

An *Ab Initio* Study of Methylcarbene and the Stereochemistry of Its Rearrangement to Ethylene

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

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada. M5S 1A1. Received October 15, 1973

Abstract: Nonempirical LCAO-MO-SCF calculations employing a double ζ basis set have been carried out to study two cross-sections of the potential surface of methylcarbene. It was found that methylcarbene has a singlet ground state with an (S_0 - T_1) separation of 0.3 kcal/mol. Calculations were also performed for ethylene and various possible transition-state structures through which the rearrangement of methylcarbene to ethylene may occur. The results suggest that this rearrangement involves the migration of a methyl hydrogen gauche to the methine proton.

Divalent reactive intermediates such as carbenes are of great theoretical interest,¹⁻⁴ since it is conceivable that these may exist either in a singlet or in a triplet state.

The simplest carbene, methylene, has been studied extensively.^{1,2,5,6} Calculations on this molecule have been reported by several workers,^{1,2} all of them predicting a triplet ground state with a singlet-triplet (S_0 - T_1) separation in the range of 25-37 kcal/mol. Experimental observations⁶ are in good agreement with the above. The reactions of methylene have also been studied. Theoretical calculations have been carried out^{2,3} for the mechanism and stereochemistry of insertion and addition.

Other carbenes, however, prefer to rearrange *via* a 1,2-shift of a vicinal hydrogen rather than undergo the above reactions.⁷ An example is methylcarbene (**1**) which rearranges to ethylene (**2**). This reaction could



occur in a variety of ways depending upon the electronic state of the reactant and the state in which the ethylene is produced.⁴ The stereochemistry of the above process was studied by Tee,⁴ who, on the basis of least motion calculations,⁸ predicted that the reaction will most probably involve a triplet methylcarbene rearranging to a "twisted" triplet ethylene. However, least motion calculations consider solely the geometries of the various

reactant and product conformations, and neglect the energy differences between them. Furthermore, prior to this publication, neither the nature and the energy of the ground state of methylcarbene nor the magnitude of separation between its various electronic states had been firmly established. Consequently, the predictions of the PLM approach⁸ are valid only if the energy differences between singlet and triplet methylcarbene are smaller than the differences in energies of the various transition states leading to the formation of the products.

Recently, Dewar reported⁹ the results of MINDO/2 type of calculations on methylcarbene. He also investigated the stereochemistry of hydrogen migration, but considered only one of the possibilities, namely the rearrangement of singlet methylcarbene to ground-state ethylene.

The purpose of our investigation was to study some of the cross-sections of the potential energy hypersurface of methylcarbene and thus examine the energetics of the various stereochemical possibilities of its rearrangement.

Computational Details

Nonempirical LCAO-MO-SCF calculations have been carried out on an IBM 370/165 computer using the IBMOL-IV system.¹⁰ With the exception of the preliminary work, all calculations employed a double ζ basis set optimized by Dunning¹¹ as shown in Table I.

Table I. Contracted^a Gaussian Basis Set for Hydrogen and Carbon

Hydrogen s set		Carbon s set		Carbon p set	
Exponents	Coefficients	Exponents	Coefficients	Exponents	Coefficients
19.2406	0.032828	4232.6100	0.002029	18.1557	0.018534
2.8992	0.231208	634.8820	0.015535	3.9864	0.115442
0.6534	0.817238	146.0970	0.075411	1.1429	0.386206
0.1776	1.000000	42.4974	0.257121	0.3594	0.640089
		14.1892	0.596555	0.1146	1.000000
		1.9666	0.242517		
		5.1477	1.000000		
		0.4962	1.000000		
		0.1533	1.000000		

^a Contracted functions are indicated in boldface type.

(9) N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9103 (1972).

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

(11) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

(1) For recent *ab initio* calculations, see (a) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969); (b) C. F. Bender and J. F. Shaefter III, *ibid.*, **92**, 4984 (1970); (c) S. Y. Chu, A. K. O. Siu, and E. F. Hayes, *ibid.*, **94**, 2969 (1972), and references therein.

(2) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Amer. Chem. Soc.*, **94**, 9095 (1972).

