Solvents were purified by standard procedures before use.[19] Reagent grade hydrocarbons were recrystallized before use.

References and Notes

(1) For part I, see ref 5.
(2) (a) D. E. G. Austen, D. J. E. Ingram, P. H. Given, and M. E. Peover, *Nature (London)*, **182**, 1784 (1958); (b) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).
(3) R. Dietz, "Organic Electrochemistry, an Introduction and Guide", M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973, Chapter V.
(4) A. Demortier and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 3495 (1973).
(5) B. S. Jensen and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 367 (1974).
(6) (a) M. E. Peover and J. D. Davies, *J. Electroanal. Chem.*, **6**, 46 (1963); (b) I. B. Goldberg and A. J. Bard, *J. Phys. Chem.*, **75**, 3281 (1971).
(7) M. Szwarc, *Acc. Chem. Res.*, **5**, 169 (1972).
(8) G. Levin, C. Sutphen, and M. Szwarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).
(9) (a) A. Rainis, R. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973); (b) *Proc. R. Soc. London*, in press.
(10) J. Jagur-Grodzinski, M. Feld, S. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965); (b) A. Rainis and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 3008 (1974).
(11) We have been informed by Professor Szwarc that, under the conditions of their measurements,[10] the dianions that have been investigated are stable for at least an hour, allowing for spectral measurements.
(12) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes", Interscience, New York, N.Y., 1968, Chapter VI.
(13) V. D. Parker, *J. Electroanal. Chem.*, **35**, app 8 (1972).
(14) O. Hammerich and V. D. Parker, *J. Electroanal. Chem.*, **36**, app 11 (1972).
(15) G. Barry, G. Cauquis, and M. Maurey, *Bull. Chim. Soc. Fr.*, 2510 (1966).
(16) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).
(17) All potential measurements made in this work were under conditions such that the data are independent of sweep rate, and the peak current ratios for the second charge transfers are greater than 0.8. In the more resistant media, corrections were applied for uncompensated resistance.
(18) R. Dietz and B. E. Larcombe, *J. Chem. Soc. B*, 1369 (1970).
(19) C. K. Mann in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1969.
(20) The data reported in this paper were obtained using solvents which had been purified by standard techniques.
(21) In order to observe this behavior, enough alumina must be present to react with most of the solvent impurities; otherwise, oxidation current cannot be observed for the dianion. On the other hand, if more alumina were added, the background hold was not necessary in order to observe the dianion oxidation.
(22) It should be emphasized that, although tetraalkylammonium ions are capable of acting as proton donors, no reactions were observed between the anion radicals or dianions with the electrolytes on the time scale of the measurements. The latter is evident from the voltammograms in Figures 1, 2, and 4 and the voltammetric data.
(23) The Stokes radii for the tetraalkylammonium ions have been calculated to be equal to: 4.71 (n-Bu$_4$N$^+$), 3.92 (n-Pr$_4$N$^+$), 2.81 (Et$_4$N$^+$), and 2.04 Å (Me$_4$N$^+$).[24] The Stokes radius of Na$^+$ in THF has been determined to be of the order of 4.0 Å.[25]
(24) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed, Academic Press, New York, N.Y., 1959.
(25) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).
(26) K. Izutsu, S. Sakura, and T. Fujinaga, *Bull. Chem. Soc. Jpn.*, **46**, 2148 (1973).
(27) (a) L. A. Avaca and A. Bewick, *J. Electroanal. Chem.*, **41**, 405 (1973); (b) M. E. Peover, "Electroanalytical Chemistry", Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1967, p 19.
(28) R. N. Adams, *Acc. Chem. Res.*, **2**, 175 (1969).
(29) An effect of supporting electrolyte concentration on peak potentials in THF has previously been noted for single charge transfers.[26]
(30) C. P. Keszthelyi, N. E. Tokel-Takvoryan, H. Tachikawa, and A. J. Bard, *Chem. Phys. Lett.*, **23**, 219 (1973).
(31) O. Hammerich and V. D. Parker, *J. Chem. Soc., Perkins Trans. 1*, 1718 (1972).
(32) N. S. Moe, unpublished work.

