iodide and bromide salts were prepared by addition of NH_4Br or KI instead of NH_4Cl. The products were shown by spectroscopy {$\nu_1(N_2O)$, 1155 (Cl^- salt), 1160 (Br^-), 1175 cm^{-1} (I^-); $\nu_3(N_2O)$, 2235 (Br^-), 2250 cm^{-1} (I^-), unobservable for Cl^- salt; $\nu(N_2)$, 2100 (Cl^-), 2110 (Br^-), 2120 cm^{-1} (I^-);[15] $\nu_1(N_2O)$ and $\nu(N_2)$ were of comparable intensity, λ_{max} 221 ($[Ru^{II}(NH_3)_5N_2]^{2+}$) and 235 nm ($[Ru^{II}(NH_3)_5N_2O]^{2+}$); the latter band decreased rapidly and a new band appeared at 299 nm, due to $[Ru^{III}(NH_3)_5OH]^{2+}$ [28]} and analysis (Table III) to be mixtures of $[Ru^{II}(NH_3)_5N_2]X_2$ and $[Ru^{II}(NH_3)_5N_2O]X_2$, with the latter complex comprising, at maximum, 70% of the product.

Table III. Analytical Data for Mixed $[Ru^{II}NH_3)_5N_2O]X_2$–$[Ru^{II}(NH_3)_5N_2]X_2$ Product

	Calcd, %[a]			Found, %		
	H	N	X	H	N	X
$[Ru^{II}(NH_3)_5N_2]Cl_2$	5.30	34.38	24.86		33.80	23.55
$[Ru^{II}(NH_3)_5N_2]Br_2$	4.04	26.21	42.72	3.98	25.87	40.42
$[Ru^{II}(NH_3)_5N_2]I_2$	3.23	20.95	54.22	3.23	21.62	52.70

[a] The calculated percentages for $[Ru^{II}(NH_3)_5N_2O]X_2$ are given in Table II.

By a similar method, but stirring the cold solution for approximately 3 min before precipitating, brick red (Cl^-) or purple (I^-) salts were obtained. These salts, which showed paramagnetism, became pale yellow on setting aside. The infrared spectra showed a band at 2020 cm^{-1} in addition to those of $[Ru^{II}(NH_3)_5N_2]X_2$ and $[Ru^{II}(NH_3)_5N_2O]X_2$. The electronic spectrum showed a band at 460 nm which decreased with time. These properties indicated the presence of $[Ru^{III}(NH_3)_5N_3]^{2+}$.[15]

(c) With $N_2H_6^{2+}$ and OH^- at Room Temperature. To a solution of $[Ru^{II}(NH_3)_5NO]I_3 \cdot H_2O$ (0.089 g) and $N_2H_6I_2$ (1.0 g) in water (7 ml) were added four pellets (0.8 g) of NaOH. The precipitate which formed on dissolution of the NaOH was removed by filtration, washed with alcohol and ether, and dried *in vacuo* over P_2O_5, yield 0.040 g. The product was a mixture of $[Ru^{II}(NH_3)_5N_2O]I_2$ and $[Ru^{II}(NH_3)_5N_2]I_2$ in similar proportion to that obtained by method b above.

Electronic spectra were measured on a Hitachi-Perkin-Elmer EPS-3T instrument; infrared spectra (as Nujol or hexachlorobutadiene mulls between KBr plates) on a Beckman IR 12 instrument. Mass spectra were obtained, at ionizing voltages of 30 and 70 V, on a Hitachi-Perkin-Elmer RMU-6D instrument. Magnetic moments were by the Gouy method. Microanalyses were by A. Bernhardt, West Germany, and Chemalytics, Tempe, Ariz.

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(28) J. A. Broomhead and L. A. P. Kane-Maguire, *ibid.*, **8**, 2124 (1969).

Ground States of Molecules. XIX.[1] Carbene and Its Reactions[2]

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Abstract: MINDO/2 calculations are reported for singlet and triplet carbene and for their reactions with methane and ethylene. The energies of the various states of carbene have been calculated as a function of HCH bond angle. The results lead to the prediction that for small bond angles the singlet state becomes progressively favored. This prediction has been tested by calculations for cyclopropylidene, cyclopropenylidene, and vinylidene.

The divalent carbon compounds known variously as methylenes or carbenes have long fascinated organic chemists,[4] and numerous theoretical studies of them have been reported.[5]

It is now recognized that compounds of this kind can exist in both singlet and triplet states, and carbene itself has been shown[6–8] to have a triplet ground state, in agreement with recent *ab initio* SCF calculations.[5]

The reactions of singlet and triplet carbene have also aroused much interest, particular attention being paid to the mechanism and stereochemistry of insertion and addition reactions. Here the only detailed calculations are those recently reported by Hoffmann, *et al.*;[9] these, however, were carried out by a procedure ("extended Hückel" method) which is known to give very poor estimates of molecular energies.

Here we report calculations for singlet and triplet carbene and their addition and insertion reactions, using a procedure (MINDO/2[10]) which has been shown to

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(1) Part XVIII: N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972).

(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126.

(3) Robert A. Welch Postdoctoral Fellow.

(4) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p. 235.

(5) For recent *ab initio* calculations and references to earlier work, see (a) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969); (b) C. F. Bender and H. F. Schaeffer III, *ibid.*, **92**, 4984 (1970); (c) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971); (d) J. F. Harrison, *ibid.*, **93**, 4112 (1971); (e) S. Y. Chu, A. K. O. Siu, and E. F. Hayes, *ibid.*, **94**, 2969 (1972).

(6) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

(7) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970); E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970).

(8) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970).

(9) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6188 (1971).

