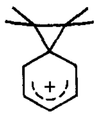
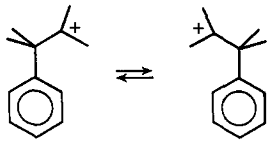
The Ethylenebenzenium Cation

Sir:

The observation that β-phenylethyl derivatives undergo facile rearrangements in solution provided Cram[1] with an early opportunity to propose the involvement of bridged carbocation intermediates. Although the original (stereochemical) evidence demanding a bridged intermediate was quickly strengthened by the kinetic studies of Winstein and his collaborators[2] the proposal was vigorously challenged by Brown,[3] who noted that the observed stereochemistry as well as the kinetic rate enhancements could easily be accounted for on the basis of a rapidly equilibrating pair of open ions. The experimental evidence against such an alternative has mounted in the past decade[4] crowned recently by the direct observation of the elusive ion in superacid media.[5] Even though the ion formed on solvolysis of β-phenylethyl derivatives is now known to possess a symmetric bridge structure[6] in its ground state, the detailed nature of its structure remains a mystery. Also unanswered is the extent to which open ethylenebenzenium ions are involved in solvolysis.

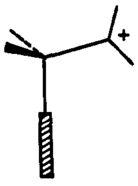




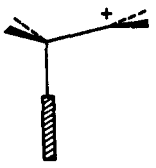
In this communication we consider a straightforward application of *ab initio* molecular orbital theory to the description of a section of the $C_8H_9^+$ potential surface. We shall be interested primarily in the predictions to the theory concerning both the equilibrium structures and relative stabilities of open and bridged forms of ethylenebenzenium ions and in a comparison of these results with related studies on the homoallyl-cyclopropylcarbinyl[7] and benzenium–benzenonium[8] systems.

Quantum mechanical methods have been described in the preceding communication.[7] Because of the large size of the molecules involved only a limited amount of geometric optimization has been performed, and our studies have been restricted to a minimal basis level.

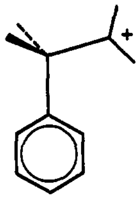
Considering initially the open forms of the ethylenebenzenium ion (I–IV),[9] the theory predicts the *orthogonal perpendicular* structure II to be the most stable. The *orthogonal staggered* (I) and *planar perpendicular* (IV) forms are related to it by single bond rotations *without activation*, while the *planar staggered* structure III is unstable with respect to either of two single bond torsions. More importantly, we find the *orthogonal perpendicular* structure to collapse *without activation* to a symmetric bridged ethylenebenzenium ion (V).[10] This lack of stable open forms is entirely consistent with the findings of our parallel study on the homoallyl–cyclopropylcarbinyl system.



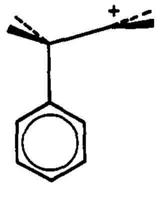
I



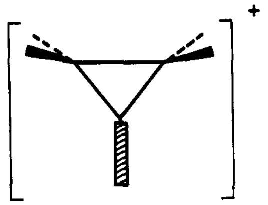
II



III



IV



V

The (partially optimized[11]) structure for symmetric bridged ethylenebenzenium is striking in comparison with those of cyclopropylcarbinyl[7] and benzenium.[8] The predicted distortion of the cyclopropyl ring away from threefold symmetry is nearly identical in both cyclopropylcarbinyl and ethylenebenzenium (angles $C_2C_1C_2'$ of 53.7 and 54.4° and C_1C_2 bond lengths of 1.609 and 1.598 Å in the two molecules, respectively), while the aromatic ring in benzenium is somewhat more perturbed from sixfold symmetry (angle corresponding to $C_3C_1C_3'$ (in ethylenebenzenium) has diminished to 110.9°) than we note here.

Table I presents theoretical STO-3G energies (relative to bridged ethylenebenzenium) for the open and bridged forms of the ethylenebenzenium. It is expected that

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[1] D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949); D. J. Cram and R. Davis, *ibid.*, **71**, 3875 (1949); see also D. J. Cram, *ibid.*, **86**, 3767 (1964).

[2] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

[3] H. C. Brown, *Chem. Soc., Spec. Publ.*, No. **16**, 140 (1962); see also H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965).

[4] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967); H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968); H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); for a different outlook see S. L. Loukas, M. R. Velkou, and G. A. Gregoriou, *Chem. Commun.*, 251 (1970), and references cited therein.

[5] G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 6877 (1971), and references therein pertaining to nmr observations on related species. These authors report evidence in favor of a structure virtually identical with that proposed by Cram two decades before.

