Stable Carbocations. CXXVI.[1] Attempted Preparation of Trimethylenehalonium Ions. Preference for Three- and Five-Membered Ring Halonium Ion Formation

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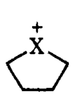
Abstract: A series of suitable alkylene dihalides have been ionized in SbF_5–SO_2 or 1:1 HSO_3F–SbF_5–SO_2(SO_2ClF) solution at low temperatures where halonium ions produced are generally stable, in an attempt to prepare four-membered ring trimethylenehalonium ions. Product ions obtained were exclusively three- or five-membered ring halonium ion, formed through ring contraction or expansion, indicating the greater thermodynamic stability of these systems over four-membered ring trimethylenehalonium ions.

We have previously reported the preparation of a variety of three-[2] and five-membered[3,4] ring halonium ions in superacid media. As an extension of this work we attempted to prepare four-membered ring halonium ions. These ions would be of interest for several reasons: (1) the effect of ring size on the stability of halonium ion could be determined, (2) ring expansion to five-membered ring ions, **1**, or ring contraction to three-membered ring ions, **2**, might be possible, and (3) four-membered ring halonium ions, **3**, are formally related to halogenated cyclopropanes, **4**, analogs of the protonated cyclopropane structures. The structural difference between ions **3** and **4** is that the halogen atom forms two σ bonds with two carbon atoms in the former and a three-center bond (two electrons) with two carbon atoms in the latter.[5]



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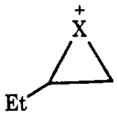

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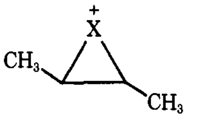

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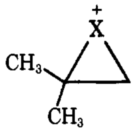

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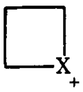

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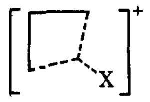

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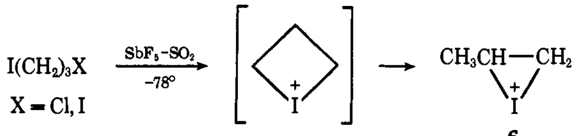
Results and Discussion

Ionization of 1,3-Dihalopropanes. When 1-halo-3-iodopropanes were treated with SbF_5–SO_2 at −78°, the propyleneiodonium ion **6** was formed. Ion **6** could be formed through the trimethyleneiodonium ion **5** which was, however, not observed as an intermediate. The isomerization to **6** must be fast. Identification of **6** was made on the basis of its pmr spectrum which has been previously observed.[2c] Alternatively, nonassisted ionization of 1-halo-3-iodopropane, followed by rapid 1,2-hydride shift and iodine participation to form **6**,

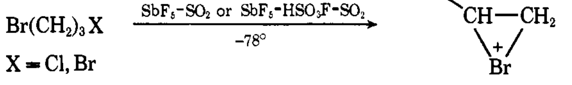


5 **6**

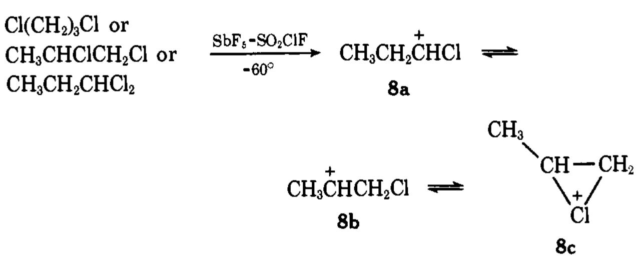
$$I(CH_2)_3X \longrightarrow [ICH_2CH_2\overset{+}{C}H_2] \longrightarrow ICH_2\overset{+}{C}HCH_3 \longrightarrow 6$$
$$X = Cl, I$$

could be considered. Based on spectroscopic data it is suggested that no species corresponding to **4** was observed, since this would be expected to show a single pmr absorption as a rapidly equilibrating halogenated cyclopropane.

