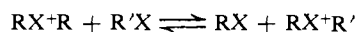# Onium Ions. IX.[1] Intermolecular Exchange Reactions of Dialkylhalonium Fluoroantimonates with Alkyl Halides and Alkylcarbenium Ions

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Abstract: Dialkylhalonium ions (except dimethyl- and diethylhalonium ions) undergo intermolecular exchange with the corresponding alkylcarbenium ion and/or with the corresponding alkyl halides under stable ion conditions at low temperature. The nature of the exchange reactions was studied by pmr spectroscopy, and is discussed.

Recently, the preparation of various types of halonium ions, including dialkylhalonium ions,[3] ethylenehalonium ions,[4] tetramethylenehalonium ions,[5] alkylarylhalonium ions,[6] and di- and trihalonium ions,[7] has been achieved. The structure of dialkylhalonium ions was studied in detail by nmr (^{1}H and ^{13}C), ir, and Raman spectroscopy.[8] Till now, however, only primary and secondary dialkylhalonium ions have been prepared and studied, while tertiary dialkylhalonium ions have not yet been observed. It is known from our studies, that dimethyl (ethyl) halonium ions are capable of alkylating a variety of n-donor bases.[3b,9] Thus, if the n donor is the excess alkyl halide, intermolecular exchange reactions could take place.

$$RX^+R + R'X \rightleftharpoons RX + RX^+R'$$

Similarly, dialkylhalonium ions may also undergo intermolecular exchange reaction with alkylcarbenium ions.

$$RX^+R + R'^+ \rightleftharpoons R^+ + RX^+R'$$
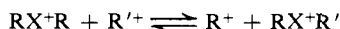
Furthermore, unsymmetrical dialkylhalonium ions could be expected to undergo disproportionation reactions.

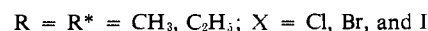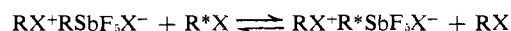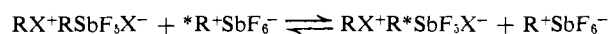$$2RX^+R' \rightleftharpoons RX^+R + R'X^+R'$$

We have now extended our studies to these reactions and report our findings.

Results and Discussion

Dimethylhalonium ions prepared from methyl halides with SbF$_5$ in SO$_2$ solution do not undergo intermolecular exchange reactions with excess of the methyl halide. The pmr spectra of these solutions show separately the presence of both dimethylhalonium ions and methyl halides from -80 to $-10°$. Similarly, dimethylhalonium ions, prepared by methylation of methyl halides with methyl fluoroantimonate, do not undergo

intermolecular exchange reaction with the excess methyl fluoroantimonate. The pmr spectra of these solutions display the absorptions of both dimethylhalonium ions and methyl fluoroantimonate from -80 to $-10°$. These results reflect the unusual stability of dimethylhalonium ions.

Similarly, diethylhalonium ions, prepared from ethyl halides with SbF$_5$–SO$_2$ solution, show the absence of intermolecular exchange reaction with excess of ethyl halides. Diethylhalonium ions also do not undergo intermolecular exchange reaction with excess ethyl fluoroantimonate in SO$_2$. The pmr spectra for these

$$RX^+RSbF_5X^- + {}^*R^+SbF_6^- \rightleftharpoons RX^+R^*SbF_5X^- + R^+SbF_6^-$$

$$R = R^* = CH_3, C_2H_5; X = Cl, Br, and I$$

$$RX^+RSbF_5X^- + R^*X \rightleftharpoons RX^+R^*SbF_5X^- + RX$$

$$R = R^* = CH_3, C_2H_5; X = Cl, Br, and I$$

solutions show the presence of both diethylhalonium ions and ethyl fluoroantimonate or ethyl halides and are temperature independent from -80 to $-10°$.

Diisopropylhalonium Ions. Isopropyl cation, prepared from isopropyl chloride and 4 (or more) mole equiv of antimony pentafluoride in SO$_2$ solution, displays in the pmr spectrum a doublet at δ 5.00 ($J = 6$ Hz) and a septet at δ 13.8 ($J = 6$ Hz). When about 10 mol % of additional isopropyl chloride was added to the above solution, the pmr doublet and the heptet were shielded to δ 4.90 and 13.0, respectively. The coupling constant was decreased to 4 Hz. Further addition of isopropyl chloride to this solution caused additional shielding of both absorptions, as well as the decreasing of the coupling constant. (Under these experimental conditions, tert-hexyl cation and a very small amount (5%) of unidentified polymeric products were also observed.) These data suggest that the following intermolecular exchange reaction has taken place. Further

