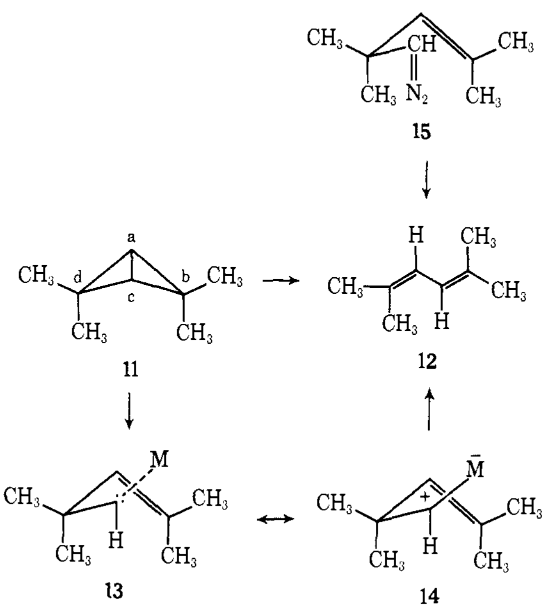
spectroscopy. Diene **10** was quite normal, showing a uv maximum in isooctane at 240 nm ($\epsilon$ 17,750). In contrast, **9** gave an abnormal uv spectrum with $\lambda_{\max}^{\text{isooctane}}$ 220 nm ($\epsilon$ 3850). The unusually short wavelength, weak absorption for **9** was consistent with expectations, since the strong methyl–methyl interactions in **9** would be expected to twist the double bonds out of coplanarity.[9] The nmr spectrum of **9** showed $H_A$ at $\tau$ 4.63 and $H_B$ at 4.12 with $J_{AB}$ = 11 cps. In comparison, **10** had $H_A$ at $\tau$ 4.54 and $H_B$ at 3.56 with $J_{AB}$ = 15 cps. Both the positions of the protons and the larger coupling constant between the vinylic protons of **10** are consistent with the assigned structures.

It is obvious that the presence of the additional bridgehead methyl group dramatically changes the course and stereospecificity of the isomerization of **1**. Whereas diene formation from **1** was stereospecific, diene formation from **8** was almost statistical. In addition, **8** failed to yield any vinylcyclopropane derivative with rhodium dicarbonyl chloride dimer.

In view of the strong influence of the additional methyl group on the rearrangement of **1** we decided to study the transition metal carbonyl-promoted rearrangement of 2,2,4,4-tetramethylbicyclo[1.1.0]butane (**11**),[10] which is isomeric with **8**. This bicyclo[1.1.0]butane derivative was of particular interest because it could not follow the same type of reaction paths followed by **1**, **4**, **6**, and **8**. In the transition metal carbonyl-promoted isomerizations observed for **1**, **4**, **6**, and **8**, the central bond and one peripheral bond of the bicyclo[1.1.0]butane moiety were cleaved in each case. We have noted[2] that this *formally* corresponds to a transition metal carbonyl-promoted retrocarbene addition or to an elimination of a carbenoid–metal complex. In each of the examples presented above, the cleavage reaction must be followed by hydrogen shift in order to produce the observed dienes. 2,2,4,4-Tetramethylbicyclo[1.1.0]butane lacks such a suitably situated hydrogen.

When **11** was treated with 5 mol % of rhodium dicarbonyl chloride dimer at 25° in chloroform for 5 min, an 83% yield of **12** was obtained. Similar treatment of **11** with 5 mol % of iridium tricarbonyl chloride dimer at 25° for 12 hr gave an 87% yield of **12**. On the surface it would appear that the presence of the two methyl groups at C-4 of **11** had completely changed the course of the rearrangement, even to the extent of changing which bonds were cleaved. The simplest explanation for these observations would be that the transition metal carbonyl complexes were promoting the cleavage of either bonds a–b and c–d, or a–d and b–c, while leaving a–c intact in a manner similar to the cleavage noted for the thermal rearrangement of bicyclo[1.1.0]butanes.[11] However, this would be quite inconsistent with the precedent set by the transition metal carbonyl-promoted isomerizations of **1**, **4**, **6**, and **8**. We feel that an alternate explanation can be provided which is consistent with our other findings. Cleavage of **11** could occur to give a metal complex of a carbenoid intermediate such as **13**. It is known that migratory aptitudes to a carbenoid center are hydrogen > vinyl > methyl.[12] Since there is no adjacent hydrogen available for migration in **13**, migration of the vinylic portion might be expected to occur, producing **12**. Such a vinyl migration should be especially favored in the case of a metal complexed carbene such as **13** which would have considerable positive charge on carbon as illustrated by its resonance contributor **14**. Thus, the metal-bonded cation, **14**, should be able to readily sustain a vinyl migration. Evidence for the feasibility of this concept was amply provided by the rhodium dicarbonyl chloride dimer promoted decomposition of **15** which occurred violently at low temperatures to yield **12** as the only volatile product.



