3280 (NH), 1703 (C=O), 1288 and 1220 cm^{-1} (C—O) and 696, 763 and 784 cm^{-1} (aromatic CH).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13 Found: C, 66.23; H, 5.59; N, 5.28.

(b) A 1.93-g (10.0 mmol) sample of **4** was heated with 5.0 cc (41 mmol) of dimethyl acetylenedicarboxylate in 10 cc of acetic anhydride for 15 min in a 130° bath; 10 mmol of CO_2 was evolved, half of which was generated during the first 30 sec. The light-brown solution was concentrated under vacuum at 11 mm and the residue recrystallized from methanol to give 2.14 g (78%) of colorless crystals, mp 129–130°; identity with the above product **3** was shown by mixture melting point and ir.

(c) A 1.51-g (10.0 mmol) sample of C-phenylglycine was heated as above with 5.0 cc of dimethyl acetylenedicarboxylate and 15 cc of acetic anhydride for 15 min at 130°. Carbon dioxide evolution was again quantitative. Workup as above yielded 2.04 g (75%) of **3**, mp 129–130°.

Conversion of 3 to 2-Methyl-5-phenylpyrrole (6). A 300-mg sample of **3** was saponified in 10 cc of boiling 30% ethanolic KOH solution. On exposure to light, the dicarboxylic acid **5** turned red. A mixture of this acid with calcium oxide was destructively distilled from a micro flask under 15 mm. The distillate, crystallized from 70% methanol, gave flakes of mp 98–99° (lit.[36] 101°). Ir and mixture melting point comparisons with an authentic sample[5] of **6** confirmed its identity.

Dimethyl 2-Ethoxy-5-phenylfuran-3,4-dicarboxylate (15). **(a)** A 0.51-g (2.5 mmol) sample of **12** did not react with 0.40 g (2.8 mmol) of dimethyl acetylenedicarboxylate at 20°. However, after 10 min at 100°, a yellow solution was formed from which excess dienophile was removed under vacuum at 0.01 mm. The residue, recrystallized from ether–petroleum ether, gave 543 mg (71%) of colorless prisms: mp 80–83°, pure mp 83–84° (ether); ir (KBr) 1735 (3-CO_2CH_3), 1691 (4-CO_2CH_3), strong bands at 1600, 1468, 1354, 1050 cm^{-1}; uv max (ethanol) 288 mμ (log ϵ = 4.27).

Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.32; H, 5.51.

(b) Similarly 2.0 g (7.5 mmol) of **13** was heated 3 hr with 2.0 g (14 mmol) of dimethyl acetylenedicarboxylate and 2 cc of xylene in a 100° bath. Workup as above gave 1.76 g (77%) of **15**, mp 82–83°, identical by ir comparison and mixture melting point with the product obtained from **12**. Benzonitrile was identified in the distillate by gas chromatography.

Alkaline Hydrolysis of 15. A 0.80-g (2.6 mmol) sample of **15** was treated with 5 g of potassium hydroxide in 10 cc of water and 15 cc of methanol for 15 hr at 20° and 2 hr at the boiling point. After diluting with water, removal of methanol *in vacuo*, and acidification with HCl, there was obtained by filtration 0.21 g (29%) of 2-ethoxy-5-phenylfuran-3,4-dicarboxylic acid (**16**), mp 158–159° dec.

Anal. Calcd for $C_{14}H_{12}O_6$: C, 60.87; H, 4.38. Found: C, 60.85; H, 4.32.

The aqueous filtrate was extracted with ether and the residue of the ether solution distilled at 175–180° (0.001 mm) (bath). The product, 192 mg (41%) of β-benzoylpropionic acid (**18**), gave colorless crystals from methylene chloride–petroleum ether, mp 113–115° (lit.[37] 116°) Identity was also confirmed by nmr.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.68; H, 5.59.

Acknowledgment. We gratefully acknowledge the financial assistance given by the Deutsche Forschungsgemeinschaft, The Fonds der Chemischen Industrie, and the National Science Foundation (H. O. B.). Also, we are indebted to Mr. H. Huber for the spectral measurements.

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(36) C. Paal, *Ber.*, **18**, 367 (1885).

(37) L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 81.

