

Theoretical Investigation of the Photochemical Unimolecular Reactions of Cyclopropene

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Ab initio SCF calculations (STO-3G) followed by a limited CI (involving a selection of the first hundred low-lying excited states of the molecule) have been carried out in order to assist the construction of MO and state correlation diagrams relative to the various reactions of cyclopropene. The idealized reaction paths exhibit the following trends. The thermal cleavage easily yields a quite stable carbenic species. In the excited state, a dichotomy is observed: (a) the singlet is likely to yield a carbene via ring cleavage; (b) the triplet, which remains unreactive would preferentially react through bimolecular processes or via hydrogen capture on the side chain. Qualitative considerations show that when both the double bond and side chain are substituted by stabilizing groups, for example, allylic groups, side-chain cleavage is observed as a competitive process.

Owing to its 54.5-kcal/mol intrinsic strain,² cyclopropene is predicted to be relatively unstable thermally. Upon excitation, the presence of a double bond provides a low-energy source of excited states able a priori to initiate the evolution toward ring opening and/or fragmentation via Norrish type I reactions. The frozen rotation of the double bond is also of interest, since it is well-known that in parent noncyclic alkenes, cis-trans isomerization constitutes the major deactivation process, preventing the system from other types of reactions.

Experimentally, the thermal reaction of cyclopropenes consists of dominant ring cleavage³ leading to a carbenic species. Thermolysis of an optically active compound⁴ shows that the racemization, whose E_a is 32.6 kcal/mol, occurs at a rate faster than the rate of conversion into a mixture of dienes and acetylenes. In other words, only a weak energy maximum, or none at all, should exist at the ground-state (GS) potential energy surface (PES) for ring opening and reclosure since carbenic rearrangements are known to proceed very easily. This very easy thermal closure of the carbenic moiety is exploited in the synthesis of cyclopropenes via the formation of carbenic species.⁵

The photochemical reactions of cyclopropenes have been recently reviewed by Padwa.⁶ Let us briefly summarize the main results. In the singlet state, ring cleavage is dominant, leading to a carbene, which, in turn, leads to a facile recyclization (racemization) or to further reactions such as insertion into a CH bond or alkyl group migration. Usually low quantum yields of transformed products are observed due to the easy reclosure of the system regenerating the starting molecule. In reality, the quantum yield of ring cleavage might be important. In the presence of phenyl substituents on the double bond and of an allylic chain borne by the saturated carbon, side-chain cleavage is also observed. This reaction is no longer found when an alkyl substituent replaces the allylic chain. Triplet cyclopropenes do not undergo ring cleavage, and sensitized

Table I. Vertical Transitions of Cyclopropene (C_{2v})

state	MO's ^b	E , eV	state	MO's ^b	E , eV
³ B ₂ ^a	³ ΠΠ*	5.42 ^c	³ A ₂	³ W _S Π*	10.30
³ B ₁	³ W _A Π*	9.45	¹ A ₂	¹ W _S Π*	10.91
¹ B ₁	¹ W _S Π*	9.75	¹ B ₂	¹ ΠΠ*	11.22

^a z axis is the C_2 axis, x is perpendicular to the plane, and y lies in the plane of the heavy atoms. ^b The MO's correspond to the nomenclature of the left side of Figure 4. ^c An E value of 5.19 eV was also obtained from Goddard et al.¹²

irradiations lead to the formation of dimers via a classical (2 + 2) addition. In some cases, intramolecular capture of hydrogen on the γ -position occurs, as reported by Padwa et al.⁶

Several calculations have been reported for cyclopropene at the semiempirical⁷⁻¹⁰ or at the ab initio level.^{11,12} An overall energy barrier of 42.6 kcal/mol has been calculated for the thermal ring opening. The final singlet species lies 36.6 kcal/mol above the initial ground state (GS). A stable triplet carbene is found 12 kcal/mol below this state and is predicted to be a somewhat long-living intermediate.¹² No rationalization of the photochemical reactivity is available, and we present here a complete theoretical analysis of the behavior of the low-lying singlet and triplet states when various reactions are simulated. The reaction paths are described in Figure 1.

Path a describes the rupture of a CH bond of the methylene unit. Path b is similar to a Norrish type I cleavage of the cycle preserving the initial bonding framework, leading to 3. Path c consists of a synchronous bond rupture and methylene rotation, leading to the carbene 4. (Compound 3 may interconvert into 4 by methylene rotation.) Finally, we have paths d and e which are limiting processes for methylene extrusion via, respectively, a synchronous two-bound process and a stepwise mechanism involving the intermediate formation of 3.