We are continuing to investigate the mechanistic details of these fascinating metal complex promoted rearrangements.

**Acknowledgment.** We are indebted to the National Science Foundation for support of this work.

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(9) For a twisted diene system such as 1,3-cyclooctadiene we have found $\lambda_{\max}$ 228 nm ($\epsilon$ 4300).

(10) For the preparation of **11** see H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Siega, *J. Amer. Chem. Soc.*, **93**, 121 (1971). We wish to thank Dr. Cherkofsky for providing us with the experimental procedure for the preparation of **11** prior to publication.

(11) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); G. L. Closs and P. E. Pfeffer, *ibid.*, **90**, 2452 (1968); and R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(12) Professor H. Shechter, private communication. We wish to thank Professor Shechter for an enlightening and helpful discussion of this problem.

(13) Alfred P. Sloan Research Fellow, 1967–1969.

(14) National Science Foundation Trainee, 1968–1971.

(15) Goodyear Fellow, 1968–1969; Dow Chemical Fellow, 1969–1970.

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## Structures and Relative Stabilities of $C_3H_7^+$ Cations

*Sir:*

There has been considerable recent interest in the $C_3H_7^+$ series of cations both from an experimental and theoretical viewpoint. A great deal of the attention has been focused on the possibility of protonated cyclopropanes and other nonclassical cations as reaction intermediates.[1] Although both semiempirical[2–6] and

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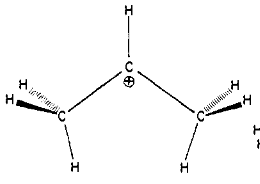
(1) For recent reviews see C. J. Collins, *Chem. Rev.*, **69**, 541 (1969); C. C. Lee, *Progr. Phys. Org. Chem.*, **7**, 129 (1970); J. L. Fry and G. J.

*ab initio*[7,8] molecular orbital calculations have been applied to the problem, there has been no extensive geometry optimization at the *ab initio* level. We have found that in the absence of preliminary data (such as geometries of very similar cations), geometry optimization is critical in species of the kind dealt with here since many of the bond lengths and angles have unusual values. Again, there are serious reservations on the current use of semiempirical techniques with charged species and, in particular, these methods may artificially favor cyclic over open structures.[3,9] We have therefore performed *ab initio* molecular orbital calculations with complete geometry optimization (subject only to specified symmetry restrictions) for the 2-propyl cation (I), methyl-eclipsed 1-propyl cation (II), methyl-staggered 1-propyl cation (IV), and corner- (III, V), edge- (VI), and face- (VII) protonated cyclopropanes.[10] In this communication, we present preliminary comments on the geometries and energies of these cations.



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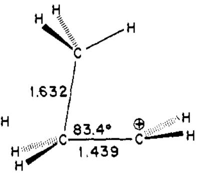

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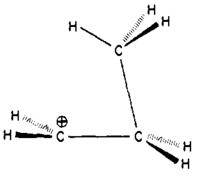

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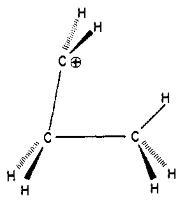

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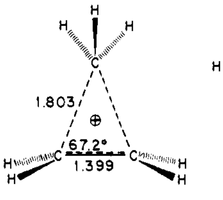

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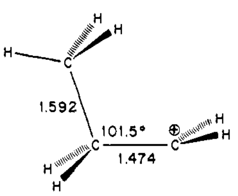

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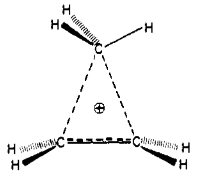
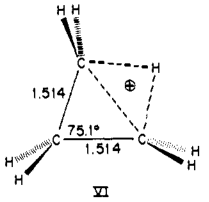
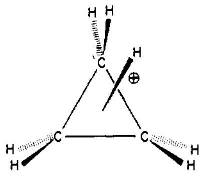


V



VI



VII

Standard self-consistent field molecular orbital theory was used. Minimization of the calculated energy with respect to the geometric parameters was carried out with the minimal STO-3G basis set[11] which has previously been applied successfully to the study of molecular geometry.[12-14] Single calculations on the STO-3G optimized geometries were then performed with the extended 4-31G basis set[15] which is more reliable for energy comparisons.[13-16] The relative energies obtained with both basis sets are listed in Table I.[17]

Table I. Relative Energies[a] of $C_3H_7^+$ Cations

| No. | Cation | Symmetry | STO-3G | 4-31G |
|---|---|---|---|---|
| I | 2-Propyl | $C_{2v}$ | 0 | 0 |
| II | 1-Propyl (methyl eclipsed) | $C_s$ | 20.5 | 16.9 |
| III | Corner-protonated cyclopropane | $C_s$ | 22.8 | 17.3 |
| IV | 1-Propyl (methyl staggered) | $C_s$ | 19.7 | 17.4 |
| V | Corner-protonated cyclopropane | $C_s$ | 22.9 | 17.4 |
| VI | Edge-protonated cyclopropane | $C_{2v}$ | 27.1 | 27.1 |
| VII | Face-protonated cyclopropane | $C_{3v}$ | 161.0 | 139.6 |

[a] Kilocalories per mole.

