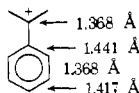
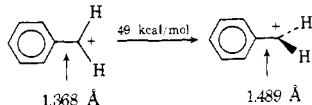


- (11) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).  
 (12) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.  
 (13) For our earlier work on the effects of solvent on the stabilities of carbocations see W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 7162 (1974).  
 (14) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).  
 (15) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971); (b) R. T. McIver, Jr., and J. R. Elyer, *ibid.*, **93**, 6334 (1971); (c) R. T. McIver, Jr., and J. H. Silvers, *ibid.*, **95**, 8462 (1973); (d) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 4728 (1972).  
 (16) (a) Benzyl cation:

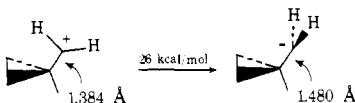


All C-H bond lengths are fixed at 1.08 Å; all CCC and CCH bond angles are fixed at 120°. (b) Cyclopropylcarbinyl cations: W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 302 (1974).

- (17) W. J. Hehre and R. W. Taft, unpublished. For a detailed discussion of related correlations see G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, in press.  
 (18) (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 5636, 6501 (1968); (b) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. W. Holtz, and R. W. Taft, *ibid.*, **94**, 4724 (1972); (c) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972); (d) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *ibid.*, **95**, 3811 (1973); (e) J. F. Wolf, P. G. Harch, and R. W. Taft, *ibid.*, **97**, following paper in this issue.  
 (19) See, for example, R. H. Boyd, R. W. Taft, A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).  
 (20) E. M. Arnett and J. M. Abboud, *J. Am. Chem. Soc.*, in press.  
 (21) Differences in rotational barriers and changes in geometry accompanying torsion about the carbonium center-substituent linkage provide further evidence that a phenyl ring interacts more effectively with an unsubstituted cation center than does cyclopropyl. Thus, torsion of CH<sub>2</sub><sup>+</sup> in the benzyl cation from a planar to an orthogonal arrangement requires 49 kcal/mol, and leads to a lengthening of the phenyl ring-carbonium center linkage of 0.121 Å.



Rotation in cyclopropylcarbinyl is less costly and leads to a smaller lengthening in connecting bond length.<sup>16b</sup>



- (22) This conclusion has also been reached independently by Dr. L. Radom (Australian National University) and Professor J. A. Pople (Carnegie-Mellon University). We thank them for communication of their results prior to publication.  
 (23) For a discussion of the cyclopropane Walsh orbitals see R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971).  
 (24) For a discussion see R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972).  
 (25) Alfred P. Sloan Fellow, 1974-1976.

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 Robert W. Taft,\* Warren J. Hehre\*<sup>25</sup>

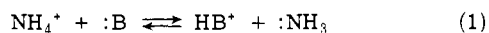
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Received December 5, 1974

## Concerning Negligible Aqueous Solvent Effects on Proton Transfer Equilibria of Aryl Carbocations<sup>1</sup>

Sir:

Utilizing pulsed ion cyclotron resonance spectroscopy,<sup>2</sup> accurate determinations of equilibrium constants,  $K_{(g)}$ , for reaction 1 in the gas phase have become available.<sup>3</sup> Com-



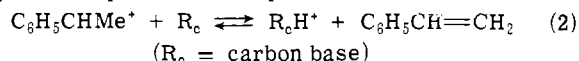
parison with corresponding equilibrium constants in aqueous solution  $K_{(aq)}$ , provides a quantitative evaluation of the medium effect of water on the proton transfer equilibrium (1), i.e.,  $K_{(g)}/K_{(aq)}$ . For simple alkyl and aryl substituted amines, medium effects 5-17 powers of ten are found.<sup>3,4</sup> These very large medium effects for proton transfer between neutral molecules are primarily associated with differential cation solvation.<sup>3,4</sup> With careful balance achieved in cation solvation,<sup>4</sup> the medium effects of water (and of acetonitrile)<sup>4b</sup> may be reduced to less than one power of ten.

