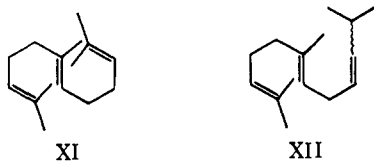
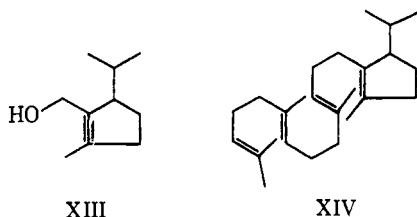


dioxide or *t*-butoxide-*t*-butyl alcohol involved a significant degree of competition between phenyl and allyl as leaving groups. Most important, however, the hydrocarbon which did result from the desired phosphorus-allyl cleavage proved to be a 3:1 isomeric mixture of XI and XII, thus making this procedure unattractive from a synthetic standpoint. The carbon-

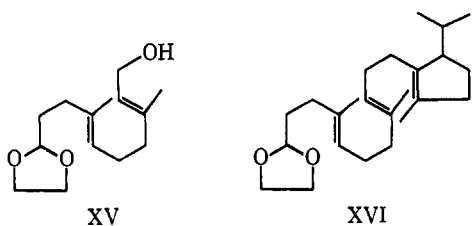


phosphorus bond can also be cleaved reductively by LiAlH_4 ,¹⁵ electrolysis,¹⁶ zinc-acid, and lithium-amine.¹⁷ However, treatment of X with LiAlH_4 led exclusively to $\text{SN}2'$ product XII. The method which demonstrated the greatest promise was the reported reduction with lithium in ethylamine at -76° , giving a 43% yield of the desired hydrocarbon XI. Since the low yield could be ascribed to competitive cleavage of phenyl and allyl (as observed for the hydroxide-water cleavages), or phenyl reduction by lithium-ethylamine, we used the tri-*n*-butylphosphonium salts, for which no such ambiguity should exist, in order to reach a successful conclusion (*vide supra*).

More highly hindered allylic systems such as the cyclopentenyl alcohol XIII¹⁸ may also be coupled with, for example, *trans*-farnesol (III) to give XIV (63%).¹⁹



Coupling of XIII with the functionalized *trans*-farnesol trisnor acetal XV¹⁰ to give acetal XVI²⁰ is further indi-



cation of the general applicability of this sequence, as is the alkylation of the intermediate ylides by alkyl iodides and bromides. The generality of this method for the preparation of pure 1,5-dienes and the preparation of 1,4-dienes by lithium aluminum hydride reduction of

(15) W. Bailey and S. Buckler, *J. Amer. Chem. Soc.*, **79**, 3567 (1957).

(16) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961).

(17) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Amer. Chem. Soc.*, **77**, 3230 (1955).

(18) The synthesis and reactions of XIII were originally pursued by R. Anderson of these laboratories and will be reported elsewhere.

(19) Nmr (CCl_4) δ 5.0-5.3 (4, broad), 2.4-2.6 (1, broad), 1.8-2.4 (14, broad), 1.65 (3, s), 1.57 (12, broad s), 1.0-1.5 (3, broad m), 0.92 (3, d, $J = 7$ Hz), 0.64 (3, d, $J = 7$ Hz).

(20) Identical with an authentic sample prepared independently. Nmr (CCl_4) δ 5.0-5.3 (3, broad), 4.75 (1, t, $J = 6$ Hz), 3.78-3.95 (4, m), 2.4-2.6 (1, broad), 1.8-2.4 (14, broad), 1.56 (9, broad s), 0.92 (3, d, $J = 7$ Hz), 0.66 (3, d, $J = 7$ Hz).

substituted allyl phosphonium salts portend some breadth of synthetic utility.

Acknowledgments. The authors are grateful to the National Science Foundation (Grant No. GP 7187) and the National Institutes of Health (Grant No. GM 10421) for financial aid.

(21) National Institutes of Health Postdoctoral Fellow, 1969-present.

E. H. Axelrod, G. M. Milne,²¹ E. E. van Tamelen
Stanford University, Department of Chemistry
Stanford, California 94305

Received November 29, 1969

Barriers in Ethyl Cations¹

Sir:

Because of geometrical restrictions, many carbonium ions cannot achieve the preferred planar structure.^{2,3} Bridgehead cations are examples of such nonplanar carbonium ions.⁴ While it would be desirable to perform rigorous and reliable molecular orbital calculations on these ions, such calculations are impossible at present because of the large size of such systems. For finding the energies associated with nonplanarity and with torsional interactions in nonplanar ions, the ethyl cation, the simplest ion for which torsional barriers are possible, is an obvious model. In addition, it is the simplest ion in which classical and bridged structures may be compared.