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

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

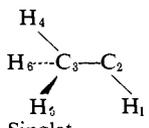
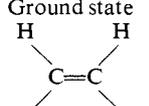
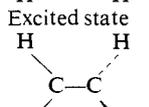
(5) (a) R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965); (b) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 1015 (1962); (c) R. J. Cvetanovic, H. E. Avery, and R. S. Irwin, *J. Chem. Phys.*, **46**, 1993 (1967); (d) T. W. Eder and R. W. Carr, Jr., *J. Phys. Chem.*, **73**, 2074 (1969); (e) D. F. Ring and B. S. Rabinovitch, *Int. J. Chem. Kinet.*, **1**, 11 (1969).

(6) (a) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961); (b) E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970); (c) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970).

(7) For some recent reviews on carbene chemistry, see (a) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969; (b) D. Bethell, *Advan. Phys. Org. Chem.*, **7**, 153 (1969); (c) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(8) For the development of the calculations applying the Principle of Least Motion (PLM), see (a) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966); (b) O. S. Tee, *ibid.*, **91**, 7144 (1969).

Table II. Molecular Parameters Used for Calculation of Geometries

Molecule	Bond	Length, Å	Bond angle, deg
Methylcarbene			
 Singlet	C ₂ -C ₃	1.48 ^c	
	C ₂ -H ₁	1.10 ^c	C ₃ H ₂ H ₁ 90 ^a
Triplet	C ₃ -H _{4,5,6}	1.104 ^c	C ₂ C ₃ H _{4,5,6} te ^b
	C ₂ -C ₃	1.46 ^c	
	C ₂ -H ₁	1.078 ^d	C ₃ C ₂ H ₁ 90 ^a
	C ₃ -H _{4,5,6}	1.104 ^c	C ₂ C ₃ H _{4,5,6} te ^b
Ethylene			
Ground state 	C-C	1.337 ^e	
	C-H	1.086 ^f	HCH 117.36
Excited state 	C-C	1.63 ^e	HCH 120
	C-H	1.086 ^f	
Transition state Structure I Structure II Structure III	For atomic coordinates see Table III		

^a This angle was used as a reaction coordinate. Lowest value used is shown above. ^b te = tetrahedral $\approx 109.5^\circ$. ^c Assumed value based on J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963), and ref 9. ^d G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971). ^e W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966). ^f H. C. Allen, Jr., and E. L. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958).

For the preliminary calculations on methylcarbene the SCF MO were expanded in terms of a minimal basis set which in turn was contracted to form a set of primitive Gaussian type functions suggested by Klessinger.¹²

The energies of the excited states were calculated by the virtual orbital technique¹³ using

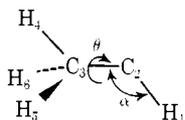
$${}^1E_1 = E_0 + (\epsilon_a - \epsilon_b) - J_{ba} + 2K_{ba}$$

$${}^3E_1 = E_0 + (\epsilon_a - \epsilon_b) - J_{ba}$$

where J_{ba} and K_{ba} are the two-electron integrals over the molecular basis and a and b are the virtual and occupied MO involved in the excitation, respectively.

Results and Discussion

Conformation of Methylcarbene. The two most important internal coordinates of methylcarbene are



α , the C₃C₂H₁ bond angle leading to the in-plane inversion about the methine carbon, and the dihedral angle θ , responsible for the torsional mode of motion along the C-C bond. Consequently, our theoretical study involved the examination of the two cross-sections $E = E(\alpha)$ and $E = E(\theta)$ of the rotation-inversion potential surface $E = E(\alpha, \theta)$ of methylcarbene.

(12) M. Klessinger, *Theor. Chim. Acta*, **15**, 353 (1969).

(13) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 161 (1951).

