

Ground States of Molecules. XX.¹ MINDO/2 Study of Some Carbenes and Their Intramolecular Rearrangements²

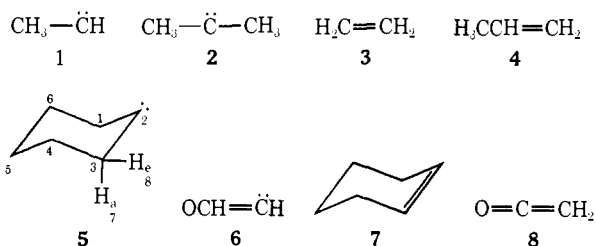
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Abstract: The MINDO/2 method has been used to study the structures of methylcarbene (1), carbenacyclohexane (\equiv cyclohexylidene, 5), and formylcarbene (6) and the course of their intramolecular rearrangements to ethylene (3), cyclohexene (7), and ketene (8), respectively. Methylcarbene is predicted to be strongly stabilized (by *ca.* 1 eV) by hyperconjugation, and the rearrangements are predicted to involve migration of hydrogen *gauche* to the methine group.

We have recently shown¹ that the MINDO/2 method⁴ gives good estimates of the heats of atomization and geometries of singlet (S_0 , S_1) and triplet (T_1) carbene and also a good account of the reactions leading to insertion of singlet (S_0) and triplet (T_1) carbene into the CH bonds of methane and their addition to the C=C bond of ethylene. The MINDO/2 method thus seems to be applicable to carbenes as well as to "normal" molecules.

While carbene itself readily undergoes insertion and addition reactions, methylcarbene (1) and dimethyl-



carbene (2) fail to react in this way, rearranging instead to ethylene (3) and propene (4), respectively.⁵ Carbenacyclohexane (\equiv cyclohexylidene, 5) and formylcarbene (6) behave likewise, 5 rearranging to cyclohexene (7) and 6 to ketene (8) instead of undergoing normal insertion or addition.

These rearrangements were of interest to us for four reasons. In the first place, some preliminary calculations⁶ in these laboratories had suggested that 1, 2, and 6 might possess rather unusual "nonclassical" structures, intermediate between the carbene and its rearrangement product. If so this could of course account for the tendency of these compounds to rearrange in preference to anything else. Secondly, the rearrangements of alkylcarbenes present an interesting conformational problem, seen most clearly in the conversion of 5 to 7. The reaction can involve migration either of axial (H_a in 5) or equatorial (H_e in 5) hydrogen. It is difficult to predict on the basis of intuition or simple

MO theory which, if either, of these alternatives should be preferred. Thirdly, we had heard⁷ that this problem was being studied experimentally. Fourthly, since we had taken care not to find out the results of these investigations in advance, this seemed an entertaining opportunity to test the predictive powers of MINDO/2.

Procedure

The MINDO/2 method is now well established.⁸ The calculations reported here were carried out using the parameters of part X.^{4b} The geometry of each structure was chosen to minimize the energy with respect to all geometrical parameters using a procedure developed by Brown⁹ and modified by Wasson,¹⁰ based on the Simplex algorithm.¹¹

The rearrangements were followed by the procedure developed in earlier papers of this series⁸ in which one uses as a reaction coordinate some geometrical parameter that varies monotonically during the reaction. For each value of the reaction coordinate the energy is minimized with respect to all other geometrical variables. A plot of energy *vs.* the reaction coordinate will then normally give a cross section of the potential surface along the bottom of the valley linking the reactants and products, corresponding to the "easiest" path for the reaction.

For convenience, the calculated heats of atomization have been converted to heats of formation using the following values for the heats of formation of gaseous carbon and hydrogen atoms: C, 170.89; H, 52.102 kcal/mol.

Since we were concerned here with the rearrangements of carbenes by hydrogen migration, and since such a rearrangement could occur in a triplet only by an intersystem crossing, calculations were carried out only for closed shell singlet forms of the carbenes since these should be the lowest singlet states (*cf.* ref 1).

Results and Discussion

Calculations were first carried out for methylcarbene (1). Figure 1 shows the geometry and heat of formation given by the Simplex minimization. As we shall see presently, this is predicted to be at best a marginally

(1) Part XIX: N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Amer. Chem. Soc.*, **94**, 9095 (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) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, E. Haselbach, and A. Harget, *ibid.*, **92**, 3854 (1970).

(5) See W. Kirmse, Ed., "Carbene Chemistry," Academic Press, New York, N. Y., 1964; *Progr. Org. Chem.*, **6**, 164 (1964).

