"vertical stabilization" in a model system for the cyclopropylcarbinyl cation. Such results are especially puzzling when viewed in terms of the resonance model of the cyclopropylcarbinyl cation.[13]

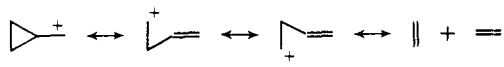
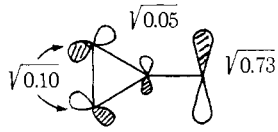


Table I, column IV, gives our calculated results for the stabilization of the cyclopropylcarbinyl cation by substituents in the 2 position. These stabilizations are all *ca.* one-tenth as large as the stabilization energies for the direct interaction of R with the carbinyl carbon given in Table I. This factor is consistent with the factor of 0.10 derived by simply taking the square of the coefficient of the in-plane p orbital at the 2 position of the ring in the LUMO of cyclopropylcarbinyl cation[14] derived from the CNDO/2 calculation.



3

The factor of 10 (derived either from the CNDO results or from the simple perturbation argument) is quite sufficient to account for Sneen's phenyl substituent effect. The factor of 250,000,000 = $10^{8.4}$, the observed substituent effect of a phenyl attached directly to the cation (Table I), is predicted to be reduced to $10^{8.4/10} = 7$ for the cyclopropylcarbinyl system, sufficiently close (especially if entropy effects are considered) to Sneen's factor of 2.2.

This analysis is also consistent with the observed relative rates for methyl and vinyl substituents on the cyclopropylcarbinyl cation. Methyl in the 2 position of the ring would be expected to accelerate the solvolysis rate by $10^{4.7/10} = 3$; the observed[2b] value is a factor of 10. Recently[15] the k_{rel} for a dimethylvinyl substituted cyclopropylcarbinyl cation has been determined as 15. The k_{rel} for the corresponding tetramethylallyl cation can be estimated[16] as $\sim 10^{13.7}$ leading to a predicted k_{rel} for the cyclopropylcarbinyl system of $10^{1.37} = 23$.

A methoxy group adjacent to an incipient cationic center accelerates the rate of solvolysis by $10^{14.17}$ Our analysis for the effect of a methoxy substituent in the 2 position of the cyclopropylcarbinyl system would predict $10^{1.4} = 25$. We would tend to agree, therefore, with Traylor's assertion[2e] that the observed[18] factor of 791 is due to some ring cleavage accompanying solvolysis.

(13) These resonance structures would, of course, be given very unequal weights. This resonance picture cannot then, however, correctly predict the extraordinary stability of the parent ion.

(14) (a) This refers only to the H_{ij}^2 parameter in the perturbation expression (eq 1). ΔE changes as well and accounts for some of the fluctuations encountered upon comparing columns 3 and 4 of Table I; these latter considerations have been alluded to by Dewar: M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965). (b) The coefficient at C_1 is small due to the mixing in of antibonding as well as bonding cyclopropane levels. Its magnitude is consistent with the known minor effect of substitution at that site.[2b]

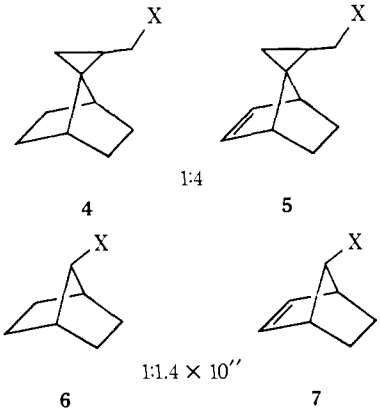
(15) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemuro, *Chem. Lett.*, 503 (1972).

(16) R. G. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(17) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Presitt, *J. Chem. Soc.*, 3641 (1955).

(18) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Amer. Chem. Soc.*, **92**, 4727 (1970).

The analysis presented here nicely rationalizes the small observed rate enhancement (a factor of 4 at 25°) experienced upon comparing compounds **4** and **5**.[2f]



4 5

6 7

Applying our treatment $10^{11.1/10} = 13$. This factor is further diminished when one considers that the strain associated with the 7 position of the norbornyl skeleton reduces still more the coefficient of the cyclopropyl p orbital at that position in the LUMO of the cation, **3**, a point made elegantly by Sargent[19] for the similar allylic systems.

In conclusion we feel that the perturbation arguments presented provide a clear qualitative explanation for the small effect of resonance stabilizing groups in the "intensely conjugated" [1a] cyclopropylcarbinyl system. The very same factor which makes cyclopropane an excellent stabilizing group, namely the concentration of electron density at one site in its interacting HOMO, assures, by depleting the coefficients at other sites, that the group is little responsive to substituent effects. The phenomenon cannot be generalized, but any case that does come up can be analyzed by the perturbation method given here. We feel that this approach has great potential in explaining the poor stabilization of other σ-delocalized ions by π donors.[18,20]

(19) T. J. Mason, M. J. Harrison, J. A. Hall, and G. D. Sargent, *J. Amer. Chem. Soc.*, **95**, 1849 (1973).