Several calculations, at various levels of sophistication, have been reported for the ethyl cation.^{3,5-8} However, the effects of extensive variation of geometry have not generally been considered, especially by the most refined methods. In this communication, we wish to report the results of two sets of *ab initio* calculations on ethyl cations which are relevant to both the rotational barrier in classical structures (planar and tetrahedral CH_2^+) and the bridge barrier for the interconversion by 1,2-hydride shift of equivalent classical structures.

The first set of calculations used the same basis set as ref 3, with two scaled s-type groups of gaussian orbitals on each hydrogen. In general, threefold rotational barriers computed by this method are accurate to within ± 0.4 kcal/mol.⁹ Five geometries were considered, and the energies are presented in Table I. For each calculation the methyl group was tetrahedral, with a CH bond length assumed to be 1.096 Å. The CH bond length in the trigonal CH_2^+ group was kept at

(1) Molecular Orbital Calculations on Carbonium Ions. III.^{2,3}

(2) Part I: J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1037 (1969).

(3) Part II: R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969).

(4) R. C. Fort and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966); G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(5) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); R. E. Davis and A. S. N. Murthy, *Tetrahedron*, **24**, 4595 (1968).

(6) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968); M. S. Isaacs, *Tetrahedron*, **25**, 3555 (1969); J. J. Dannenberg and T. D. Berke, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. PHYS 163.

(7) F. Fratev, R. Janoschek, and H. Preuss, "Arbeitsbericht der Gruppen Quantenchemie," Max-Planck Institut für Physik und Astrophysik, No. 10, 1968, p 140; *Int. J. Quantum Chem.*, **3**, 893 (1969).

(8) During the course of this work we became aware of a similar *ab initio* study on the ethyl cation: G. V. Pfeiffer and J. G. Jewett, *J. Amer. Chem. Soc.*, **92**, 2143 (1970).

(9) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968); W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

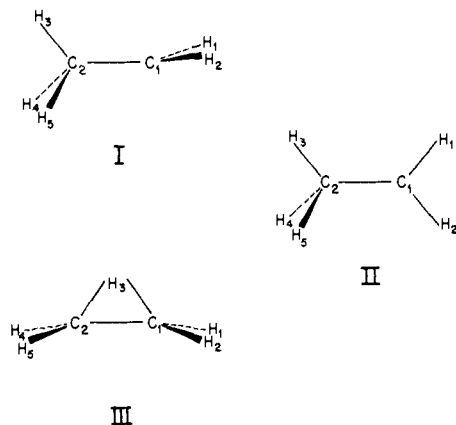


Figure 1. Geometries of classical and bridged ethyl cations.

1.084 Å, and a constant CC length, 1.48 Å, the previous determined energy value,³ was used. In calculations 1 and 2, the methylene center was kept planar. As a model for torsional energies in nonplanar cations, calculations 3, 4, and 5 were carried out with the CH₂⁺ group tetrahedral in staggered, intermediate (smallest two dihedral HCCH angles = 30°), and eclipsed rotational conformations.

These results suggest that, if the CH₃ and CH₂⁺ groups are held in tetrahedral and planar geometries, respectively, the sixfold rotational barrier is effectively zero.^{3,7} However, when the CH₂⁺ group is made rigidly tetrahedral, the sixfold barrier becomes threefold, and the barrier height rises to 2.8 kcal/mol, approximately the value for ethane.^{9,10} Interestingly, the energy required to distort the methyl and ethyl cations out of the RCH₂⁺ plane is very similar, despite the difference in the attractive and repulsive energy changes for each system (Table I). This similarity in distortion energy suggests that it may be possible to use the methyl and ethyl cations as fairly reliable models for the behavior of more highly substituted carbonium ions.

The second series of molecular orbital calculations made use of the recently developed STO-3G minimal basis set.¹¹ Standard molecular ζ values were used.¹¹ The results of such calculations are known to parallel closely those based on a minimal Slater-type orbital set (STO). In STO-3G, each STO is replaced by a least-squares-fitted sum of three gaussian functions. Also, the computations are sufficiently rapid that complete minimization of the energy with respect to several geometrical parameters is possible. Previous studies have shown that this basis set leads to good agreement with experimental geometries.¹²

In Table II, we present energies found for the three structures illustrated in Figure 1. In calculations 6 and 7, the bond angles were held at tetrahedral (CH₃) and trigonal values (CH₂⁺) and the bond lengths optimized. This leads to $r_{\text{CH}}(\text{CH}_3) = 1.095 \text{ \AA}$, $r_{\text{CH}}(\text{CH}_2^+) = 1.115 \text{ \AA}$, and $r_{\text{CC}} = 1.495 \text{ \AA}$ for structures I and II. The very small difference between the two energies confirms the