(10) (a) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

Table I. Properties of Carbene

	Heat of formation, kcal/mol		Bond length, Å			Bond angle, deg		
State	MINDO/2	Obsd	MINDO/2	*Ab initio* SCF	Obsd	MINDO/2	*Ab initio* SCF	Obsd
S_0	95.8	91.9,[a] 86 ± 6[b] 94.6–94.5[d]	1.097	1.100[c]	1.11[b]	107	105.4,[c] 108,[e] 105[f]	102.4[b]
T_1	67.5	48[g]	1.062	1.069,[c] 1.096[h]	1.078[i]	142	132,[c] 138,[e] 132.5[f]	136[i]
S_1	97.0		1.050			180	148,[e] 180[f]	140 ± 15[i]

[a] W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*. **48,** 1109 (1968). [b] G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961). [c] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971). [d] W. A. Chupka, *J. Chem. Phys.*, **48**, 2337 (1968); W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *ibid.*, **50**, 1938 (1969). [e] J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969). [f] J. F. Harrison, *ibid.*, **93**, 4112 (1971). [g] F. Field and J. A. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 117. [h] C. F. Bender and H. F. Schaeffer III, *J. Amer. Chem. Soc.*, **92**, 4984 (1970). [i] G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).

give satisfactory estimates of molecular geometries and heats of formation for a wide variety of organic molecules, including ions, radicals, and triplet states,[11,12] and also of reaction paths and activation energies for a number of reactions.[10,11,13]

Theoretical Procedure

The calculations reported here were carried out with the original version of MINDO/2, using the parameters of part X.[10b] Calculations for triplet states were carried out by an extension[14] of the "half-electron" method,[15] originally introduced in a SCF π approximation but extended here in an obvious manner to MINDO/2.

The geometry of each structure was chosen to minimize the energy, using a procedure developed by Dr. A. Brown based on the SIMPLEX algorithm.[16] This was modified[17] by interrupting the search as the minimum is approached and constructing a new simplex from computed steepest descent step sizes for valence force coordinates, thus avoiding false minima and usually speeding up convergence.

There are three states of carbene to be considered: the triplet state (T_1) in which two carbon AO's are singly occupied by electrons with parallel spins; a singlet state (S_0) in which one carbon AO is empty while a second contains two unshared electrons; and a second singlet state (S_1), again with two singly occupied AO's. The energy of S_0 is given by the usual closed shell procedure while those of S_1 and T_1 are given simultaneously by the half-electron method.[14]

Results and Discussion

A. Geometries and Energies. Table I shows our calculated equilibrium geometries and heats of formation for the three states, S_0, S_1, and T_1, of carbene. The calculations in fact lead to heats of atomization; these were converted to heats of formation using the following experimental values for heats of formation of gaseous atoms: C, 170.89; H, 52.102 kcal/mol. The version of MINDO/2 used here leads to CH bond lengths that are systematically too long by 0.1 Å; the values in Table I have been corrected for this. Table I also shows the latest experimental data for singlet and triplet carbene. Herzberg[6] had originally concluded from spectroscopic studies that triplet carbene is linear. Subsequently Wasserman, *et al.*,[7] showed that the molecule must in fact be bent, with an apical angle of *ca.* 136°, from studies of the esr spectrum of carbene in a matrix at +4°K. This observation led Herzberg and Johns[18] to reinvestigate the spectroscopic data, arriving at the conclusion that they are in fact consistent with the structure proposed by Wasserman, *et al.*[7]

Table I also lists the results of three recent *ab initio* SCF calculations.[5] Two of these[5a,b] followed earlier work in using assumed lengths for the CH bonds but probably represent the most refined treatments of this type so far reported. In the third[5c] the energy was minimized with respect to both the CH bond lengths and the HCH bond angle. *Ab initio* methods cannot, of course, give meaningful estimates of heats of atomization.

It will be seen that the MINDO/2 geometries for S_0 and T_1 are in quite good agreement with experiment and the results of the *ab initio* calculations. The calculated bond angle for S_1 differs considerably from the estimate by Herzberg and Johns[18] and from the value calculated by Bender and Schaeffer;[5b] however, a very recent calculation by Harrison[5d] supports our prediction that S_1 is linear. The distinction may not in fact be too significant since all calculations agree in predicting the potential surface for S_1 to be very flat for bending, the energy varying very little with bond angle over the range 120–180°.

The singlet–triplet separation (S_0–T_1) calculated here (28 kcal/mol) is in reasonable agreement with the calculations of Harrison and Allen[5a] (33 kcal/mol), Pople, *et al.*[5c] (37 kcal/mol), and Harrison[5d] (25 kcal/mol), and with an estimate (38 kcal/mol[19]) from electron impact studies.

Our calculations depend of course on the assumption

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(11) For a review, see M. J. S. Dewar, *Fortschr. Chem. Forsch.*, in press.

(12) (a) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970); (b) N. Bodor and M. J. S. Dewar, *ibid.*, **92**, 4270 (1970); (c) N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. D. Worley, *Tetrahedron*, 26, 4109 (1970); (d) M. J. S. Dewar and W. W. Schoeller, *ibid.*, 27, 4401 (1971); ; (e) M. J. S. Dewar, E. Haselbach, and S. D. Worley, *Proc. Roy. Soc., Ser. A*, **315**, 431 (1970); (f) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *Angew. Chem., Int. Ed. Engl.*, **9**, 738 (1970).

(13) (a) M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **91**, 7521 (1969); (b) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, **92**, 3505 (1970); (c) A. Brown, M. J. S. Dewar, and W. W. Schoeller, *ibid.*, **93**, 1481 (1971); (d) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4290, 4291, 4292 (1971); (e) M. J. S. Dewar and M. C. Kohn, *ibid.*, 94, 2704 (1972).

(14) M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. D*, 646 (1970).

(15) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 90, 1953 (1968).

(16) J. A. Nelder and R. Mead, *Computer J.*, 7, 308 (1964).

(17) M. J. S. Dewar and J. S. Wasson, unpublished work.

(18) G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).