We wish to report the observation of extremely large medium effects of water ( $K_{(g)}/K_{(aq)} \approx 10^{25}$ ) for reaction 1 with carbon base precursors of aryl carbocations. Such ions as a class are apparently poorly solvated (the hydration energy may be estimated<sup>3,4</sup> at about 50 kcal) due to the absence of exposed atomic sites with appreciable positive charge. The very extensive delocalization of the cationic charge throughout such relatively large cations has been thought to assure this condition and in particular to maintain the poor proton donating ability of C-H bonds.<sup>5</sup> This picture of cation solvation<sup>6</sup> has been associated with the basis for the Deno-Long-Boyd (DLB)  $H_0$  acidity function for carbon bases.<sup>6f</sup>

The standard free energies for reaction 1 in the gas phase,  $\delta_R \Delta G^\circ_{i(g)}$ , have been obtained by the method reported previously using standards developed in prior work.<sup>4b</sup> The results are listed in Table I together with the corresponding aqueous standard free energies,  $\delta_R \Delta G^\circ_{i(aq)}$ . The values of  $\delta_R \Delta G^\circ_{i(aq)}$  are based upon measurements in acids ranging from dilute aqueous to about 90% (wt) H<sub>2</sub>SO<sub>4</sub>. The latter have been extrapolated to the former condition by use of the DLB  $H_0$  function.<sup>7</sup> It will be noted that there is a nearly constant difference ( $\Delta$ ) of  $\sim 35 \pm 1$  kcal (i.e.,  $K_{(g)}/K_{(aq)} \approx 10^{25}$ ) between the corresponding free energy changes. Although pyridinium ions in general give very much smaller solvent effects for reaction 1, a special one, 2,6-di-*tert*-pyridinium,<sup>8</sup> is found to give the same solvent effect as for the aryl carbocations. Since it is expected that the *tert*-butyl groups will completely hinder aqueous hydrogen-bonding to the N; and the NH<sup>+</sup> groups, this conjugate acid-base pair meet the same criteria for poor solvation of the acid-base pair as for the aryl carbocations.<sup>8c</sup>

The following points may be singled out for specific comment.

(1) A plot of the  $-\delta_R \Delta G^\circ_{i(g)}$  vs. corresponding  $-\delta_R \Delta G^\circ_{i(aq)}$  values from Table I is linear with approximately unit slope and intercept,  $\Delta = 35$  kcal. Thus, for

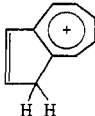



reaction 2, a range of structural effects of  $\sim 23$  kcal is accompanied by essentially no solvent effect ( $K_{2(g)}/K_{2(aq)} \approx 1$ ). Although  $\delta_R \Delta G^\circ_{i(aq)}$  values are unavailable for nonaryl and less stable aryl carbocations, we believe it is unlikely that this striking result applies to them (cf. point 5 below).

(2) The DLB acidity function has been confirmed by our measurements in the absence of solvent as a valid measure of intrinsic effects of molecular structure on protonation of carbon bases leading to aryl carbocations. In view of the large medium effects observed<sup>3,10</sup> for proton transfer equilibria with other classes of bases, B, this result appears limited to the DLB acidity function.

(3) The present results are analogous to the findings of Chandhuri, Jagur-Grodzinski, and Swarc<sup>11</sup> that the free energies of formation of free aryl carbonium radicals by reduction of polynuclear aromatic hydrocarbons are essentially the same in the gas phase and in solutions of tetrahydro-

Table I. Aryl Carbocations: Gas Phase and Aqueous Basicities, Relative to NH<sub>3</sub>

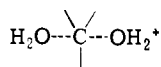
Carbon base	Aryl carbocation	$-\delta_R \Delta G^\circ_{i(g)}^a$	$-\delta_R \Delta G^\circ_{i(aq)}^b$	$\Delta^c$
Styrene	C <sub>6</sub> H <sub>5</sub> CHMe <sup>+</sup>	-2.0		
$\alpha$ -Methylstyrene	C <sub>6</sub> H <sub>5</sub> CMe <sub>2</sub> <sup>+</sup>	3.4	$\sim -31^{6b}$	$\sim 34$
Hexamethylbenzene	Me <sub>6</sub> C <sub>6</sub> HMe <sup>+</sup> <sup>9</sup>	4.5	$-30.7^{6a}$	35.2
1,1-Diphenylethylene	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CMe <sup>+</sup>	7.9	$-26.8^{6a}$	34.7
Azulene		21.2	$-14.9^{6c-f}$	36.1
2,6-Di- <i>tert</i> -butylpyridine		26.4 <sup>d</sup>	$-7.74^{8b}$	34.1

<sup>a</sup> Standard free energy change for reaction 1 in the gas phase, kcal mol<sup>-1</sup>, 298°K. <sup>b</sup> Standard free energy change for reaction 1 in aqueous solution, obtained from pK values of cited references and pK = 9.24 for NH<sub>4</sub><sup>+</sup>. <sup>c</sup>  $\Delta = -\delta_R \Delta G^\circ_{i(g)} + \delta_R \Delta G^\circ_{i(aq)} = 1.36 \log(K_{(g)}/K_{(aq)})$ . <sup>d</sup> We are indebted to Professor D. H. Aue for communicating to us their similar unpublished result.

furan. Here again charge delocalization is so extensive in the aryl carboanion radicals as to effectively eliminate hydrogen bonding or other "chemical" solvation at specific atomic sites.