$$([CH_3]_2CH)_2Cl^+ + CH_3C^+HCH_3 \rightleftharpoons$$
$$CH_3C^+HCH_3 + ([CH_3]_2CH)_2Cl^+$$
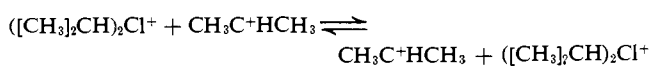
addition of isopropyl chloride to the above solution until the ratio of (CH$_3$)$_2$CHCl:SbF$_5$ = 2:1 was reached resulted in a pmr spectrum displaying a doublet at δ 2.20 ($J = 6$ Hz) and a broadened heptet at δ 7.1 (at $-85°$). The pmr spectrum is temperature dependent; both the doublet and the heptet collapsed into broadened singlets at $-30°$.

On the other hand, when 4 equiv of isopropyl chloride was treated with 1 equiv of antimony pentafluoride in

(1) Part VIII: G. A. Olah, J. J. Svoboda, and A. T. Ku, *J. Org. Chem.*, **38**, 4447 (1973).

(2) Postdoctoral Research Investigator, 1972–1973.

(3) (a) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); (b) G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *ibid.*, **96**, 884 (1974).

(4) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 947 (1968); (b) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587, 6988 (1968).

(5) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968).

(6) G. A. Olah and E. B. Melby, *J. Amer. Chem. Soc.*, **94**, 6220 (1972).

(7) G. A. Olah, Y. K. Mo, E. G. Melby, and H. Lin, *J. Org. Chem.*, **38**, 367 (1973).

(8) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).

(9) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 2562 (1970).

SO$_2$ solution at $-60°$ the pmr of the solution again showed a doublet (at δ 2.00) and a heptet (at δ 6.5). These two absorptions were deshielded when additional antimony pentafluoride was added. These data suggest intermolecular exchange reaction of diisopropylchloronium ion with isopropyl chloride has taken place.

$$([CH_3]_2CH)_2Cl^+ + (CH_3)_2CHCl \rightleftharpoons$$
$$(CH_3)_2CHCl + ([CH_3]_2CH)_2Cl^+$$
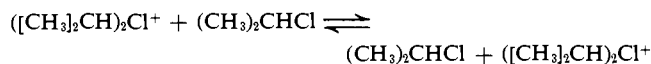
When the molar ratio of SbF$_5$:CH$_3$CHClCH$_3$ was increased to 2:1, temperature–dependent pmr spectra (two singlet absorptions at δ 2.20 and 7.10) were observed. Thus, the intermolecular exchange process is reversible (see previous discussion). The absence of proton–proton coupling indicates the exchange reaction also involves the methine proton. One possible explanation is the following cleavage and exchange reaction.

$$([CH_3]_2CH)_2Cl^+ \rightleftharpoons CH_3C^+HCH_3 + CH_3CHClCH_3 \rightleftharpoons$$
$$CH_3C^+ClCH_3 + CH_3CH_2CH_3$$
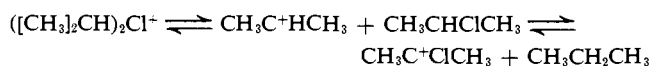
In order to prove whether this possible exchange reaction occurs, we have prepared the dimethylchlorocarbenium ion from 2,2-dichloropropane and antimony pentafluoride in SO$_2$ solution,[10] and mixed it with an equimolar amount of propane. The pmr spectrum of the resulting solution is identical with that of 2 equiv of isopropyl chloride in SbF$_5$-SO$_2$ solution.

The second intermolecular exchange reaction can be that involving alkylation of the C–H single bond[11] through a two-electron, three-centered bonded carbonium ion transition state (I).[12] These data are
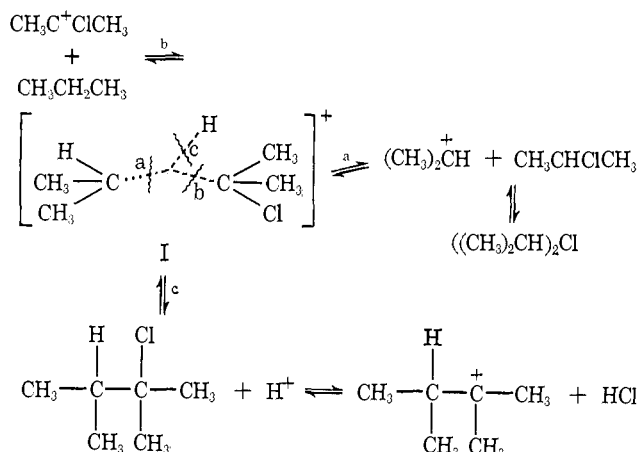
significant because they show the competing σ- vs. n-donor ability toward an electrophile (in this case isopropyl cation). Isopropyl cation alkylates the n-donor chlorine atom of isopropyl chloride to form diisopropylchloronium ion. It is also capable of alkylating the σ-donor C–H single bond[11] of isopropyl chloride forming the carbonium ion I. There are three possible ways to cleave I (depicted as a, b, and c). It could cleave to isopropyl chloride and isopropyl cation via a. Protolytic cleavage via b could give dimethylchlorocarbenium ion and propane. Deprotonation of I could generate the alkylation product, 2,3-dimethyl-2-chlorobutane, which is further ionized to tert-hexyl cation (an