(6) Unpublished work by Dr. W. W. Schoeller.

(7) Professor Alex Nickon, personal communication.

(8) For a review see M. J. S. Dewar, *Fortschr. Chem. Forsch.*, **23**, 1 (1972).

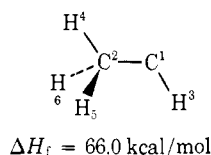
(9) See A. Brown, M. J. S. Dewar, and W. W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).

(10) J. S. Wasson, unpublished work; see ref 1.

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

Table I. Calculated Formal Charges in Methylcarbene

Atom	1	2	3	4	5	6
Formal charge	-0.0952	+0.1472	-0.0113	-0.0356	-0.0106	+0.0055



Bond length, Å	Bond angle	Dihedral angle
$\bar{12} = 1.414$	$\bar{213} = 120.3^\circ$	$\bar{4213} = 173.7^\circ$
$\bar{13} = 1.101$	$\bar{124} = 111.9^\circ$	$\bar{5213} = 51.8^\circ$
$\bar{24} = 1.108$	$\bar{125} = 110.5^\circ$	$\bar{6213} = 295.8^\circ$
$\bar{25} = 1.106$	$\bar{126} = 113.2^\circ$	
$\bar{26} = 1.108$		

Figure 1. Calculated geometry and heat of formation (ΔH_f) at 25° for methylcarbene (**1**). Here and subsequently the dihedral angle $ijkl$ is defined as the angular displacement of kl relative to ij , measured anticlockwise along the direction $j \rightarrow k$.

stable structure. It does, however, correspond nicely to that expected for "classical" **1**. The usual^{1,4,6} correction of 0.1 Å has been applied to CH bond lengths.

The heat of formation of methylcarbene is not known. If the CC bond is localized,¹² the heats of formation (ΔH_f) of **1** and carbene itself should differ by about the same amount as the corresponding difference (7.9 kcal/mol¹³) between ethylene and propene. The difference between the values calculated for **1** and for carbene¹ is, however, 30 kcal/mol. The discrepancy seems far too large to be due to any failing of MINDO/2 and suggests that there may be a very strong interaction between the methyl group and the carbenoid center. If so, this could of course be one of the factors responsible for the reduced carbenoid activity of **1**.

Since **1** is the conjugate base of the ethyl cation there should be a strong hyperconjugative interaction between the empty carbenoid 2p AO and the appropriate adjacent CH bonds (*i.e.*, $\bar{25}$ and $\bar{26}$ in Figure 1). The same type of interaction occurs in the ethyl cation, $C_2H_5^+$, the heat of formation of which is consequently less by 41 kcal/mol¹⁴ than that of CH_3^+ . The corresponding interaction in **1** should of course be less than in $C_2H_5^+$ because it leads to separation of charge ($CH_3^{\delta+}-CH^{\delta-}$). This, however, might be partly counterbalanced by a second hyperconjugative interaction between the remaining CH bond ($\bar{24}$ in Figure 1) and the carbenoid lone pair, leading to a transfer of charge in the opposite direction and resulting in a kind of hyperconjugative backcoordination. The calculated formal charges in **1**, shown in Table I, do indeed follow this pattern. There is a large net transfer of charge from methyl to methine, due to hyperconjugation involving the empty 2p AO, and at the same time H(4)

(12) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 140.

(13) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

(14) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Bureau of Standards, Washington, D. C., 1969.

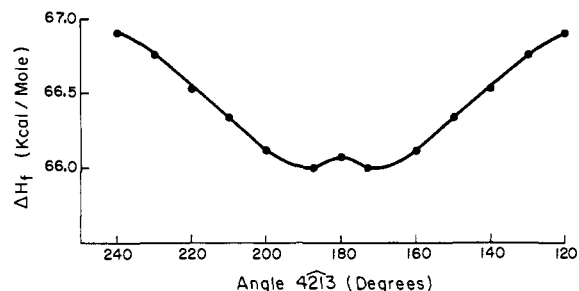


Figure 2. Plot of calculated heat of formation (ΔH_f) vs. the dihedral angle $\bar{4213}$ (Figure 1) for rotation about the CC bond in methylcarbene.

is more negative than H(5) or H(6). It therefore seems very likely that our calculation is correct in predicting a large stabilization of **1** by hyperconjugation, the magnitude of this (~ 22 kcal/mol relative to ethylene/propene; see ref 12) being about two-thirds that (~ 33 kcal/mol) in the ethyl cation.

