first the process where R and R' are saturated

moieties. The radical $R\dot{C}O$ has two low-lying available states: a bent ground state with the odd electron in a σ orbital and a linear excited state with the odd electron in a π orbital. In the π radical there is still a CO double

σ Radical π Radical

bond but the p bonding occurs in a plane perpendicular to the orbital axis of the odd π electron. For the formyl radical (R = H) the bent $^2A'$ state lies 1.1 eV below the linear $^2A''$ or $^2\Pi$ state.[5,51]

Let us now draw the state correlation diagram for α cleavage of ground singlet and excited n,π^* singlet (or triplet) states of a saturated ketone. In the usual manner we restrict the electron count to the two carbonyl π electrons, the pair of oxygen n electrons, and the two σ electrons originally in the CC bond which is cleaved. The results are shown in Figure 10. Contrary to the reactions studied in the previous reaction, there is *no* crossing of the singlet surfaces. However, since the $R\dot{C}O$ σ and π radicals, and thus the corresponding diradicals $D_{\sigma,\sigma}$ and $D_{\sigma,\pi}$ formed by weak interaction between $R\dot{C}O$ and $\cdot R'$, lie close in energy, the singlet surfaces will *come very close* in the region of the diradical photoproduct. We speak of a surface *touching*.[51d]

Another important feature is as follows. To the ground singlet σ,σ diradical photoproduct $D_{\sigma,\sigma}$ corresponds a triplet σ,σ diradical with nearly equal energy. Since the wave function of this triplet is symmetric (4σ, 2π electrons) with respect to the molecular plane, it cannot correlate with the low-lying n,π^* triplet. The triplet σ,σ diradical must therefore correlate with the lowest symmetric triplet of reactant, *i.e.*, the π,π^* triplet of ketone. In saturated ketones, there is little doubt that this triplet state lies above both singlet and triplet n,π^* states.[52] The energy surface of this triplet will therefore come down, *cross* both surfaces generated by the n,π^* states, and correlate with ground triplet state of product diradical[50d] (see further the section on the general reaction types). As it comes down along the reaction coordinate, the triplet π,π^* state acquires progressively triplet σ,σ^* character (with same spatial symmetry).

These results are confirmed in an *ab initio* calculation of the α cleavage of acetone. The corresponding acetyl radical $CH_3\dot{C}O$ is found to have a bent $^2A'$

(49) (a) R. G. W. Norrish, *Trans. Faraday Soc.*, 33, 1521 (1937); (b) J. W. Kraus and J. G. Calvert, *J. Amer. Chem. Soc.*, 79, 5921 (1957). (c) For a review of the photochemistry of cyclic saturated ketones, see R. Srinivasan, *Advan. Photochem.*, 1, 83 (1963).

(50) For important recent work on the nature of the intermediates in the α-cleavage reaction, see (a) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *J. Amer. Chem. Soc.*, 94, 7221 (1972); (b) P. J. Wagner, F. A. Kelso, and K. G. Zepp, *ibid.*, 94, 7450 (1972); (c) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, 92, 6974 (1970); (d) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *ibid.*, 93, 7213 (1971). Figure 2 of this paper (adapted from R. K. Boyd, G. B. Carter, and K. O. Kutsche, *Can. J. Chem.*, 46, 175 (1968)), suggested for the behavior of the different energy surfaces, compares well with Figures 10 and 11 here.

(51) (a) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 469. (b) G. Herzberg, "The Spectra and Structures of Simple Free Radicals," Cornell University Press, 1971, p 186. (c) In the linear geometry, which is an *equilibrium* geometry for the π radical but a *nonequilibrium* geometry for the σ radical, the two states are degenerate. (d) The term "touching" which we use henceforth for neighboring symmetric and antisymmetric surfaces corresponds, in $H\dot{C}O$, to what is traditionally called a "glancing intersection." The surfaces separate quadratically.[27b] In other examples considered in this section, such as $CH_3\dot{C}O$, the surfaces separate linearly. The author is grateful to Professor Tucker Carrington for pointing out this distinction.

(52) In formaldehyde, for instance, the π,π^* triplet is calculated in an extensive 120-configuration interaction calculation to be at 4.99 eV compared with $^3n,\pi^*$ at 3.01 eV and $^1n,\pi^*$ at 3.43 eV (R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, 53, 1368 (1970); see in particular Table VII).

ground state, and a linear $^2A''$ excited state lying 1.25 eV above it. The energy curves in Figure 11 have been computed for cleavage to a *bent* geometry.[53] For cleavage to a linear geometry, the σ,π diradical states $D_{\sigma,\pi}$ would be lowered (as indicated in the figure) and the σ,σ diradical states $D_{\sigma,\sigma}$ raised. As predicted, there is no intersection between the two lowest singlet states. However, there is a "touching" of the surfaces in a dissociation path which leads to a linear acetyl radical.[51c,d] If the excited molecule remains on the (singlet or triplet) n,π^* surface throughout, it then relaxes automatically to its linear equilibrium geometry, at which point its energy is quasidegenerate with that of the ground-state molecule. Internal conversion to a linearly ground-state molecule with excess C_1C_2O bending vibrational energy should then be extremely facile. Alternatively one can imagine, especially if steric constraints make the opening of the C_1C_2O angle difficult, that intersystem crossing (from $^1n,\pi^*$ state) or internal conversion (from $^3n,\pi^*$ state) to the symmetric triplet state occurs near the crossing point ($R_{C_1C_2} = 2.05$ Å in Figure 11). Certainly the existence: (1) of a simple pathway, with a single interval conversion in the triplet manifold, from $^3n,\pi^*$ state to diradical product; (2) of an extremely favorable intersystem crossing point (see further, the discussion of Figure 17b) must be relevant to the much faster cleavage observed in triplet states.[50d] Finally there is the possibility of direct cleavage in the $^3\pi,\pi^*$ state, if it can be excited.