Similarily, when 1-halo-3-bromopropanes were treated in the same way at −78°, the pmr spectra of these solutions showed the formation of propylenebromonium ion **7** and a small amount of an as yet unidentified species. On the other hand, when 1,3-dichloropropane was ionized in SbF_5–SO_2ClF solution at −60°, the pmr spectrum of the solution showed two, equal-intensity, sharp singlets at δ 3.00 and 6.24. This result does not agree with the formation of propylenechloronium ion which had not been prepared previously despite numerous attempts.[2c] The pmr spectrum was temperature dependent in a reversible way. The deshielded singlet was broadened more than the shielded singlet as the solution was cooled from −60 to −102° (Figure 1). In addition, we found that 1,1- and 1,2-dichloropropane exhibited identical pmr spectra and behavior when dissolved in SbF_5–SO_2ClF solution. These observations clearly suggest the formation of rapidly equilibrating ions **8a**, **8b**, and **8c**.



7



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[1] Part CXXV: G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, in press.

[2] (a) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 947 (1968); (c) G. A. Olah, J. M. Bollinger, and J. Brinch, *ibid.*, **90**, 2587 (1968).

[3] G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).

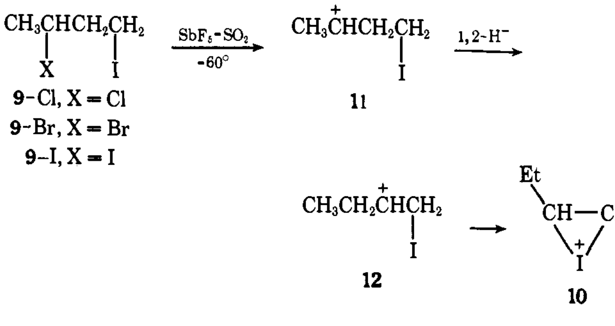
[4] G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968).

[5] For a discussion of the three-center bond, see G. A. Olah, *ibid.*, **94**, 808 (1972).

Figure 1 also shows that the methyl protons are not involved in the exchange with the other three protons, as the methyl proton resonance is temperature independent. Some broadening is probably due to vicinal proton–proton coupling and also to the increasing of viscosity of the medium at low temperature. On the other hand, the broadening of peak at δ 6.24 (at −105°) is presumably due to the slow intramolecular proton exchange. Thus, ion **8c** could have a longer lifetime and the pmr absorption of the methine and methylene protons should be different since the proton shifts of methine and methylene protons are about 1.6 ppm different in propylenebromonium ion.[2c] We thus conclude that propylenechloronium ion **8c** may be formed as an intermediate only at very low temperature.

Furthermore, the methyl shift of ions **8** is similar to that of propylenebromonium and -iodonium ions (δ 2.98 and 3.32, respectively). The methyl proton shifts of ions **8a** and **8b** are predicted to be about δ 1.6 and 4.2, respectively (based on comparison with the ethylmethylchlorocarbenium ion and chloromethyldimethylcarbenium ions, respectively[2c]). The average methyl shift of ions **8a** and **8b** is δ 2.9 and is thus also close to the observed value of δ 3.00. Similarily, the average shift of methylene and methine protons in propylenebromonium ion is calculated to be δ 6.40. It is further known that proton shifts of the homolog halonium ions are more deshielded in iodonium ions than in bromonium and chloronium ions.[2b] Thus, the actual average proton (CH and CH_2) shift of ion **8c** should be shielded from δ 6.4 (the observed value is 6.24). By using the above model ions and the isopropyl cation, the average proton (CH and CH_2) shifts of ions **8a** and **8b** are calculated to be δ 7.3 and 8.4. These data are deshielded from the experimentally observed values, suggesting that the lifetime of ion **8b** must be short, and that it can only be formed as a transient intermediate. It is thus indicated that the chlorine atom, instead of stabilizing the charge by forming a σ bond, **8c**, or *via* chlorine back donation, **8a**, destabilizes ion **8b** by its inductive effect. We are thus presently unable to tell the relative amounts of individual ions (**8a**, **8b**, or **8c**) present in the rapidly equilibrating system.