Stereochemistry of Carbene Rearrangements. Correlation of ab Initio Molecular Orbitals as an Aid to the Investigation of the Electron Redistribution Mechanism

Julianna A. Altmann, Imre G. Csizmadia, and Keith Yates*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 1A1. Received November 11, 1974

Abstract: Nonempirical LCAO-MO-SCF calculations employing a double ζ basis set have been carried out to examine the reaction profile of the rearrangement of methylcarbene to ethylene. The investigation also involved a charge distribution analysis on the basis of which a mechanism for the electron redistribution process has been proposed. This mechanism has been further supported by a detailed study of the change in molecular orbital density contours along the reaction coordinate. An energy level correlation diagram for the singlet carbene to ethylene process, based on the calculated MO distribution pattern, shows no correlations between bonding levels in the reactant and antibonding levels in the product. Thus the reaction is predicted to be thermally allowed in the Woodward-Hoffmann sense.

The thermal rearrangement of carbenes to olefins is well known[1] to organic chemists. Since carbenes could conceivably exist as singlets or triplets, this reaction could, in principle, involve either the conversion of a singlet carbene to an olefin in its ground state, or the conversion of a triplet carbene initially to an excited triplet olefin which rapidly decays to its ground state. Orbital symmetry considerations[2] to predict which of the above conversions should be favored cannot be utilized because of the lack of a common symmetry element in reactant and product. An alternative qualita-

tive quantum mechanical approach, which is based on the correlation of nodal characteristics of the molecular orbitals involved in a reaction and does not require any symmetry considerations, is the so called "MO Following technique".[3] It was reported[3] that application of this technique to the carbene rearrangement predicts the ground state process to be "allowed" and thus preferred. However, this approach is truly applicable only to molecules whose electronic ground state is unquestionably singlet. It is clear that, in the present case, the choice of the favored conversion depends entirely
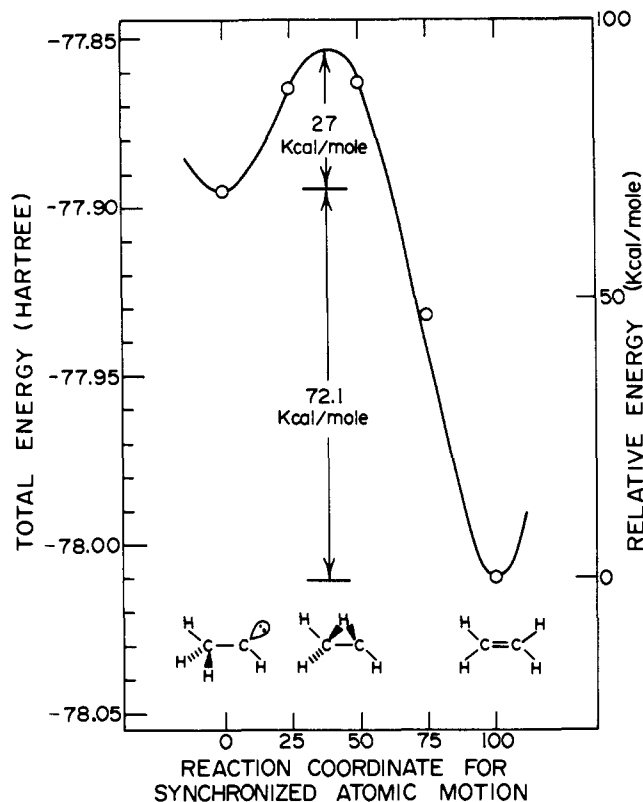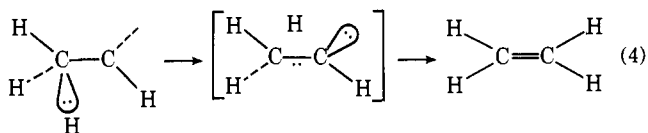
Table I. Variation of the Total Energy with the Position of the Migrating Hydrogen[a] along the Reaction Coordinate of the Preferred Stereochemical Mode of the Rearrangement

Percent reaction	Distance (m), Å[d]			E_0, hartree[b]	m_0, Å[c]
	1.0	1.1	1.2		
0				−77.8964109	
25	−77.8576763	−77.8675777	−77.8647195	−77.868060	1.13
50	−77.8521676	−77.8603521	−77.8630550	−77.86305514	1.19
75	−77.9288571	−77.936000	−77.9311135	−77.9360527	1.11
100				−78.0115556	

[a] Defined as the vertical distance (m) of the migrating hydrogen from the carbon–carbon single bond. [b] Minimized energy using equation in text. [c] Distance at minimum energy. [d] Only the three points around the minimum of the curve are given in this table. In the case of the geometry corresponding to 50% reaction, other points up to $m = 1.5$ Å were also considered for minimization.

on the nature of the most stable electronic state of the carbene.