Intuitively one might have expected **1** to have a strictly staggered conformation, H(3) being trans to H(4). The corresponding dihedral angle ($\bar{4213}$) is not, however, equal to 180° . This asymmetry is also reflected by the charges at H(5) and H(6) in Table I. To check this curious result we calculated the heat of formation as a function of the dihedral angle $\bar{4213}$. The results are shown in Figure 2. It will be seen that the symmetrical eclipsed ($\bar{4213} = 120$ or 240°) forms represent maxima in the energy, the two minima being slightly twisted forms of the staggered conformer. The calculated barrier to rotation (0.9 kcal/mol) is probably too low since MINDO/2 tends² to underestimate such barriers. The value found by Hoffmann, *et al.*,¹⁵ from an extended Hückel calculation (0.6 kcal/mol) is even lower.

Next we studied the rearrangement of **1** to ethylene **3** by migration of "cis" hydrogen (atoms 5 and 6 in Figure 1) or "trans" hydrogen (atom 4). The reaction coordinate was in each case the corresponding HCC angle ($\bar{125}$ or $\bar{124}$ in Figure 1). In the former, the hydrogen migrates toward the empty 2p AO of the carbenoid center, in the latter toward the filled lone pair AO. On this basis one might perhaps expect cis migration to be favored, the two processes resembling Wagner-Meerwein type rearrangements of a carbonium ion and a carbanion, respectively.¹⁶

Figure 3 shows plots of the calculated heat of formation (ΔH_f) against the reaction coordinate for each of the two modes of rearrangement. It will be seen that rearrangement by cis migration is predicted to require little or no activation, **1** being only marginally stable to this reaction. Indeed, the structure in Figure 1 may not even represent a minimum in the potential surface but merely a very flat maximum. The SIMPLEX

(15) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

(16) See M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949; "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965).

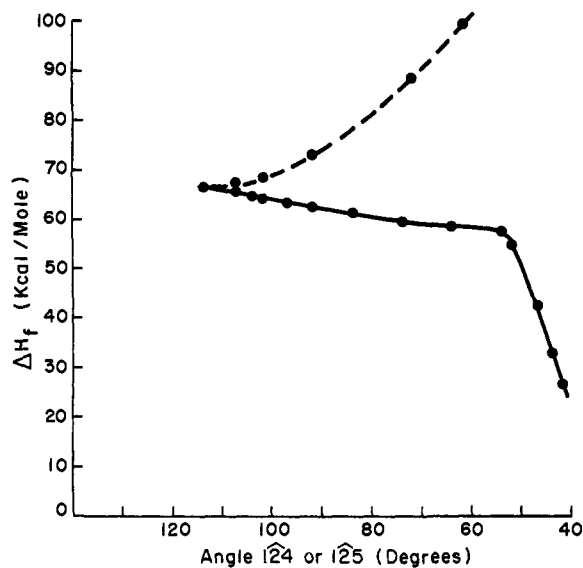


Figure 3. Plot of calculated heat of formation (ΔH_f) against the appropriate reaction coordinate ($\angle 125$ or $\angle 124$) for the rearrangements of methylcarbene (1) to ethylene (3) by cis (-) or trans (- -) migration of hydrogen.

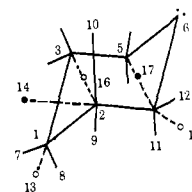
procedure can converge in such cases. On this basis one would expect **1** to rearrange to **3** in the time of a molecular vibration. The failure of **1** to give normal carbenoid reactions is then easily understood. It is also easy to see why the preliminary studies⁶ led to the incorrect prediction that **1** has a nonclassical structure. The potential surface for the cis rearrangement is almost flat in the region near $\angle 124 = 60^\circ$ and the original version⁹ of SIMPLEX was even more prone to give false solutions in such cases than the improved one¹⁰ used here.

The situation is, however, quite different for trans migration. This is predicted (see Figure 3) to be a very unfavorable process. Indeed, we could study it only by enforcing retention of the trans geometry by keeping the dihedral angle 3124 fixed. Otherwise rotation occurred about the CC bond, converting the trans migration into a cis one. In the enforced trans geometry, the energy rises steadily as the reaction proceeds. One would therefore predict cis migration to be the favored mode of rearrangement in cases where rotation about the CC bond is inhibited.