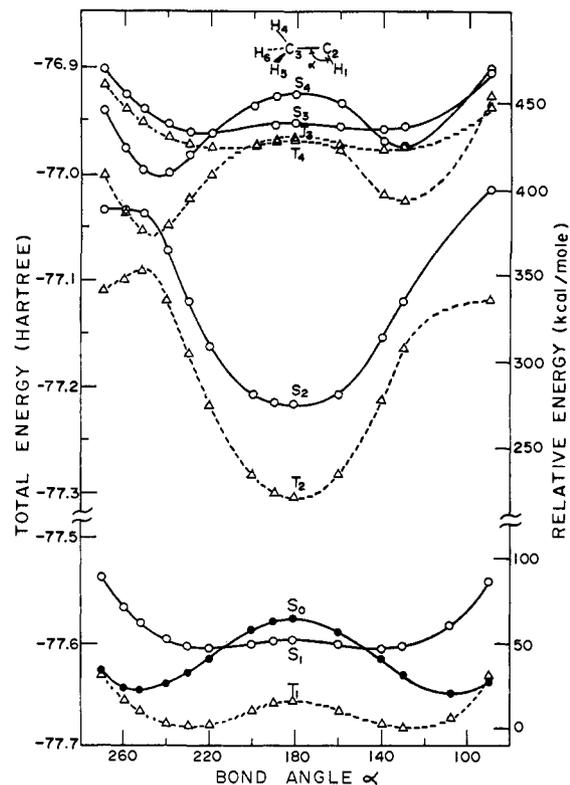


Figure 1. Variation of total energy as a function of the CCH bond angle, α (in-plane inversion potential), for the ground (S_0), first four excited singlet (S_i), and triplet (T_i) states of methylcarbene as computed using a minimal basis set.

For the first cross-section the internal coordinate was chosen to be the bond angle α , and a series of preliminary calculations were carried out to generate $E = E(\alpha)$ using a minimum size basis set. The geometrical parameters used for the calculations are listed in Table II. The $E(\alpha)$ plot for the closed shell ground (S_0) state and the first four excited singlet (S_i) and triplet (T_i) states is shown in Figure 1. It is apparent that methylcarbene, like methylene itself, prefers a bent geometry. In the S_0 state the minimum on the curve corresponds to a conformation having an α value of 107.8° , whereas in the T_1 state the optimal bending angle is 130° . The curve associated with the S_1 state appears to be quite flat with a shallow minimum at an α value of 140° . It is interesting to note that the curves for both the S_2 and T_2 states have their minima at $\alpha = 180^\circ$, meaning that the molecule in these states favors a linear geometry. According to Figure 1 methylcarbene should have a triplet ground state with an adiabatic (S_0 - T_1) separation of 21.6 kcal/mol. The first excited singlet state (S_1) also lies fairly low, only 24.9 kcal/mol above the S_0 state.

For further refinement of the preliminary work, the calculations were repeated using a double ζ atomic basis set. Our results are summarized in Table III and illustrated in Figure 2. As was expected, the general appearance of the curves is very similar to that obtained from the minimal basis set (Figure 1), although the α values of the lowest energy conformations in the various states are slightly shifted toward larger bond angles.¹⁴

(14) The minimum on the curve obtained for the S_0 state appears at $\alpha = 111.8^\circ$, on the curve for the T_1 state at $\alpha = 133.5^\circ$, and on the curve for the S_1 state at $\alpha = 144.4^\circ$.

Table III. Variation of Total Energy with the CCH Angle β^a in the Ground State and the First Four Excited States of Methylcarbene^b

β , deg	States				
	S_0	S_1/T_1	S_2/T_2	S_3/T_3	S_4/T_4
100	-77.8881039	-77.800210	-77.493197	-77.518667	-77.459202
		-77.862631	-77.512250	-77.539528	-77.479219
110	-77.8928781	-77.819898	-77.519182	-77.518808	-77.476034
		-77.879599	-77.534063	-77.537123	-77.501902
120	-77.8906673	-77.832935	-77.538042	-77.518654	-77.483954
		-77.889537	-77.552598	-77.531600	-77.514703
130	-77.8883572	-77.840220	-77.553532	-77.517334	-77.483674
		-77.893438	-77.569013	-77.527185	-77.516839
140	-77.8729344	-77.843143	-77.565728	-77.514887	-77.478358
		-77.892778	-77.583686	-77.523657	-77.511982
150	-77.8615764	-77.842962	-77.574127	-77.511077	-77.470239
		-77.889021	-77.596016	-77.519773	-77.503178
179	-77.8424125	-77.838201	-77.580515	-77.502030	-77.459622
		-77.878489	-77.612561	-77.511521	-77.467810
215.6	-77.8688922	-77.842621	-77.566901	-77.512716	-77.461487
		-77.893076	-77.587796	-77.521885	-77.487865
226.5	-77.8814421	-77.840953	-77.554797	-77.516244	-77.462622
		-77.895926	-77.572105	-77.525880	-77.485905
248.2	-77.8964109				

^a Where $\beta = (360 - \alpha)$. For definition of α see Figure 2. ^b Calculations employed a double ζ basis set.