The potential energy surfaces in Figure 11 are by no means the first potential surfaces calculated for an α-cleavage reaction.[54] In an extremely thorough pioneering calculation,[54a] Morokuma and his collaborators have studied both the coplanar and noncoplanar cleavage of formaldehyde to $H\dot{C}O + H$. They calculate the dissociation path respectively in the ground, lowest triplet, and singlet excited states, starting with relaxed geometries and optimizing geometries throughout the different pathways. In both excited states they find a preference (lower activation energy) for a strongly *noncoplanar* cleavage. Although it is by no means certain that the excited molecular system necessarily follows a fully optimized pathway (the nuclear motion along the reaction coordinate is as fast as, and can compete with, any other nuclear motion which tends to relax the excited molecule from its Franck–Condon ground state geometry), their results serve to remind

Figure 11. Energy surfaces for α cleavage of acetone: (- - -) triplet energies; (O) unreliable energies.

us that the coplanar motion is only a "model" motion which may not always be preferred in real life.[48]

Another interesting feature of Morokuma's calculation is the form of the lowest triplet surface. Since there is no symmetry element in the noncoplanar cleavage, the $^3n,\pi^*$ (A'') and $^3\sigma,\sigma^*$ (A') states can mix. Hence the lowest triplet state surface is essentially that which would be obtained, in Figure 11, by joining the $^3n,\pi^*$ curve for $R_{C_2C_3} < 2.12$ Å to the $^3\sigma,\sigma^*$ curve for $R_{C_2C_3} > 2.12$ Å. Cleavage in the n,π^* triplet state than leads directly to the σ,σ diradical and becomes a likely mechanism[54a] (see further, the discussion of Figure 19).

Another pioneering calculation is that of Fink,[54b] who studied the cleavage of pyramidal excited formaldehyde. Fink's potential energy surfaces for the lowest excited singlet state and two lowest excited triplet states correspond again to those expected from Figure 11 for a noncoplanar cleavage. Their aspect is therefore very similar to that of the central scheme of Figure 19, which we will discuss later.

α **Cleavage of Enones and Dienones.** If the ketone which undergoes cleavage is conjugated, the corresponding π-radical product is stabilized relative to the σ-radical product. For example, in the α cleavage of an enone such as acrolein the π radical gains the stabilization due to allylic resonance. In $H\dot{C}O$ the σ radical was more stable by 1.1 eV. Hence there can be reasonable doubt as to which of the two "acrolyl-2" radicals

σ Radical   π Radical

lies lower in energy.[55] Almost certainly the two lowest

(53) Several computational difficulties arise in the calculation of these surfaces. They can be ascribed to the change in symmetry of the lowest lying empty orbital of the reactant near $R_{C_2C_3} = 2$ Å (π at shorter distances, σ at larger distances). (a) A more extensive configuration interaction scheme than available is necessary in order to mix the triplet (σ,σ^*) configuration with the triplet (π,π^*) configuration and thus allow the energy surface of the triplet (σ,σ) diradical to correlate properly with the triplet π,π^* state of this reactant. (b) In regions (short distances) where the lowest empty orbital is of π^* nature, the 3 by 3 configuration interaction procedure (mixing of σ^2, $\sigma\pi^*$ and π^{*2}) is less effective at lowering the energy of ground singlet than at larger distances (mixing of σ^2, $\sigma\sigma^*$, σ^{*2}), whence the circles (unreliable points) at $R = 1.92$ and 2.02 Å, corresponding to an overestimated energy for ground singlet.

(54) (a) D. M. Hayes and K. Morokuma, *Chem. Phys. Lett.*, 12, 539 (1972). The experimental work pertaining to a more favorable nonplanar departure of the hydrogen atom is that of J. Solomon, C. Jonah, P. Chandra, and R. Bersohn, *J. Chem. Phys.*, 55, 1908 (1971). (b) W. H. Fink, *J. Amer. Chem. Soc.*, 94, 1073, 1078 (1972). (c) For an early qualitative attempt at interpreting the photochemistry of formaldehyde, see E. W. Abrahamson, J. G. F. Littler, and K.-P. Vo, *J. Chem. Phys.*, 44, 4082 (1966).

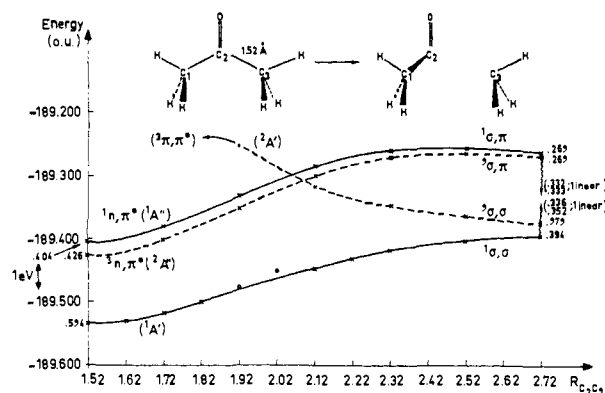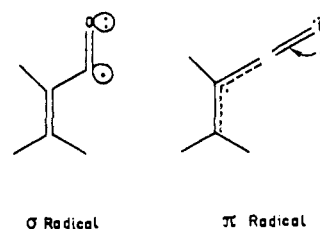(55) A restricted minimal basis set Gaussian calculation on acrolyl gives a σ radical ground state favored by 0.80 eV. (The energy surfaces for cleavage of methyl-2-acrolein have been calculated and resemble those of Figure 11.) On the other hand, an INDO calculation yields a π-radical ground state, favored by 0.87 eV (J. Roncin, private communication to the author, 1973). The truth is probably somewhere in between; it would therefore be extremely useful to carry out an unrestricted Hartree–Fock calculation with an extended basis set on acrolyl. The author is grateful to Dr. J. Roncin and Professor Mrs. R. Marx for many helpful discussions on this problem.
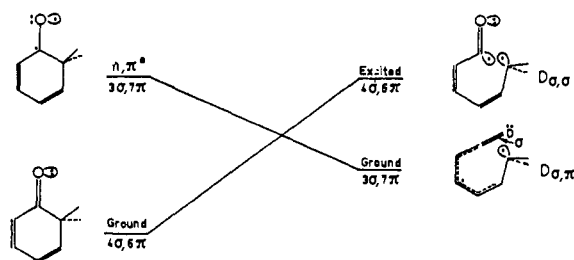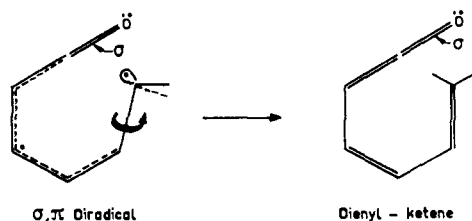
3496