Such rotation is indeed inhibited in carbenacyclohexane (**5**) by the barrier to conformational inversion of the six-membered ring. As a first step to studying the corresponding rearrangement of **5** to cyclohexene (**7**), we first calculated the geometries and heats of formation of **5** and **7**. The results are shown in Figures 4 and 5. The geometries were optimized with respect to all geometrical parameters except for the lengths of two of the CH bonds in **7**.

The original version of MINDO/2 predicted cyclohexane to be too stable by *ca.* 10 kcal/mol. The same is true of cyclohexene ($\Delta H_f(\text{expt}) = 1.7$ kcal/mol¹³). The fact that both differences are similar suggests that the error will probably remain much the same for other similar compounds, in particular **5**.

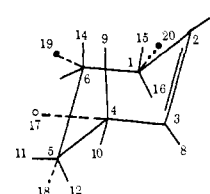
If we are correct in deducing that **1** is highly stabilized by hyperconjugation, **5** should be stabilized to a still greater extent since it is an analog of **2**. The compari-



$$\Delta H_f = 39.2 \text{ kcal/mol}$$

Bond lengths, Å	Angles, deg
$\overline{12}$, 1.514	$\overline{213}$, 109.6; $\overline{11,4,12}$, 105.4
$\overline{24}$, 1.529	$\overline{124}$, 111.7; $\overline{42,14}$, 127.3
$\overline{46}$, 1.454	$\overline{246}$, 107.8; $\overline{64,15}$, 126.8
$\overline{17}$, 1.119	$\overline{465}$, 115.2; $\overline{1,16,17}$, 129.9
	$\overline{718}$, 106.6; $\overline{6,17,16}$, 122.9
	$\overline{92,10}$, 102.0;

Figure 4. Calculated heat of formation (ΔH_f), bond lengths, and angles in pentamethylenecarbene (**3**). Here 13, 14, and 15 are dummy atoms lying on lines bisecting the corresponding HCH angles and 16 and 17 are the midpoints of lines joining atoms 2 and 3, and atoms 4 and 5, respectively.



$$\Delta H_f = -9.7 \text{ kcal/mol}$$

Bond lengths, Å	Angles, deg
$\overline{12} = \overline{34} = 1.451$	$\overline{123} = \overline{234} = 122.2$
$\overline{23} = 1.307$	$\overline{345} = \overline{216} = 112.6$
$\overline{16} = \overline{45} = 1.489$	$\overline{456} = 111.4$
$\overline{56} = 1.485$	$\overline{127} = \overline{438} = 116.7$
$\overline{27} = 1.085$	$\overline{54,17} = \overline{61,20} = 115.1$
$\overline{4,10} = \overline{5,11} = 1.119$	$\overline{65,18} = \overline{56,19} = 124.8$
	$\overline{94,10} = \overline{15,1,16} = 102.2$
	$\overline{11,5,12} = \overline{13,6,14} = 99.8$
Dihedral angles (see Figure 1)	
	$\overline{1234} = 19.6^\circ$
	$\overline{2345} = \overline{3216} = 332.1^\circ$

Figure 5. Calculated geometry and heat of formation (ΔH_f) for cyclohexene. The $\overline{4,10}$ and $\overline{5,11}$ bond lengths were assumed to be 1.119 Å.

Table II. Comparisons of Calculated Heats of Formation^a

Hydro-carbon	ΔH_f	Carbene	ΔH_f	Diff	Stabilizn
CH ₄	-16.2 ^b	CH ₂	95.8	112.0	
C ₂ H ₆	-22.8 ^b	CH ₃ -CH	66.0	88.8	23
C ₆ H ₁₂	-36.2 ^c	C ₆ H ₁₀	39.2	75.4	37

^a ΔH_f ; kcal/mol at 25°. ^b Reference 4b. ^c N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **92**, 4270 (1970).

sons in Table II suggest that this is the case. The last column of Table II gives estimates of the overall stabilizing effect of substitution in carbene, including both the contributions of changing CC bond type¹² and hyperconjugation.