(19) F. Field and J. A. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 117.

that our parametric treatment will allow adequately for electron correlation in carbene, using parameters derived from compounds of normal quadrivalent carbon. As a referee has pointed out, this seems not to be the case in linear CH_2 because we predict a separation of the S_0 ($^1A_1$) and S_1 ($^1B_1$) states of 23 kcal/mol whereas both should converge (to $^1\Delta_g$) as the bond angle increases to 180°. The correlation effects here are, of course, extreme since in a one-electron description of the S_0 state the HOMO and LUMO are degenerate. Evidently we overestimate the energy of S_0 by *ca.* 23 kcal/mol. The error should, however, decrease with decreasing bond angle. An additional estimate can be made from the excitation energy of singlet (S_0) carbene (bond angle, 102.4°) which we calculate to be 26 kcal/mol whereas the observed zero-zero transition is at about 1.5 eV (35 kcal/mol). Our estimate of the S_0–T_1 separation may therefore well be too large by about 10–12 kcal/mol, leading to an estimate in good agreement with that (22 kcal/mol) from a very recent and detailed *ab initio* study.[5e]

Recently Carr, Eder, and Topor[20] have claimed on the basis of photochemical studies that the singlet–triplet separation in carbene is very small (1–2 kcal/mol). The electron impact value[19] is admittedly quite uncertain since the species involved were not definitely identified while the *ab initio* calculations are open to the usual criticism that such procedures do not give acceptable estimates of heats of atomization. It is also possible that use of a larger basis set, in particular one including d AO's, might decrease the separation somewhat. However, the success of *ab initio* SCF methods in predicting the relative energies of small molecules[21] and the agreement between the *ab initio* values and the MINDO/2 calculations reported here make it very difficult to believe that the new low value can be correct. It seems likely that the singlet-triplet separation is not less than 15 kcal/mol and that the photochemical experiments must consequently have been misinterpreted.

In order to estimate the bending and stretching force constants, detailed calculations were carried out for about 40 different geometries for each state. The results were fitted to the following[22] quartic potential function.

$$2\delta E = F_{ii}(\delta S_i)^2 + F_{iii}(\delta S_i)^3 + F_{iiii}(\delta S_i)^4 \qquad (1)$$

Here δE is the change in energy due to change δS_i in the bond lengths or in the bond angle. The results are shown in Table II.

The average error in δE, found from eq 1 with the force constants of Table II, was 3–4%, except for points near the minimum where the accuracy is limited by that of the Simplex minimization, and for the bending force constant for S_1 (see below). The stretching constant (F_{11}) for S_0 is in good agreement with the values commonly found for CH bonds[23] and is greater, as one would expect, than the values calculated for T_1 and S_1. That for T_1 agrees quite well with the *ab initio* value of Bender, *et al.*[5b] (6.8 mdyn/Å). The bending constant for T_1 is also in reasonable agreement with the *ab initio*[5b] value (0.21 mdyn Å/rad^2).

Table II. Calculated Force Constants for Carbene

State	$F_{11} = F_{22}$, mdyn/Å	F_{33}, mdyn Å/rad^2
S_0	5.14	0.31
T_1	6.14	0.28
S_1	6.26	(0.14)

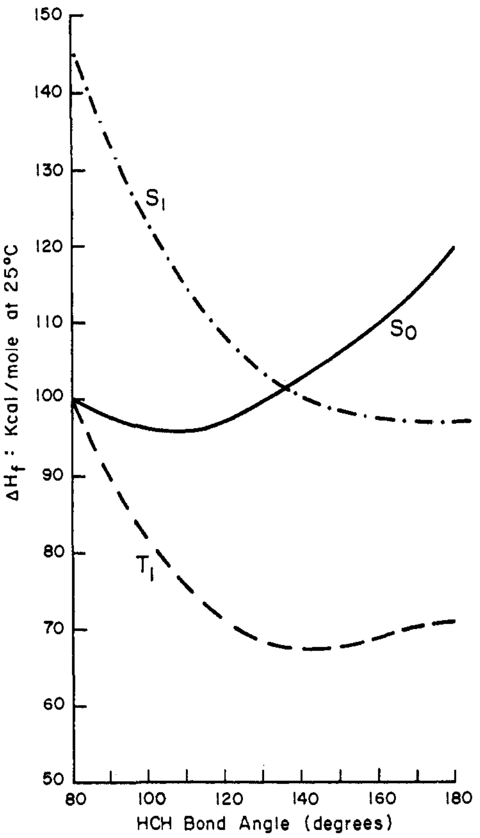

Figure 1. Plot of heat of formation (ΔH_f; kcal/mol at 25°) *vs.* HCH bond angle for S_0 (—), T_1 (- - -), and S_1 (-·-·).

Figure 1 shows a plot of heat of formation against bond angle for the three states. It will be seen that the plot for S_1 is very flat, being almost horizontal over the range 150–180°. Since a potential function of this form cannot be fitted by the expression of eq 1, our value for F_{33} (Table II) is not very significant.

The potential surfaces indicated in Figure 1 resemble those deduced by Harrison and Allen in the ordering of states and in the prediction that the S_0–T_1 separation should decrease with decreasing bond angle (θ). However, we differ from them in our prediction that S_0 and T_1 should actually cross at $\theta = 80°$. As a check on this we calculated the energies of the two states for some derivatives of carbene with the results shown in Table III.

Note that the S_0–T_1 separation in cyclopropylidene is, as predicted, much less than in carbene itself. The ground state is still predicted to be T_1 rather than S_0, even though the corresponding CCC bond angle is only *ca.* 60°; this, however, is not in disagreement with

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[20] R. W. Carr, Jr., T. W. Eder, and M. G. Topor, *J. Chem. Phys.*, **53**, 4716 (1970).

[21] L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).

[22] M. A. Parisean, I. Suzuki, and J. Overend, *J. Chem. Phys.*, **42**, 2335 (1965).

[23] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945.