(20) (a) C. F. Wilcox and H. D. Banks, *J. Amer. Chem. Soc.*, **94**, 8231 (1972); (b) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965); (c) H. C. Brown, F. J. Chloupeck, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964); (d) E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963).

(20e) NOTE ADDED IN PROOF. Professor P. v. R. Schleyer has recently informed us of unpublished work with H. Alper on the solvolysis of 2-substituted cyclopropylcarbinyl derivatives that yields a good correlation against σ^+ with a ρ of -3.6 including the methoxy substituent. Even if this substituent sensitivity represented solely "vertical" stabilization (contrary to the evidence in ref 2e) the central conclusion of this communication would still hold. Also, in Table I if the reaction of ethane to ethyl cation is used as the reference the cation stabilization energies are reduced by a factor of about 0.66.

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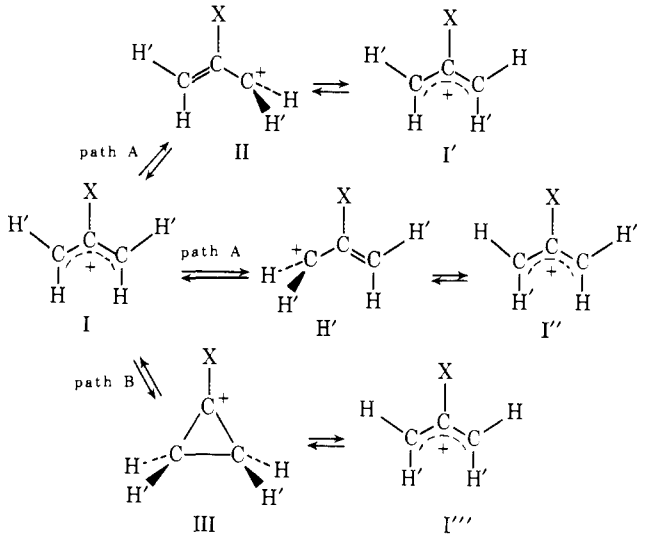
Effects of Substituents on the Mechanism of Stereomutation of Allyl Cations

Sir:

The stereomutation of allyl cations (I → I′, I″, I‴) can, in principle, take place by two mechanisms, either (Scheme I, paths A and A′) by simple stepwise rotation

Scheme I

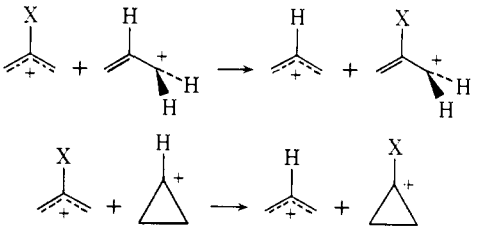


of the terminal methylene groups, *i.e. via* a perpendicular allyl cation (II or II′) or (path B) by disrotatory closure to a cyclopropyl cation (III) followed by disrotatory ring opening in the opposite sense.[1]

All experimental observations of allyl cation stereomutations have been shown to proceed *via* path A or have been assumed to do so.[1,2] This is not surprising, since all cases reported have involved alkyl substitution on the terminal carbons. Such substitution is expected to favor path A over path B. *Ab initio* molecular orbital calculations[3] suggest that for the unsubstituted allyl cation, path A should indeed be favored since the perpendicular allyl cation (II, X = H) is predicted to be lower in energy than the cyclopropyl cation (III, X = H) by about 4 kcal mol^{-1} (6–31G* basis set). Substitution by carbocation-stabilizing groups X should tend to reverse this behavior by preferentially stabilizing III over II. This possibility has now been examined by theoretical calculations with substituents X = CH_3, NH_2, OH, and F.

The theoretical method used is *ab initio* molecular orbital theory with the STO-3G basis set.[4] The framework geometries to which the groups X are attached are taken as the optimized geometries of the unsubstituted ions.[3] The groups CH_3, NH_2, and OH are assumed to be tetrahedral, planar trigonal, and bent (tetrahedral bond angle), respectively, with C–H = 1.09 Å, N–H = 1.04 Å, and O–H = 1.00 Å (taken from the optimized geometries[5] for X–CH_2^+). The C–X bond lengths were optimized in each case yielding the results in Table I.

Previous work has shown that the STO-3G basis set does not always give accurate energies for reactions involving changes in bond type.[2,6] Therefore, the differences in STO-3G energies of I–III may not provide reliable relative energies of these species. Much better results are expected if the STO-3G energy changes in reactions which conserve bond type (isodesmic reactions[6a]) such as eq 1 and 2 are employed.