Ionization of Dihalobutanes. We also examined the behavior of 1,3-dihalobutanes, including the iodo compounds where the leaving group was varied, $CH_3CHXCH_2CH_2I$ (**9**, X = Cl, Br, and I). Ionization of **9** in SbF_5–SO_2 solution at −60° give only the ethylethyleneiodonium ion **10**. Obviously ionization took place at the secondary carbon atom to give intermediately ion **11**, which then underwent 1,2-hydride shift to ion **12**. Iodine participation in ion **12** would form the stable ethylethyleneiodonium ion **10**. On the other hand, when 1,2- and 1,3-dibromobutanes as well as the dichlorobutanes were treated with SbF_5–SO_2 solution in a similar fashion, only the tetramethylenehalonium ions **1** (X = Br or Cl) were observed. The formation of **1** is an unusual reaction for a cationic species in strong acid media where one usually finds nonbranched cations rearranging to branched ones, but rarely the reverse. The driving force for this rearrangement is assumed to be the formation of the very stable five-membered ring ion.

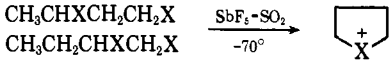


9-Cl, X = Cl
9-Br, X = Br
9-I, X = I

11

12

10



1-Cl, X = Cl
1-Br, X = Br

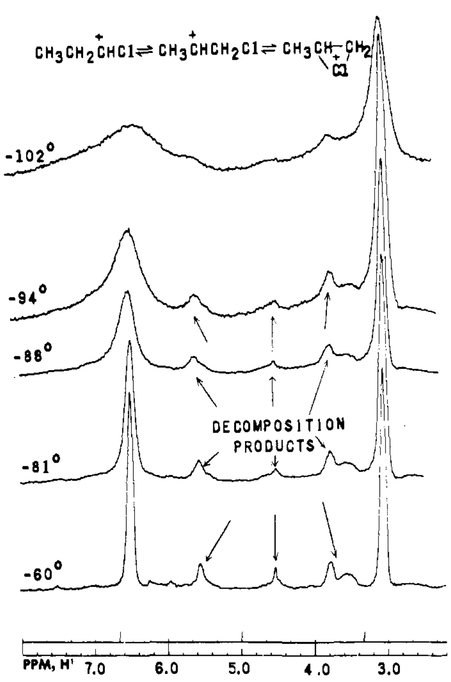
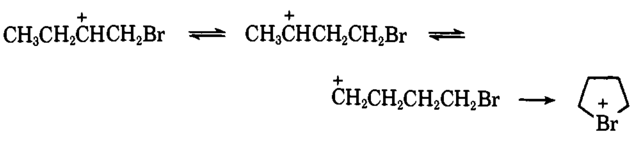


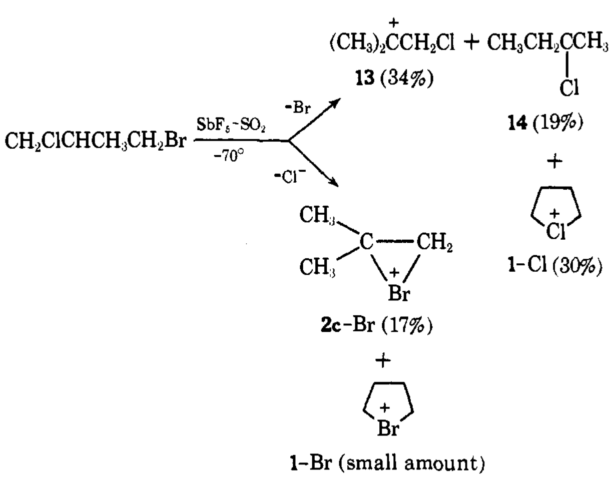
Figure 1. Temperature-dependent pmr of dichloropropane in SbF_5–SO_2ClF solution.