To study the rearrangement of **5** to **7** in complete detail would involve a huge amount of computation

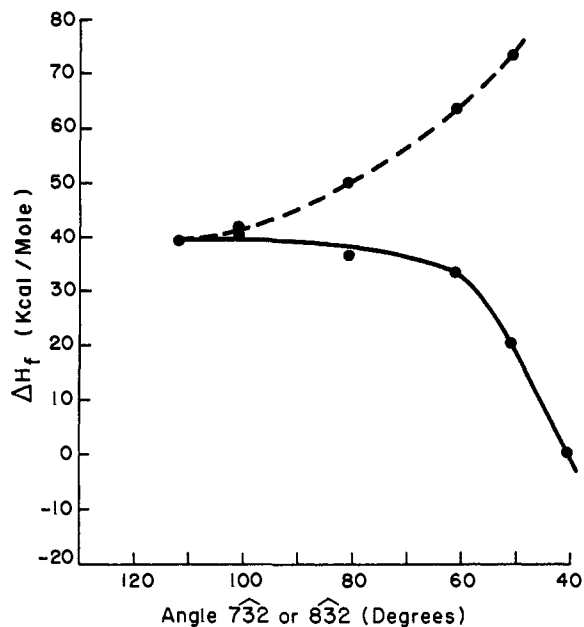


Figure 6. Plots of heat of formation (ΔH_f) against the angles $\widehat{732}$ or $\widehat{832}$ for rearrangement of **5** to **7** by migration of axial (—) or equatorial (· · ·) hydrogen.

since the system has no symmetry whatsoever. Forty-eight independent geometrical variables would be involved. It was for this reason that we assumed the lengths of two of the CH bonds in calculating the geometry of **5** (see Figure 5). However the results for the rearrangement of **1** to **3** had indicated a very large difference between the cis and trans routes and our main purpose was merely to see whether this difference extends to the rearrangement of **5** to **7**. In this limited context it seemed reasonable to make certain assumptions concerning the geometry of the part of the molecule not adjacent to that taking part in the reaction since the errors so introduced seemed likely to be similar for both modes of rearrangement.

We therefore assumed that the lengths of the bonds between carbon atoms 1, 2, 3, and 5 in the notation of Figure 4 (*i.e.*, $\overline{12}$, $\overline{13}$, $\overline{35}$) were the same throughout, having the same values as in cyclohexene, that the lengths of CH bonds formed by those atoms were likewise constant, and that the corresponding HCH bond angles were also constant. All the remaining bond lengths and bond angles, and all the dihedral angles, were varied.

Calculations were carried out for migration of axial hydrogen (atom 7) and equatorial hydrogen (atom 8),

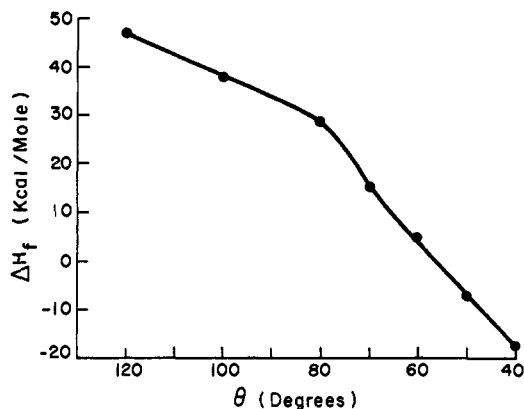


Figure 7. Plot of heat of formation (ΔH_f) vs. the H-C-CH angle (θ) for rearrangement of formylcarbene (**4**) to ketene (**6**).

the reaction coordinates being respectively the angles $\overline{732}$ and $\overline{832}$ (*cf.* structure **5**). Figure 6 shows plots of energy against these coordinates for the two modes of rearrangement. It will be seen that they duplicate the essential features of Figure 3. There is an overwhelming preference for migration of the axial hydrogen, corresponding to the cis migration in **1**. The difference between the two routes may of course be reduced by leakage from one to the other by proton tunnelling; even so we feel that it is large enough for a rather confident prediction that rearrangement of **3** must be highly stereospecific, only axial hydrogen migrating so long as the conformational integrity of the ring is maintained.

Note that the point at $\overline{732} = 100^\circ$ in Figure 6 implies a small activation energy (1.4 kcal/mol) for the axial rearrangement. This, however, may well be due to our failure to optimize the geometry completely. To do so would have required an unreasonable amount of computer time. Even with the simplifying assumptions indicated above, the calculation of each point in Figure 6 took 35 min on a CDC 6600 computer.

The last calculation was concerned with formylcarbene (**6**). This was predicted to be definitely unstable with respect to rearrangement to ketene (**8**). Figure 7 shows a plot of the calculated heat of formation (ΔH_f) of **6** as a function of the H-C-CH angle (θ) which should have a value of *ca.* 120° for **6** itself. It will be seen that ΔH_f decreases steadily and rather rapidly with decreasing θ , implying that **6** should probably start to rearrange even during its formation. The available experimental evidence is consistent⁵ with this, no products other than **8** having been observed in reactions producing singlet **6**.