We had previously carried out an ab initio study[4] for a model reaction, the conversion of methylcarbene (I) to ethylene (II) in which we first focused our attention to the *conformational properties* of the reactant. Examination of the two major cross-sections[5] of the potential-energy hypersurface of methylcarbene (I) predicted that the most stable electronic state is the singlet (S_0),[6] but that the first triplet (T_1) lies extremely close.[7] On the other hand, when the *stereochemistry of the rearrangement* was investigated,[4] it was found that one of the modes corresponding to a singlet I to ground state II conversion was highly favored. This mode involved the migration of a hydrogen gauche to the methine proton as shown in eq 2. The above mode involves more

$$CH_3-\ddot{C}H \longrightarrow CH_2{=}CH_2 \quad (1)$$

$$\quad\;\; I \qquad\qquad\quad II$$

$$(2)$$

$$II$$

atomic motion than any of the other stereochemical possibilities considered.[8] Consequently, it appeared that the stereochemistry must be controlled solely by the change of electron density during the migration. The objective of this investigation was to find a mechanism for the electronic redistribution which would justify the preference for the favored stereochemical mode.

Computational Details

All computations have been carried out on an IBM 370/165 computer.

The reaction profile was investigated by means of nonempirical LCAO-MO-SCF calculations using the IBMOL-IV system[9] and employing a double ζ basis set optimized by Dunning.[10]

The net atomic charges were obtained from Mulliken population analysis.[11]

The position of the migrating hydrogen along the reaction coordinate was optimized by varying its distance (m) from the carbon–carbon single bond. The minimum was found by fitting the points into quadratic eq 3

$$E = E_0 + \tfrac{1}{2}k(m - m_0)^2 \quad (3)$$

where E and E_0 denote the energies, k is a constant, and m

and m_0 represent the distances corresponding to E and E_0, respectively. The results are shown in Table I.

The shapes of the molecular orbitals were obtained from two-dimensional cross-sections using the computer program SNOOPY.[12]

Results and Discussion

The Reaction Profile. In our previous paper,[4] we reported the relative order of preference of various stereochemical modes for the rearrangement based on the comparison of the energetics of the barriers at half-reaction. However, it should be noted that the above ordering, and in particular the preference for reaction 2, may be influenced by the position of the transition state on the reaction coordinate. Consequently it was felt necessary to investigate the reaction profile of the favored stereochemical mode. Our results are summarized in Table I and illustrated in Figure 1. Each point on the curve was obtained by optimizing the position of the migrating hydrogen (cf. Table I) and allowing all the other atoms of the molecule to move synchronously along the reaction coordinate. This treatment was found to give a good description of the loosening of the carbon–hydrogen bond during the migration.

It is apparent from the shape of the curve in Figure 1 that the transition state is somewhat earlier than half-reaction.[13] This is reasonable and in fact would be expected, according to Hammond's postulate,[14] for an exothermic reaction requiring relatively small activation energy. Because of the fact that the difference in both energy and geometry between the actual transition state and that at 50% reaction has been found to be relatively small, comparison of the energetics at either of these positions on the reaction coordinate is expected to give the same ordering of modes. Thus our original assignment involving the gauche-hydrogen migration in the preferred mode has been further substantiated.

The mechanism of the electron redistribution for the rearrangement was investigated by means of two different techniques: (1) charge distribution studies; and (2) correlation of the molecular orbitals. These will be outlined in detail in the following parts of this article.

Charge Distribution Analysis. Observation of the charge redistribution during the rearrangement allows insight into the nature of the migrating hydrogen. Three possibilities may be considered: (1) a migrating hydride ion; (2) a migrating proton; (3) some combination of the former two.

The first of these possibilities is known[15] to occur commonly in the case of carbonium ion rearrangements, and the second type is expected to be involved[16] in the case of carbanions. Since carbenes are neutral, neither of these mechanisms could apply unless some charge separation develops during the migration. Consequently, the variation of the net charges of the atoms along the reaction coordinate was examined. Our results for the two carbon atoms (i.e., the