Methodology

The ab initio SCF-CI method used here has been previously described.¹³⁻¹⁵ It consists of a STO-3G calcula-

(1) This laboratory is part of the ERA No. 549 of CNRS.
 (2) P. v. R. Schleyer, J. E. Williams, Jr., and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970). Recent theoretical results have been published during the course of this study: J. D. Dill, A. Greenberg, and J. F. Liebman, *J. Am. Chem. Soc.* **101**, 6814 (1979); M. S. Gordon *ibid.*, **102**, 7419 (1980).
 (3) R. D. Streeper and P. D. Gardner, *Tetrahedron Lett.*, 767 (1973). See also: R. D. Streeper, *Diss. Abstr. Int. B.* **33**(2), 647 (1972); R. Srinivasan, *J. Chem. Soc. D*, 1041 (1971); *J. Am. Chem. Soc.*, **91**, 6250 (1969).
 (4) J. E. York, W. Dittmar, R. J. Stevenson, and R. G. Bergman, *J. Am. Chem. Soc.*, **95**, 5680 (1973); **94**, 2882 (1972).
 (5) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).
 (6) A. Padwa, *Acc. Chem. Res.*, **12**, 310 (1979). During the typing of this manuscript an important publication by A. Padwa, T. J. Blacklock, D. M. Cordova, and R. Loza, *J. Am. Chem. Soc.*, **102**, 5648 (1980), had appeared. Experimental findings and a mechanistic proposal in close agreement with those of our study may be found there.

(7) J. A. Pincock and R. J. Boyd, *Can. J. Chem.*, **55**, 2482 (1977).
 (8) J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 7536 (1973).
 (9) J. Pancir and R. Zahradnik, *Tetrahedron*, **32**, 2257 (1976).
 (10) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1298 (1975).
 (11) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **14**, 305 (1969).
 (12) J. H. Davis, W. A. Goddard III, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 2427 (1972); **98**, 4015 (1976); T. K. Ha, F. Graf, and H. H. Guenthard, *J. Mol. Struct.*, **15**, 335 (1973).
 (13) A. Devaquet, A. Sevin, and B. Bigot, *J. Am. Chem. Soc.*, **100**, 2009 (1978).

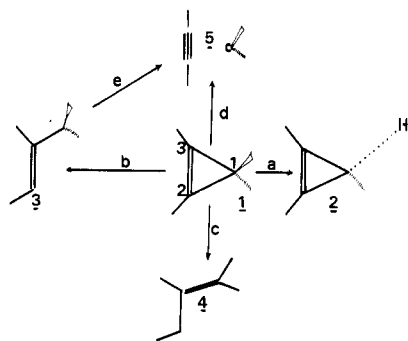


Figure 1. Description of the various calculated paths.

tion^{16a} followed by a CI involving a careful selection of the first hundred mono- and diexcited configurations built on the six highest occupied and the four lowest unoccupied MO's.^{16b}

We have taken for cyclopropene the geometry that has been previously optimized by using the ab initio STO-3G-SCF method.¹⁷ The resulting structure is in good agreement with experimental determinations.¹⁸ In all calculations, the CH bond lengths have been kept constant and equal to their initial value. The CC bond lengths have been optimized for structures 2–4 for the lowest singlet root of the CI. Then, a linear variation of all the geometrical parameters that are involved in a given process is assumed between the initial molecule and the final target. We thus obtain model processes allowing a simple description of reactivity based on the familiar concepts of MO's and corresponding valence states. Owing to the use of a minimal basis and to a limited CI step, we can only predict semiquantitative PES's. However, relative comparisons of the various processes remain of chemical significance and afford a simple basis for a complete discussion or, eventually, for more sophisticated calculations, if very precise data are required.

No experimental result is available dealing with the vertical transitions of cyclopropene itself. Our calculated values are reported in Table I.

It is important to note that, with the exception of the $\pi\pi^*$ singlet–triplet couple,¹⁹ the other valence states appear in pairs close in energy: $^1W_a\pi^*$ and $^1W_s\pi^*$. They correspond to the excitation of one electron from the anti-symmetric and symmetric Walsh MO's of cyclopropene to π^* (see Figure 4, left). The values that are found are expected to be overestimated since important bond relaxation might be predicted to stabilize these states.

(14) A. Sevin, B. Bigot, and A. Devaquet, *Tetrahedron*, **34**, 3275 (1978).

(15) B. Bigot, A. Devaquet, and A. Sevin, *J. Org. Chem.*, **45**, 97 (1980), and references therein.