Detection of Alkylcyclopropane Intermediates during Carbonium Ion Rearrangements in Antimony Pentafluoride Tritiated Fluorosulfonic Acid

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Abstract: During the rearrangement of many butyl, amyl, and hexyl cations in the SbF_5–HSO_3F system, a species forms which can exchange a single proton with the acid. The species may be regarded as either a protonated cyclopropane, or a proton and a cyclopropane moiety. It has been detected in both chain branching isomerizations and those leading to a methyl shift, but not in the isomerization of the neopentyl to the *t*-amyl cation.

It has been shown that butyl, amyl, and hexyl cations can be trapped by hydride transfer from methylcyclopentane in 2 *M* SbF_5–HSO_3F to give kinetically controlled products.[1] Various results suggested that protonated alkylcyclopropanes were intermediates in many of the rearrangements observed, It was hypothesized that such a species might contain a loosely bound proton that would be susceptible to exchange with the acid, and the current work was undertaken to examine this theory. Indeed, it may be demonstrated that a number of simple rearrangements do proceed through the formation of such a species which, in general, can be detected after adding a small amount of water to the acid, thus increasing the concentration of nucleophiles and catalyzing the exchange.

Cyclopropyl intermediates in these and similar rearrangements have been proposed before;[2–6] some of the earliest studies of the cleavage of representative ring

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(1) G. M. Kramer, *J. Amer. Chem. Soc.*, **91**, 4819, 1969.

(2) F. E. Condon in "Catalysis," Vol. 6, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p 119–122, a review.

(3) P. S. Skell and I. Starer, *J. Amer. Chem. Soc.*, **82**, 2971 (1960).

(4) N. C. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966).

(5) H. Hart and R. H. Schlosberg, *ibid.*, **88**, 5030 (1966).

(6) A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).

systems having been reported by Demjanow,[7] Gustafson and Popper,[8] and Kotz.[9] However it was not until the work of Baird and Aboderin[6] that compelling evidence for the existence of protonated cyclopropane as a real intermediate developed. Much of the current literature has recently been reviewed by Collins.[10]

Brouwer and Oelderik[11] suggested that protonated methylcyclopropane is an intermediate in the isomerization of *sec*-butyl-1-^{13}C to *sec*-butyl-2-^{13}C cations in the HF–SbF_5 system and Saunders, Rosenfeld, and Hagen[12] also implicated this species in the rearrangement of *sec*-butyl cations in SbF_5–SO_2FCl. Based on the temperature dependence of nmr spectra they proposed that protonated methylcyclopropane is about 7.5 kcal/mol richer in energy than the *secondary* ion. This estimate is in accord with the finding of only traces of methylcyclopropane in the deamination of butylamine,[3] and other qualitative estimates of the stabilities of these species.[13]

The present work is consistent with these views in that it is shown that during the isomerization of an isobutyl cation to a 2-butyl cation an intermediate is formed which exchanges a proton with the acid. The data do not allow one to decide if the intermediate is best described as a point, edge- or face-protonated species, or if it should be considered as methylcyclopropane plus a proton. Nevertheless, it may be noted that Brouwer has provided a thermodynamic argument indicating that a protonated entity is most likely present,[14] and we are inclined to accept this result.

The present investigation was carried out with tracer quantities of tritium in 2 *M* SbF_5–HSO_3F solutions. It was found that alkyl cations could generally be trapped by hydride transfer from methylcyclopentane after some exchange of protons with the acid had occurred. The extent of exchange depends mainly upon the presence of nucleophiles in the acid and the intermediates through which the ions pass as isomerization proceeds.

Experimental Section

Experiments were carried out at −50° in nmr tubes. Most of the work was done with commercially available HSO_3F to which enough T_2O was added to yield a specific activity of about 1 mCi/ml. The behavior of this system could be approximated by adding 5% H_2O to redistilled HSO_3F. Reactions were also carried out under relatively "anhydrous" conditions using redistilled HSO_3F and with intermediate concentrations of water.

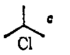
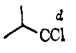
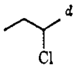
Mixtures containing 0.5 ml of acid and 0.25 ml of a solution of alkyl halides in methylcyclopentane were shaken for 10 sec and allowed to separate. Blank experiments indicated essentially no reaction occurred until the solutions were mixed. Products were recovered by vacuum distillation at −50° and then analyzed by gas chromatography and an internal flow through radiation detector. The alkyl halide concentration with respect to the acid was 0.1 *M* in all experiments.