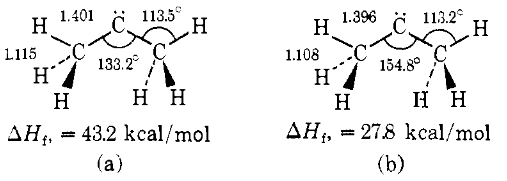
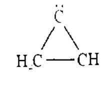
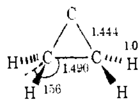
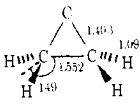
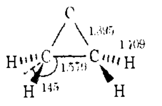
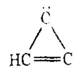
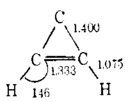
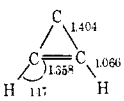
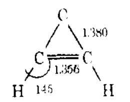
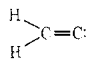
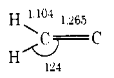
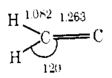
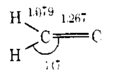


Figure 2. Bond lengths (Å), bond angles, and heats of formation (ΔH_f; kcal/mol at 25°) for states of dimethylcarbene: (a) S_0, (b) T_1.

Table III. Geometries and Heats of Formation of Carbenes

Compound	S_0	T_1	S_1
	Bond lengths (A), bond angles, and heats of formation (ΔH_f; kcal/mol at 25°) for states of carbene.		
	 ΔH_f 79.9	 77.6	 95.2
	 ΔH_f 97.8	 132.0	 149.5
	 ΔH_f 104.1	 124.6	 151.3

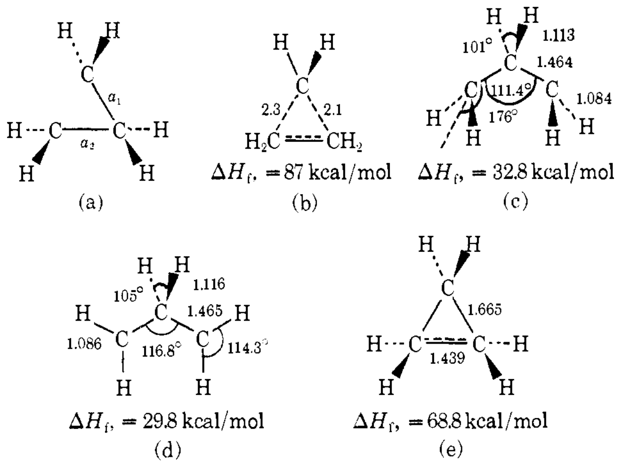


Figure 3. (a) Coordinates for the (C_2H_4 + CH_2 (T_1)) system; (b–e) bond lengths (Å) and heat of formation (ΔH_f; kcal/mol at 25°) for the transition state for addition (b), for the triplet trimethylene biradical in its ground state (c) and a twisted conformation (d), and for the transition state for interconversion of isomeric trimethylene biradicals (e).

the results indicated in Figure 2 since the relative energies of the states must depend on the types of bonds involved. In vinylidene, where the bond angle is formally zero, the ground state is predicted to be a singlet, a prediction which should be capable of test, at any rate in the case of appropriate derivatives. The ground state of cyclopropenylidene is also predicted to be a singlet; here, however, S_0 is selectively stabilized since it is in effect the conjugate base of the aromatic cyclopropenium ion whereas T_1 is analogously related to the nonaromatic cyclopropenyl radical.[24]

Calculations were also carried out for dimethylcarbene with the results indicated in Figure 2. Here the S_0–T_1 separation again decreased with decreasing bond angle, being small (~5 kcal/mol) over the range 80–120°.

B. Reactions of Carbene. It is well known[25] that the reactions of carbene are of considerable complexity, a variety of possible processes commonly taking place with comparable ease. This is due in part to the very great inherent reactivity of carbene, its reactions consequently having low activation energies so that the differences between different reactions are very small, and in part to the even greater reactivity of the "hot" carbene molecules produced by photolysis of diazomethane or ketene. The situation is further complicated by the possibility of deactivation of the initially formed S_0 carbene to the triplet (T_1) ground state so that products may be formed by reaction of either with suitable substrates. Here we report detailed calculations for the reaction of both S_0 and T_1 carbene with ethylene and methane, as prototypes of the characteristic addition and insertion processes.

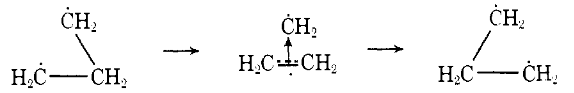
In studying these reactions we followed the usual expedient of plotting the energy as a function of a suitable reaction coordinate.[26] For each value of the reaction coordinate, the energy was minimized with respect to all the other geometric parameters by our Simplex procedure. In "normal" reactions,[25] where the reactants and products are linked by a single valley on the potential surface, a plot of the energy so calculated against the reaction coordinate will give a cross section of the potential surface along the lowest points in the valley linking reactants and products. The maximum in such a plot will then correspond to the transition state.

Preliminary studies indicated that the preferred mode of approach of triplet (T_1) carbene to ethylene was that indicated in Figure 3a, the system having a plane of symmetry passing through the carbon atoms and bisecting the methylene groups. The reaction coordinate (r_1) was taken to be

$$r_1 = a_1 - a_2 + 1 \qquad (2)$$

Figure 4 shows the reaction paths as a plot of energy against the reaction coordinate (r_1) of eq 2. The product of the reaction is predicted to be the trimethylene biradical, the triplet form of cyclopropane being unstable. The reaction is predicted to have an activation energy of 5 kcal/mol. Figure 3b shows the structure of the transition state A. Figures 3c and 3d show the structure of the product B in two conformations, the first corresponding to that of Figure 3a and the second to one derived from it by rotation of the "radical" methylene groups through 90°.

The resulting biradical can in principle undergo scrambling of the methylene groups *via* a π complex intermediate, *viz.* eq 3. The right-hand section of



(3)

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(24) See M. J. S. Dewar, *Tetrahedron Suppl.*, 8 (1), 75 (1966).

(25) H. M. Frey in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 217.

(26) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941.