(16) (a) Using the Gauss 70 series of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana. The closed-shell hamiltonian [C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1960)] and the "restricted Nesbet" open-shell hamiltonian [R. K. Nesbet, *ibid.*, **35**, 555 (1963)] were used independently, the best energy being selected at each point, for each state. (b) We thus obtain data allowing an easy elaboration of MO and state correlation diagrams on which the description of reactivity is based.

(17) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5340 (1971).

(18) P. H. Kasai, R. J. Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). D. R. Lide, Jr., *ibid.*, **33**, 1514 (1960). Calculated and experimental (in parentheses) values are as follows: C=C 1.277 Å (1.300); C—C 1.493 Å (1.515); C=C—H 150.3° (149.9); H—C—H 112.5° (114.7); =C—H 1.075 Å (1.070); C—H 1.087 Å (1.087). Both calculated and experimental C=C bond lengths are shorter than usual.

(19) It is now well established that $^1\pi\pi^*$ is not correctly described by minimal basis calculations. Only bases including diffuse function are able to accommodate correctly its diffuse character. C. F. Bender, T. H. Dunning, Jr., H. F. Schaefer III, W. A. Goddard III, and W. J. Hunt, *Chem. Phys. Lett.*, **15**, 171 (1972).

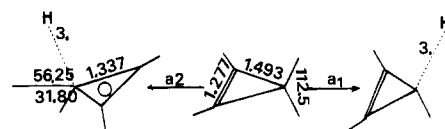


Figure 2. Model ruptures of the methylene CH bond. In path a_1 , the H—C=C bond angles are frozen to their initial values. In path a_2 , a linear variation of the geometrical parameters is assumed from cyclopropene to the optimal intermediate.

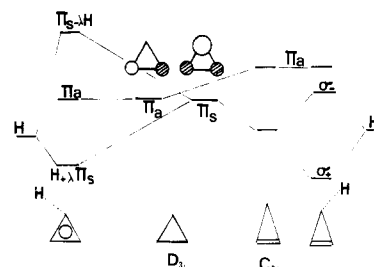


Figure 3. Perturbation scheme showing the interaction of H (1s atomic orbital) with the π_s, π_a couple of MO's, in the case of D_{3h} and C_{2v} geometries.

Particularly, relaxation of the double bond would compensate to some extent the destabilization due to the population of π^* .²⁰ When aromatic substituents are linked to the double bond, an important energy lowering is predictable for both singlet and triplet $\pi\pi^*$ states. This effect would not be important for alkyl substituents.²¹

After these considerations, one must keep in mind that all the processes that will be described in the following sections are mainly related to cyclopropenes where strong conjugative interactions are not present. Qualitative arguments will be used to extend the conclusions to the case of aryl-substituted compounds. We will now examine the various reactions paths of Figure 1.

Hydrogen Departure, Path a

Two model processes have been tested. The first one consists of a CH rupture which preserves the starting geometry of the ring and roughly corresponds to a Jahn–Teller distorted cyclopropyl radical at the end of the process.²² The second one consists of a CH rupture with concomitant rearrangement of the ring structure leading to the geometry that has been independently optimized for the $C_3H_3^+$ cation. Both processes are described in Figure 2. The related MO diagrams only differ in that the relative order of the frontier MO's depends on the shape of the final system. Let us first examine the perturbational scheme of Figure 3. Starting from the D_{3h} cyclopropyl unit, where π_a and π_s are degenerate, one observes that distortion toward C_{2v} lowers π_s since the bonding interaction is increased and the antibonding interaction is decreased. At the same time, π_a is destabilized

(20) In alkenes, the destabilization caused by the partial filling of π^* acts as a driving force for spontaneous cis/trans isomerization. In this case, concomitant rotation and bond stretching are observed.

(21) The singlet absorption of stilbene has a maximum at 2800 Å (4.43 eV). The lowest triplet state of cis-stilbene is found at an energy lower than 3 eV. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1967. See also G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964). The corresponding values are 8.1 and 4.0 eV for singlet and triplet ethylene, as calculated in ref. 19.

(22) D. Poppinger, L. Radom, and A. Mark, *Chem. Phys.*, **23**, 437 (1977); N. C. Baird, *J. Org. Chem.*, **40**, 624 (1975); G. E. Palmer, J. R. Bolton, and D. R. Arnold, *J. Am. Chem. Soc.*, **96**, 3708 (1974); D. R. Arnold, R. W. Humphreys, W. Leigh, and G. E. Palmer, *ibid.*, **98**, 6225 (1976); P. Bischof, *ibid.*, **99**, 8145 (1977); R. C. Binham and M. J. S. Dewar, *ibid.*, **95**, 7180, 7182 (1973).