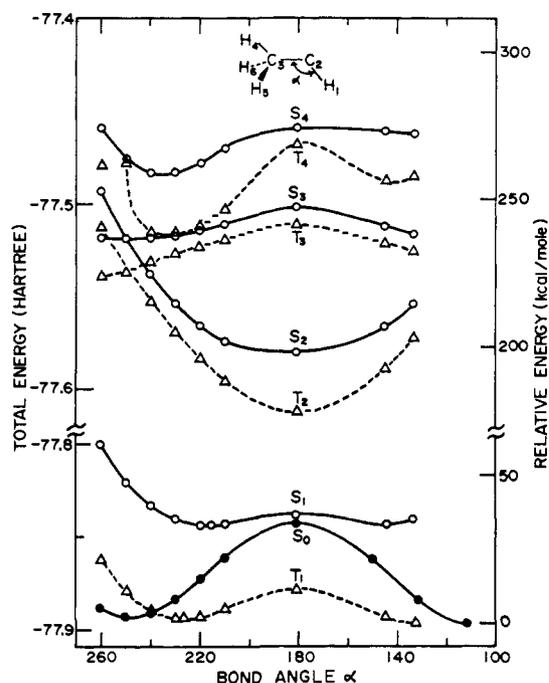


Figure 2. Variation of total energy as a function of the CCH bond angle, α (in-plane inversion potential), for the ground (S_0), first four excited singlet (S_i), and triplet (T_i) states of methylcarbene as computed using a double ζ basis set.

However, the relative energies of the two lowest states are significantly different from the preliminary results. The adiabatic (S_0 - T_1) separation decreased to 0.3 kcal/mol, with the S_0 state being the lowest energy state when the methylcarbene is in its most stable staggered conformation. On the other hand, when the molecule assumes its less stable eclipsed conformation, the order of the stabilities of the S_0 and T_1 states reverses to a similar extent.¹⁵ A crossover of the two states occurs at an α value of 121° .

These results suggest that methylcarbene may have either a singlet or a triplet ground state depending on

(15) The adiabatic (S_0 - T_1) gap is 0.45 kcal/mol for the eclipsed conformation.

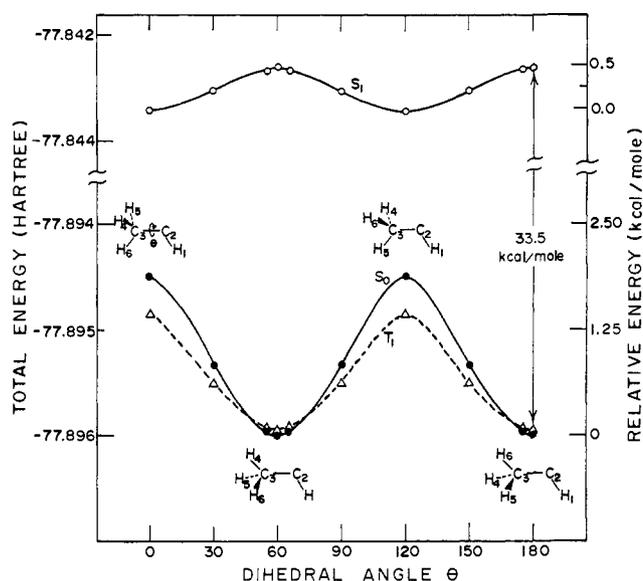


Figure 3. Variation of total energy as a function of the C-C torsional angle, θ (rotation-potential), for the ground (S_0), first excited singlet (S_1), and triplet (T_1) states of methylcarbene.

whether it assumes a staggered conformation or it is forced into an eclipsed conformation by means of some geometrical constraints. Furthermore, the close energy gap between the two states suggests that the generation of any one of the pure spin states could be an extremely demanding experimental task.¹⁶

For the other cross-section the internal coordinate was chosen to be the dihedral angle θ .¹⁷ The results obtained in the form of $E = E(\theta)$ for the three lowest states are shown in Figure 3 and the actual values are

(16) As a referee has pointed out, it is probable that correlation energies in singlet states are somewhat higher than in triplet states, which would result in an overestimation of the (S_0 - T_1) separation by the SCF method. Furthermore, a recent very refined theoretical study of methylene (including differential correlation energy) revealed that addition of d orbitals to the basis set decreases the (S_0 - T_1) gap substantially (C. F. Bender, H. F. Schaefer III, D. R. Franceschetti, and L. C. Allen, *J. Amer. Chem. Soc.*, **94**, 6888 (1972)). Thus an alternative interpretation of our results is that the methylcarbene ground state is most probably a singlet.