Figure 12. State correlation diagram for α cleavage of cyclohexadienones.

the higher energy σ,σ diradical can conceivably lead to a bicyclic product

O,O Diradical   Bicyclo-[3.1.0]-hexenone

singlet states (and the two lowest triplet states) will "touch" in the region of the primary photoproduct.

If we add an additional double bond to the conjugated system, the π radical is most probably the stable form. The diradical states $D_{\sigma,\pi}$ arising from the cleavage of *hexadienones* should lie slightly below the σ,σ diradical states $D_{\sigma,\sigma}$. The correlation diagram for the ground and n,π* singlet excited states of a cyclohexadienone skeleton is shown in Figure 12. The excited n,π* singlet now correlates with ground diradical product, but its surface remains close to the other singlet surface in the product region since $D_{\sigma,\pi}$ and $D_{\sigma,\sigma}$ are close in energy. Thus, there is a slight crossing at the very end of the reaction path. In a first approximation the surfaces are again in a "touching" situation (rigorously we could include this reaction in the crossing family).

The n,π* *triplet* will parallel the behavior of the n,π* singlet, with a slightly lower energy throughout the reaction path. As to the π,π* triplet, the extensive delocalization in the parent dienone suggests that its starting energy is now *below* that of the (^{1}n,π*, ^{3}n,π*) pair of states.[56] Since it correlates with the triplet *excited* diradical state $D_{\sigma,\sigma}$ its rising surface will cross that of the two descending states corresponding to the ground diradical states $D_{\sigma,\pi}$ (see further the section on general reaction types).

The ultimate fate of the two primary diradical products should be different. The σ,π diradical, corresponding to the more stable hexadienon-2-yl π radical, can lead to a dienylketene[57] by simple rotation of the terminal methylene radical center. On the other hand

O,π Diradical   Dienyl — ketene

The σ,σ diradical in its singlet state correlates with the ground state of the starting material. But in its triplet state it also correlates with triplet π,π* state, so this mechanism does not disagree with the suggestion[59] by Hart that photochemical isomerization of cyclohexadienones to bicyclo[3.1.0]hexenones originates from the π,π* photoreactive state. Here, therefore, we appear to have a one-to-one correspondence between resonance structures, electronic states, and primary product.

Fragmentation of Aromatic Ethers. Isomerization of Furans to Cyclopropenyl Ketones.[60–62] The parent reaction in this series is the mercury ($^3P_1$)-sensitized isomerization of 2-cyclopropenecarboxaldehyde,[60a] followed by decarbonylation. It is reasonable to assume
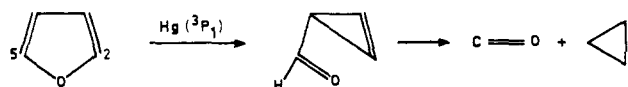
that the primary photochemical reaction step is cleavage of a carbon–oxygen bond to form a 1,5 diradical. In some beautiful semiempirical plus CI calculations on this reaction, Poquet and Chaillet have obtained strong evidence[61] that the cleavage occurs in the lowest triplet π,σ* state of furan. The σ* orbital is localized in the C-O-C fragment, excitation to which should naturally favor the observed bond cleavage.[63]

As in the previous systems two different diradicals, with σ,π or σ,σ symmetry, can be generated by the

(56) There is ample evidence (ref 57, Figures 1–4) that the π,π* singlet lies no more than 1 eV above the (n,π*) states. The energy difference between singlet and triplet π,π* states in acrolein[58] is calculated to be +2 eV; unless this difference is reduced drastically in the higher conjugated homolog our suggestion seems well founded.

(57) (a) G. Quinkert, *Pure Appl. Chem.*, **33**, 285 (1973). Professor Quinkert's beautifully clear description of the electronic mechanism of photoisomerization of cyclohexadienones was instrumental in leading us to the notion of surface crossings between singlet states. (b) The first direct observation of a ketene intermediate in the α cleavage of a dienone is due to O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).

(58) M. Jüngen and H. Labhart, *Theor. Chim. Acta*, **9**, 345 (1968).

(59) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 5296 (1968). Bicyclo[3.1.0]hexenone may also arise from the ketene: J. Griffiths and H. Hart, *ibid.*, **90**, 3297 (1968).

(60) (a) R. Srinivasan, *Pure Appl. Chem.*, **16**, 65 (1968); (b) E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968); **93**, 6129 (1971).

(61) The author is extremely grateful to Drs. E. Poquet and M. Chaillet for calling his attention to this reaction. Detailed calculations on this reaction, as well as a thorough study of its mechanism, have been carried out by these authors and will be published elsewhere.

(62) For related reactions, see (a) (fragmentation of thiophenes) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, **89**, 3501 (1967); (b) (photoisomerization of isoxazoles) E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966); J. P. Ferris, F. A. Antonucci, and R. W. Trimmer, *ibid.*, **95**, 919 (1973); and references therein; (c) (photochemistry of the corresponding dehydroaromatics) T. Matsuura and Y. Ito, *Tetrahedron Lett.*, 2283 (1973), and references therein. (d) Excited pyrroles do not give fragmentation products (for a review, see A. Lablache-Combier and M. A. Rémy, *Bull. Soc. Chim. Fr.*, 679 (1971); this could be due to the higher energy of the appropriate CNC σ* orbital (or, in the alternative interpretation of an n,π* photoreactive state,[62] to the absence of such a state in pyrrole).