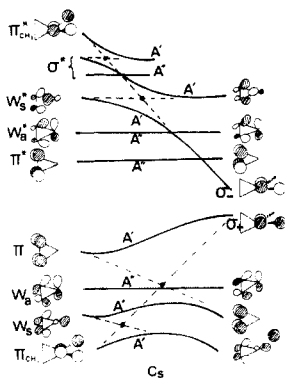


Figure 4. MO correlation diagram for C-H bond rupture derived from the SCF calculation. The dominant contributions are emphasized and the schematic drawing outlines the main phase relationship.

since the antibonding interaction is increased. Interaction of the resulting set with H (right side) leads to the formation of σ_+ and σ_- , where strong mixing of π_s and 1_s of H is expected (nearly degenerate interaction). On the other hand, similar interactions with the D_{3h} MO's lead to nondegenerate mixings: π_a remains unchanged while the lowest combination is rather concentrated on H and the highest is concentrated on the π system. Hence, we have two different frontier MO orderings for paths a_1 and a_2 . Within the set of the Walsh MO's, only small energetic changes are observed.

The calculated MO diagram of Figure 4 is schematically drawn for path a_1 . For path a_2 , the corresponding one would be obtained by taking the final MO order of the left of Figure 3. The various MO's are labeled with respect to the symmetry plane, (C_s symmetry) which is preserved during the reaction. The various contributions have been slightly emphasized in order to follow more easily the "natural" MO correlations.^{13,14} This diagram can be obtained by two successive steps: (1) the correlations of the Walsh MO's are straightforward since they are not affected to a great extent in the process; (2) the dominant contributions of π and π^* are preserved (broken line for π , solid line for π^*). The π -type bonding MO of CH_2 tends to yield σ_+ , and the corresponding antibonding MO, $\pi_{\text{CH}_2}^*$, tends to reach σ_- for the same reasons (broken lines). Several crossings should occur, and once these are taken into account in the SCF step of the calculation, the resulting full-line pattern is obtained.

In order to construct the related state correlation diagram, let us focus our attention on the various states of the final system. We will first examine the distorted geometry of path a_1 . Due to the quasi-degenerate situation of σ_+ and σ_- , we must consider the various electronic configurations built on these MO's,²⁵ namely, σ_+^2 , σ_-^2 , and ${}^1,3(\sigma_+^1\sigma_-^1)$, all being of A' symmetry. After CI, we find at low energy a singlet-triplet pair of diradicals, 1,3D , nearly degenerate in energy and of dominant covalent character, whose eigen functions are, respectively, $\sigma_+^2 - \sigma_-^2$ and ${}^3(\sigma_+^1\sigma_-^1)$. We then find a second singlet-triplet pair of diradicals, quite degenerate in energy, ${}^1,3D'$, and of A'' symmetry. It results from another covalent electronic distribution involving the partial filling of the π^* MO. A high-energy gap, greater than 4 eV, results between this couple and 1,3D . The first ionic state lies far above these

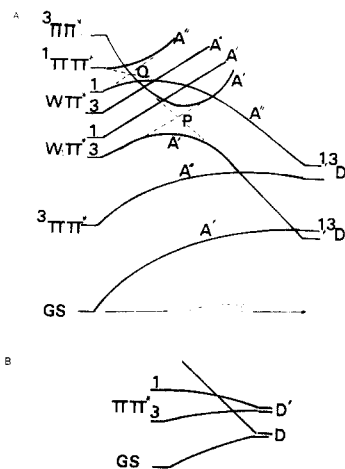


Figure 5. (A) State correlation diagram for C-H bond rupture. The same correlations are valid for both paths a_1 and a_2 . Part B corresponds to the presence of an aryl substituent, able to stabilize the ${}^1\pi\pi^*$ state of the system.

species and needs not to be discussed here.

With the final geometry corresponding to path a_2 , energetic changes occur. On the one hand, 1D now bears a slight polarity, $\text{C}_3\text{H}_3^+\cdots\text{H}^-$, and is destabilized by 0.5 eV. A weaker destabilization is found for the triplet species. Drastic changes are found for the ${}^1,3D'$ couple: since the relaxation of the bond length lowers the energy of π^* , the electronic distribution involving the population of this MO is greatly stabilized, and, as an end result, the ${}^1,3D'$ couple now lies in the vicinity of 1,3D , the energetic separation being only 1 eV.