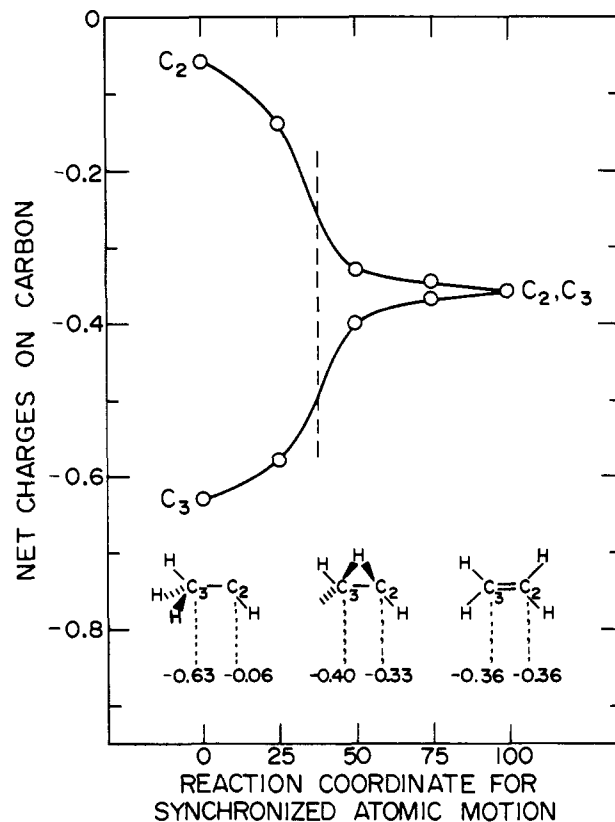Figure 1. Energy profile for the singlet methylcarbene-ethylene inter-conversion along the favored stereochemical path.

Figure 2. Variation of the net atomic charges of C_2 and C_3 along the reaction coordinate of the favored stereochemical mode in the CH_3—$CH \rightarrow CH_2=CH_2$ rearrangement.

methyl carbon and the carbenic center), on which the largest change in charge density occurs, are illustrated in Figure 2. It is immediately apparent from the shape of the curves that the transfer of charge from the methyl carbon to the carbenic carbon does not occur gradually along the reaction coordinate. Instead, the bulk of the charge is transferred in the early part of the reaction and, after the midpoint (i.e., 50% conversion), only minor changes occur. This early charge transfer implies that the migrating hydrogen pulls its electron pair along toward the center of the C–C bond as illustrated below. Thus it seems reasonable to suggest that, in the early stage of the rearrangement, the migrating hydrogen resembles a pseudo-hydride ion.

(4)

At midpoint, however, because of the additional electron density in the vicinity, a negative charge has developed on the carbenic carbon. In addition, this carbon possesses a lone pair which may be classified as σ type[17] and thus would readily accept a proton. Based on the above, it is unlikely that, in the latter part of the reaction (after the transition state), the migrating hydrogen would continue its motion toward the lone pair as a pseudo-hydride ion.

On the other hand, if the migrating hydrogen was a pseudo-proton, its motion toward the now negatively charged carbenic carbon would be expected to be highly accelerated.

Consequently, the simplest description of the mechanism of the electronic rearrangement is to envisage an electron pair "following" a migrating hydrogen toward the center of the carbon–carbon bond spreading its density rapidly about that bond until it is fully delocalized and thus becomes the

new ethylenic π bond. After the transition state, the hydrogen continues its motion as a pseudo-proton toward the lone pair which, because of its spatial environment,[18] does not contribute to the π bond but is utilized for the formation of the new C–H bond.

Molecular Orbital Analysis. Since in the MO theory the spatial behavior of an electron pair is described by a molecular orbital, an electronic rearrangement can be monitored visually by analyzing the molecular orbitals along the reaction coordinate. For instance, if an electron pair is "migrating", as it was suggested in the previous section, its migration path (i.e., the electron redistribution process) could be determined from the change in the shape of the corresponding molecular orbital with the extent of reaction. Furthermore, the fate of the lone pair on the carbene may also be determined with the aid of this technique.

Based on the above, we have obtained a number of electron density contours corresponding to the occupied and virtual molecular orbitals of methylcarbene, the species at half-reaction, and ethylene. Our objective was to correlate these MO's by "following" them from reactant to transition state to product assuming that the number of nodal planes of a given molecular orbital remains unchanged during the rearrangement. This type of correlation appeared to be doubly challenging because, apart from its utility in substantiating the proposed mechanism, it may also be regarded as a rigorous justification of the qualitative MO Following technique[3] the basis of which is continuity of nodal characteristics along the reaction coordinate.