In both of these cases, the ethylethylenehalonium ions may form, but are unstable. This is not surprising when the halogen is chlorine, since we have been previously unable to prepare ethylenechloronium ions with less than three methyl substitutes. The ethylethylenebromonium ion must also lack thermodynamic stability or exist in equilibrium with the open-chain ion. Subsequent 1,2-hydride shifts and bromine participation would lead to the thermodynamically more stable tetramethylenebromonium ion, **1-Br**.



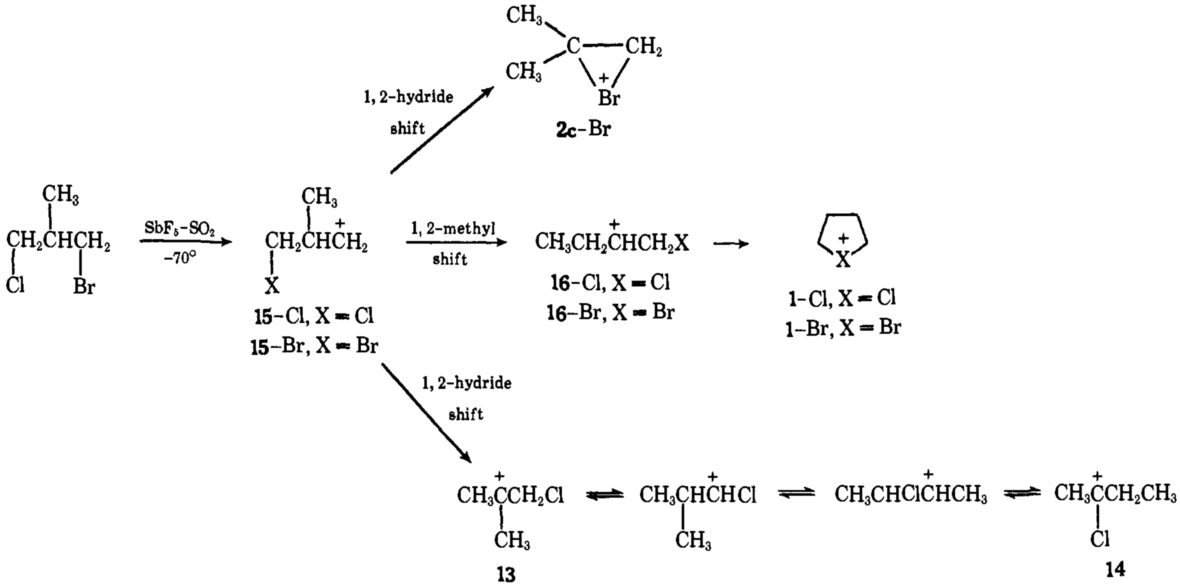
1-Br

Ionization of 1,3-Dihalo-2-methylpropanes. We next studied the ionization of 1,3-dihalo-2-methylpropanes in SbF_5–SO_2 solution. In the case of 1-bromo-3-chloro-2-methylpropane, the pmr spectrum of the solution shows the presence of four major separate ions (**13**, 34%; **14**, 19%; **1-Cl**, 30%; and **2c-Cl**, 17%) as well as a small amount of **1-Br**. This is the first observation of bromine ionizing more readily than



chlorine in a bromide chloride in SbF_5–SO_2 solution. Indeed, the preference is nearly 5:1 corresponding to 83% of the products formed by bromide loss and 17% by chloride loss.