(4) The introduction of heteroatoms in the aryl carbocation-conjugate base pair may frequently lead to deviant behavior. Thus, for example, 1,3,5-trimethoxybenzene differs by  $\sim 4$  kcal from the behavior in Table I ( $-\delta_R \Delta G^\circ_{i(g)} = 15.8$ ;  $-\delta_R \Delta G^\circ_{i(aq)} = -23.2$ ;<sup>6f</sup>  $\Delta = 39$  kcal). This deviation may be attributed to hydrogen bonding between the acidic medium and the methoxy groups of the base. A figure of  $\sim 1$  kcal/OCH<sub>3</sub> for the standard free energy change for such an interaction appears reasonable.<sup>12</sup> Since such hydrogen bonding will be strongly reduced in the trimethoxybenzenium ion, the heteroatom effect in this example is associated principally with the free base. With an OH substituent, for example, hydrogen-bonding theory anticipates a deviation (in the opposite direction) caused primarily by hydrogen bonding in the cationic state.<sup>13</sup> As noted above, the behavior of 2,6-di-*tert*-butylpyridine in Table I represents very special rather than general behavior for a heteroatomic system.<sup>8c</sup>

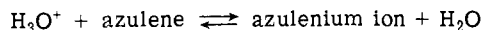
(5) The aryl carbocations of Table I involve a variety of structures. The common behavior suggests a cationic heat of solution in water of  $\sim 50$  kcal as a rough estimate for limiting physical ion-dipole and ion-induced dipole solvation of the generally accessible univalent cations which do not involve specific cation-molecule "chemical" bonding. Specific bonding interactions leading to heats of hydration exceeding this value include H bonding of water molecules with acidic protons of the cation<sup>5,6</sup> and Lewis acid-base bonding,<sup>14</sup> e.g.,



Thus, solvation energies (as indicated by activity coefficient behavior) for stable aryl carbocations, tetra-*n*-butylammonium and tetraphenylphosphonium ions are very similar but are distinctly smaller than for H bonding cations, e.g., anilinium ions and hydrated K<sup>+</sup> and Ag<sup>+</sup> ions.<sup>6f</sup> Both the ionization of HONO<sub>2</sub><sup>15</sup> to NO<sub>2</sub><sup>+</sup> and HONO<sub>16</sub> to NO<sup>+</sup> have been shown by Deno to approximately follow the *H<sub>R</sub>* acidity function based upon hydration of triarylcationium ions indicators.<sup>17</sup> The large triarylmethyl cations and the small NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> cations have only one apparent common structural feature dictating the suggested similar but poor solvation, i.e., no acidic protons. The behavior of NO<sup>+</sup> (in particular) is illuminating in suggesting that large cationic solvation energy may depend upon more subtle considerations than the presence of exposed charge localized at such

relatively small atomic centers as those of oxygen and nitrogen.

(6) While the 10<sup>25</sup> medium effects of water reported here are extremely large for proton transfer equilibria between neutral bases, even larger solvent effects may be anticipated if more highly solvating cations replace NH<sub>4</sub><sup>+</sup> in reaction 1 and water is replaced by more basic solvating solvents. Thus, for example, it may be crudely estimated from available data that the medium effect of water is  $\sim 10^{35}$  for the proton transfer equilibrium