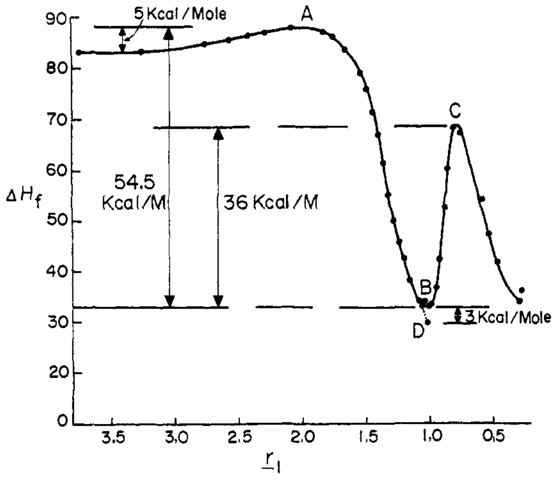

Figure 4. Plot of the calculated heat of formation (ΔH_f; kcal/mol at 25°) *vs.* the reaction coordinate r_1 (eq 2) for addition of triplet (T_1) carbene to ethylene and for rearrangement of the resulting biradical.

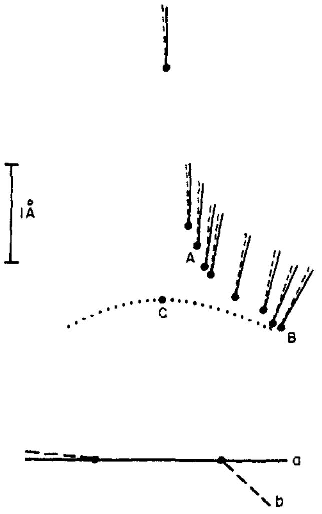

Figure 5. Geometry of approach of T_1 carbene to ethylene. The dots indicate successive positions of the carbon atom of the carbene and the attached tails the orientation of the hydrogen atoms. The carbene molecule is seen edge on, the full line representing the nearer CH bond and the dotted line the more distant one. The molecule lies in a plane perpendicular to the paper, *i.e.*, in a plane perpendicular to that bisecting the C=C bond. Lines a and b indicate the initial and final position of the hydrogen atoms at the central carbon atom of the resulting biradical $\cdot CH_2CH_2CH_2\cdot$. The dotted line indicates the reaction path for rearrangement of the biradical (eq 2), C being the transition state.

Figure 4 shows the corresponding reaction path. The calculated activation energy is very high (36 kcal/mol), implying that the rearrangement should not be observed in practice. This would, of course, be expected since the intermediate π complex (C) should contain one electron in an antibonding MO, a circumstance which explains the failure of radicals to undergo facile Wagner–Meerwein rearrangements.[27]

Figure 3e shows the structure of the π complex transition state C. The antibonding effect of the extra electron is seen very clearly from a comparison of this with the corresponding π complex from ethylene and methyl cation ("corner protonated cyclopropane") in which the CC distances (1.419 and 1.628 Å[28]) are much smaller.

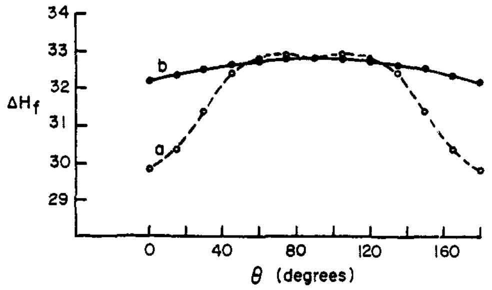

Figure 6. Plot of calculated heat of formation (ΔH_f; kcal/mol at 25°) *vs.* angle of twist (θ) of the terminal methylene groups from the C_3 plane in trimethylene biradical: (a) synchronous rotation of both methylenes, conrotatory and disrotatory; (b) one methylene is rotated, the other is fixed at θ = 90°.

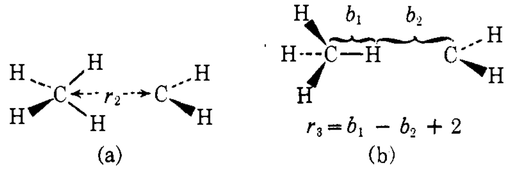

Figure 7. Reaction coordinates (r_2 and r_3) for the two modes of approach of triplet (T_1) carbene to methane. Distances in Å.

The geometry of the reaction path is indicated in Figure 5. The carbene initially approaches the ethylene symmetrically as though it were about to form the π complex of Figure 3e. Before doing so, however, it veers to one side, forming the biradical directly. There are therefore three distinct valleys on the potential surface, two analogous to that indicated in Figure 5 and leading directly to the two equivalent biradical products, and the third (indicated by a dotted line in Figure 5) linking the products *via* the symmetrical π complex of Figure 3e.

The conformation of Figure 3c is not the stable form of the biradical, that indicated in Figure 3d being lower in energy by 3.0 kcal/mol. The intermediate configuration, with one methylene perpendicular to the C_3 plane and one parallel to it, is 2.3 kcal/mol higher in energy than the stable planar form. Figure 6 shows the calculated potential surface for interconversion of isomeric planar structures by synchronous rotation of both methylenes and by rotation of one only. In the former case, no difference was found between disrotation and conrotation. The energies calculated here for the various species, and the geometry of the perpendicular biradical (Figure 3c), are in general agreement with the results of a recent very detailed *ab initio* study of the trimethylene system by Salem.[29]

The potential surface for the reaction of T_1 carbene with methane also contained two valleys. One corresponded to the mode of approach indicated in Figure 7a which should lead to direct insertion, the other to the mode of approach of Figure 7b which should lead to abstraction of hydrogen with formation of a pair of methyl radicals. Figure 7 also shows the reac-

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[27] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 18, C71 (1951); "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949; "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[28] N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **93**, 6685 (1971).

[29] L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970); *J. Chem. Soc. D*, 382 (1971).

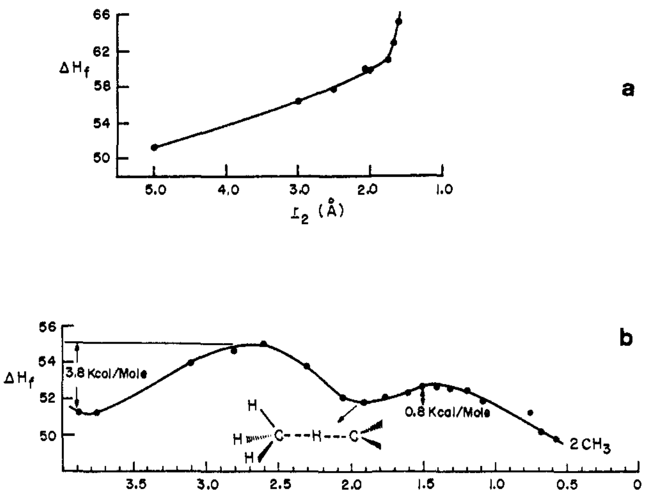

Figure 8. (a) Reaction path for the process indicated in Figure 7a; (b) corresponding path for Figure 7b.

tion coordinates (r_2 and r_3) used to calculate the corresponding reaction paths (Figure 8).