The fact that the five-membered ring ion contained chlorine was further checked by gas chromatography of the quenched solution in Na^+OMe^-–MeOH. Quenching indicated that the ion was mostly the tetramethylenechloronium ion with a small amount of the tetramethylenebromonium ion also present. It is interesting to note the difference in stable ion formation when the leaving group is changed from chlorine to bromine. Presumably, ionization of both halogens would give the primary cations **15**. A simple 1,2-hydride shift of cations **15**-Cl and **15**-Br will form ions **13** and **2c**-Br, respectively. Ion **13** shows no chlorine participation to form the 1,1-dimethylethylenechloronium ion **2c**-Cl. The open-chain structure of ion **13** has been discussed in our early work.[2c] The 1,2-methyl shift in ions **15** will give ions **16** which then through 1,2-hydride shift will generate the tetramethylenehalonium ions **1**. The intermediate ions **16** were also involved in the ionization of 1,2- and 1,3-dihalobutanes with SbF_5–SO_2 solution (see previous discussion). Ion **16**-Cl would rearrange to ion **1**-Cl, but not to the methylethylchlorocarbenium ion **14**. Thus, ion **14** could be formed from either ion **13** by subsequent 1,2-hydride and 1,2-methyl shifts or other intermediates. When 1-chloro-3-iodo-2-methylpropane was treated in the same way, there was one major product formed by elimination of chloride ion, *i.e.*, the 1,1-dimethylethyleneiodonium ion.[2b] A small amount of unidentified product ions was also observed in the pmr spectrum, which were different in nature from those obtained in the ionization of 1-bromo-3-chloro-2-methylpropane.



Ionization of Dimethyl-β-haloethylcarbinol. We also prepared the two dimethyl-β-haloethylcarbenium ions, **17**-Cl and **17**-Br. In both cases the *gem*-dimethyl group consisted of triplets due to coupling with the methylene protons through the sp^2 carbon, and appeared at low field, δ 4.1. This is a clear indication that the ions are open-chain ions and not bridged.[2c] Ion **17**-Cl was obtained from the ionization of dimethyl-β-chloroethylcarbinol (**18**) in 1:1 HSO_3F–SbF_5–SO_2 solution while ion **17**-Br could be generated from the ionization of either dimethyl-β-bromoethylcarbinol (**19**) or 1,3-dibromo-3-methylbutane in HSO_3F–SbF_5–SO_2 solution at −78°.

$$XCH_2CH_2C(CH_3)_2Y \xrightarrow[-78°]{1:1\ HSO_3F\text{-}SbF_5\text{-}SO_2} XCH_2CH_2\overset{+}{C}(CH_3)_2$$

18, X = Cl; Y = OH
19, X = Br; Y = OH
20, X = Br; Y = Br

17-Cl, X = Cl
17-Br, X = Br

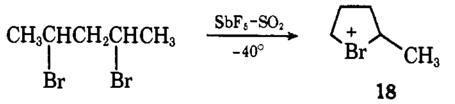
Table I. Pmr Spectral Data of Dimethyl-β-haloethylcarbenium Ions (Halo-*tert*-amyl Cations) in HSO_3F–SbF_5–SO_2 Solution[a–c]

Halogen (X)	CH_2X	CH_2C^+	CH_3
Cl	4.22 (t) (4.7)	4.74 (m)	4.08 (t) (4.4)
Br	4.02 (t) (5.2)	4.87 (m)	4.05 (t) (4.5)

[a] Chemical shifts are in parts per million from external (capillary) TMS at −60°. [b] Abbreviations used: (t) = triplet and (m) = multiplet. [c] Numbers in parentheses are coupling constants in hertz.

The pmr spectra of these ions are summarized in Table I. The ions were solvolyzed in methanol–sodium methoxide at −78° and gave the appropriate methyl ethers in good yield. Identification of the various ethers was made on the basis of their pmr spectra. All attempts to prepare the dimethyl-β-iodoethylcarbenium ion **17**-I from the corresponding alcohol resulted in the formation of a species whose most prominent absorption was an unsymmetrical doublet at δ 3.65 with *ca.* 1.0-Hz coupling and absorptions in the olefinic region. This spectrum may be that of the 1,1-dimethylallyl cation, although we were unable to generate this ion by a more straightforward route and, therefore, cannot be certain of its structure. A small amount of the same species appeared in the spectrum of **17**-Cl, but there was a greater amount of it detectable in solution with **17**-Br.