(1)

(2)

The STO-3G energy changes for reactions 1 and 2 together with the energy differences for the unsubstituted $C_3H_5^+$ ions derived from the more accurate 6–31G* calculations[3] lead to the relative energies listed in Table II.

Table I. Optimized C–X Bond Lengths for Substituted Planar Allyl (I), Perpendicular Allyl (II), and Cyclopropyl (III) Cations

Bond	C–X bond lengths, Å		
	I	II	III
C–CH_3	1.536	1.552	1.495
C–NH_2	1.402	1.424	1.290
C–OH	1.391	1.405	1.278
C–F	1.354	1.370	1.271

Table II. Calculated Relative Energies of Substituted Planar Allyl (I), Perpendicular Allyl (II), and Cyclopropyl (III) Cations

Substituent (X)	Rel energies,[a] kcal mol^{-1}		
	I	II	III
H	0[b]	34.8[b]	39.2[b]
CH_3	0	32.8	18.8
NH_2	0	41.6	−33.5
OH	0	35.6	−9.8
F	0	39.4	14.9

[a] Except for X = H, calculated from the STO-3G energy changes for reactions 1 and 2 and the 6–31G* relative energies for the parent ions (X = H). [b] 6–31G* relative energies.[3]

The important difference between the cyclopropyl cation (III) and the planar (I) and perpendicular (II) allyl cations as far as substituents X are concerned is that in III the positive charge is strongly localized at the central carbon atom whereas in I and II most of the charge is located on the terminal carbons. Thus, in III, there is a relatively empty π-type orbital on the central carbon atom capable of a strong stabilizing interaction with π-donating substituents X. These qualitative considerations are confirmed by our calculations. We note the following points in particular.

(1) The C^+–X bonds in the substituted cyclopropyl cations (III) are substantially shorter than "normal" C–X bonds reflecting the considerable degree of double bond character. The C^+–X bond lengths are, in fact, similar to the corresponding lengths calculated[5] for the substituted methyl cations X–CH_2^+. The C–X bonds

(1) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Chem. Soc.*, **91**, 5174 (1969).

(2) (a) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, **92**, 4025 (1970); (b) N. C. Deno, R. C. Haddon, and E. N. Nowak, *J. Amer. Chem. Soc.*, **92**, 6691 (1970); (c) V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971); (d) V. Buss, P. v. R. Schleyer, and L. C. Allen, *Top. Stereochem.*, **7**, 253 (1972); (e) H. O. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1972).

(3) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(4) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). (b) The calculations were carried out with the Gaussian 70 system of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., Program No. 286.

(5) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, in press.

(6) (a) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970); (b) L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971); (c) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).

in the planar (I) and perpendicular (II) allyl cations on the other hand are altered to a much smaller extent.

(2) For methyl and fluoro substituents, the energy of the cyclopropyl cation is lowered beneath that of the perpendicular allyl cation and we predict that in these cases stereomutation of the allyl cation should proceed *via* ring closure and opening (*i.e.*, path B).

(3) The stabilization of the cyclopropyl cation by hydroxy and amino substituents is so great that these species are not only more stable than the substituted perpendicular allyl cations (II) but should be significantly more stable than the corresponding planar allyl cations (I). This conclusion is consistent with experimental observations that cyclopropane substitutions which may involve 1-RO- and 1-R_2N-cyclopropyl cation intermediates proceed without ring opening,[7] and with the direct observation of the 1-dimethylaminocyclopropyl cation.[8]

Finally, our results will hopefully provide added interest to the experimental attempts to observe closure of a substituted allyl cation to a cyclopropyl cation.[9]

Acknowledgments. It is a pleasure to acknowledge useful discussions with Professor Th. H. de Boer. This work was supported at Carnegie-Mellon University by National Science Foundation Grant No. GP-25617 and at Princeton by National Science Foundation Grant No. GP-29078X, by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-La Roche, Inc., Nutley, N. J. We thank the Australian National University Computer Centre for a generous allocation of computer time.

(7) W. J. M. van Tilborg, S. E. Schaafsma, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **86**, 417 (1967); J. Szmuskovica, D. J. Duchamp, E. Cerda, and C. G. Chidester, *Tetrahedron Lett.*, 1309 (1969); H. H. Wasserman and M. S. Baird, *ibid.*, 1729 (1970); 3721 (1971); W. J. M. van Tilborg, G. Dooyewaard, H. Steinberg, and Th. J. de Boer, *ibid.*, 1677 (1972). A case which may involve a 1-fluorocyclopropyl cation is also known: P. Weyerstahl, G. Blume, and C. Miller, *ibid.*, 3869 (1971).