Although there is a valley in the potential surface corresponding to the mode of approach of Figure 7a, it does not lead anywhere. The energy rises steadily as the carbene approaches, neither abstraction nor insertion taking place (Figure 8a). The alternative mode of approach leads, however, to abstraction (Figure 8b) with the formation of two methyl radicals. The activation energy predicted for this process is 3.8 kcal/mol, close to that (5.0 kcal/mol; Figure 4) for addition of T_1 carbene to ethylene.

The reactions of triplet carbene have been studied in considerable detail.[30] It now seems to be generally agreed that triplet carbene adds to the double bond of olefins[31] in a nonstereospecific manner,[30a,32] indicating the formation of an intermediate trimethylene biradical. It also seems to be generally agreed[33] that triplet carbene reacts with paraffins by abstraction of hydrogen to form a methyl radical and an alkyl radical rather than by insertion. Products formally derived by insertion in fact arise by combination of the pairs of radicals formed initially by abstraction. Our calculations are of course in complete agreement with these results.

No estimates of the absolute activation energies of these processes are available. Competition studies indicate that the activation energies for addition to ethylene and for abstraction of hydrogen from methane are similar, again in agreement with our predictions, our calculated difference being too small to be significant.

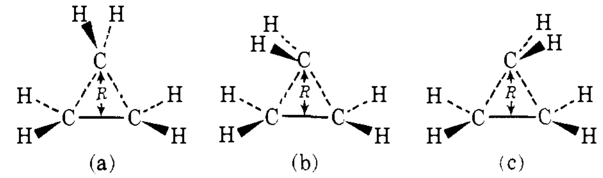

Figure 9. Three modes of approach of singlet carbene to ethylene that correspond to valleys on the potential surface.

Calculations were next carried out for the addition of singlet (S_0) carbene to ethylene. The potential surface for this reaction proved to be unexpectedly complicated, containing three distinct valleys that correspond to the modes of approach indicated in Figure 9. These were studied in the usual way, taking the distance (R) between the carbene carbon and the midpoint of the ethylene CC bond as the reaction coordinate (Figure 9).

Figures 10 and 11 show plots of energy *vs.* R for three possible modes of approach. In the first (Figure 10), the methylene carbon was constrained to approach in the plane bisecting the C=C bond. The optimum geometry for each value of R was as indicated in Figure 9a, having C_{2v} symmetry. While this path leads directly to the product (cyclopropane) in its ground state, it requires considerable activation (10 kcal/mol).

When no constraints were applied, the methylene carbon still preferred to approach in the plane bisecting the HCH angles of the ethylene. At larger values of R, there were two minima in the energy, separated by maxima and corresponding to the rotamers of Figure 9b and 9. In each case there is a plane of symmetry passing through the carbon atoms. Figure 11a shows the reaction path for approach *via* structures of the type of Figures 9b, and 11b the corresponding path for structures of the type of Figure 9c. The symbolism is that indicated in the caption to Figure 5. In neither case is any activation involved. As R decreases, the valley corresponding to the structure of Figure 9c fades out, the stable species at smaller values of R having structures corresponding to Figure 9b. The paths in Figures 11a and 11b merge at this point. As R decreases further, the valley corresponding to the species of Figure 9b in turn merges with that for the symmetrical approach (Figure 9a). The final sections of all three paths (Figures 10 and 11) thus coincide.

Skell, *et al.*,[34] have pointed out that since carbene is the conjugate base of methyl cation (CH_3^+), both should approach ethylene in a similar manner to form an intermediate π complex by interaction of the empty AO of CH_3^+ or CH_2 with the filled MO of ethylene (*cf.* ref 27). On this basis the preferred approach should be that corresponding to Figure 9b or 9c, not that of Figure 9a in which the filled π MO interacts with the filled lone-pair AO of the carbene. Skell, *et al.*, favored the approach of Figure 9c, a conclusion supported by Closs and Closs[35] and preliminary studies in these laboratories.[36]

Hoffmann[37] has pointed out that the approach of

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(30) See the following papers and papers cited in them: (a) T. W. Eder and R. W. Carr, Jr., *J. Phys. Chem.*, 73, 2074 (1969); (b) H. M. Frey and R. Walsh, *J. Chem. Soc. A*, 2115 (1970); (c) R. A. Cox and K. F. Preston, *Can. J. Chem.*, 47, 3345 (1969).

(31) S. Ho, I. Unger, and W. A. Noyes, *J. Amer. Chem. Soc.*, **89**, 5091 (1967); D. R. Ring and B. S. Rabinovitch, *J. Phys. Chem.*, 72, 191 (1968); C. McKnight, E. K. C. Lee, and F. S. Rowland, *Ber. Bunsenges. Phys. Chem.*, 72, 236 (1968); T. W. Eder and R. W. Carr, *J. Phys. Chem.*, 73, 2074 (1969); R. W. Carr and G. B. Kistiakowsky, *ibid.*, 70, 118 (1966).

(32) See W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 26.

(33) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *J. Amer. Chem. Soc.*, 82, 5001 (1960); 83, 1934 (1961); R. W. Carr, *J. Phys. Chem.*, 70, 1970 (1966); B. M. Herzog and R. W. Carr, *ibid.*, 71, 2688 (1967).

(34) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 78, 4496 (1956); P. S. Skell and A. Y. Garner, *ibid.*, 78, 5430 (1956).

(35) G. L. Closs and L. E. Closs, *Angew. Chem.*, 74, 431 (1962).