Ionization of **2,4-dibromopentane** in SbF_5–SO_2 solution at −40° gave the 2-methyltetramethylenebromonium ion **18**. Identification of ion **18** was made on the basis of its pmr spectrum reported by Olah and Peterson.[3]



$$\underset{}{CH_3\underset{Br}{C}HCH_2\underset{Br}{C}HCH_3} \xrightarrow[-40°]{SbF_5\text{-}SO_2}$$

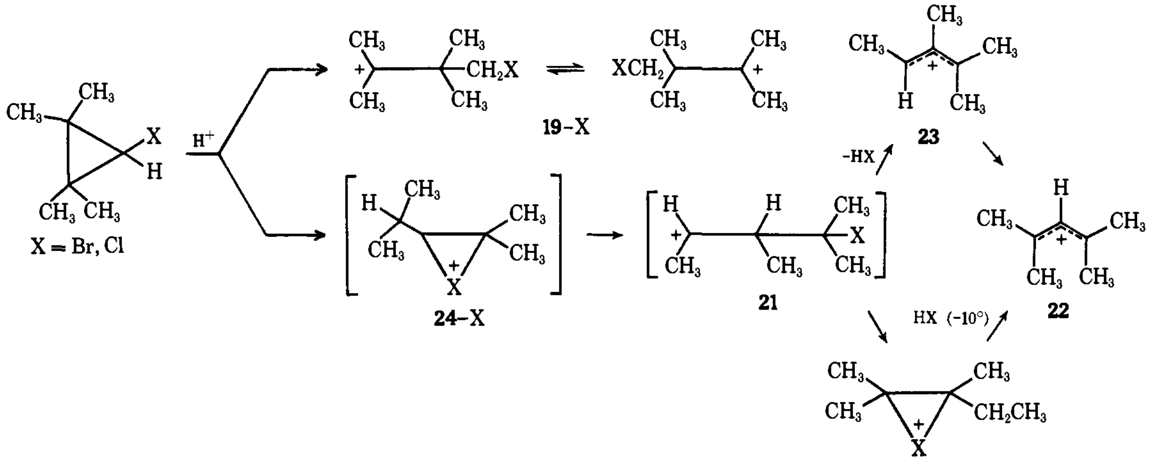
18

Protonation of 1,1,2,2-Tetramethylhalocyclopropanes. One area of additional interest in terms of possible four-membered ring halonium formation was the protonation of 1,1,2,2-tetramethylhalocyclopropanes. We had observed[6] previously that 1,1,2,2-tetramethylbromocyclopropane was protonated in 1:1 SbF_5–HSO_3F in SO_2 solution to give a species whose pmr spectrum consisted of two singlets in the ratio of 6:1 and which we then suggested might be due to the rapidly

$$\left.\begin{array}{c} (CH_3)_2\overset{+}{C}C(CH_3)_2Cl \\ \mathbf{19}\text{-Cl} \\ \delta\ 3.10\ (12\ H,\ CH_3),\ 4.30\ (2\ H,\ CH_2Cl) \\ (CH_3)_2\overset{+}{C}C(CH_3)_2CH_2Br \\ \mathbf{19}\text{-Br} \\ \delta\ 3.07\ (12\ H,\ CH_3),\ 4.10\ (2\ H,\ CH_3Br) \end{array}\right\}\begin{array}{l}\text{in 1:1 } SbF_5\text{–}HSO_3F\text{–}SO_2 \\ \text{at } -60°\end{array}$$

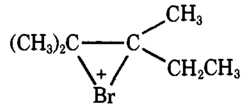
equilibrating ion

$$\underset{\mathbf{19}\text{-Br}}{(CH_3)_2\overset{+}{C}C(CH_3)_2CH_2Br} \rightleftharpoons \underset{\mathbf{19}\text{-Br}}{(CH_3)_2CCH_2Br\overset{+}{C}(CH_3)_2}$$

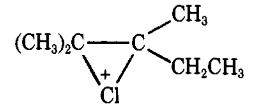


We have now examined the chlorine containing ion **19**-Cl for which a similar result was obtained. Attempts to cool the ions to −110° in an effort to obtain the frozen-out spectra were not successful. Only broadened pmr spectra were observed. These results indicate the kinetic process is of considerably low energy. Quenching solutions of the ions in MeONa–MeOH at −78° gave good yields of the expected methyl ethers (contaminated with several minor products) as indicated by the pmr spectra of the products.