The state correlation diagram of Figure 5A results. Due to avoided crossings at the MO level, between occupied MO's, nonmonotonous correlations are expected for the PES's whose leading configurations involve a variation of the electronic population of these MO's.¹³ This is schematically indicated by weak curvatures along the correlations. The GS is linked to 1D while, at least formally, the triplet state ${}^3\pi_{\text{CH}_2}\pi_{\text{CH}_2}^*$ tends to correlate with 3D . The ${}^1,3\pi\pi^*$ couple, of A'' symmetry, is linked to ${}^1,3D'$, but the situation is complicated by the presence of valence states like ${}^1,3W_a\pi^*$ (A') and ${}^1,3W_s\pi^*$ (A''), all being correlated with high-lying states of the final species. Several avoided crossings result: at point P, ${}^3W_a\pi^*$ and the dissociative PES avoid themselves, and at point Q the same occurs for ${}^1\pi\pi^*$ and ${}^1W_s\pi^*$.

The calculated PES's of Figure 6 are in complete agreement with this analysis. In this figure, two different sets of PES's have been reported: path a_1 is drawn with solid lines and path a_2 with broken lines.

The qualitative description of the reactivity is simple: ${}^3\pi\pi^*$ is not reactive in this process since in both paths high energy barriers prevent this state from reaching 3D via internal conversion at point S, or, even worse, at point R. The same is true for the lowest excited singlet that has to overcome an appreciable barrier in both cases. Thus, as experimentally found, no reactive channel is available at low energy.

(25) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972). The first singlet eigenfunction is $-0.89\sigma_+^2 + 0.36\sigma_-^2 - 0.16\sigma_+\sigma_-^1$ and the second is $0.58\sigma_+\sigma_-^1 - 0.63\sigma_+\sigma_-^1 + 0.63\sigma_+\sigma_-^1\pi_a^1$. The first triplet eigenfunction is pure ${}^3\sigma_+\sigma_-^1$, the second is $-0.70\sigma_+\sigma_-^1\pi_a^1 + 0.52\sigma_+\sigma_-^1\pi_a^1$. In spite of their complexity all distributions are mainly covalent (weak polarity for the system); this is indicated by the equivalence of singlet and triplet distributions as in usual covalent diradicals and by the analysis of local charges.

(23) See, for calculated examples, L. Salem and W. L. Jorgensen, "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973.

(24) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953); see also the following papers.

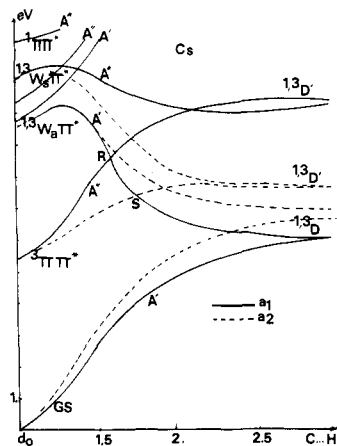


Figure 6. Calculated potential energy curves for paths a_1 and a_2 . The reaction coordinate only refers to the CH distance in path a_1 , but in path a_2 concomitant ring relaxation takes place. Both sets of curves are drawn together in order to allow qualitative comparisons.

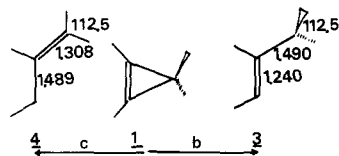


Figure 7. Simulated geometry changes in paths b and c. Linear variations of the parameters are assumed along the whole path. Unless noted, all angles in 3 and 4 are 120° . Only C-C bond lengths have been optimized.

In the presence of an aromatic substituent on the double bond, $^1\pi\pi^*$ might be lowered to such an extent that it becomes the *first* excited singlet state. In this case, if $^1D'$ is stabilized enough a reaction of the first singlet becomes likely. This is schematically indicated in Figure 5B. The corresponding reaction of the first triplet is less likely since, in this case, the lowering of $^3\pi\pi^*$ should be such that before reaching $^3D'$ a noticeable energy gap should be overcome. In other words, the triplet would be handicapped by its great stability. This qualitative result accounts for the experimental fact that when both an aromatic substituent on the double bond and an allylic chain on the methylene are present, side-chain cleavage is observed in the singlet state while the triplet remains unreactive for this process.

Ring Cleavages, Paths b and c

We will first examine path b, which preserves a symmetry plane, and then discuss the variation brought about by a concomitant methylene rotation. In order to simulate these processes, we have used the geometry constraints described in Figure 7.