(63) An alternative possibility is that the cleavage occurs in the triplet n,π* state. The concomitant enrichment of electrons in the π system at C_2 in the n,π* transition of furan could force, by electron repulsion between π and σ electrons at C_2, the cleavage of the C_2O bond just as α cleavage in alkanones is brought about by π enrichment at the carbonyl carbon atom. In this respect the π_2,π_4 state could also be the photoreactive state.
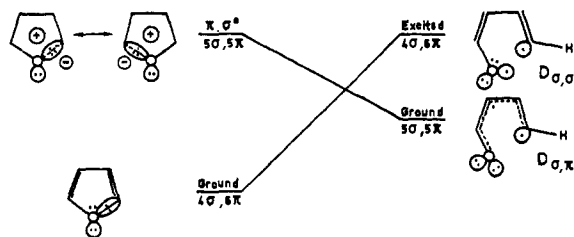
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Figure 13. State correlation diagram for fragmentation of furans.
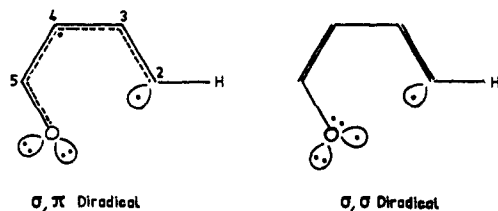
Figure 14. State correlation diagram of ring opening of azirines.

cleavage

σ,π Diradical   σ,σ Diradical

The σ,π diradical, which is strongly stabilized by pentadienylic-type resonance, is a likely precursor for C_2C_4 closure to cyclopropene-2-carboxaldehyde. We can now draw the state correlation diagram (Figure 13) on the basis of the Poquet–Chaillet mechanism.

In the usual manner the electron count includes the two oxygen n electrons, the two σ electrons originally in the OC_2 bond and the six π electrons of furan ring. Then furan has 4σ,6π electrons, while π,σ* excited furan has 5σ,5π electrons. And, whereas the σ,σ diradical has also 4σ,6π electrons and correlates with ground reactant, the σ,π diradical has 5σ,5π electrons, and correlates with excited reactant.

The correlation diagram demonstrates a touching of ground singlet and π,σ* excited singlet (or triplet) states, with probably a slight surface crossing in the final phases of the cleavage. The triplet π,σ* surface will behave identically with the singlet π,σ* surface. Finally the lowest triplet π,π* state also correlates with the excited σ,σ diradical (in its triplet state).

Ring Opening of Azirines.[64] Substituted azirines undergo ready photochemical cycloaddition with olefins, aldehydes, ketones, etc., to yield five-membered rings of the pyrroline (X = CR_1R_2) or 3-oxazoline (X = O) type. Intermediates which have been proposed for
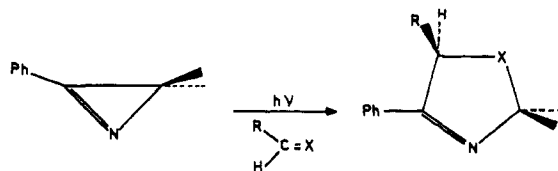
this cycloaddition derive from cleavage of the starting material and are all of zwitterionic 1,3 dipolar type.[64a,b]

This reaction is very similar, formally at least, to the three previous reactions studied in this section: n,π* excitation[64b] leads to cleavage of a carbon–carbon bond

α to the locus of excitation (nitrogen atom).[65] Three radical centers are thereby created (a π bond with two orbitals and the two σ atomic orbitals in the ruptured bond). One therefore expects the primary, ring-opened, photoproduct to be one of two low-lying radicals of different symmetry (where we have pointed

σ,σ Diradical   σ,π Diradical
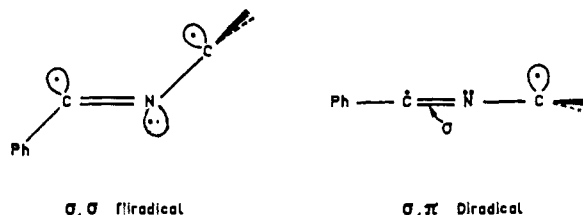
out the "ketiminoid" in-plane nature of the double bond in the σ,π diradical). These neutral resonance structures for the ring-opened azirine are as appropriate as the ionic structures I and II. Therefore we appear to have a situation with a large number of states. However, the reader will remember that when allowed by symmetry, as in a σ,σ type radical with two orbital centers of same symmetry, a molecule with a broken bond can have both covalent and ionic character.[14] In other words it can be *partly diradical, partly zwitterionic.* This is particularly true if substitution on the two termini is highly unsymmetrical, as in phenylazirines. Therefore here the σ,σ diradical structure and the benzonitrile methylene ylide zwitterionic structure I are simply two resonance structures corresponding to the *same singlet state* of the molecule. Similarly, structure II is another ionic resonance structure, for the linear geometry of the σ,σ diradical, contributing again to the same singlet state. Of course, there is also a triplet state corresponding to the σ,σ diradical structure. The correlation diagram for ground and n,π* excited states will therefore resemble that of Figure 10[66] with the admixture of additional ionic resonance structures (Figure 14). *Ab initio* computations of the ground and three lowest excited-energy surfaces for 2H-azirine it-

(64) (a) A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, *Pure Appl. Chem.*, 33, 269 (1973); J. *Amer. Chem. Soc.*, 95, 1945, 1954 (1973); (b) P. Claus, Th. Doppler, N. Gakis, M. Georgarakis, H. Giezendanner, P. Gilgen, H. Heingartner, B. Jackson, M. Märky, N. S. Narasimhan, H. J. Rosenkranz, A. Wunderli, H.-J. Hansen, and H. Schmid, *Pure Appl. Chem.*, 33, 339 (1973), and references therein; (c) B. Singh, A. Zweig, and J. B. Gallivan, J. *Amer. Chem. Soc.*, 94, 1199 (1972); (d) W. Seiber, P. Gilgen, S. Chaloupka, H. J. Jansen, and H. Schmid, *Helv. Chim. Acta*, 56, 1679 (1973).