To determine the average number of protons exchanged in the products the system was calibrated by two methods. In the first, methylcyclopentyl ions were allowed to equilibrate in the acid for 5 min or more, and then they were trapped by reaction with methylcyclohexane. The specific activity of the recovered methylcyclopentane and cyclohexane was assumed to be associated with 11 exchanged protons. A second and more convenient calibration method utilized internal standards. Thus cyclohexane was formed during all trapping experiments with methylcyclopentane and it contained 5 ± 1 exchanged protons (using commercial HSO_3F). The relative activity of cyclohexane in experiments with this acid was therefore used as an internal standard and the exchange measured in this way agreed well with that estimated from calibrating runs made on fully exchanged methylcyclopentane, either before or after a particular experiment. When using the more anhydrous acids, calibrations were made by fully exchanging methylcyclopentyl ions in portions of the acids to which 5% water was added.

Results and Discussion

Three butyl chlorides, *t*-butyl chloride, 2-chlorobutane, and isobutyl chloride, were employed in studies of the C_4^+ system. The results of typical experiments are shown in Table I.

Table I. Kinetically Controlled Product Distributions in 2 *M* $SbF_5/H(T)SO_3F$, −50°

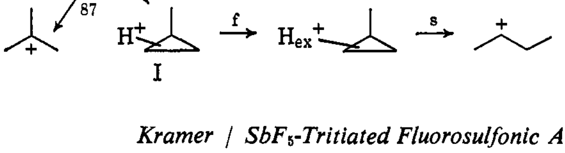
Reactant	Conv[a]	*i*-C_4H_{10}, %	H_{ex}[b]	*n*-C_4H_{10}, %	H_{ex}
 [c]	100	100	0.2		
 [d]	∼18	87	<0.1	13	0.9
 [d]	∼90			100	<0.1

[a] The conversions are approximations based on the detection of unconverted reactants in the products. Material balances are not well known. [b] H_{ex} is the average number of protons exchanged in the trapped isomer. The error is less than ±20% of the indicated value. [c] With commercial HSO_3F. [d] With 2% H_2O.

t-Butyl chloride yields isobutane which has undergone little exchange. Thus even in the relatively wet acid the *t*-butyl cation has a substantial lifetime with respect to exchange. This is consistent with the fact that the ion may be observed by nmr spectroscopy and hence is expected to have a half-life of more than about 0.001 sec.

The behavior of 2-chlorobutane and isobutyl chloride is particularly informative. In the acid containing 2% water, 2-chlorobutane appears to ionize to the *sec*-butyl ion which extracts a hydride ion from methylcyclopentane before it exchanges protons with the acid. Thus the secondary ion is also relatively stable and may be trapped before proton loss through any process occurs. In the same acid isobutyl chloride is more slowly converted and yields 87% isobutane which is barely exchanged and 13% *n*-butane with essentially one exchanged proton. The proton exchange must preceed formation of the secondary butyl ion and is strong evidence for the formation of a protonated methylcyclopropane intermediate during the rearrangement of the isobutyl ion, Scheme A. The exchange

Scheme A



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(7) N. Demjanow, *Ber.*, **28**, 22 (1895).

(8) G. Gustafson and O. Popper, *J. Prakt. Chem.*, **2**, 58, 458 (1898).

(9) A. Kotz, *ibid.*, 174 (1903).

(10) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969).

(11) D. M. Brouwer and J. M. Oelderik, *Pet. Chem. Preprints*, **13**, 184 (1968).

(12) M. L. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6882 (1968).

(13) N. C. Deno, D. La Vietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457, (1968).

(14) D. M. Brouwer, *Rec. Trav. Chim.*, **87**, 1435 (1968).

behavior would be incompatible with the proposal of a methyl shift in which I might resemble a transition state because none of the simple alkyl cations exchange protons readily with the acid. Thus even isobutane obtained from isobutyl chloride has acquired little tritium indicating that the primary cation is also relatively stable with respect to exchange (or that it rearranges to the *t*-butyl ion and protonated methylcyclopropane faster than it transfers a proton to the acid).

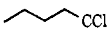
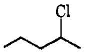
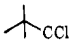
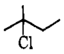
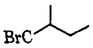
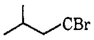
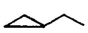
It is important to note that the observations on the latter compounds were made with 2% water in the acid. In more anhydrous systems the exchange is so slow that rearrangement of the isobutyl ion occurs with negligible exchange in both product butanes while with 5% water the exchange of the *sec*-butyl ion is strongly catalyzed making it difficult to interpret the data. Thus with 0, 2, and 5% water the *n*-butane obtained from 2-chlorobutane contained 0.002, 0.08, and 1.4 exchanged protons.