A very simple MO diagram is associated with path b as shown in Figure 8a: π and π^* are unaffected while W_a and W_a^* , respectively, yield p_+ and p_- , the in-phase and out-of-phase mixing of p lobes on the terminal carbons. The associated correlation diagram (Figure 8b) is straightforward: $^3W_aW_a^*$ and the GS are linked to $^1,3D'$ triplet and singlet covalent diradicals, respectively, as is observed in the related Norrish type I reactions^{13,14,26} or in the parent ring cleavage of azirine²⁷ or diazirine.²⁸ The singlet-triplet

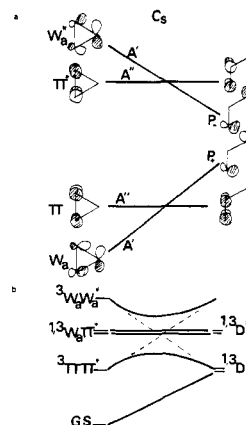


Figure 8. (a) MO correlation diagram corresponding to path b. (b) State correlation diagram corresponding to path b.

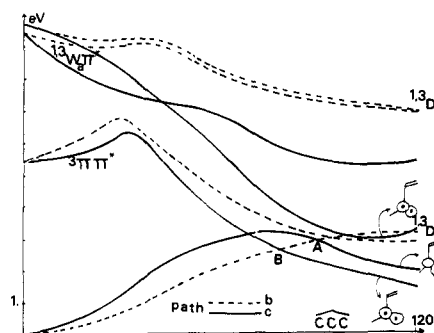


Figure 9. Calculated potential energy curves for paths b and c. The reaction coordinate varying from the initial $C=C-C$ angle to 120° is adequate for the description of path b. This is no longer correct for path c where bond rearrangement and methylene rotation are linked. Nevertheless, it remains useful to draw both sets of potential energy curves on the same figure in order to show that isoenergetic regions of the hyperspace exist around points A and B. It is reasonable to assume that travelling from the surface corresponding to path b to the surface corresponding to path c around these points should not require the overcoming of noticeable energy barriers.

couple $^1,3W_a\pi\pi^*$ correlates monotonously with excited forms of the final species, $^1,3D^*$. The calculated PES's of Figure 9 (broken lines) illustrate this analysis.

No extremum is found along the GS PES, and the low activation energy (3.4 eV) which is obtained reflects the intrinsic ring strain. A noticeable energy barrier also exists along the $^3\pi\pi^*$ PES, resulting from the avoided crossing with the dissociative PES. The high-energy excited states $^1,3W_a\pi\pi^*$ lead to the dissociation via an exothermal process.

Let us now examine the changes that occur when the methylene is rotated and the CC bonds are allowed to relax. This time a complex series of events is involved: ring opening, rotation of the CH_2 , and bond reorganization, since at the end of the reaction, the stable carbenic species 4 is obtained.

Since no symmetry element is preserved along this process, all the crossings are avoided at the state level. The actual shapes of the PES's are then essentially ruled by the relative position of the various states at the end of the overall geometrical changes (solid lines of Figure 9). We have already seen that the optimization of the final

(28) B. Bigot, R. Ponec, A. Sevin, and A. Devaquet, *J. Am. Chem. Soc.*, **100**, 6575 (1978).

(29) D. R. McLaughlin, C. F. Bender, and H. F. Schaefer, *Theor. Chim. Acta*, **25**, 352 (1972); J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1974); P. M. Siegbahn, *J. Am. Chem. Soc.*, **99**, 7716 (1977); R. R. Lucchese and H. F. Schaefer, *ibid.*, **99**, 6765 (1977).

(26) B. Bigot, A. Sevin, and A. Devaquet, *J. Am. Chem. Soc.*, **100**, 2639 (1978).

(27) B. Bigot, A. Sevin, and A. Devaquet, *J. Am. Chem. Soc.*, **100**, 6924 (1978).

structure does not yield a true allylic moiety but a rather localized double bond. Thus, the carbenic end is roughly independent, and a weak conjugation is found. The first low-energy state of the carbenic species is a triplet, whose electronic configuration recalls the classical 3B_1 configuration of CH_2 . We call it "pseudo- 3B_1 ". Only 0.5 eV above this state we find the singlet GS carbene, "pseudo- 1A_1 ", where the two paired electrons lie in the plane of the molecule, localized in a hybrid on C_1 . Then, we find a singlet counterpart of the low-lying triplet, "pseudo- 1B_1 ". The energetic separation between these low-energy configurations is very similar to the ones previously obtained for CH_2 by using the same method (see the following paragraph relative to the formation of CH_2). At high energy, we find a triplet state corresponding to an excitation of the allylic system.