(17) The dihedral angle $ijkl$ is defined as the angular displacement of kl relative to ij , measured counterclockwise along the direction $k \rightarrow j$.

Table IV. Variation of Total Energy with the $H_6C_3C_2H_1$ Dihedral Angle,^a θ , for the Ground (S_0), First Excited Singlet (S_1), and Triplet (T_1) States of Methylcarbene

State	Dihedral angle θ , deg	Total energy, hartree
S_0	0	-77.8929957
	30	-77.8946793
	55	-77.8963530
	60	-77.8964109
T_1	0	-77.893726
	30	-77.895041
	55	-77.895861
	60	-77.895926
S_1	0	-77.843446
	30	-77.843061
	55	-77.842711
	60	-77.842621

^a For the definition of the dihedral angle see text.

summarized in Table IV. The curves are symmetrical, closely analogous to the well-known threefold rotational potential curves of ethane. The calculated rotational barrier for the S_0 state is 2.14 kcal/mol, for the T_1 state 1.38 kcal/mol, and for the S_1 state -0.52 kcal/mol, the latter value indicating that the eclipsed conformation in that state is slightly more stable.

A summary of our results for methylcarbene is shown in Table V.

Table V. Summary of the Results of Calculations for Methylcarbene and Ethylene

	Methylcarbene			Ethylene		
	S_0	T_1	S_1	S_0	T_1	S_1
$\angle H_2C_2C_3$, deg	111.8	133.5	144.4	121.35	120	120
Total energy, hartree	-77.8964109	-77.895926	-77.843446	-78.0115556	-77.910064	-77.716596
Rotational barrier, kcal/mol	2.14	1.38	-0.52 ^a		63.7 ^c	185.2 ^c
Heat of formation ΔH_f , kcal/mol	84.8	85.1	117.9	12.5 ^b		

^a The negative value indicates that the eclipsed conformation is more stable than the staggered conformation. ^b Value taken from literature.¹⁹ ^c The values quoted refer to the barrier to cis-trans isomerization.

Molecular Rearrangement of Methylcarbene. The second part of our study involved the stereochemistry of the rearrangement of methylcarbene to ethylene. In order to be able to construct a correlation diagram for this process, the energies of both the ground and excited states of ethylene had to be calculated. The molecular parameters used for the calculations are listed in Table II¹⁸ and the energies obtained are reported in Table V. The energy value obtained for ground-state ethylene was then used to calculate the heat of formation of methylcarbene by means of the following equation.¹⁹ Since $\Delta H_f(\text{ethylene})$ is well

$$\Delta H_f(\text{carbene}) - \Delta H_f(\text{ethylene}) \approx E_{\text{SCF}}(\text{carbene}) - E_{\text{SCF}}(\text{ethylene})$$

known²⁰ and the quantities on the right-hand side of the equation are available from our calculations, ΔH_f -

(18) For the ground-state conformation D_{2h} symmetry, and for the excited states C_2 symmetry, was used.

(19) The equivalence below holds only approximately because ΔE_{corr} is not added to the right-hand side of the equation. This is equivalent to assuming that the correlation energy of methylcarbene is identical with that of ethylene.

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

(carbene) may be calculated. The values obtained are $\Delta H_f(\text{carbene}) = [(E_{\text{SCF}}(\text{carbene}) - E_{\text{SCF}}(\text{ethylene})) + \Delta H_f(\text{ethylene})$