[6] Following the nomenclature proposed by G. A. Olah (*ibid.*, **94**, 808 (1972)), ions of this type are termed ethylenebenzenium.

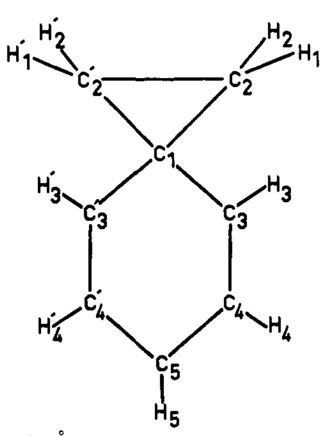
[7] Preceding communication: W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972).

[8] W. J. Hehre and J. A. Pople, *ibid.*, in press.

[9] For the open ethylenebenzenium ions we have used standard geometries derived from those of benzene (M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970)) and bisected and eclipsed forms of the ethyl cation (W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971)). Preliminary optimization studies on these molecules indicate that the reported trends are valid.

[10] A previous theoretical (CNDO) study gave this same result, but full impact was lacking because of the method's considerable bias in favor of ring structures. Indeed, calculations by the same author using the extended Hückel method gave opposite results: E. I. Snyder, *ibid.*, **92**, 7529 (1970); see, also, G. W. Van Dine and R. Hoffmann, *ibid.*, **90**, 3227 (1968).

[11] The values for geometrical parameters not considered in the optimization procedure are given in parentheses.



$r(C_1C_2) = 1.598$ Å
$r(C_2C_2') = 1.460$ Å
$r(C_3C_4) = (1.400$ Å)
$r(C_2H_1) = (1.080$ Å)
$r(C_4H_4) = (1.080$ A)
$\angle C_2C_1C_2' = 54.4°$
$\angle C_1C_3C_4 = 122.1°$
$\angle C_4C_5C_4' = (120.0°)$
$\angle H_{12}C_2C_2'$[12] $= 158.2°$
$\angle H_3C_3C_1 = 118.3°$
$\angle H_5C_5C_4 = (120.0°)$

$r(C_1C_3) = 1.431$ Å
$r(C_4C_5) = (1.400$ Å)
$r(C_3H_3) = (1.080$ Å)
$r(C_5H_5) = (1.080$ A)
$\angle C_3C_1C_3' = 115.8°$
$\angle C_3C_4C_5 = (120.0°)$
$\angle H_1C_2H_2 = 115.7°$
$\angle H_4C_4C_3 = (120.0°)$

Table I. Energy Data (kcal/mol)

Molecule	STO-3G
Bridged ethylenebenzenium (V)	0
Orthogonal perpendicular ethylenebenzenium (II)	35.4
Orthogonal staggered ethylenebenzenium (I)	42.3
Planar perpendicular ethylenebenzenium (IV)	46.5
Planar staggered ethylenebenzenium (III)	48.8

the relative energies of the open ions will be lowered some 10–15 kcal/mol by further geometric optimization and by extension of the basis function beyond minimal.[13] It is not anticipated, however, that such an effect will alter the stated conclusions.

In this and in the preceding communication[7] we have provided two examples of the interaction of an electron-deficient center with an area rich in density. The similarity is striking and we believe extends well beyond our present applications.

Acknowledgments. The author gratefully acknowledges Professor Lionel Salem (Orsay) for his comments and criticisms on the manuscript.

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[12] $H_{12}C_2$ refers to the line bisecting the plane formed by carbon 2 and hydrogens 1 and 2.

[13] This latter behavior is to be expected in light of our experience with the homoallyl–cyclopropylcarbinyl system; see ref 7.

[14] Also part of the Laboratoire de Physico-Chimie des Rayonnements associated with the CNRS.