While the water concentration is important for the purpose of detecting exchange it plays a minor role in affecting the isomerization of the ions after they are formed. Thus, isobutyl chloride yields 75–85% isobutane and 15–25% *n*-butane with up to 5% water in the acid. The extent of reaction of the alkyl halide is more strongly influenced by the water concentration, isobutyl chloride being 70, 18, and ~5% converted in systems containing 0, 2 and 5% H_2O.

Similarly, 2-butyl chloride is increasingly converted in the more anhydrous acid. After reaction the recovered butyl chloride is also found to contain some tritium. This is unusual as none of the other alkyl halides acquired radioactivity during the exchange studies. It is unlikely that the radioactive butyl chloride was formed by nucleophilic attack of Cl^- on a *sec*-butyl cation because no radioactive 2-chlorobutane is obtained during the reaction of isobutyl chloride. The mechanism of this exchange is uncertain but evidently is dictated by the behavior of the protonated substrate, $[C_4H_9ClH]^+$.

Exchange information for the amyl system is reported in Table II. *t*-Amyl chloride, neopentyl chloride, 1-bromo-2-methylbutane, and 1-bromo-4-methylbutane all yield isopentane with little exchange. The tritium incorporation obtained in these cases may be due to a relatively slow proton transfer to solvent followed by reprotonation but the more significant fact is that much less than one proton is exchanged in the primary, secondary, and tertiary ions which are presumed intermediates in the reaction. Thus from none of these species is proton exchange with solvent a dominating reaction.

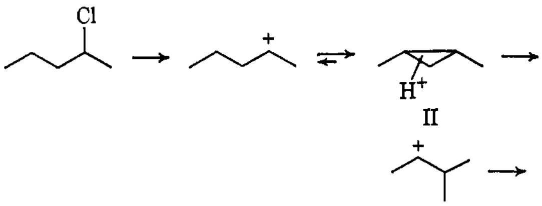
Table II. Kinetically Controlled Product Distributions in 2 *M* SbF_5–$H(T)SO_3F$, −50°

Reactant	*i*-C_5H_{12}	H_{ex}[a]	*n*-C_5H_{12}	H_{ex}
	79	0.9	21	0.1
	91	1.0	9	0.3
	100	0.1		
	100	0.2		
	100	0.2		
	100	0.1		
	100	1.0		
	79	1.9	21	0.8
	97	1.1	3	1.1

[a] All experiments used commercial HSO_5F

By way of contrast, consider the reaction of 2-chloropentane. This yields mainly isopentane containing one exchanged proton and *n*-pentane with little exchange. This behavior is consistent with the formation of a protonated dimethylcyclopropyl intermediate, II, which contains one labile proton that exchanges with solvent before ring cleavage occurs (Scheme B). If II were the intermediate a small amount of *n*-pentane containing an exchanged proton should also be formed corresponding to the behavior of *cis*-1,2-dimethylcyclopropane shown in Table II. The latter reaction will account for the exchange observed in the *n*-pentane rather nicely.

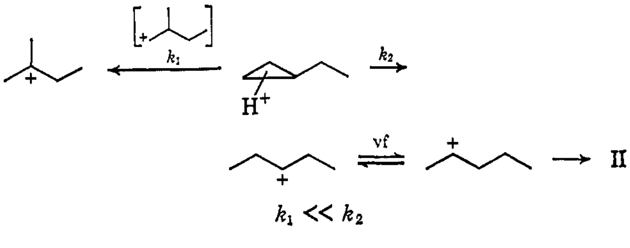
Scheme B



Thus the data suggest that a protonated cyclopropane is an intermediate in the chain branching isomerization of C_5 cations. Brouwer has suggested that this species is best regarded as a protonated cyclopropane rather than as a proton and an alkylcyclopropane molecule and the exchange information is compatible with either view. As with the C_4 system the exchange results do not provide structural information about the cyclopropyl intermediate beyond indicating that one rather than two, three or more protons are rendered extremely labile.