(65) Our calculations show that the nitrogen n orbital has a large admixture of $\sigma_{C_2C_3}$ character (as would be expected for nitrogen substitution of the appropriate cyclopropane Walsh orbital). So the *photoreactive state has partial* σ_{CC,π^*} *character,* which explains the facile cleavage of the C_2C_3 bond.

(66) (a) The σ imine radical moiety should be more stable than the π imine radical moiety (by analogy with formyl); thus the σ,σ diradical is expected to be the more stable diradical. (b) The electron count involves, in the usual manner, the C=N π electrons (2), the CC σ electrons (2), and the nitrogen n electrons (2).
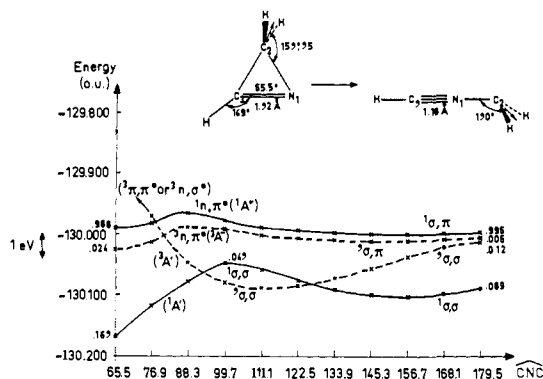
Figure 15. Energy surfaces for ring opening of 2H-azirine: (- - -) triplet energies; (O) unreliable energies.

self confirm this diagram. If one opens the ring progressively to a bent geometry, a structure with slightly ionic character is found. Net charges of $+0.16$ on the methylene carbon and -0.16 on the iminoid carbon are obtained, indicating *a diradical state with slight 1,3 dipolar character*. One can also open the ring progressively to the linear geometry depicted in II. The energies of the ground, n,π^* singlet, and triplet states in this case are depicted in Figure 15. Also illustrated is the second triplet state (originally π,π^* or n,σ^* whichever configuration lies lowest)[67] which ultimately correlates with triplet σ,σ diradical state.

The interesting features of Figure 15 are the following.

(1) A relatively close approach of ground singlet to the n,π^* pair of states for a $\angle$CNC angle of $\sim 100°$. One can still speak in loose terms of a "touching" although the energy separation is now 1.5 eV.

(2) A rapid descent of the symmetric triplet, which probably[53a] originates in the π,π^* state, *below* the ground state in the 100–120° angle region. For such geometries the ground state is essentially *diradical* like. A significant amount of ionic character in the wave function would not allow the triplet (σ,σ) diradical to lie, as it does, well (20 kcal/mol) below the singlet (σ,σ) diradical.

(3) As the $\angle$CNC angle opens up even further, toward the linear geometry, an increase in the energy of this same triplet, and a stabilization of the ground singlet state. The latter has now acquired closed-shell zwitterionic character. The calculated net charges (C_3, 0.37, N_1, 0.11, C_2, -0.46) are in good agreement with the dipolar resonance structure II (although the positive charge is concentrated on carbon rather than on nitrogen).

(4) The large barrier between azirine and linear dipole in ground singlet but small barrier in excited singlet are in excellent agreement with the recently demonstrated *photochemically, but not thermally reversible* trans-

formation of 2,2,3-triphenyl-2H-azirine to the benzonitrile diphenylmethylide dipole.[64d]

Altogether our calculations indicate that the ring-opened azirine should be capable of dual reactivity, depending on its geometry when it is intercepted by a second molecule: diradical like (bent) or 1,3 dipolar like (linear). They also indicate that reactive dipolar intermediates such as II are best reached by internal conversion (from ^{1}n,π^* state) or intersystem crossing (from ^{3}n,π^* state) at a $\angle$CNC angle of 100°.

State Correlation Diagrams for the Two General Reaction Types

Our investigation of eight different photochemical reaction types has revealed two families of coplanar reactions. One family has an intersection between a surface leading to a zwitterion and a surface leading to a diradical. The second family has an approximate touching between two surfaces each of which leads to a distinct diradical. A careful look at the *geometry* of the reacting system also shows a major difference between these two families.

σ,π **Bitopic Reactions.** In the hydrogen abstraction, aza aromatic photoreduction, and ketone-to-olefin additions, *i.e.*, the reactions characterized by a crossing of singlet surfaces, two radical centers are created. We call these reactions *bitopic* reactions. For instance, in the hydrogen abstraction by ketones, a σ-radical center is created on the carbon atom from which the hydrogen atom is abstracted, while a π-radical center is created in the π-electron system of the carbonyl bond. This second radical center is essentially localized on the carbon atom adjacent to oxygen, but it partially reaches oxygen. In the hydrogen abstraction by carbenes, a
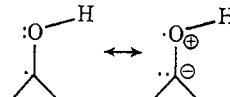
σ-radical center is again created on an alkane carbon atom while a π center is created on the abstracting carbon atom which becomes a methyl radical center.

In all cases, therefore, two radical centers, one of σ symmetry and one of π symmetry, are created. The bitopic reactions studied here can therefore be specifically labeled σ,π-bitopic reactions.[68] Their major characteristic is as follows. Let the radical centers be labeled respectively A and B. There is competition in the product between a diradical state D (σ_A, π_B) and two zwitterionic states,[14] $Z_1(\sigma_A{}^2)$ and $Z_2(\pi_B{}^2)$. If we use the group-theoretical notation of the C_s point group, the diradical has A$''$ symmetry and the zwitterions A$'$ symmetry. In the now-familiar case where the diradical state lies well below the lowest zwitterionic state Z_1, there is an intersection between ground symmetric (A$'$) singlet and excited antisymmetric (A$''$) singlet or triplet. The general state correlation diagrams for σ,π bitopic reactions are shown in Figure 16. The left-hand diagram is restricted to the two lowest singlets.