**Acknowledgment.** We are pleased to acknowledge helpful discussions with Professor W. J. Hehre.

## References and Notes

- (1) This work has been supported in part by a grant from the National Science Foundation.
- (2) (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4313 (1971); (c) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972); (d) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4728 (1972).
- (3) (a) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972); (b) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972).
- (4) (a) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *J. Am. Chem. Soc.*, **95**, 3811 (1973); (b) R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, in press.
- (5) R. W. Taft, *J. Am. Chem. Soc.*, **82**, 2965 (1960).
- (6) (a) N. C. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959); (b) N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *ibid.*, **82**, 4719 (1960); (c) J. Schulze and F. A. Long, *ibid.*, **86**, 322 (1964); (d) F. A. Long and J. Schulze, *ibid.*, **83**, 3340 (1961); **86**, 327 (1964); (e) E. M. Arnett, *Prog. Phys. Org. Chem.*, **1**, 223 (1963); (f) R. H. Boyd in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 3.
- (7) Small differences between Deno's *H<sub>R</sub>'* function, Long's *H<sub>0</sub>* function based upon azulenes (ref 6f), and Boyd's  $-\log a_{\text{H}^+}$  (activity of hydrogen ion relative to tetraethylammonium ion) can make up to about 1 kcal difference in  $\delta_R \Delta G^\circ_{i(aq)}$  values of Table I. We regard this as a sufficiently small uncertainty for present purposes that the  $\delta_R \Delta G^\circ_{i(aq)}$  values used are based upon pK values as given in references 6a, 6b, and 6f.
- (8) (a) F. E. Condon, *J. Am. Chem. Soc.*, **87**, 4494 (1965); (b) H. C. Brown and B. Kanner, *ibid.*, **88**, 986 (1966). (c) Further, stabilization of cations by polarizable hydrocarbon substituents is suggested to apply nearly equally in the gas phase and aqueous solution only when the absence of hydrogen-bonding prevents dispersal of cationic charge to the solvent. Cf. also E. M. Arnett and J. F. Wolf, *ibid.*, **95**, 978 (1973).
- (9) Cf. W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. V. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7162 (1974).
- (10) (a) M. Taagepera, W. H. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 1369 (1972); (b) R. T. McIver, Jr., and J. H. Silvers, *ibid.*, **95**, 8462 (1973); (c) R. Yamdagni, T. B. McMahon, and P. Kebarle, *ibid.*, **96**, 4035 (1974).
- (11) J. Chandhuri, J. Jagur-Grodzinski, and M. Swarc, *J. Phys. Chem.*, **71**, 3063 (1967).

- (12) R. W. Taft, D. Gurka, L. Joris, P.v.R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, 4801 (1969).  
 (13) (a) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **84**, 3778 (1962); (b) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962).  
 (14) Cf., for example, R. H. Boyd, R. W. Taft, A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).  
 (15) Cf. F. Westheimer and M. S. Kharasch, *J. Am. Chem. Soc.*, **68**, 1871 (1946).  
 (16) K. Singer and P. A. Vamplew, *J. Chem. Soc.*, 3971 (1956).  
 (17) N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *J. Am. Chem. Soc.*, **81**, 2344 (1959).

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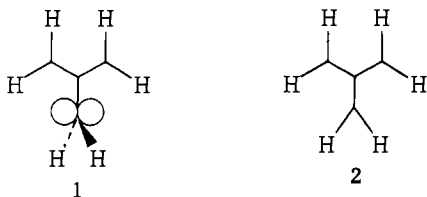
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Received December 23, 1974

## The Lowest Singlet State of Planar Trimethylenemethane

Sir:

Two calculations<sup>1,2</sup> have appeared that predict for singlet trimethylenemethane a large (>1 eV) barrier to the rotation of the nonconjugated methylene group from the orthogonal (**1**) to the planar (**2**) geometry. In contrast, in a re-



cent theoretical study Yarkony and Schaefer<sup>3</sup> found a much smaller (2.8 kcal/mol) barrier to rotation in the lowest singlet, *provided* that the symmetry of the wave function for the planar geometry was allowed to relax from  $D_{3h}$  to  $C_{2v}$ . The latter result is in much better accord with the experimental observation that racemization competes with rearrangement in chiral methylenecyclopropanes.<sup>4,5</sup> This communication shows that the Yarkony-Schaefer result is, indeed, correct and can be readily understood on the basis of previously published work.<sup>6</sup>

In fully delocalized  $D_{3h}$  trimethylenemethane, it is impossible to find a combination of degenerate molecular orbitals that do not both have amplitude on at least one common atom. In the lowest singlet state, where the two electrons in these orbitals have opposite spin, the Pauli exclusion principle does not prohibit the simultaneous occupancy of an AO common to both MO's. Therefore, the wave function for this state contains ionic terms, corresponding to the simultaneous occupancy of the same AO by the two electrons in the degenerate MO's. These terms are of high energy, because of the large value for the one-center electron repulsion integral. If, however, one methylene group in the molecule is twisted, as in **1**, so that the wave function becomes that for an allyl radical plus an electron essentially localized in a p orbital, then the two nonbonding orbitals have no atoms in common, and the high energy ionic terms, present in the wave function for the fully delocalized singlet, are absent. The resulting decrease in the electron repulsion energy has been calculated to be greater than 2 eV.<sup>6</sup> Although this decrease in two-electron energy is achieved only at the expense of raising the one-electron energy from  $2\sqrt{3}\beta$  to  $2\sqrt{2}\beta$ , the former effect is larger in magnitude than the latter, and it has been used<sup>2,6</sup> to explain the large barrier calculated<sup>1,2</sup> for conversion of orthogonal **1** to fully delocalized singlet trimethylenemethane.