(8) E. Jongejan, W. J. M. van Tilborg, Ch. H. V. Dussen, H. Steinberg, and Th. J. de Boer, *ibid.*, 2359 (1972).

(9) For the first apparent examples of such closures, see D. Cantacuzène and M. Tordeux, *ibid.*, 4807 (1971); J. C. Blazejewski, D. Cantacuzène, and C. Wakselman, *Tetrahedron*, submitted for publication; private communication from Dr. Cantacuzène.

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Facile Methylation of Metal Complexes to Give Unusual Metal–Alkyl Cations

Sir:

In recent years several methods have been developed to produce σ-carbon bonds to transition metals. The two most common methods involve either (1) metathesis of a metal–halide by alkyllithium or Grignard reagents or (2) oxidative addition of alkyl or acyl halides to transition metal complexes.[1,2] The former reagents function as nucleophiles and maintain the oxidation state and coordination number of the metal. The latter reagents are cleaved at the carbon–halogen bond by the transition metal *via* an SN2 mechanism,[3] and both organic halide fragments are found to be coordinated in the resultant complex, *i.e.*, an increase of two in the oxidation state of the metal is accompanied by an increase of two in the coordination number.

A reaction between a basic transition metal center and a strong alkylating agent containing a weakly coordinating anion should produce metal–carbon bonds *via* a *single-site* oxidative addition in which only the alkyl group is added to the metal. We report here examples of such reactions whereby unusual cationic metal–alkyl complexes may be prepared by the facile alkylation of *low-valent, coordinatively unsaturated* metal complexes by methyl fluorosulfonate, as well as trimethyloxonium hexafluorophosphate. We have also observed that other types of complexes react with CH_3FSO_3 to give a variety of reactions, such as oxidation of the metal, halogen abstraction, and alkylation of a coordinated phenyldiazo group,[4] all of which are similar to the recently reported results of Eaborn, *et al.*[5]

In a typical reaction 0.60 g of Rh(ttp)Cl, ttp = bis(3-diphenylphosphinopropyl)phenylphosphine,[6] in 50 ml of refluxing benzene was treated with 0.5 ml of CH_3FSO_3 under nitrogen. A yellow solid began precipitating immediately, and after 30 min of refluxing the resultant solid was collected on a filter, washed with ether, and dried, yield 0.66 g (95%). The molar conductivity of the compound is 74 cm^2 ohm^{-1} mol^{-1} in nitromethane, which confirms the ionic formulation $[Rh(ttp)Cl(CH_3)]FSO_3$.

Anal. Calcd for $C_{37}H_{40}ClFO_3P_3RhS$: C, 54.54; H, 4.91; Cl, 4.36. Found: C, 54.63; H, 4.91; Cl, 4.16.

To confirm that the methyl group had added to rhodium, a careful comparison of the infrared and nmr spectra of $[Rh(ttp)Cl(CH_3)]FSO_3$ (I) and the corresponding deuterated complex $[Rh(ttp)Cl(CD_3)]FSO_3$ (II) was undertaken. The infrared spectra (KBr disks) of I and II were virtually identical except for weak absorbances at 2130 and 2258 cm^{-1} in II which are assigned as the symmetric and asymmetric C–D stretching frequencies, respectively, and the absorbances at 1210 cm^{-1} in I and 915 cm^{-1} in II which are assigned as a deformation of the CH_3 and CD_3 groups, respectively.[7]

The proton nmr spectra of I and II in the τ 7–8 region are shown in Figure 1.[8] The Rh–CH_3 resonance is somewhat obscured by the resonances due to the

(1) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968), and references therein.

(2) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970), and references therein.

(3) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

(4) The authors gratefully acknowledge the experimental results of K. D. Tau, J. A. Tiethof, J. Riker, and W. H. Myers concerning these other types of reactions that occur with CH_3SO_3F.

(5) C. Eaborn, N. Farrell, J. L. Murray, and A. Pidcock, *J. Organometal. Chem.*, **55**, C68 (1973).

(6) (a) T. E. Nappier, Jr., and D. W. Meek, *J. Amer. Chem. Soc.*, **94**, 306 (1972); (b) T. E. Nappier, D. W. Meek, R. M. Kirchner, and J. A. Ibers, *ibid.*, **95**, 4194 (1973).

(7) (a) D. E. Clegg and J. R. Hull, *Spectrochim. Acta, Part A*, **23**, 263 (1967); (b) C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 3054 (1970).

(8) The nmr spectrum over the range τ 1.5–10.5 is consistent with the spectrum of ttp, showing *only* peaks for the phenyl protons at $\tau \sim 2.6$, in addition to the peaks shown in Figure 1.