The principal points that emerge from these calculations are: (1) the 2-propyl cation I is the lowest energy form of $C_3H_7^+$. The energy difference between the 1- and 2-propyl cations (~17 kcal mol$^{-1}$ with 4-31G) is in close agreement with a recent experimental value[18] (16 kcal mol$^{-1}$). The minimum energy conformation I has a somewhat widened CCC bond angle of 126.0°. (2) In agreement with all previous conclusions,[2-5,7,19] the face-protonated cyclopropane VII is a highly unfavorable geometry for $C_3H_7^+$. (3) The methyl-eclipsed (II) and methyl-staggered (IV) 1-propyl cations and the corner-protonated cyclopropanes III and V all have similar energies. The potential surface has not been fully determined at the 4-31G level but the points that are available suggest a moderately flat region linking II, III, IV, and V. For example, a 1,2-methyl shift (II → III → II') requires only 0.4 kcal mol$^{-1}$ activation energy. (4) The methyl-staggered 1-propyl cation IV differs somewhat from the classical formulation. The CCC bond angle is decreased to 101.5°, the cation $CH_2^+$ center is nonplanar (as with the ethyl cation[13,20]) being bent 5.4° *toward* the methyl group, and the C–C bond lengths[21] are unequal ($C_1$–$C_2$ = 1.474 Å, $C_2$–$C_3$ = 1.592 Å). (5) The methyl-eclipsed 1-propyl cation II has an even more distorted geometry with the CCC angle reduced to 83.4° and could therefore alternatively be regarded as a distorted corner-protonated cyclopropane. However, despite the closer approach of the methyl group, the cationic

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Karabatsos in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 14. See also R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964); C. C. Lee and D. J. Woodcock, *ibid.*, **92**, 5992 (1970); G. J. Karabatsos, C. Zioudrou, and S. Meyerson, *ibid.*, **92**, 5996 (1970).

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(4) H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Lett.*, 5821 (1968).

(5) H. Kollmar and H. O. Smith, *ibid.*, 1833 (1970).

(6) H. Kollmar and H. O. Smith, *Angew. Chem., Int. Ed. Engl.*, **9**, 463 (1970).

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(8) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6380 (1970).

(9) This conclusion also emerges from a comparison of the present *ab initio* results with those from modified CNDO calculations on the same $C_3H_7^+$ species.[5]

(10) Corner- and edge-protonated cyclopropanes are taken as the forms with the bridging carbon or hydrogen equidistant from two carbon atoms. The bridging hydrogen in face-protonated cyclopropane is equidistant from all three carbon atoms.

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(17) The STO-3G and 4-31G relative energies are quite similar but the numerical values given in the following discussion refer to the 4-31G calculations.

(18) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(19) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, **92**, 3469 (1970); R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **92**, 3471 (1970).

(20) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970).

(21) All bond lengths in this paper are in ångströms (Å).

CH$_2^+$ plane remains bent (4.2°) toward this group. The C–C bond lengths (C$_1$–C$_2$ = 1.439 Å and C$_2$–C$_3$ = 1.632 Å) move closer to the values for methyl-bridged structures III and V. This species, II, is predicted (by the 4-31G basis set) to be the most stable form after I, and may well correspond to the only other potential minimum in the complete C$_3$H$_7^+$ surface. It could have important implications regarding mechanistic schemes recently proposed[1] to rationalize results of experimental studies of reactions which may involve protonated cyclopropanes. The coupled methyl rotation and bond angle distortion process (II → IV) requires surprisingly little energy (0.5 kcal mol$^{-1}$). (6) Rotation of the methyl group in corner-protonated cyclopropane (III → V) is practically free corresponding to the sixfold barrier. An analogous situation is the methyl rotation in the $C_s$ form of CH$_5^+$ in which the ethylenic moiety can be considered to be replaced by H$_2$.[22] In III and V both CH$_2$ groups are bent by about 11° from the C=C line *away* from the methyl group. The bridging C–C bond length is 1.803 Å and the other C–C bond has shortened to 1.399 Å. The CCC angle (at the nonbridging carbon) is now 67.2°. (7) Edge-protonated cyclopropane VI is found to have a higher energy than either the corner-protonated or the 1-propyl forms (II–V). A 1,3-hydride shift (II → VI → II″) requires about 10 kcal mol$^{-1}$. The C–C bond lengths are 1.516 and 1.849 Å while the bridging hydrogen is 1.315 Å from either carbon.