The carbon core-electrons were omitted from the present analysis. The shapes of the molecular orbitals were obtained from two dimensional cross-sections using two perpendicular planes (plane A and B) as shown in Figure 3. For correlational purposes, however, only one of the cross-sections were used, the selection being dependent upon the better
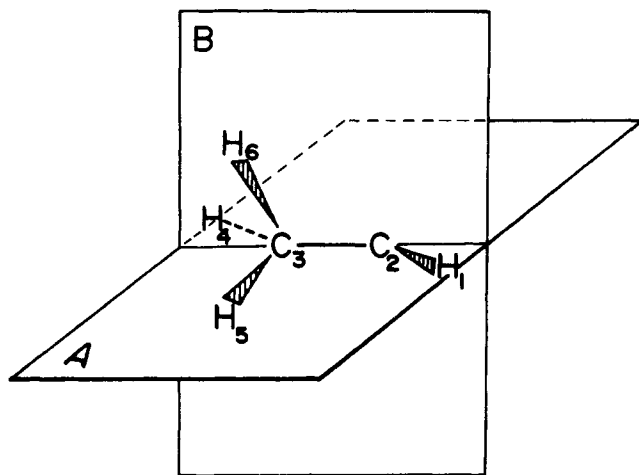
Figure 3. Molecular geometry and principal planes (A and B) of methylcarbene.

visibility of the nodal properties. Thus in the case of the occupied orbitals, the ones corresponding to the σ bonds lying in plane A (i.e., $H_4C_3C_2H_1$ bonds) were correlated by means of their plane A cross-sections. The two other orbitals involving the σ bonds H_5C_3 and H_6C_3 as well as the C_3C_2 π bonds were correlated with the aid of their plane B cross-sections. A similar technique was used for the correlation of the virtual orbitals.[19]

The density contours of the six valence electron pairs[19] are illustrated in Figure 4. The heavy lines connecting the MO's indicate the correspondence and the direction (shown by the arrows) along which correlation was being performed. As is apparent, in each set, the nodal characteristics are preserved.

Let us now "follow" the MO's along the reaction coordinate. MO3 is fully bonding, has no nodes and, following it from left to right (i.e., reactant to transition state to product), there is a close correspondence with respect to the MO contours. MO4 has one vertical node which is preserved throughout the rearrangement. A similar argument applies to MO5 having a horizontal node. Notice the close correspondence between the shape of the reactant MO's and that of the transition state suggesting that these electrons are not involved in the rearrangement. This is not the case, however, for MO6 which corresponds to the bonding electron pair of the migrating hydrogen. Following this orbital along the reaction coordinate (indicated by the heavy arrows), with conservation of its horizontal nodal plane, reveals that in fact it correlates with the π bond of ethylene. Notice that, in the transition state, the electron pair is fully delocalized about the two carbon atoms and the migrating hydrogen. The occurrence of the apparent cross-correlation is what was expected and will be explained in detail in the next section. Continuing our correlation and following MO7 across, it is clear that this MO, just as the first three considered, is not involved in the rearrangement. It has two vertical nodal planes, and its shape shows essentially no change during the process. Finally let us examine MO8, the highest occupied molecular orbital corresponding to the lone pair on the carbenic center. The sp² type hybridization at that center is clearly noticeable from the contour. Following MO8 along the reaction coordinate, it is apparent that it correlates with MO7, the highest occupied σ-type orbital of ethylene (σ C-H), thus showing that the lone pair of carbene is indeed responsible for the formation of the new C-H bond.

An important point should be mentioned here, namely that the shape of MO8 of the transition state is almost identical with that of the reactant, except that the sp² lobe on the carbenic center has contracted somewhat. This means that, as the reaction progresses, the lone pair becomes more localized. The more localized the electron pair, the more it becomes susceptible for the formation of a σ bond and the less available for the formation of a π bond. This observation constitutes further evidence against the involvement of the lone pair in the formation of the π bond.

The cross-correlation involving MO6 of the methylcarbene may be justified as follows. It has been observed that the energy of a given MO increases with increasing number of nodes. On the other hand, it is also known that π-type orbitals are generally of higher energy than σ-type orbitals regardless of their nodal characteristics. Thus in the case of ethylene, MO8 (the π orbital having only one nodal plane) is of higher energy than either MO6 or MO7, although the latters possess two nodal planes. Should this exception not have occurred, the π orbital would have actually been MO6, and no cross-correlation would have been observed. A similar argument applies to MO7 of the transition state which also has π character and thus is of higher energy than MO6. In this case, however, MO7 is only second highest in energy because of the presence of a nonbonding orbital corresponding to the lone pair.

For all these reasons, therefore it is clear that the correlation scheme is in good agreement with the proposed mechanism.

The foregoing discussion is summarized by the correlation diagram shown in Figure 5. The diagram illustrates the relative energetics of all the valence orbitals and the six lowest lying orbitals of the virtual manifold. It is of great importance to realize that there is no cross-correlation between the occupied and the virtual levels. If there were such cross-correlations, then this particular stereochemical mode for the rearrangement would have been "forbidden" according to the Woodward-Hoffmann[2] definition. Therefore reaction 2 should also be regarded as the stereochemical mode "allowed" by the conservation of nodal properties,[3] or in other words, by principle of maximum overlap which underlines orbital symmetry[2] arguments.