Table I. *Ab Initio* Energies for Planar and Tetrahedral Structures^a

Calculation	Geometry	ΔV_{att}^c	ΔV_{rep}^d	ΔE
Ethyl Cation ^b				
1	Structure I, CH ₂ planar	0.0	0.0	0.0
2	Structure II, CH ₂ ⁺ planar	-0.1 ^e	0.1 ^e	0.0 ^e
3	CH ₂ ⁺ tetrahedral, staggered ($\phi = 60^\circ$) ^f	-263.4 ^e	296.1 ^e	32.6 ^e
4	CH ₂ ⁺ tetrahedral, intermediate ($\phi = 30^\circ$) ^f	0.9 ^g	0.5 ^g	1.4 ^g
5	CH ₂ ⁺ tetrahedral, eclipsed ($\phi = 0^\circ$) ^f	2.3 ^g	0.5 ^g	2.8 ^g
Methyl Cation				
	Planar	0.0	0.0	0.0
	Tetrahedral	-0.2 ^h	32.7 ^h	32.5 ^h

^a All energies in kcal/mol. ^b See Figure 1 and text. Tetrahedral geometry for CH₃ assumed. ^c Sum of nuclear-electron attractions. ^d Sum of positive (repulsive) energies: electron-electron and nuclear-nuclear interactions and electron kinetic energies. ^e Relative to the energy of the planar form of I (calculation 1) -78.24224 hartrees = -2128.971 eV (1 hartree = 27.210 eV = 627.502 kcal/mol). ^f HCCH torsional angles. ^g Relative to the energy for the tetrahedral, staggered ion (calculation 3). ^h Relative to the energy of the planar form; total energies: -39.20731 hartrees = -1066.831 eV.

earlier conclusion that *rigid* rotation gives effectively a zero sixfold barrier.³

Table II. STO-3G¹¹ Energies for Geometrically Optimized Ethyl Cation Structures

Calculation	Geometry ^a	E^b	ΔE^c
6	Structure I, lengths optimized ^d	-77.406062	1.25
7	Structure II, lengths optimized ^d	-77.406059	1.25
8	Structure I, full optimization	-77.408055	
9	Structure II, full optimization	-77.407703	0.22
10	Structure III, full optimization	-77.389859	11.42

^a See Figure 1 and text. ^b Total energies in hartrees. ^c Energies in kcal/mol relative to calculation 8 (the predicted equilibrium geometry). ^d Tetrahedral CH₃ and trigonal CH₂⁺ assumed.

In calculations 8 and 9, *all* geometrical parameters in structures I and II were varied, the only restriction being the retention of a single reflection plane as shown. As a result of change of bond angles away from the previously fixed values, the energy of structure I is lowered by 1.25 kcal/mol and that of structure II by 1.03 kcal/mol. Thus, if the bond angles are allowed to change during internal rotation about the C-C bond, a sixfold barrier of 0.22 kcal/mol is predicted, structure I having the lowest energy.

Full details of the predicted STO-3G equilibrium geometry of this and other small hydrocarbons will be presented in a future publication. One feature of interest in C₂H₅⁺ is that the angle C₁C₂H₃ in structure I is reduced to 102.2°, which may be interpreted as a partial approach toward a bridged protonated-ethylene struc-

(10) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968); K. S. Pitzer, *Discuss. Faraday Soc.*, **10**, 66 (1951); D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958).

(11) W. J. Hehre, R. F. Stewart, and J. A. Pople, *ibid.*, **51**, 2657 (1969).

(12) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, in press.

ture. However, the CH_2^+ plane for structure I is displaced 2.9° upward from the C-C line toward H_3 . This corresponds to a small distortion toward a staggered ethane type of geometry.

Calculation 10 refers to the symmetrically bridged structure III which is found to be 11.4 kcal/mol less stable than the most stable classical form (I). This is close to the *ab initio* value previously calculated (9.0 kcal/mol, without full optimization),³ and in very good agreement with Pfeiffer and Jewett's value (12.1 kcal/mol, with partial minimization).⁸ The CH_2 groups are bent away from the bridging hydrogen (H_3), and 2.5° from the C-C line as shown (III). The perpendicular distance of the bridging proton from the C-C bond is 1.15 Å.