The behavior of ethylcyclopropane can be understood with a very similar analysis. It is to be expected that it will initially cleave to a *sec*-amyl ion containing one exchanged proton if exchange on the ring system is slow relative to cleavage and this is found. Formation of the secondary ion is to be preferred to cleavage through a relatively high energy primary like transition state or intermediate ultimately leading to the *t*-amyl ion, although a small amount of *t*-amyl$^+$ could be formed *via* this route. Most of these ions should, however, arise *via* the isomerization of the *sec*-amyl ions first formed and these should acquire a second exchanged proton by passing through intermediate II as discussed above. This reaction sequence is outlined in Scheme C.

Scheme C



The 1,2 hydride shift interconverting secondary cations should occur rapidly in accord with their generally accepted behavior and especially with recent measurements on the butyl system.[12] The bulk of the *t*-amyl ions should therefore contain two exchanged protons as is observed.

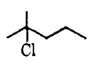
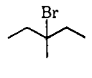
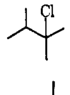
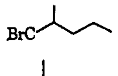
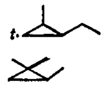
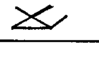
1,1-Dimethylcyclopropane cleaves readily upon protonation and thus acquires one exchanged proton. In this case a tertiary ion may be formed directly after protonation and it is not surprising that formation of the ion is substantially faster than exchange in the ring system. A major result of the exchange studies in the C_5 system is the detection of a single labile proton in the chain branching reaction and the existence of such a species is naturally expected in the related reactions of higher molecular weight cations. It may be noted that only with neopentyl chloride where rearrangement from a primary cation to a tertiary may occur is evidence for the formation of a cyclopropane lacking.

There are two alternatives to explain our failure to detect an exchangeable proton during the rearrangement of the neopentyl cation. One is that protonated 1,1-dimethylcyclopropane does form but undergoes cleavage faster than proton exchange so that failure to find the loose proton is a consequence of the kinetics and the experimental conditions. If this is correct further studies with more aqueous systems may detect the proton.

Alternatively one may postulate that ionization of neopentyl chloride is anchimerically assisted by the electrons in a neighboring C–C bond leading to a transition state which is stabilized by electron release from three methyl groups. In addition this transition state could look much like a tertiary cation and lead directly to *t*-amyl cation. This mechanism would be much less important in the somewhat analogous isobutyl chloride solvolysis because the secondary ion like transition state that could lead directly to the *sec*-butyl cation should be 10–15 kcal/mol more difficult to stabilize.

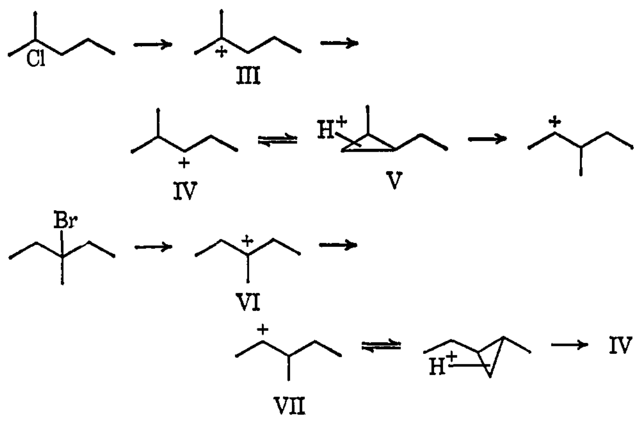
The behavior of representative compounds in the hexyl system is shown in Table III. The tertiary halides, 2-chloro-2-methylpentane, 3-bromo-2-methylpentane, and 2-chloro-2,3-dimethylbutane, convert to the corresponding paraffins with little rearrangement. 2,3-Dimethylbutane can be obtained with just traces of methylpentanes and acquires a little tritium, possibly through partial olefin formation during solvolysis of the chloride since 1,1,2-trimethylcyclopropane yields the same intermediate 2,3-dimethylbutyl cation which can be trapped with only one exchanged proton.

Table III. Kinetically Controlled Product Distributions in 2 *M* SbF_5–HSO_3F, −50°

Reactant	2,3-DMC_4	H_{ex}	2-MC_5	H_{ex}	3-MC_5	H_{ex}
			97	0.2	3	1.3
			9	1.4	91	0.4
	100	0.3				
			93	0.4	7	1.4
			62	1.5	38	1.9
	100	0.9				

The behavior of the methylpentanes is particularly informative. Thus the 2- and 3-methylpentyl ions formed upon solvolysis of the halides can be trapped before much isomerization occurs. In each case the initial ion appears to have undergone little exchange while the product ion contains slightly more than one exchanged proton. These results are consistent with the mechanism of Scheme D. Thus the tertiary cations first formed are assumed to undergo a hydride shift and ring closure leading to a protonated methylethylcyclopropane, V. This species contains the mobile proton which rapidly exchanges before cleavage to *sec*-2- and -3-methylpentyl ions occurs.