Experimental data have usually been treated in terms of edge- and corner-protonated cyclopropanes.[1] However, we find that neither of these structures is an energy minimum. Instead, a new species of highly unusual structure II has emerged from this study as a probable intermediate. The structure of II illustrates the dangers inherent in arbitrary distinctions between "classical" and "nonclassical" carbonium ions. Even "classical" carbonium ions may have structures which differ appreciably from those normally assumed.

A full presentation of these results and discussion in the light of experimental data[1] and previous theoretical work[2–8] will be presented in a forthcoming paper.

**Acknowledgments.** This work was supported by NSF Grants No. GP-9233 and GP-9338. Some computer time was provided by Mellon Institute and Princeton University.

(22) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, **5**, 361 (1970); W. A. Lathan, W. J. Hehre, and J. A. Pople, unpublished data.

(23) Princeton University Fellow, 1968–1969; American Cyanamid Fellow, 1969–1970.

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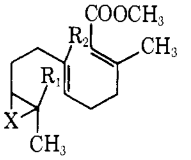
## Synthetic Imino Analogs of *Cecropia* Juvenile Hormones as Potentiators of Juvenile Hormone Activity

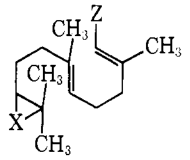
*Sir:*

2,3-Iminosqualene[1] is a potent inhibitor of the enzymes which convert 2,3-oxidosqualene to lanosterol[1] or pentacyclic triterpenes.[2,3] The C$_{18}$[4] and C$_{17}$[5] juvenile hormones (JH) of *Cecropia* (I and II) possess in common with 2,3-oxidosqualene a trisubstituted oxirane ring located at one end of the molecular chain. It seemed of interest, therefore, to synthesize imino analogs of I and II and to study their biological activity. While the results of such studies could not be predicted, several reasonable possibilities could be envisaged. For example, (1) the imino compounds might be devoid of JH activity themselves but capable of strong binding to one or more sites which are crucial to JH action resulting in hormone inhibition (or antihormone activity), (2) III and IV might prevent the enzymic conversion of I and II to other molecular structures which are the true juvenile hormones, (3) III and IV might prevent the metabolic destruction of JH, or (4) they might be even more active hormones than the natural JH. The results reported below seem to support the third of these hypothetical situations.

The imino JH analogs III and IV were synthesized by taking advantage of the method used previously[1] for the transformation of an oxirane derivative to an azirane structure. For the synthesis of III the oxido derivative of *trans,trans*-farnesyl acetate[6] (V) was treated with excess lithium azide in dimethoxyethane–acetic acid at 25° for 17 hr to form a hydroxy azide[7a] which was converted by reaction with *p*-toluenesulfonyl chloride–pyridine to the corresponding tosyloxy azide,[7a] purified by chromatography on silica gel ($R_f$ 0.65, CH$_2$Cl$_2$), and reductively cyclized by excess lithium aluminum hydride in ether (0°, 30 min, and 25°, 10 min) to give VI (25% from V).[7] Oxidative esterification of VI by the manganese dioxide–cyanide–methanol procedure[8] yielded the desired imino ester III (35% yield), without the necessity for protection of the imino function.

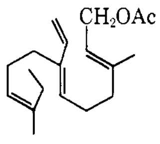
The synthesis of IV was accomplished starting from the readily available[9] tetraene VII. Reaction of VII



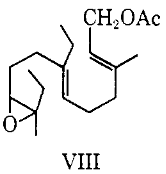


I, R$_1$ = R$_2$ = C$_2$H$_5$; X = O
II, R$_1$ = C$_2$H$_5$; R$_2$ = CH$_3$; X = O
III, R$_1$ = R$_2$ = CH$_3$; X = NH
IV, R$_1$ = R$_2$ = C$_2$H$_5$; X = NH

V, X = O, Z = CH$_2$OAc
VI, X = NH, Z = CH$_2$OH



VII



VIII

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(1) E. J. Corey, P. R. Ortiz de Montellano, K. Lin, and P. D. G. Dean, *J. Amer. Chem. Soc.*, **89**, 2797 (1967).

(2) E. J. Corey and P. R. Ortiz de Montellano, *ibid.*, **89**, 3362 (1967).

(3) See also (a) E. J. Corey and S. K. Gross, *ibid.*, **90**, 5045 (1968); and (b) E. J. Corey, K. Lin, and H. Yamamoto, *ibid.*, **91**, 2132 (1969).

(4) H. Röller, K. H. Dahm, C. C. Sweeley, and B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, **6**, 179 (1967).

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