(67) Here, as in the α cleavage of saturated ketones, the *orbitally* allowed correlation is between ^{3}n,σ^* state and triplet σ,σ diradical state. Hence, if the $^3\pi,\pi^*$ state is the lowest symmetric triplet of reactant (as in formaldehyde[52]) its proper (*state* allowed) correlation with triplet σ,σ diradical, which arises *via* the exchange mixing of $^3\pi,\pi^*$ and ^{3}n,σ^* configurations, may involve an *energy barrier* corresponding to an avoided crossing. In both cases the size of the triplet–triplet mixing is proportional to $K_{\pi n,\pi^* \sigma^*} - K_{\pi \sigma^*, \pi^* n}$. If this term is large (the one-center densities πn and π^*n on O, $\pi^* \sigma^*$ and $\pi \sigma^*$ on C_2, Figure 11, give two-center Coulomb integrals which *reinforce* each other) the barrier may be small. The author is grateful to Professor J. Michl for drawing his attention to this problem.

(68) The photodissociation of a hydrogen molecule in its $^1\Sigma_u{}^-$ state or the quasicoplanar photodissociation of the ($\sigma_{CC},\sigma_{CC}{}^*$) state of ethane to two methyl radicals, would be σ,σ bitopic reactions. Two-step pericyclic reactions are also formally bitopic reactions. In particular, the two-step coplanar decomposition of cyclobutane to two ethylene molecules is a σ,σ bitopic reaction (relative to the molecular plane). The author is grateful to Dr. Alain Devaquet for a discussion of this problem.
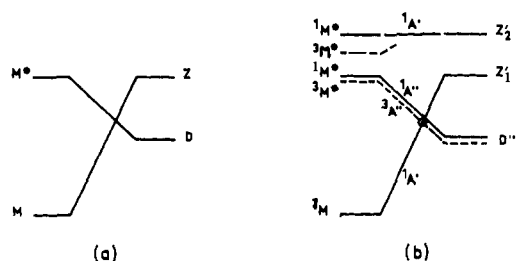
Figure 16. General state correlation diagrams for σ,π bitopic reactions: (a) simplified; (b) complete; (O) intersection with favorable intersystem crossing.

Figure 17. General state correlation diagrams for $\sigma(\sigma,\pi)$ tritopic reactions when D' below D'': (a) simplified; (b) complete (ref 72) (higher states include a second D''-type diradical state and two other Z'-type zwitterionic states); (O) intersection with favorable intersystem crossing.

The right-hand diagram includes both triplet states and is more specific in its labeling (D'', antisymmetric; Z_1' and Z_2' symmetric). Both diagrams assume the lowest pair of excited states to have A'' character, as do n,π^* states. Correspondingly the second excited singlet state will probably have A' character, as would a π,π^* state. It correlates with the second zwitterionic state Z_2'. The $^3\pi,\pi^*$ state correlates with some high-energy symmetric diradical state not represented in the figure.

Several brief remarks concerning Figure 16b are appropriate. In the particular case of the carbene abstraction reaction, the diagram would have to be modified to account for the fact that the ground state of reactants is the $^3M^*$ state. The circle surrounding the intersection of the $^3A''$ state and the ground $^1A'$ state indicates a triplet–singlet intersection where intersystem crossing should be relatively good. It is well known[14b] that the largest spin–orbit coupling matrix elements occur when the odd electron must switch from a σ-type orbital to a π-type orbital on the reverse, as is the case here.

Figure 16b shows that σ,π-bitopic reactions should occur easily in the singlet n,π^* state. In the triplet n,π^* state the energetic features are equally favorable.[69] However, a subsidiary requirement is facile intersystem crossing from triplet diradical primary product to final singlet product. In both n,π^* states the intersection with ground singlet surface, with facile internal conversion, or facile intersystem crossing (Figure 16b, circle) is a leakage point back to ground state reactant. The theory agrees well with experimental results for Norrish type II photoprocesses.[25]

Finally these diagrams give some insight as to solvent influence or photoprocesses. For instance, in a highly polar solvent, singlet Z is expected to fall below singlet D, at least to the extent that the nuclear coordinate for solvent rearrangement is able to follow the nuclear coordinate for the photochemical reaction.[70] There is no surface crossing any more. The reacting system may then find that the best manner to come within "radiationless-transition distance" of the ground surface is via the triplet state.[71] This might account for the

strong influence of polar solvents on the multiplicity of the photoreactive state in the hydrogen abstraction by ketones.[22a]

$\sigma(\sigma,\pi)$ Tritopic Reactions. In the α cleavage of ketones, whether saturated or unsaturated, and in the ring opening of furans and azirines, the electronic excitation and concomitant changes in geometry create three radical centers. We call these reactions tritopic reactions. The reader will easily verify that two of the radical centers (those resulting from cleavage of an in-plane single bond) have σ character, while the third center is delocalized in the π system. These reactions, which were all characterized by surface touchings, are specifically $\sigma(\sigma,\pi)$ tritopic reactions. The label $\sigma(\sigma,\pi)$ indicates that bond rupture has yielded a σ radical center on one fragment and an alternative σ,π pair of centers on the other fragment. Since each of the three centers can formally carry 0, 1, or 2 electrons, the manifold of electronic states of photoproduct is more varied than in bitopic reactions. First of all, there are formally three diradical states (or more properly pairs of states), depending on which pair of orbitals is occupied. If the σ radical centers are labeled A and B, and the π center is labeled BCD, these states correspond respectively to the configurations $\sigma_A\sigma_B$, $\sigma_A\pi_{BCD}$, and $\sigma_A\pi_{BCD}$. One of these states $(\sigma_B\pi_{BCD})$, where σ and π electrons are partially localized on the same atom B, has a very high energy. It corresponds to heterolytic cleavage of bond AB, and has mixed covalent and ionic character according to the scheme
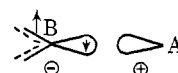
The two remaining low-lying diradical states have respectively A'' symmetry (σ,π diradical $D_{\sigma\pi} = D''$) and A' symmetry (σ,σ diradical $D_{\sigma,\sigma} = D'$). These diradical states will generally provide the two lowest (singlet, triplet) pairs of states of photoproduct, with D' and D'' competing for ground (singlet, triplet) pair of states. Accompanying these two diradical states are three zwitterionic singlet states, all of symmetry $^1A'$, corresponding to simultaneous occupation of one of the three radical loci by two electrons. One of these states should not be too far above D' and D'', due to favorable configuration interaction mixing between σ_A^2, σ_B^2 and π^2. The correlation diagrams for the various states in a $\sigma(\sigma,\pi)$ tritopic reaction are shown in Figure 17