(36) M. J. S. Dewar and W. W. Schoeller, Combined Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 2, 1970, Paper 603.

(37) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

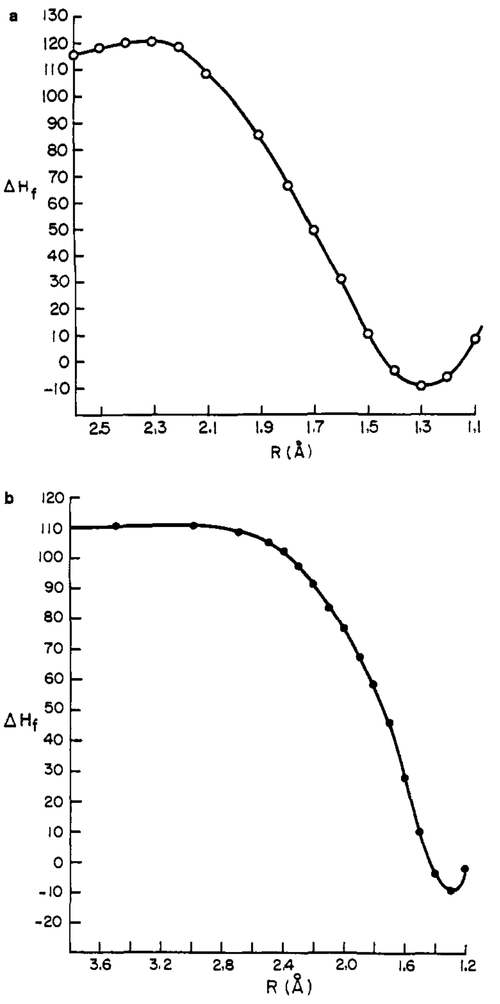

Figure 10. Plots of calculated heat of formation (ΔH_f; kcal/mol at 25°) *vs.* R (a) for the symmetrical approach of Figure 9a; (b) for the approach of Figure 9b.

Figure 9a should be "forbidden" in terms of the conservation of orbital symmetry. He also reported EH calculations that supported the approach of Figure 9b, at any rate for large values of R.

Our calculations support these predictions but indicate that the barrier to the "forbidden" reaction *via* Figure 9a is quite low. Indeed, since photolysis of diazomethane normally produces "hot" molecules of carbene with more than 10 kcal/mol of energy, this path may be feasible in the gas phase or in the case of intramolecular addition.

The plot of Figure 10b indicates that while no activation is involved in the reaction of carbene with ethylene, the energy begins to fall appreciably only when the reactants are closer than the sum of their van der Waals radii. The same is true for the approach of Figure 9c. Since geometries intermediate between the two are of higher energy, steric effects due to substituents could well introduce a low barrier to the path of Figure 9c. Although the overall reaction could still occur without activation, this would have the effect of circumscribing the required mode of approach and so decreasing the Arrhenius preexponential factor. Such an effect would of course account for the results of Closs and Closs without requiring the reaction to occur by the path of Figure 9c.

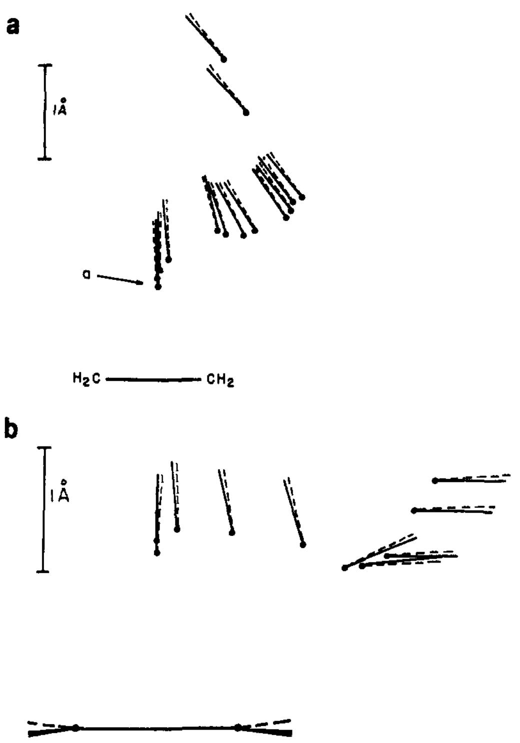

Figure 11. Reaction paths (*cf.* Figure 5) for the initial approach of (a) Figure 9b; (b) Figure 9c.

If the reaction is regarded as a pericyclic process, the approach of Figure 9b or 9c is favored according to Evans' principle[38] by the fact that the corresponding transition states are aromatic (isoconjugate with cyclopropenium cation) whereas that for the approach of Figure 9a is antiaromatic (isoconjugate with cyclopropenium anion). In this case, however, the product corresponds to the "forbidden" antiaromatic reaction. The form of the potential surface, with two distinct valleys corresponding to reactant and product, respectively, is therefore analogous to those recently observed in other antiaromatic reactions and interpreted in terms of Evans' principle.[39] Here the effect is less striking because the overall reaction is so extremely exothermic that the valleys merge without incident.

We have also carried out calculations for the reaction of singlet carbene with methane. This reaction has recently been studied by Hoffmann, *et al.*,[9] using the extended Hückel method. They concluded that insertion takes place by the abstraction–combination mechanism suggested by Benson,[40] transfer of hydrogen from methane to carbene taking place while the carbon atoms are 2.5 Å apart and the rest of the reaction path apparently resembling that for combination of a pair of methyl radicals (which they also calculated). They found the insertion reaction to have an activation energy of 7 kcal/mol; however, as they point out, this could have been an artifact of the procedure used in which fixed values were assigned to most of the geometrical parameters, no attempt being made to minimize the energy by varying them.

Preliminary studies[36] had shown that MINDO/2 pre-

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[38] See M. J. S. Dewar, *Angew. Chem.*, 83, 859 (1971).

[39] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 93, 4291, 4292 (1971).

[40] S. W. Benson, *Advan. Photochem.*, 2, 1 (1964); W. B. Moore and S. W. Benson, *ibid.*, 2, 219 (1964).