Recently Nickon and coworkers[20] carried out a series of thermal and photochemical Bamford-Stevens reactions in order to investigate the stereochemistry of vicinal hydrogen shift in carbenes. Using rigidly locked norbornyl ketones such as brexan-5-one (III) shown below in which the carbonyl carbon represents the potential carbene site, the rate ratio k_{exo}/k_{endo} for the thermal migration was found to be 138.
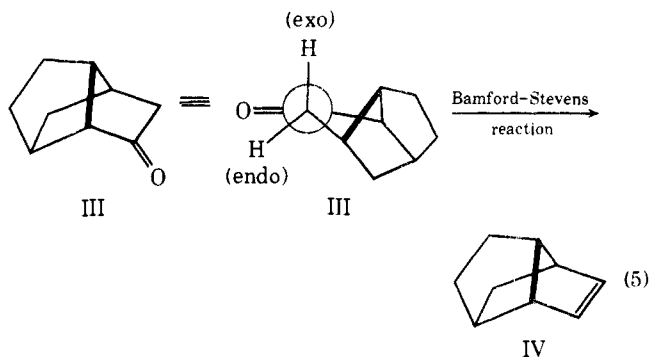
In contrast, the photolytic rearrangement was observed to be much less stereoselective.[22]

If we make the reasonable assumption that the thermal process involves a singlet carbene,[23] then because of the structure of the brexyl system,[24] the migration of the exo hydrogen simulates the motion toward the empty p orbital of the carbenic center, whereas migration of the endo hy-
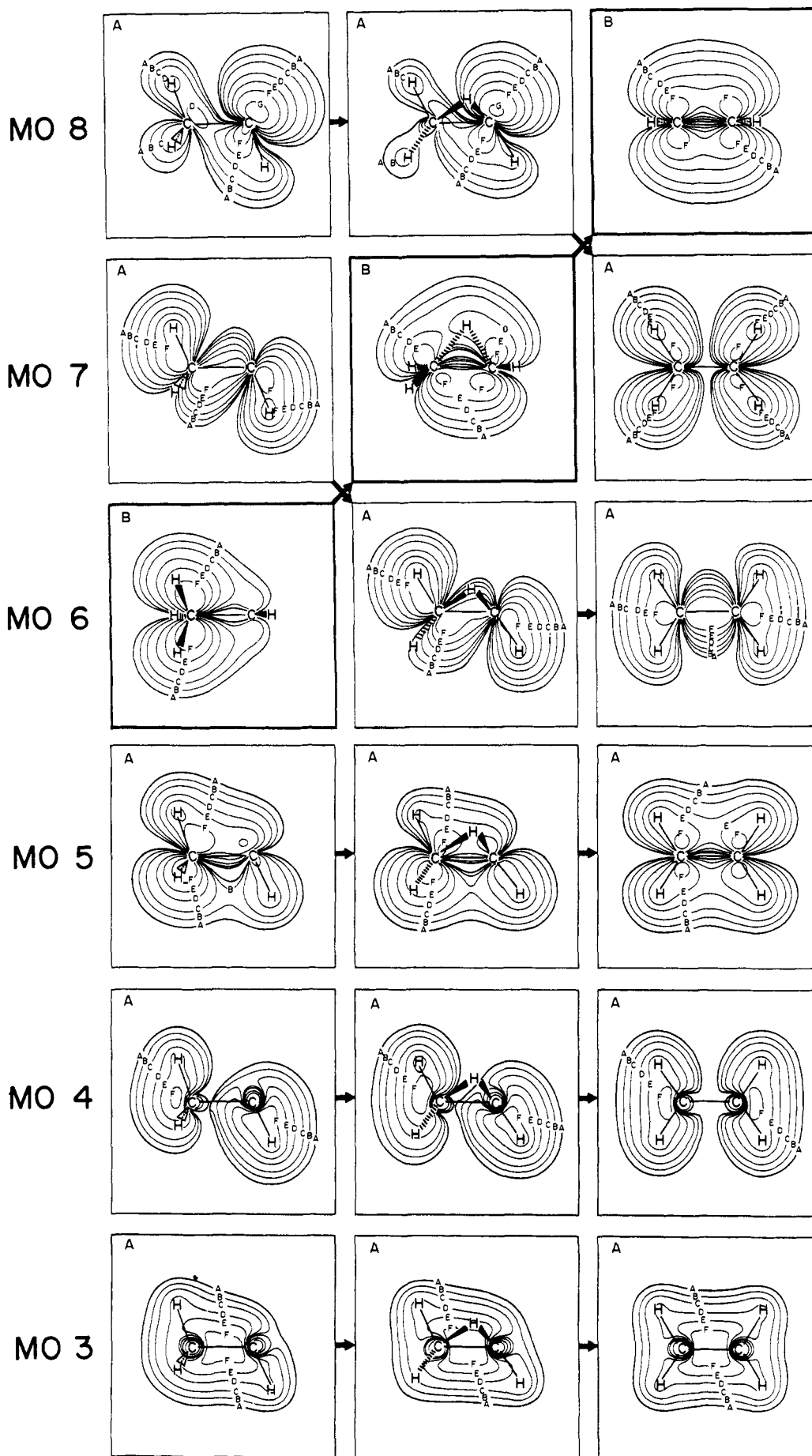
Figure 4. Valence electron molecular orbital density contours in cross-sections A and B for methylcarbene, the half-reaction species and ethylene. (For the definitions of the principal planes A and B see Figure 3.) The capital letters A and B at the upper left hand corner of the individual plots represent the cross-section plane as shown in Figure 3. The density contour labels A, B, C, D, E, and F represent 0.002, 0.004, 0.008, 0.02, 0.04, and 0.08 electron/bohr³, respectively.
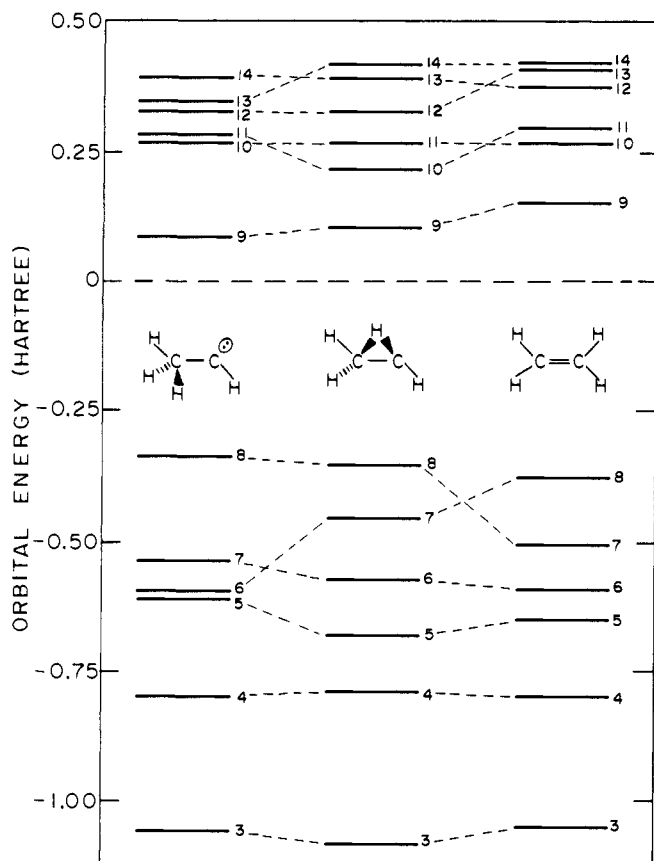
Figure 5. Orbital energy correlation diagram for the methylcarbene-ethylene rearrangement. The computed near-Hartree-Fock MO levels are plotted to scale.

drogen resembles motion toward the lone pair. Thus the exo-preference confirms our prediction (i.e., reaction 2) for thermal rearrangement.