Let us first deal with the singlet GS PES's. It must be remarked that on the drawing of Figure 9, the reaction coordinates are independent for each process and cannot be easily related. Nevertheless, it can be seen that if we only refer to the CCC opening angle, the face-to-face PES lies below the corresponding one obtained for concomitant opening and rotation. A rough picture of the process can be proposed as follows. At the beginning of the reaction, the process follows preferentially the face-to-face motion (retention of bond lengths, no rotation of CH_2). Then, when the CCC angle is around 90 – 95° , methylene rotation takes place, inducing a very important bond relaxation and leading in the end to the stable carbenic species. The overall energy barrier can be estimated by the energy that is necessary to reach point A (~ 3.0 eV). The reverse reaction, i.e., formation of cyclopropene from the carbene species, is not spontaneous since an energy activation of 0.8 eV is necessary. This reaction is even less likely to occur if the system has reached, via intersystem crossing, the more stable "pseudo- 3B_1 " triplet carbene (via the point B). It follows that cyclopropene re-formation competes with other possible evolution processes of the carbene.

The situation is fairly different when the excited states are dealt with. This time the lowest potential energy gradient corresponds at the beginning to path c, for all the low-lying PES's. In particular, the first excited singlet spontaneously yields the pseudo- 1B_1 species, which may interconvert around point A to the more stable pseudo- 3B_1 triplet. The final moiety possesses through this process an excess of internal energy which is able to induce the overcoming of the reclosure barrier: we thus obtain a simple racemization process which is very easy in the singlet excited state. An energy barrier exists along the low-lying ${}^3\pi\pi^*$ PES, and we thus conceive that ring opening through this state remains unfavorable, competing with other eventual processes such as dimerization. This absence of triplet reactivity is found in experimental studies.⁶

The pseudo- 3B_1 form of the carbene is a true stable intermediate. A noticeable energy barrier prevents it from reclosing (1.0 eV)³⁰ via intersystem crossing at or near point B, and a rather long lifetime is predicted for this species. However, one must keep in mind that if the pseudo- 3B_1 form is reached through a photochemical process (for example via a cascade from an upper singlet PES), an excess of internal energy is stored by the system, making it able to eventually reclose or undergo further rearrangements

(30) Owing to the fact that all the crossings are avoided, this time ${}^3\pi\pi^*$ is repelled by the descending ${}^3W_a\pi^*$ PES. A neat reduction of the barrier height results, and a nonmonotonous PES is found for the highest triplet PES.

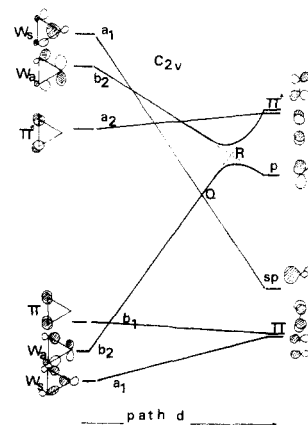


Figure 10. MO correlation diagram for path d.

or fragmentations. Since these processes usually involve energy barriers higher than or in the range of 1 eV, the quantum yield of formation of the resulting products will be small compared to the quantum yield of racemization.

If the double bond is substituted by aromatic groups (see the preceding paragraph relative to CH cleavage), the first low-lying singlet will be ${}^1\pi\pi^*$. By analogy with the behavior of ${}^3\pi\pi^*$, an energy barrier will exist along its PES before the final system is reached. The eventual presence of singlet states near in energy should greatly reduce the barrier height, as is the case when one compares processes b and c for the ${}^3\pi\pi^*$ PES (see also ref 30). Then behavior roughly comparable to the case of nonsubstituted (or alkyl-substituted) structures is predicted, and carbene formation should remain easy in the singlet state.

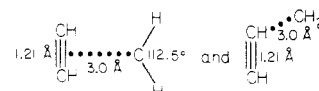
Methylene Formation, Paths d and e

The fragmentation of cyclopropene into acetylene and carbene (methylene), has been simulated in two limiting cases. The first one, path d, consists in a stretching of the CH_2 unit along a direction which preserves the initial C_{2v} symmetry of the system. Path e results from the stretching of CH_2 , taking the open form 3 as a starting point. (Of course, paths b and e are linked in the overall process.) The stable form 4 is not likely to fragment this way since the CH_2 unit is part of a double bond.

Path d will be treated first and we will then examine the variations brought about by the two-step mechanism. The final geometries correspond to standard bond lengths for acetylene; the HCH angle has been kept equal to its initial value, intermediate between the equilibrium geometries of the CH_2 singlet and triplet.³¹ The final distance between CH_2 and acetylene was fixed to 3 Å, where only a weak coupling between both entities remains.