included in Table V. The calculated heat of formation for methylcarbene in the S_0 state is 84.8 kcal/mol but an experimental value is not available for comparison. However, the heat of formation of methylene was reported to be in the range of 91.9²¹-94.6²² kcal/mol. The difference between these and our estimate, *i.e.*, $\Delta\Delta H_f = \Delta H_f(\text{HCH}) - \Delta H_f(\text{CH}_3\text{CH}) = 7.1-9.8$ kcal/mol, agrees remarkably well with the average $\Delta\Delta H_f$ of methyl substitution in olefins (*e.g.*, $\Delta H_f(\text{CH}_2=\text{CH}_2) - \Delta H_f(\text{CH}_3\text{CH}=\text{CH}_2) = 7.9$ kcal/mol²⁰). On the other hand, as Dewar pointed out²³ such comparisons are truly applicable only to molecules with localized bonds. He reported⁹ the calculated heat of formation of singlet methylcarbene as being 66.0 kcal/mol. The large discrepancy between his value and that estimated by the localized bond approach was attributed to "stabilization of methylcarbene by hyperconjugation."⁹ It was shown²⁴ that double ζ basis set calculations usually predict the heats of formation within 10 kcal/mol of the experimental value. In the present case this is undoubtedly due to the unavoidable neglect of ΔE_{corr} in the thermochemical equation above. Therefore it is conceivable that our estimate is somewhat higher than the correct value.

The correlation diagram, constructed for methylcarbene and ethylene, is shown in Figure 4. The diagram reveals that the first excited state (T_1) of ethylene lies 8.6 kcal/mol below the ground state (S_0) of methylcarbene. Considering the finding that the S_0 and T_1 states of methylcarbene are almost degenerate, two alternative mechanisms may be envisioned for its rearrangement: mode 1, singlet (S_0) methylcarbene rearranging to ground-state (S_0) ethylene, or mode 2, triplet (T_1) methylcarbene rearranging to form initially an excited triplet (T_1') ethylene, which in turn would decay to the ground (S_0) state product. The former process may involve the migration of a hydrogen being either syn or anti to the carbenic hydrogen. In the case of the triplet-triplet conversion the anti process is expected to be more favorable since the migration to a "twisted" ethylene need not be accompanied by any torsion of the C-C bond. Although the former route is thermodynamically favored, it is not unlikely that the

(21) W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

(22) W. A. Chupka, *J. Chem. Phys.*, **48**, 2337 (1968).

(23) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 141.

(24) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **23**, 369 (1972).

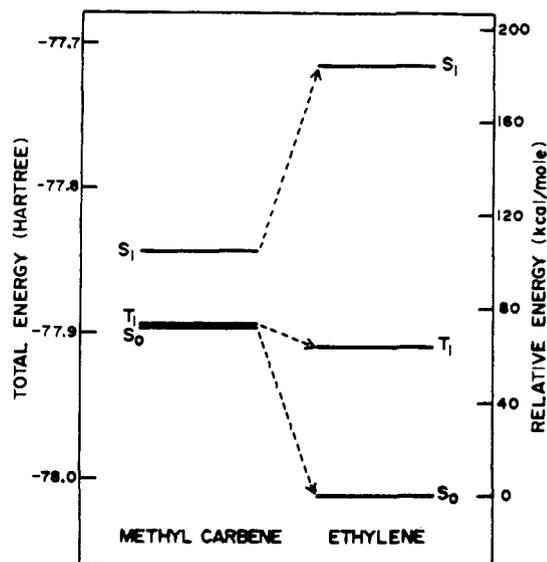


Figure 4. Correlation diagram of methylcarbene and ethylene as computed employing a double ζ basis set.

Table VI. Atomic Coordinates of the Optimized Transition-State Structures Considered for the Rearrangement of Methylcarbene to Ethylene

Atom	Coordinates (atomic units)		
	x	y	z
Structure I			
1	1.7461	2.52348	0.0
2	0.0	1.45975	0.0
3	0.0	-1.45975	0.0
4	-2.15571	0.34031	0.0
5	0.51199	-2.44885	1.73935
6	0.51199	-2.44885	-1.73935
Structure II			
1	1.72074	2.42561	0.0
2	0.0	1.32133	0.0
3	0.0	-1.32133	0.0
4	-1.87187	-2.1942	0.0
5	-1.13379	0.30806	1.96378
6	1.5025	-2.3734	-0.94945
Structure III			
1	0.97911	2.38506	1.44575
2	0.0	1.32133	0.0
3	0.0	-1.32133	0.0
4	-1.48316	0.38083	-1.48316
5	0.51199	-2.31014	1.73935
6	0.51199	-2.31014	-1.73935

^a For definition see text.

latter mode is faster if its barrier to the conversion (T_1-T_1') is lower.