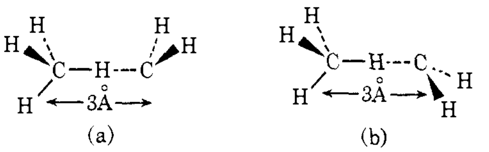

Figure 12. Geometries minimizing the energy of the system (CH_4 + (singlet)CH_2) when the carbon atoms are 3.0 Å apart.

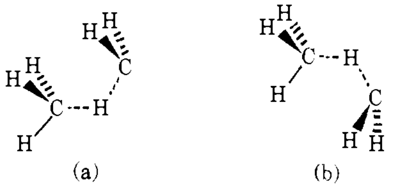

Figure 13. A later stage in the reactions *via* (a) eclipsed and (b) staggered conformations, the CC distance being 2.0 Å.

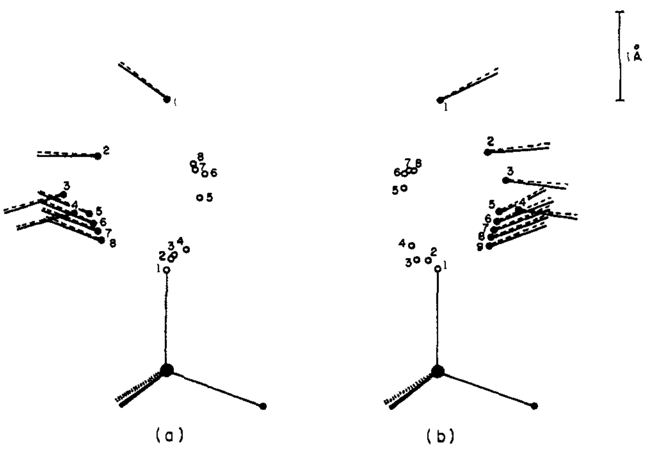

Figure 14. Calculated reaction paths for insertion of singlet carbene into methane. The numbers indicate successive positions of the carbene carbon and the hydrogen of the methane undergoing insertion. Path a leads to eclipsed ethane, path b to staggered ethane.

dicts insertion to take place by a concerted mechanism by sideways attack by carbene on a CH bond of methane. We have now studied the reaction path in detail, using the CC bond distance as the reaction coordinate.

The preferred initial approach by the carbene is along the axis of the CH bond (Figure 12), as suggested by Benson[40] and in agreement with the results of Hoffmann, *et al.*[9] However, we find that there are two alternative minima for each CC distance, corresponding to conformations in which the CH bonds are eclipsed and staggered, respectively (Figure 13a,b).

At *ca.* 3.0 Å the methylene moves to one side or the other of the CH bond undergoing attack (Figure 13), depending on whether the CH bonds are staggered (*i.e.*, Figure 12a → Figure 13a) or eclipsed (*i.e.*, Figure 12b → Figure 13b).

In the range of CC distances between 2.0 and 1.9 Å the relevant hydrogen atom of methane moves across to the carbene carbon, giving a stretched form of eclipsed or staggered ethane. The detailed course of the reaction is illustrated in Figure 14 which indicates the geometry of the system at various points along the reaction path. Here there is no question of the reaction not being concerted since the transfer of hydrogen occurs only when the carbon atoms are well within bonding distance.

The results reported here differ from those of Hoffmann, *et al.*, in two main respects, *i.e.*, the distance at which hydrogen is transferred from the methane carbon to the carbene one, and our prediction that the potential surface contains two distinct valleys corresponding to formation of eclipsed and staggered ethane. The latter discrepancy may well have been due to the fact that Hoffmann, *et al.*, did not minimize their energies with respect to all parameters. The former probably reflects an apparently general failing of the EH method, *i.e.*, its tendency to favor nonbonded structures over bonded ones.[41]

Figure 15 shows plots of the calculated heats of formation against the carbon–carbon distance (r) for the two paths (eclipsed and staggered) leading to insertion. It will be seen that neither reaction involves any activation. The sudden change in slope at r = 2.0 Å corresponds to the point where the hydrogen of methane migrates to the carbene carbon (see points 4 and 5 in Figure 14). The migration takes place with little change in the CC distance but involves a large decrease in energy.

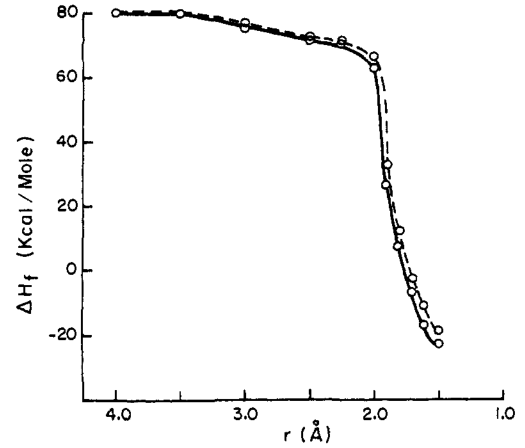

Figure 15. Plot of calculated heats of formation *vs.* the C–C distance for the eclipsed (····) and staggered (–) paths for insertion of singlet carbene into methane.

No activation energies have been measured for the insertion of singlet carbene into CH bonds but the lack of selectivity shown in these reactions indicates that the activation energies must be very small. Different CH bonds react at virtually identical rates unless steric effects are present.

It should perhaps be added that the detailed shapes of potential surfaces may not be very relevant in a mechanistic sense in cases where no activation is involved, for it is very unlikely that the heat liberated during the reaction will be dissipated so rapidly that the reaction will follow the bottom of the valley leading downhill to the product.

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(41) A good example is provided by the methyl isocyanide–acetonitrile rearrangement where EH predicts[42] the transition state to be an ion pair whereas MINDO/2 predicts[43] it to be a π complex. The experimental evidence favors[43] the latter.

(42) G. W. Van Dine and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 3227 (1968).

(43) M. J. S. Dewar and M. C. Kohn, *ibid.*, **94**, 2704 (1972).