(69) In cases where reaction can be obtained by excitation to a lowest lying $^3\pi,\pi^*$ state (C. D. De Boer, W. G. Herkstroeter, A. P. Marchetti, A. G. Schultz, and R. H. Schlessinger, J. Amer. Chem. Soc., 95, 3963 (1973)), it most probably occurs via internal inversion, from rising $^3\pi,\pi^*$ surface to descending $^3n,\pi^*$ surface, in the triplet manifold.

(70) The extent to which solvent nuclear motion can rapidly adjust to reactant nuclear motion is unknown; see H. O. Kalinowski and H. Kessler, Top. Stereochem., 7, 295 (1972) for a case where solvent influence is surprisingly small on thermal activation energies to polar transition states. The author is grateful to Professor J. Durup for a stimulating discussion of this point.
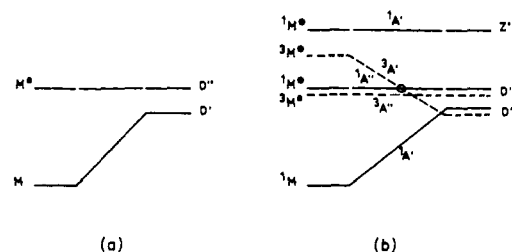
(71) The relative energy of triplet and singlet diradical states in molecules with zwitterionic ground states is not well known. The separation is essentially given by twice the exchange integral between the odd orbitals; for certain 1,4 diradicals the triplet might lie from 5 to 10 kcal/mol below the singlet.
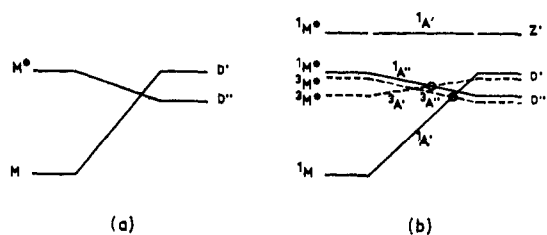
Figure 18. General state correlation diagrams for $\sigma(\sigma,\pi)$ tritopic reactions when D'' below D': (a) simplified; (b) complete (ref 72) (higher states include a second D''-type diradical state and two other Z'-type zwitterionic states); (O) intersections with favorable intersystem crossing.

Figure 19. General state correlation diagrams for noncoplanar bitopic (formerly σ,π) and tritopic (formerly $\sigma(\sigma,\pi)$) reactions.

(D' more stable than D'')[72] and Figure 18 (D'' more stable than D').[72]

Special mention should be made of the behavior of the two lowest triplet states in the right-hand side diagrams of Figures 17 and 18. In Figure 17, where the symmetric diradical D' is more stable than its antisymmetric counterpart D'', as in the α cleavage of saturated ketones,[52] we have placed the lowest triplet state ^{3}M* of reactant just below the lowest singlet, as for a pair of n,π* states. The second triplet is then a relatively high-lying π,π* triplet state, of A' symmetry. It correlates therefore with ground diradical triplet state, and in so doing crosses the (^{1}A'', ^{3}A'') pair of states, with a favorable intersystem crossing point at the intersection with ^{1}A''. The diagram reveals a crossing of triplet surfaces and a favorable point for the decay from excited singlet to a triplet leading to diradical product. This favorable region may account for the 1–4 $\times$ 10^8 sec^{-1} intersystem crossing rate from the excited singlets of cyclic ketones, as found by Lee and collaborators.[73]

A direct reaction pathway to ground diradical product D' from triplet π,π* state is thus revealed. Another simple pathway within the triplet manifold, with only one internal conversion point, would start in the triplet n,π* state. The excited diradical D'' is probably best obtained directly from lowest (n,π*) singlet excited state.

The presence (Figure 18) of an antisymmetric (σ,π) diradical D'' ground state, as in hexadienones, indicates a relatively stable π site for the odd electrons, as would arise from a highly conjugated system. The lowest triplet is then generally the π,π* triplet of A' symmetry.[56] It now correlates with the *higher* diradical triplet state. In so doing it again crosses (but in the opposite sense!) the (^{1}A'', ^{3}A'') pair of states. The scheme now shows *two* favorable intersystem crossing points; one at the (^{3}A', ^{1}A'') intersection and one at the intersection of ^{3}A'' with ground singlet ^{1}A'. However, in both of these regions, intersystem crossing from higher state to lower state tends to bring the system back to reactant geometry.

Altogether the ground diradical D'' seems best attained directly *via* the lowest singlet state, or alternatively in the triplet manifold, from ^{3}n,π* state directly or from $^3\pi,\pi$* state with a single internal conversion. Excited diradical product D' by necessity requires a triplet pathway.
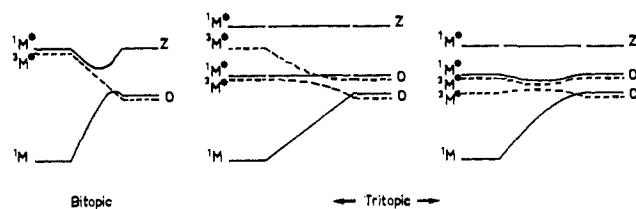
Nature of the Diradical State and Multiplicity of the Photoreactive State Predictions.