The barrier for the triplet-triplet conversion (mode 2) was calculated in the following way: a transition-state geometry was assumed by allowing the atoms of the molecule to move synchronously to a position halfway between their initial and final spatial position. This was achieved by averaging all the bond lengths and bond angles between reactant and product. The position of the migrating hydrogen was then optimized as shown in

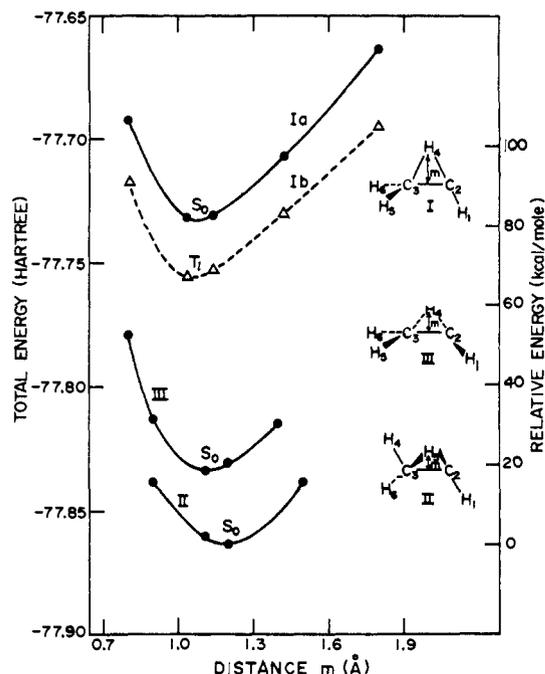


Figure 5. Optimization of the position of the migrating hydrogen [defined as the distance, m , of the migrating hydrogen from the center of the C-C bond] in the various possible transition-state structures considered for the rearrangement of methylcarbene to ethylene.

Figure 5, curves Ia and Ib. The conformation having minimum energy (structure I) has a CCH_{migr} angle of 49.4° . Similar types of calculations were carried out for each of the transition-state structures (II and III) involved in the singlet-to-ground state conversion as illustrated in Figure 5. Curve II corresponds to the S_0 state of the transition state conformation for syn migration of mode 1 and curve III to that for the anti migration of mode 1.²⁵ The corresponding optimum conformations were found to have CCH_{migr} angles of 54.3 and 52.2° for structure II (syn) and III (anti), respectively. The atomic coordinates of the optimized transition state structures (I, II, and III) are given in Table VI.

The diagram summarizing the energetics of the rearrangement is shown in Figure 6. It is apparent that the rearrangement of singlet methylcarbene to ground-state ethylene (mode 1) is preferred over the triplet-triplet route (mode 2) both kinetically and thermodynamically. For the former process, of the two stereochemical alternatives, the syn migration is predicted to be more facile than the anti migration because of the low barrier (20.9 kcal/mol) involved. This is somewhat surprising since intuitively it might have been expected that the hydrogen would preferentially migrate toward the lobe with a lone pair rather than toward the initially empty p orbital on carbon. But if one considers that, as the rearrangement proceeds, the electron density of the σ bond (C-H_{migr} bond) progressively diffuses to all three atoms (*i.e.*, CH_{migr} C) involved in the migration, then the preference for mode 2 is not at all unlikely.²⁶

(25) For these two only the S_0 states are shown since they were the lowest in energy in the manifold.

(26) The above rationalization is qualitatively in accord with the mixing of the orbitals in Zimmerman's MO Following approach,²⁷ as applied to this rearrangement.

(27) H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972).

Our results agree with those of Dewar,⁹ who also found the syn migration to be favored over the anti migration. In contrast, the triplet-triplet conversion was found to be slightly preferred by least motion considerations.⁷ It seems therefore that the rearrangement is non-least-motion-controlled.

Conclusions

Our results were arrived at by a limited optimization procedure regarding the geometries of the various C_2H_4 species under consideration. A complete optimization of these and in particular the transition-state geometries could change the relative energies by several kcal/mol. This is not expected to influence the overall stereochemical consequences of the rearrangement which involves the *relative ordering* of the energies of the individual species. On the other hand, since optimization generally lowers the energy, it is likely that the barriers to the migrations would decrease substantially. Consequently, the barrier to the preferred syn mode should be regarded as an upper limit, bearing in mind that the reaction is known to be extremely facile.