In the case of the photochemical reaction, however, because of the excess energy available, there is a strong probability that the generated carbene will not be in its most stable state. Consequently, our predictions regarding the stereochemistry of the rearrangement do not apply here.

Conclusions

The reaction profile of the favored stereochemical mode indicates that the actual transition state occurs somewhat earlier than half-reaction. However, this is not expected to upset our previously proposed[4] relative order of preference of the various stereochemical modes for the rearrangement. Therefore our previous assignments, and in particular our prediction regarding the most favorable mode (i.e., reaction 2), may now be considered as being further substantiated. As shown by the correlation diagram (Figure 5), this mode is allowed by the conservation of orbital symmetry approach[2] as well. Furthermore, the recent experimental observations of Nickon and coworkers[20] are also in agreement with our prediction. In contrast, least motion calculations[21] have shown that this particular mode is extremely unfavorable. Therefore it was proposed that the preference is because of stereoelectronic factors and, in connection with this, a mechanism for the electron redistribution process was suggested. The mechanism was initially based on charge distribution analysis, and it involves the migration of a σ-electron pair to populate a new π bond and the utilization of the nonbonding electron pair for the formation of a

new σ bond. Because of the fact that the above mechanism is further supported by the correlation of molecular orbitals, it is reasonable to conclude that it is indeed an accurate description of the movement of the electrons during the rearrangement.