Scheme D

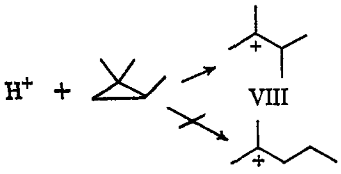


Ion V should open to these products in the 62:38 ratio obtained with the parent compound. Thus some of the radioactivity found in 2-methylpentane when starting with 2-methylpentyl chloride is associated with the back-reaction and the same is true of the radioactive 3-methylpentane obtained in the reaction of 3-bromo-3-methylpentane. However, since somewhat more activity is found in isomers corresponding in structure to the reacting alkyl halide than can be accounted for entirely by the back-reaction, partial exchange through olefin formation is indicated.

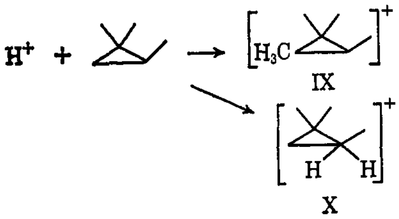
1-Bromo-2-methylpentane yields 3-methylpentane containing more than one exchanged proton and 2-methylpentane with less than one, but no *n*-hexane. This conduct together with the fact that the *t*-2-methylpentyl ion can be trapped under identical conditions before undergoing substantial rearrangement to the 3-methylpentyl system indicates that the primary ion obtained in solvolysis cyclizes to protonated methylethylcyclopropane in competition with the hydride shift to the tertiary ion. Assuming that all the 3-methylpentane comes from this route enables one to estimate that the ratio of the tertiary hydride shift to cyclization is about 4:1 which is nearly the same as found in the butyl system.

1,1,2-Trimethylcyclopropane converts cleanly to the 2,3-dimethyl-2-butyl cation in this acid, Scheme E. Thus although two tertiary ions of roughly equivalent stability may be formed cleavage occurs to yield VIII exclusively. The system therefore appears to distinguish

Scheme E



between the protonated cyclopropanes IX and X, probably on the basis that the charge in IX is delocalized between a tertiary and a secondary type of site whereas in X it is delocalized between a tertiary and a primary site. Structures IX and X might represent either intermediates or transition states involved in the cleavage reaction, no judgment being offered at this time.



A similar distinction is also apparent in the reaction of 1-methyl-2-ethylcyclopropane where cleavage to a *sec*-hexyl ion might have been expected to compete with the formation of *sec*-methylpentyl ions but in fact was not observed. Again the cleavage of 1,2-dimethylcyclopropane in the C_5 system to a branched rather than linear secondary cation indicates that charge delocalization between a pair of virtual secondary sites stabilizes the protonated structure significantly more than delocalization between a primary and secondary site.

While we believe that charge delocalization in the protonated substrate governs the course of reaction some of our colleagues have suggested that steric hindrance to protonation may also play a role. In comparing ions IX and X it is clear that formation of the latter will require the protonation of a partially shielded carbon atom and hence ought to be slower than the formation of IX. It is difficult to provide a quantitative estimate of the extent of interference to be assigned to shielding by one methyl group, especially without knowing the exact reaction coordinate for the system. Thus if proton attack initially occurs on an edge or from the side of the molecule below the CH_3 group the steric barrier would be minimal while if approach is from the front side and in the plane of the ring it might be sufficient to dominate the reaction. A proper evaluation of the extent of steric control on the reaction might be obtained by a careful kinetic study of the rates of cleavage of model compounds but this has not yet been done.

In summary it has been shown that many alkyl cation rearrangements in the butyl, amyl, and hexyl systems in 2 *M* SbF_5–HSO_3F occur with the intervention of a protonated alkylcyclopropane, the proton being labile with respect to exchange in the acid containing a small amount of water. Such a species has been detected both in reactions leading to chain branching and in those which could have been formulated with simple methyl shifts such as in the isomerization of the *t*-2-methylpentyl to the *t*-3-methylpentyl ion. Simple methyl shifts are not compatible with much of the data except in the case of neopentyl chloride where rearrangement to the *t*-amyl system occurred without extensive exchange.

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