It is crucial to note, however, that it is not the geometry (i.e., the spatial relationship between the orbitals) of **1** that lowers its energy relative to that of the fully delocalized planar singlet, but rather the fact that the nonbonding MO's of **1** have no atoms in common. *Provided* that the wave function in the planar geometry (**2**) is essentially the same as that in the orthogonal one (**1**), namely that of allyl plus an electron localized in a p orbital, the energy of **2** will be approximately the same as that of **1**. Since the wave function for allyl plus p has only  $C_{2v}$  symmetry, its utilization in **2** necessitates a reduction in the symmetry demanded of the wave function for **2** from the  $D_{3h}$  symmetry of fully delocalized trimethylenemethane. This explains the large drop in energy, calculated by Yarkony and Schaefer,<sup>3</sup> when the symmetry required of the singlet wave function for **2** is relaxed from  $D_{3h}$  to  $C_{2v}$ . Indeed, comparison of the MO's for singlet **2**, with  $D_{3h}$  and  $C_{2v}$  symmetry required of the total wave function, reveals the expected change from the MO's of fully delocalized trimethylenemethane to essentially those of allyl plus p.<sup>7,8</sup>

The failure of previous calculations<sup>1,2</sup> to predict correctly the energy required to convert **1** to **2** arises from their failure to arrive at the correct wave function for planar singlet trimethylenemethane. Calculations that employ the half-electron<sup>1</sup> or Nesbet<sup>2</sup> method for dealing with open-shell systems lead to the same set of MO's for singlet as for triplet states. However, in planar trimethylenemethane the proper MO's for the two states are quite different. The triplet does, indeed, utilize the familiar set of trimethylenemethane MO's that gives a fully delocalized  $D_{3h}$  wave function,<sup>3</sup> since the two electrons in the nonbonding MO's have the same spin and so are kept from simultaneously appearing in the same AO. Because no such exclusion prohibition exists for these two electrons in the singlet, the fully delocalized  $D_{3h}$  wave function contains high energy ionic terms, and the optimum MO's for the planar singlet are essentially those of allyl plus a p orbital.<sup>9</sup> Although the pitfalls in computing wave functions for open-shell atoms with SCF methods that lead to the same orbitals for triplets and singlets have been noted previously,<sup>10</sup> the case of the lowest singlet state of planar trimethylenemethane provides a striking example of the spurious results that can be obtained in calculating wave functions for open-shell molecules.

**Acknowledgment.** I wish to thank Professor W. von E. Doering for reawakening my interest in the trimethylenemethane problem and the National Science Foundation and the Eli Lilly Company for support.

## References and Notes

- (1) M. J. S. Dewar and J. W. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).
- (2) W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).
- (3) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974).
- (4) E. F. Ullman, *J. Am. Chem. Soc.*, **82**, 505 (1960); J. J. Gajewski, *ibid.*, **93**, 4450 (1971); W. von E. Doering and L. Birladeanu, *Tetrahedron*, **29**, 449 (1973); W. von E. Doering, private communication.
- (5) Triplet trimethylenemethane does not appear to be involved in the racemization. For instance, W. von E. Doering and S. Buchwalter (private communication) find that oxygen has no effect on the rate, distribution of products, or stereochemical characteristics of the rearrangement of optically active *trans*-2,3-dicyanomethylenecyclopropane.
- (6) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973).
- (7) I wish to thank Mr. Yarkony and Professor Schaefer for providing me with the MO's obtained from their calculation.<sup>3</sup>
- (8) A wave function of  $C_{2v}$  symmetry will result in a distortion to an optimized geometry that also has  $C_{2v}$  symmetry. With a wave function that is essentially that of allyl plus p, the unique carbon-carbon bond will be longer than the other two. In contrast, the wave function for the other component ( $^1A_1$  in  $C_{2v}$ ) of the  $^1E'$  state ( $D_{3h}$  symmetry)<sup>3</sup> can be shown to lead to an optimized geometry in which the unique bond will be shorter than the other two. These distortions may, of course, be viewed as a consequence of the theorem of H. A. Jahn and E. Teller, *Proc. Roy. Soc., London, Ser. A*, **161**, 220 (1937).
- (9) Although the contribution of these ionic terms can also be reduced through the formalism of configuration interaction (CI), mixing of config-