$$C_6F_5Ag + (CH_3)_3SiCl \xrightarrow[Et_2O]{100°} C_6F_5Si(CH_3)_3\text{[20]} + C_6F_5H + C_6F_5\text{–}C_6F_5 \text{ (trace)} + AgCl \quad (6)$$

$$C_6F_5Ag + CH_3I \xrightarrow[\text{neat}]{25°} C_6F_5\text{–}CH_3\text{[21]} + AgI \quad (7)$$

$$C_6F_5Ag + C_6H_5I \xrightarrow[DMF]{110°} C_6F_5\text{–}C_6H_5\text{[4]} + AgI \quad (8)$$

$$C_6F_5Ag + C_6H_5CH_2Br \xrightarrow[Et_2O]{25°} C_6F_5CH_2C_6H_5\text{[22]} + AgBr \quad (9)$$

$$C_6F_5Ag + CH_3COCl \xrightarrow[\text{neat}]{30°} C_6F_5COCH_3\text{[23]} + AgCl \quad (10)$$

The experiments summarized in eq 3–10 demonstrate the utility of the perfluoroaromatic silver compounds as synthetic intermediates. It is believed that their use for the preparation of organometallic compounds by reaction with the corresponding halides will prove to be of particular value. The insolubility of the silver halides makes possible the preparation of compounds of elements above silver in the electromotive series as well as those below.

Perfluorophenylsilver was shown to undergo exchange with *trans*-2-iodoperfluoro-2-butene to form *trans*-perfluoro-1-methylpropenylsilver.[24]

$$C_6F_5Ag + CF_3CF{=}CICF_3 \xrightarrow[Et_2O]{50°} C_6F_5I + trans\text{-}CF_3CF{=}C(CF_3)Ag \quad (11)$$

Such exchange reactions are expected to yield information as to the nature of carbon–silver bonds and the electronic properties of perfluoro groups as well as to provide syntheses for new silver compounds. Our present results show that the tendency of perfluoro groups to compete for silver ion is

$$CF_3CF{=}C(CF_3)\text{-} > C_6F_5\text{-} > (CF_3)_2CF\text{-}$$

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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[24] Initial experiments have yielded only *trans*-1-methylpropenylsilver from both *cis*- and *trans*-2-iodoperfluoro-2-butene. These results suggest that *cis*-$CF_3CF{=}C(CF_3)Ag$ is easily converted into its trans isomer.

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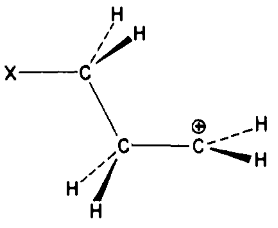
Received August 20, 1970

Rotational Barriers in 1-Propyl Cations

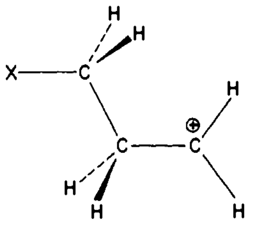
Sir:

It is well known[1] that sixfold rotational barriers are generally very small. In particular, it has recently been shown[2–4] that the barrier in the ethyl cation is close to zero when regular tetrahedral and trigonal bond angles are assumed and is raised only slightly (to 0.22 kcal mol^{-1}) when distortions are allowed. The effect of a single methyl substituent[5] as in the 1-propyl cation (I, II, X = H) is to make the barrier twofold and raise its value to 2.2–2.5 kcal mol^{-1}. The most stable conformation is I, which we call the *perpendicular* form, while the least stable conformation is the *eclipsed* form II.

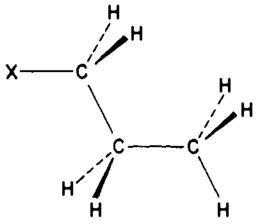
In order to study the relative stabilizing effects of substituents X in I and II, we have performed *ab initio* LCAO–SCF molecular orbital calculations with the STO-3G basis set[6] on the 1-propyl and a number of substituted 1-propyl cations. This procedure has given a reasonably satisfactory description of the rotational barriers in neutral hydrocarbons.[3,7] Standard values[8] of bond lengths and angles have been used with the additional values C$^+$–C = 1.49 Å, C$^+$–H = 1.12 Å as determined for the ethyl cation.[3] The carbonium center is taken to be trigonal.



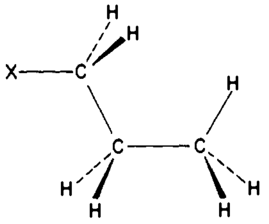
I



II



III



IV

The results of our calculations (Table I) show that the most stable conformation for all these cations is the *perpendicular* form (I). As expected, all these twofold barriers are larger than in the ethyl cation. A striking feature is the considerable variation of the barrier with the (distant) substituent X. This behavior is in contrast to the calculated barriers to rotation of the

Table I. Total Energies (hartrees) and Potential Barriers (kcal mol^{-1}) for Substituted 1-Propyl Cations