As for methylcarbene, it was shown that increasing the basis set results in the decrease of the singlet-triplet separation from 21.6 kcal/mol to approximately zero. A very recent, and probably one of the most refined, theoretical studies of methylene, by Bender, *et al.*,¹⁶ resulted in similar conclusions. In our case this decrease warrants caution in the assignment of the ground electronic state. It is suggested that methylcarbene

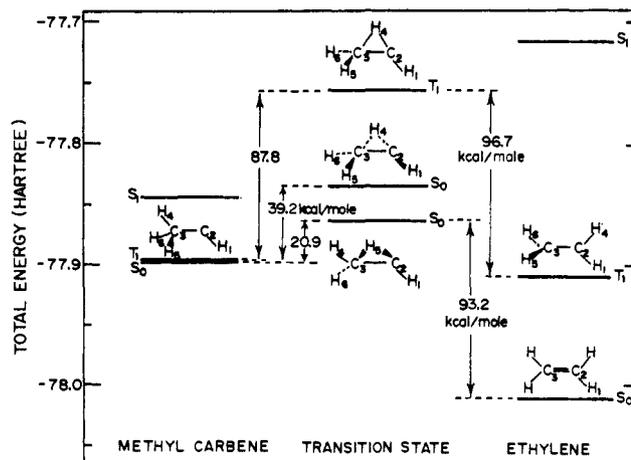


Figure 6. A summary of thermodynamic and kinetic stabilities of selected low-lying states of various C_2H_4 species.

most probably has a singlet ground state, with the reservation that for a better understanding of the (S_0 - T_1) spacing a complete study of the energy surface is necessary.

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Stereochemistry of the Thermal Addition of β -Pinene to Maleic Anhydride

Richard K. Hill,* John W. Morgan, Raghav V. Shetty, and Martin E. Synerholm

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602, and the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08540. Received October 9, 1973

Abstract: Two stereochemical aspects of the thermal ene reaction between β -pinene and maleic anhydride have been investigated, the configuration of the allylic hydrogen transferred in the reaction and the preference for endo *vs.* exo orientation. Two routes are described to a stereospecifically labeled β -pinene in which the C-3 hydrogen trans to the *gem*-dimethyl bridge is replaced by deuterium. Use of this material in ene reactions with maleic anhydride and dimethyl acetylenedicarboxylate showed that $95 \pm 5\%$ of the deuterium is transferred. Determination of the absolute configuration at the new asymmetric center in the adduct as *R*, by degradation to (*S*)-(+)-3-methylpentanoic acid, revealed that the major adduct is **2b**, formed by endo addition. Of four possible transition-state orientations A-D, C is established as the preferred pathway.

The thermal addition of an alkene to another olefin possessing an allylic hydrogen, the so-called "ene" reaction, is one of the simplest reactions of organic chemistry.¹ Though radical² and other mechanisms³ have been advanced, the addition is usually considered to proceed in a symmetry-allowed concerted process^{4,5}

(1) For reviews, see (a) H. M. R. Hoffmann, *Angew. Chem.*, **81**, 597 (1969); (b) E. C. Keung and H. Alper, *J. Chem. Educ.*, **49**, 97 (1972).
(2) H. A. Chia, B. E. Kirk, and D. R. Taylor, *Chem. Commun.*, 1144 (1971).
(3) C. Agami, M. Andrac-Taussig, and C. Prevost, *Bull. Soc. Chim. Fr.*, 173 (1966); C. Agami, M. Andrac-Taussig, C. Justin, and C. Prevost, *ibid.*, 1195 (1966).

via a six-membered cyclic transition state (eq 1), unless prohibited by steric factors.⁶ Consistent with the concerted mechanism are two important stereochemical observations: (a) the new C-C and C-H bonds are formed *cis*,⁷ and (b) asymmetric induction occurs in the adduct

(4) R. T. Arnold and J. F. Dowdall, *J. Amer. Chem. Soc.*, **70**, 2590 (1948).
(5) S. Dai and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **94**, 3953 (1972).
(6) J. Lambert and J. J. Napoli, *J. Amer. Chem. Soc.*, **95**, 294 (1973).
(7) (a) K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **651**, 141 (1962); (b) L. E. Friedrich, J. A. Kampmeier, and M. Good, *Tetrahedron Lett.*, 2783 (1971).