From the correlations of Figures 16–18 and from the previous discussion of this section, we can suggest a general conclusion. *In coplanar σ,π bitopic or $\sigma(\sigma,\pi)$ tritopic reactions antisymmetric diradicals originate preferentially in singlet or triplet n,π* states, while symmetric diradicals originate preferentially in triplet π,π* states.* By preferential pathway we mean that which involves the least number (here, zero) of radiationless transitions regardless of the relative excitation energies of the competing states. In certain cases (Figure 17b) the system may prefer a lower energy pathway with a greater number of radiationless transitions (one, from ^{1}n,π* or ^{3}n,π* to reach the symmetric diradical D', as is probably the case in azirines). However, a high vertical excitation energy does *not* preclude the involvement of an electronic state in a photochemical reaction. For instance, in the α cleavage of alkanones, a triplet sensitizer with an energy *below* the $^3\pi,\pi$* excitation energy could still specifically sensitize the $^3\pi,\pi$* state, and possibly make the reaction more efficient than with ^{3}n,π* sensitization, if it were to donate its energy to the ^{3}A' state at the point along the reaction coordinate just *above* its crossing point with the ^{1,3}A'' states (Figures 11 and 17b). This would be analogous to the Hammond–Saltiel "nonvertical" energy transfer.[74]

In noncoplanar situations where the singlet–singlet crossings and triplet–triplet crossings are strongly avoided, Figure 19 shows that the correlations are different. The lowest (formerly n,π*) singlet excited state cannot reach ground diradical product any more. Only the lowest triplet state, whatever its parent symmetry, can do so. Thus, *in strongly noncoplanar photochemical reactions of the previous type, the ground diradical product originates preferentially in the lowest triplet state, whatever the local symmetry of this excited state.* The second triplet state and the first excited singlet state of reactant correlate consistently with excited product.[54a,b]

If these predictions are correct, the ratio of quantum yields in triplet state and in singlet state for a series of Norrish type II hydrogen abstraction reactions should increase progressively if the most likely pathway is constructed to be progressively less coplanar. Confidence in such predictions must be tempered by the uncertainties on which they are based, concerning in particular internal-conversion and intersystem-crossing probabilities. The peculiarities of each reaction surface must also be taken into consideration.

(72) It should be noted that in the case of the σ,σ diradical D' admixture of ionic character in the singlet wave function is allowed, leading to partial zwitterionic character (cf. ring opening of azirines).

(73) R. G. Shortridge, C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1863 (1971).

(74) G. S. Hammond and J. Saltiel, *J. Amer. Chem. Soc.*, **85**, 2516 (1963); J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973); in part, pp 14 sqq.

State Crossings vs. Orbital Crossings. This paper has dealt with states and has purposely avoided reference to approximate wave functions such as molecular orbitals. The reader may wonder whether the *state crossing* observed in bitopic reactions is accompanied by an *orbital crossing*. The answer is negative. In reactant the n orbital lies well below the π orbital (ground configuration n^2, excited configuration $n\pi^*$). In product the top σ (originally n) orbital is still slightly beneath the π orbital (ground configuration $\sigma\pi$; lowest excited configuration σ^2; Figures 1, 3, and 6). The
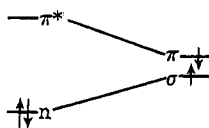
orbital model is still, however, extremely useful in interpreting the mechanism of certain reactions.[75] Thus in the Norrish type II reaction, the removal of the fourth σ electron into the π "sink" allows hydrogen abstraction to proceed with low energy *via* a three-center three-electron transition state.

Conclusion

In this article we have gathered a number of major photochemical reactions into two families: σ,π bitopic reactions and $\sigma(\sigma,\pi)$ tritopic reactions. This was made possible by consideration of the "tetralogy" (two D, two Z) of states which accompanies a diradical situation.[14] Many other fundamental photochemical reactions have not been considered: Woodward–Hoffmann allowed pericyclic reactions,[13,76] cis–trans photoisomer-

izations,[77] electron-transfer reactions,[78] valence isomerizations,[79] photosubstitution reactions of coordination compounds,[80] heterolytic photosubstitution reactions,[81] etc. Furthermore, reactions belonging to related bitopic[68] or tritopic families will most certainly be found, although none have been considered here.

Our hope is to ultimately classify all these reactions together in a coherent manner, based on the behavior of ground and excited electronic surfaces. Such a classification, together with a study of the factors which guide photochemical reactions, is in preparation.[82]

(75) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 7239 (1968). Columns IV and V, Table III of this paper also show that the orbital energies ϵ_n and ϵ_π do not cross.

(76) For a recent theoretical treatment of photochemical pericyclic reactions, see (a) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969); (b) J. Langlet and J. P. Malrieu, *ibid.*, **94**, 7254 (1972); (c) J. Michl, *Mol. Photochem.*, **4**, 257 (1972); (d) N. D. Epiotis, "Configuration Interaction Theory of Pericyclic Reactions," submitted for publication to *J. Amer. Chem. Soc.*

(77) (a) G. N. Lewis, T. T. Magal, and D. Lipkin, *J. Amer. Chem. Soc.*, **62**, 2973 (1940); (b) G. S. Hammond and J. Saltiel, *ibid.*, **84**, 4383 (1962); (c) G. S. Hammond in "Reactivity of the Photoexcited Molecule," Interscience, New York, N. Y., 1967, p 119.

(78) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

(79) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **86**, 2307 (1964). (b) A. W. Burgstahler and P. L. Chien, *ibid.*, **86**, 2940 (1964). (c) For a review, see N. Ivanoff and F. Lahmani in "Eléments de Photochimie Avancée," P. Courtot, Ed., Herman Publishers, Paris, 1972, p 131.

(80) For a review, see V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

(81) E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968); G. P. de Gunst and E. Havinga, *Tetrahedron*, **29**, 2167 (1973).

(82) Unpublished work in collaboration with W. G. Dauben and N. J. Turro.