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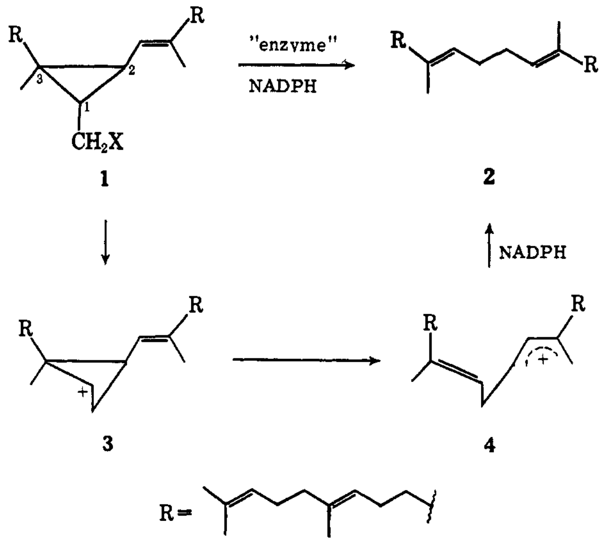
Solvolysis of *trans*-2,2-Dimethyl-3-(2′-methylpropenyl)cyclobutyl Tosylate. Model Reactions Relevant to Squalene Biosynthesis

Sir:

The reductive coupling of farnesyl pyrophosphate to squalene (**2**) proceeds through the C-30 intermediate, presqualene pyrophosphate,[1] the structure of which (**1**, X = OPP) now seems firmly established.[2,3] The rearrangement pathway **1** → **3** (or equivalent delocalized species) → **4**, terminated by a stereospecific hydride transfer from NADPH (Scheme I), has been suggested[1b,2,3b,4] as a mechanism for the **1** → **2** transformation.[5]

Scheme I



While this mechanism finds precedent in the rearrangements of cyclopropylcarbinyl compounds,[6] the heterolytic reactions of *trans*-chrysanthemol derivatives (**1**, R = CH_3) in solution lead principally to ring cleavage products.[7,8] In order to determine whether the subsequent steps in Scheme I would occur in the absence of enzymatic control, we have investigated the reactions of the C-10 cyclobutyl tosylate, **6**-OTs, a potential precursor to cation **3** (R = CH_3).[9] The corresponding C_{30} pyrophosphate has in fact been proposed as an additional enzymic intermediate between presqualene pyrophosphate and squalene.[2b] The trans isomer was selected in view of the stereochemistry

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[1] (a) H. C. Rilling, *J. Biol. Chem.*, **241**, 3233 (1966); (b) W. W. Epstein and H. C. Rilling, *ibid.*, **245**, 4597 (1970).

[2] (a) H. C. Rilling, C. D. Poulter, W. W. Epstein, and B. Larsen, *J. Amer. Chem. Soc.*, **93**, 1783 (1971); (b) J. Edmond, G. Popják, S-M. Wong, and V. P. Williams, *J. Biol. Chem.*, **246**, 6254 (1971).

[3] (a) R. V. M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, 218 (1971); (b) L. Altman, R. C. Kowerski, and H. C. Rilling, *J. Amer. Chem. Soc.*, **93**, 1782 (1971); (c) R. M. Coates and W. H. Robinson, *ibid.*, **93**, 1785 (1971).

[4] E. E. van Tamelen and M. A. Schwartz, *ibid.*, **93**, 1780 (1971).

[5] A similar scheme, but with ultimate deprotonation, may be involved in the biosynthetic coupling of geranyl-geranyl pyrophosphate to phytoene (dehydro 2, R = *trans,trans*-homofarnesyl): W. W. Epstein, private communication; R. J. H. Williams, G. Britton, J. M. Charlton, and T. W. Goodwin, *Biochem. J.*, **104**, 767 (1967). The synthesis of prephytoene and its role in carotene biosynthesis have recently been reported: L. J. Altman, L. Ash, R. C. Kowerski, W. W. Epstein, B. R. Larsen, H. C. Rilling, F. Muscio, and D. E. Gregonis, *J. Amer. Chem. Soc.*, **94**, 3257 (1972).

[6] For leading references, see G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972).

[7] (a) L. Crombie, R. P. Houghton, and D. K. Woods, *Tetrahedron Lett.*, 4553 (1967); (b) R. B. Bates and D. Feld, *ibid.*, 4875 (1967); (c) C. D. Poulter, S. G. Moesinger, and W. W. Epstein, *ibid.*, 67 (1972).

[8] A small amount of 2,7-dimethyl-2,6-octadien-4-yl methyl ether (methyl ether of 8) has recently been obtained from methanolysis of 2,5,5-trimethyl-2,6-heptadien-4-yl dimethylsulfonium fluoroborate, presumably by way of 1 (R = CH_3, X = +) and 4 (R = CH_3): B. M. Trost, P. Conway, and J. Stanton, *Chem. Commun.*, 1639 (1971).

[9] A similar investigation has been independently carried out by C. D. Poulter, *et al.*, *J. Amer. Chem. Soc.*, **94**, 5921 (1972).