The MO diagram corresponding to this path is quite similar to the one obtained in the CH_2 extrusion of diazirine²⁸ (see Figure 10). The antibonding Walsh MO, W_a^* , is correlated with the sp hybrid of CH_2 and W_a^* tends to yield the empty p AO of CH_2 . π and π^* of cyclopropene yield the corresponding MO's on acetylene. W_s and W_a , respectively, tend to yield the other couple of π/π^* MO's of acetylene. At point Q, an allowed crossing between the

(31) The final situation is as shown below. The HCH angle has not been modified. Its value is intermediate between the 1A_1 and 3B_1 equilibrium values (see ref 29).



anization at the end of the reaction path. A stable carbenic species is obtained. From this intermediate, reclosure is quite easy though not spontaneous. Thus, the eventuality of competing rearrangement processes must be taken into account, toward propyne or allene, for example.

(b) Photochemically, a striking difference is observed between singlet and triplet reactivities. In all cases, the low-energy $^3\pi\pi^*$ state is found to be unreactive and is therefore likely to lead to phosphorescence or bimolecular reactions such as (2 + 2) additions. If the first singlet state is populated, ring cleavage is observed through an overall synchronous opening and methylene rotation. We thus obtain a carbenic species possessing an excess of energy and which is able either to reclose (photochemical racemization) or to lead to further reactions. Side-chain cleavage may be observed if, at the same time, substituents are present on the double bond in order to lower the $^1\pi\pi^*$ energy and if a stabilizing group is attached to the C_3 position in order to stabilize the final diradical species.

(c) A word of caution must be added regarding the role of Rydberg states in *vapor-phase* reactions. These states are not likely to interfere with the low-lying triplet states,

but they may appear in the close vicinity of the first valence singlet state of alkyl-substituted cyclopropenes. Recent theoretical studies have shown that, for model reactions, the mixing of the Rydberg and the valence states ("derydbergization") is very easy and takes place at the beginning of the reaction.³² To a rough approximation these states might be considered as relatively low-energy reservoirs. Theoretical studies are in progress in this field.³³

(d) A very recent work by Padwa et al.³⁴ proposes a dissociation-reassociation mechanism to account for the formation of rearranged cyclopropenes upon photoexcitation. This mechanism is in very good agreement with our findings.

Registry No. Cyclopropene, 2781-85-3.

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Electrochemical Reduction of Bridgehead Iodides

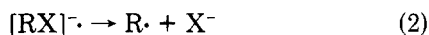
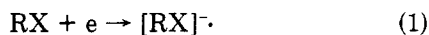
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Electroreduction of bridgehead iodides, 1-iodoadamantane, 1-iodobicyclo[2.2.2]octane, 1-iodobicyclo[2.2.1]heptane, 1-iodobicyclo[2.1.1]hexane, 6-iodotricyclo[3.1.1.0^{3,6}]heptane, iodocubane, and 1-iodotricyclo[4.1.0.0^{2,7}]heptane, at a mercury cathode is described. Polarographic studies of the iodides dissolved in dimethylformamide containing tetrabutylammonium perchlorate supporting electrolyte revealed that reduction is associated with a single two-electron wave in each case. Initially, the half-wave reduction potentials become progressively more negative as the s character of the bridgehead carbon exocyclic bonding orbital increases, but then there is a dramatic reversal of this trend. Several possible explanations are advanced to account for this behavior. Analysis of the product obtained from controlled-potential electrolysis of each iodide showed the corresponding hydrocarbon to be formed in moderate to high yield via a two-electron pathway.

The area of electroorganic chemistry has assumed increasing importance over recent years. One aspect which has generated considerable interest is that dealing with electroreduction of the carbon-halogen bond¹⁻⁵ for which the generally-accepted mechanism is that proposed some time ago by Elving and Pullman⁶ (eq 1-4).



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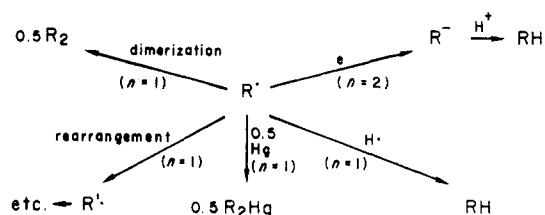
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Scheme I



For most haloalkanes, i.e., those in which the system does not lead to stabilization of the radical ion, $[\text{RX}]^-$, steps 1 and 2 are frequently assumed to be concerted;^{2,7} in other words, the radical anion can be regarded as a transition state rather than as an intermediate and in such cases the primary electron-transfer reaction is potential determining. At the same time, haloalkanes other than allyl, benzyl, and some tertiary halides generally display a single two-electron wave because reduction of the radical (eq 3) occurs at a less negative potential than that required

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