To determine whether the bridged structure III is a saddle point on the potential surface (transition state) or a local minimum (intermediate) in the degenerate rearrangement of one classical ethyl cation to another, a computation was carried out in which H_3 was moved 0.05 Å parallel to the C-C bond and the planes $\text{H}_4\text{C}_2\text{H}_5$ and $\text{H}_1\text{C}_1\text{H}_2$ were rotated counterclockwise by 1° . This lead to an energy lowering of 40 cal/mol, indicating that III is a transition state and not a metastable species (intermediate). Thus, these calculations predict a gas-phase activation barrier of 11.4 kcal/mol for 1,2-hydride shifts in the ethyl cation.¹³

Acknowledgments. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49(638)-1625, the National Science Foundation (GP 9233 and GP 9338), the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (AI-07766). Some of the computer time was provided by Princeton University and Mellon Institute.

(13) For related, recent results in strong acid media, see P. C. Myhre and E. Evans, *J. Amer. Chem. Soc.*, **91**, 5641 (1969); P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969).

(14) National Science Foundation Predoctoral Fellow, 1965-1969; Ph.D. Thesis, Princeton University, 1969.

(15) Princeton University Fellow, 1968-1969; American Cyanamid Fellow, 1969-1970.

James E. Williams, Jr.,¹⁴ Volker Buss¹⁵
Leland C. Allen, Paul v. R. Schleyer

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

William A. Lathan, Warren J. Hehre
John A. Pople

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received August 20, 1969

Activated Complex for Hydrogen Migration in the Ethyl Cation. *Ab Initio* Calculations

Sir:

We wish to report the results of *ab initio* LCAO-MO SCF calculations concerning the structure of the ethyl cation.¹ The results of the calculations bear on two related problems of experimental and theoretical interest. First, we are concerned with the relative stabilities of open or "classical" and hydrogen-bridged or "nonclassical" ethyl cations. Second, we wish to ex-

(1) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970). We express our appreciation to Professor Schleyer for providing us with the results of this work before publication.

amine whether a hydrogen-bridged structure is best described as an activated complex or an intermediate for 1,2 hydride migration in the ethyl cation. Of course these calculations apply only to the gas phase and solvation effects may alter the equilibrium geometry and structure of carbonium ions in solution.

Previous semiempirical calculations for C_2H_5^+ have given conflicting predictions concerning the structure of the ethyl cation: some reports indicate the bridged structure to be more stable² while other reports find the open structure as the more stable conformation.³ *Ab initio* calculations including the present work indicate that the bridged structure is less stable than the classical conformation.^{1,2b,4} In Table I we give the energies for

Table I. Energies for Bridged and Classical Structures

Structure ^a	E^b	ΔE^c
A	-78.22466	12.43
B	-78.22519	12.10
C	-78.22920	9.58
D	-78.24446	

^a For a description of the structures see Figure 1 and text. ^b Total energies in hartrees. ^c Energies in kcal/mol relative to structure D.

the bridged and classical structures shown in Figure 1. The basis set for these calculations consists of gaussian lobe functions with Whitten's exponents and coefficients for each function.⁵ The H(1s) function is represented by a linear combination of five gaussian functions. All of the calculations reported here were obtained with the five-term hydrogen function split into two parts which were then individually subject to linear minimization by the SCF procedure. A basis set of this quality has had excellent success in yielding molecular geometries in close agreement with experiment.⁶ We have examined a large number of conformations of C_2H_5^+ in an effort to find relative energies and optimal geometries for the open and bridged forms. In addition we wished to understand the bonding environments in these conformations and have performed population analyses on each of the conformations studied. The details of the energy terms of the numerous conformations studied as well as population analyses for these conformations will be presented in a full paper. We describe here points of immediate interest.

For the open or classical ethyl cation we first consider a structure with the CH_3 group tetrahedral with $r_{\text{CH}} = 1.091$ Å, the CH_2 group trigonal with $r_{\text{CH}} = 1.086$ Å, and a plane of symmetry through one of the CH_3 hydrogens and the CC bond. Energy minimization with respect to the CC bond length yields $r_{\text{CC}} = 1.51$ Å. The choice of a planar cationic center has previously been shown to yield the equilibrium confor-

(2) (a) T. Yonezawa, H. Nakatsuji, and H. Kato, *ibid.*, **90**, 1239 (1968); (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); (c) J. J. Dannenberg and T. D. Berke, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract No. PHYS 163.

(3) R. Hoffman, *J. Chem. Phys.*, **40**, 2480 (1964); R. E. Davis and A. S. N. Murthy, *Tetrahedron*, **24**, 4595 (1968); G. Klopman, private communication, 1969.

(4) J. E. Williams, Ph.D. Thesis, Princeton University, 1969.

(5) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

(6) For a summary of some results see L. C. Allen in "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Lowdin, Ed., Academic Press, New York, N. Y., 1966.