The present approach has the added advantage that it is generally applicable to other systems, particularly those where other approaches cannot be used because of the lack of appropriate symmetry elements.

Finally on the basis of our present study, we may conclude that the model employed by Zimmerman[3] in his qualitative treatment of the present rearrangement accurately reflects the quantum chemical behavior of the system.

References and Notes

(1) For recent work, see: (a) S. S. Olin and R. M. Venable, *J. Chem. Soc., Chem. Commun.*, **104** (1974); (b) M. Pomerantz and T. H. Whiterup, *J. Am. Chem. Soc.*, **95**, 5977 (1973); (c) M. B. Sohn and M. Jones, Jr., *ibid.*, **94**, 8280 (1972); (d) L. A. Paquette and G. H. Birnberg, *ibid.*, **94**, 164 (1972); (e) D. H. White, P. B. Condit, and R. G. Bergman, *ibid.*, **94**, 1348 (1972); (f) R. A. Keppel and R. G. Bergman, *ibid.*, **94**, 1350 (1972); (g) D. F. Eaton, R. G. Bergman, and G. S. Hammond, *ibid.*, **94**, 1351 (1972).

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, and references therein.

(3) H. E. Zimmerman, *Acc. Chem. Res.*, **5**, 393 (1972).

(4) J. A. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **96**, 4196 (1974).

(5) The two cross-sections referred to are associated with the in-plane inversion $[E = E(\alpha)]$ at the carbenic center and the rotation $[E = E(\theta)]$ about the C–C bond.

(6) It was found that both the singlet (S_0) and the triplet (T_1) methylcarbene prefer a bent geometry, the ground singlet (S_0) staggered conformation being the most stable (the rotational barrier was found to be 2.14 kcal/mol). In contrast, it was observed that, if the molecule would be forced into an eclipsed conformation by means of some geometrical constrains, then the triplet (T_1) state would be its most stable state.

(7) The (S_0–T_1) separation was found to be 0.3 kcal/mol.

(8) See ref 4 for the other stereochemical possibilities.

(9) A. Veillard, "IBMOL: Computation of Wave Functions for Molecules of General Geometry, Version 4", IBM Research Laboratory, San Jose, Calif.

(10) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970). Note: same basis set as used in ref 4.

(11) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(12) R. F. W. Bader, private communication.

(13) The maximum on the curve corresponds to 39.1% reaction.

(14) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(15) For a recent review on intramolecular hydride shifts in carbonium ions, see S. P. McManus and C. A. Pittman, Jr., In "Organic Reactive Intermediates", Academic Press, New York, N.Y., 1973, p 290.

(16) Intramolecular proton transfer in carbanions was postulated on the basis of kinetic isotope effects. See, for example, D. J. Cram, *Surv. Prog. Chem.*, **4**, 45 (1968).

(17) According to our previous study,[4] the carbenic center is essentially sp^2 hybridized. This has been also confirmed by the shape of the highest occupied MO of methylcarbene (see next section in text).

(18) The bulk of the density (according to the shape of the MO) is situated in the molecular plane, whereas the π-bond density is above and below that plane.

(19) Because of the limited space, the density contours corresponding to the virtual orbitals are not shown but are available from the authors upon request. Nevertheless they were correlated by means of the same technique as used for the occupied set, and the results are shown on the final correlation diagram (Figure 5).

(20) A. Nickon, F. Huang, R. Weglein, K. Matsuo, and H. Yagi, *J. Am. Chem. Soc.*, **96**, 5264 (1974).

(21) O. S. Tee and K. Yates, *J. Am. Chem. Soc.*, **94**, 3074 (1972).

(22) The ratio k_{exo}/k_{endo} in that case was found to be 4.8.

(23) This assumption is based on the mild experimental conditions used for the generation of the carbene.

(24) The brexyl system is distorted relative to a regular norbornyl system in that the C=O bond is not bisecting the H_{exo}–CH_{endo} dihedral angle. Instead, the dihedral angle between the carbonyl oxygen and H_{exo} has increased to almost 90°, whereas the other angle involving H_{endo} decreased to almost 30°.