The products formed upon protonation of 1,1,2,2-tetramethylchloro- and 1,1,2,2-tetramethylbromocyclopropane are very dependent on the nature of the acid mixture. In "wet" acid (if the intensity of the H_3O^+ peak in the solvent is about equal to half of the acid 1:1 HSO_3F–SbF_5) considerable protonation took place to form **20**-Br and **20**-Cl, along with the formation of **19**-Br and **19**-Cl, respectively. If the acid medium is



20-Br



20-Cl

fluorosulfuric acid (in SO_2), the intermediate **21**, presumably, can eliminate a molecule of HX to give the allylic cation **23** as the only observed species.[6]

The intermediate **20**-X loses HX at higher temperatures (near −10°) with rearrangement, perhaps through **24**-X, to give the allylic cation **22**. Interestingly, both halonium ions **20**-X and **24**-X, where X is bromine, upon formation (by protonation of the halocyclopropane, to a moderate extent, but, more cleanly by ionization of the appropriate dihalide) initially show about 5% formation of **23**. Subsequent decomposition gives (for which higher temperatures are required) almost entirely **22**.[6] These observations are somewhat reminiscent of Deno's observations of a base-dependent rearrangement which occurs in H_2SO_4.[7] Our rearrangement path appears to be dependent on the concentration and the nucleophilicity of the base. An alternative and perhaps supplementary explanation is that a competition exists between the two possible sites of protonation. We do not have sufficient data, yet, to indicate a detailed mechanism.

Experimental Section

Materials. The following compounds were purchased from Aldrich Chemical: 1,3-dichloropropane, 1,3-dibromopropane,

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[6] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968).

[7] N. C. Deno and R. R. Lastromirsky, *ibid.*, **90**, 4085 (1968).

1-bromo-3-chloropropane, 1,2-dichlorobutane, 1,3-dichlorobutane, 1,2-dibromobutane, and 1,3-dibromobutane. 1,1-Dichloropropane, 1,2-chloropropane, 1,1-dichlorobutane, and 1,3-dibromo-3-methylbutane were obtained from the Chemical Samples Co. (Columbus, Ohio). 1,3-Diiodopropane was obtained from Fisher Scientific Co. 1-Chloro-3-iodopropane was prepared by the method of Henry.[8] 1-Bromo-3-chloro-2-methylpropane was prepared by the method of Asinger.[9] 1-Chloro-3-iodo-2-methylpropane and 3-chloro-1-iodobutane were also prepared by literature methods.[10,11] 3-Bromo-1-iodobutane was prepared as described in ref 8, starting with 1,3-dibromobutane. This preparation also yielded some 1,3-diiodobutane. 4-Chloro- and 4-iodo-2-methyl-2-butanal were prepared according to the procedure of Späth and Spitzy.[12] 4-Bromo-2-methyl-2-butanol (bp 57–60° (5 mm)) was prepared in 45% yield using methyl β-bromopropionate in the above procedure.[12]

Preparation of Ions and Their Nmr Studies. Solutions of ions in antimony pentafluoride–sulfur dioxide or fluorosulfuric acid–antimony pentafluoride–sulfur dioxide solution were prepared as described previously.[2,3] Where low-temperature spectra were required, SO_2ClF was used instead of SO_2 as solvent.

Relative quantities of ions produced were determined by integration of the pmr spectra. The percentages quoted are averages of at least two experiments which generally showed good arrangement. Care was exercised to keep concentration of ions low to avoid complications of selective precipitation. Even so, solid material was sometimes observed to form at low temperature. This material was probably excess SbF_5–SO_2 complex crystallizing out. Solutions containing five-membered ring halonium ions were quenched in $NaOCH_3$–CH_3OH and the products were analyzed by vpc in order to confirm identification made on the basis of nmr spectra.