Substituent (X)	Energy I	Energy II	Barrier
CH_3	−154.57682	−154.57088	3.73
H	−115.99294	−115.98893	2.52
F	−213.42878	−213.42542	2.11
OH	−189.81070	−189.80925	0.91
CN	−206.51636	−206.51498	0.87

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Table II. Total Energies (hartrees) and Potential Barriers (kcal mol^{-1}) for Substituted Propanes

Substituent (X)	Energy III	Energy IV	Barrier
CH_3	−155.46457	−155.45878	3.63
H	−116.88512	−116.87924	3.69
F	−214.33172	−214.32621	3.46
OH	−190.70912	−190.70356	3.49
CN	−207.43037	−207.42457	3.64

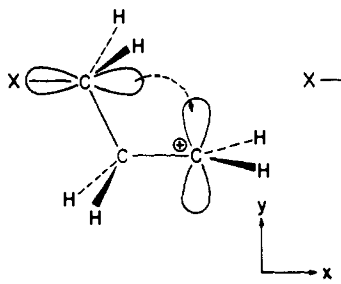
terminal methyl groups in the similarly substituted *propanes*, III *vs.* IV (Table II). Indeed, in these propanes, the barrier is effectively independent of the substituent X.

To gain insight into the mechanism of these effects it is instructive to look at some aspects of the electron distribution as, for example, the Mulliken gross population[9] of the "empty" 2p orbital at the positive carbon center (which we shall call the 2p(C$^+$) orbital) shown in Table III. We can see that in the *eclipsed* forms of the 1-propyl cations, the 2p(C$^+$) populations are approximately the same as in the ethyl cation and virtually invariant with respect to X. On the other hand, the 2p(C$^+$) populations in the *perpendicular* conformations are significantly greater than in the ethyl cation and strongly dependent on the substituent X, the populations being greatest (X = CH_3) and least (X = CN) in the cases where the barriers are greatest and least, respectively. These results suggest that (i) the CH_2X group does *not* interact with the 2p(C$^+$) orbital in the *eclipsed* conformation and (ii) the dominant effect producing the barrier is preferential stabilization of the *perpendicular* conformation through interaction of the CH_2X group with the 2p(C$^+$) orbital, leading to its increased population.

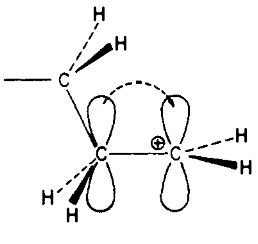
Table III. Populations of the 2p(C$^+$) Orbital in Substituted 1-Propyl Cations and the Ethyl Cation

Substituent (X)	Conformation I	Conformation II
CH_3	0.148	0.113
H	0.135	0.113
F	0.143	0.113
OH	0.132	0.116
CN	0.125	0.110
Ethyl cation	0.112	0.112

Analysis of overlap and atomic populations[9] (not reported in detail here) indicates that this interaction takes place by two mechanisms, *viz.*, (a) overlap of the $2p_x$ orbital on C_3 with the 2p(C$^+$) orbital on C_1 (see V) and (b) increased overlap population (compared with the ethyl cation) of the $2p_y$ orbital on C_2 with the 2p(C$^+$) orbital on C_1 (see VI). In the *eclipsed* conformation (II), (a) cannot occur at all because of symmetry restrictions and, for the same reason, the CH_2X group cannot contribute directly to (b) either. This is reflected in overlap populations of the 2p(C$^+$) orbital in this conformation which are effectively independent of the substituent X. On the other hand, in the *perpendicular* form, the two effects (a and b) both occur and are magnified when X is electron releasing (*e.g.*, X = CH_3) and diminished when X is electron withdrawing (*e.g.*, X = CN), leading to higher and lower barriers, respectively.



V



VI

The classical approach to the calculation of the effect of substituents on carbonium ions is based on the Kirkwood–Westheimer model in which the cation is represented as a point charge.[10] This model, of course, predicts that the substituents, X, should not influence the rotational barrier (the energy difference between I and II). In contrast, the present quantum mechanical calculations predict that the effect of a γ substituent should depend significantly on the conformation at the cation center. Experimental tests are underway to differentiate between these predictions.

Acknowledgment. This research was supported in part by National Science Foundation Grants GP-9338 and GP9233.

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The Stereochemistry of SN1 Displacement at a Vinylic Carbon

Sir:

It has been reported recently that the SN1 solvolysis of two vinylic halides, namely of the 1,2-dianisyl-2-phenylethenyl[1a] and the 1-cyclopropylpropen-1-yl system,[1b] entails complete randomization of configuration. Presumably, a linear vinylic cation is formed as an intermediate, which on nucleophilic attack affords the cis and trans isomer with equal probability.[1]

The findings of Rappoport and Bergman raise the question whether complete "racemization" is a general feature of SN1 solvolysis of vinylic systems, perhaps as a consequence of the ready accessibility of either face of the vinyl cation in an intramolecular scrambling process or whether the special stability of the two systems studied merely allowed attainment of a symmetric solvation shell before covalent collapse to the products occurred.

In order to answer these questions we sought to study a vinylic system which would give rise to a less stable

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