Ions not described in detail (pmr spectra) in this paper were already reported and characterized in our previous studies.

Nmr spectra were obtained on a Varian A-56-60A nmr spectrometer equipped with a variable-temperature probe. Chemical shifts are referred to external TMS.

Acknowledgment. Support of the work by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(8) L. Henry, *Bull. Soc. Chim. Fr.*, 17, 93 (1897).

(9) F. Asinger, G. Geisler, and M. Hoppe, *Chem. Ber.*, **91**, 2130 (1958).

(10) H. O. Dakin, *J. Biol. Chem.*, **164**, 617 (1946).

(11) H. B. Hass and H. C. Huffman, *J. Amer. Chem. Soc.*, **63**, 1234 (1941).

(12) E. Späth and W. Spitzy, *Chem. Ber.*, **58**, 2275 (1925).

Secondary Deuterium Isotope Effects. The Transition State in the Reverse Diels–Alder Reaction of 9,10-Dihydro-9,10-ethanoanthracene. A Potentially General Method for Experimentally Determining Transition-State Symmetry and Distinguishing Concerted from Stepwise Mechanisms[1]

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Abstract: Secondary α-deuterium isotope effects were studied in the reverse Diels–Alder reaction of 9,10-dihydro-9,10-ethanoanthracene, and its *-11,11-*d_2 and *-11,11,12,12-*d_4 derivatives, in an effort to determine the symmetry of the Diels–Alder transition state. The isotope effects of the d_2/d_0 adducts (k_2/k_0) and the d_4/d_0 adducts (k_4/k_0) in diphenyl ether solvent at 219.84 ± 0.015° were measured simultaneously with a ratio mass spectrometer. The isotope effects for each run were tested for their mechanistic significance. The possibility of having two different transition states for the dideuterated adduct, depending on whether protium or deuterium were next to the bond being broken, was taken into consideration. For the concerted, symmetrical transition state, $(k_2/k_0)^2 - (k_4/k_0) \equiv x = 0$; for a stepwise transition state, $x = (1 - k_2/k_0)^2 \equiv y$. The average isotope effect at 219.84 ± 0.015° for $k_2/k_0 = 0.924 \pm 0.005$, and the average isotope effect for $k_4/k_0 = 0.852 \pm 0.007$. The difference between the mechanistic extremes was 0.6%. The most positive mean value of the mechanistic index, x/y, was determined to be 0.043, indicating a transition state displaced only 4.3% from the concerted extreme. Therefore, it is concluded that the mechanism is concerted, with a symmetrical or nearly symmetrical transition state. This conclusion is *independent* of the absolute values of the observed isotope effects; it depends only on a comparison of k_4/k_0 and $(k_2/k_0)^2$. The only assumptions involved in this conclusion are: (1) that a "rule of the geometric mean" type assumption is valid in comparison of reactant and transition state; (2) that $f_A \neq f_B$ (where f_A is the isotope effect at bond C_9–C_{12} and f_B is the isotope effect at bond C_{10}–C_{11}) unless the mechanism is concerted; (3) that the mean value of x/y has significance within the experimental scatter of the data. These are the only assumptions required, and each of them is believed to be valid, (1) and (2) to a high degree of precision, and (3) to precision indicated by the statistical analysis.

The symmetry of the Diels–Alder transition state is still uncertain.[2] Theoretical[3a] and experimental[3b] evidence seems to indicate that in most reactions a concerted transition state is preferred. It is also uncertain just how much higher in energy the free-radical transi-

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[1] (a) Previous paper: E. D. Kaplan and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 6644 (1967); (b) supported in part by the Petroleum Research Fund, administered by the American Chemical Society, through Graduate Fellowship No. GF-70, and in part by the National Science Foundation through Grant No. GP-22,803; (c) taken from M.