(10) G. A. Olah and M. B. Comisarow, J. Amer. Chem. Soc., **91**, 2955 (1969).

(11) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, J. Amer. Chem. Soc., **93**, 1251 (1971), and references therein.

(12) G. A. Olah, J. Amer. Chem. Soc., **94**, 808 (1972).

observable product, see previous discussion). The formation of tert-hexyl cation is an irreversible process. This has been evidently shown by the increase in concentration of tert-hexyl cation when a solution of isopropyl chloride in SbF$_5$-SO$_2$ (ratio from 2:1 to 1:2) is kept at $-30°$ for longer periods of time.

The rather complex intermolecular exchange reactions of the diisopropylchloronium ion can be divided into three types: (i) exchange with isopropyl chloride when 2 or more equiv of isopropyl chloride is treated with SbF$_5$, (ii) exchange with isopropyl cation when isopropyl chloride is treated with 2–4 equiv of antimony pentafluoride (isopropyl cation is formed when 4 or more equiv of SbF$_5$ are used), and (iii) two different intermolecular exchange reactions, proceeding through carbenium ion I, occur when 0.5–2 equiv of isopropyl chloride is treated with SbF$_5$ in SO$_2$ solution. It is also possible that a small degree ($<5\%$) of intermolecular exchange reaction involving I takes place in both (i) and (ii) even though it cannot be detected by nmr under the experimental conditions.

Isopropyl bromide behaves differently from isopropyl chloride when treated with SbF$_5$-SO$_2$ solution. When 4 equiv of isopropyl bromide was treated with SbF$_5$ in SO$_2$ solution, diisopropylbromonium ion was formed and could be observed at $-95°$, even in the presence of excess isopropyl bromide. The pmr spectrum (at $-95°$) of the solution showed two doublets at δ 2.10 ($J = 7$ Hz) and 1.71 ($J = 7$ Hz) and two heptets at δ 5.87 ($J = 7$ Hz) and 4.40 ($J = 7$ Hz) for diisopropylbromonium ion (60%) and unassociated isopropyl bromide (40%), respectively. The pmr spectrum is temperature dependent. As the temperature is raised, these peaks begin to merge, and they coalesce to a doublet (δ 1.94) and heptet (δ 5.28) at $-40°$. Changes in concentration of isopropyl bromide apparently do alter the equilibrium, indicating that isopropyl bromide is, indeed, taking part in the equilibrium processes. This is reflected in the observed change in the ratio of the doublet and heptet absorptions. These data are consistent with the intermolecular exchange reaction of diisopropylbromonium ion with isopropyl bromide.

$$([CH_3]_2CH)_2Br^+ + (CH_3)_2CHBr \rightleftharpoons$$
$$(CH_3)_2CHBr + ([CH_3]_2CH)_2Br^+$$
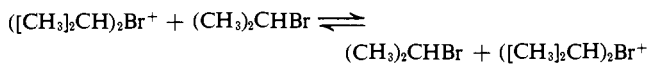
Isopropyl cation was formed when 4 or more equiv of SbF$_5$ in SO$_2$ was treated with isopropyl bromide at $-60°$. It underwent an intermolecular exchange reaction with diisopropylbromonium ion when isopropyl bromide was added to the above solution. The ex-

$$([CH_3]_2CH)_2Br^+ + (CH_3)_2CH^+ \rightleftharpoons (CH_3)_2CH^+ + ([CH_3]_2CH)_2Br^+$$

change reaction is similar to that of diisopropylchloronium ion.

When 4 equiv of isopropyl iodide was treated with SbF$_5$ in SO$_2$ solution at $-78°$, diisopropyliodonium ion was formed in the presence of unassociated isopropyl iodide. The pmr spectrum of the solution ($-50°$) displays two doublets (at δ 2.27 and 1.98) and two heptets (at δ 5.89 and 4.53) for diisopropyliodonium ion and isopropyl iodide, respectively. The pmr spectrum is temperature dependent and is similar to that of diisopropylbromonium ion, except that the coalescence temperature is higher ($-8°$). These data show that the intermolecular exchange reaction of diisopropylio-
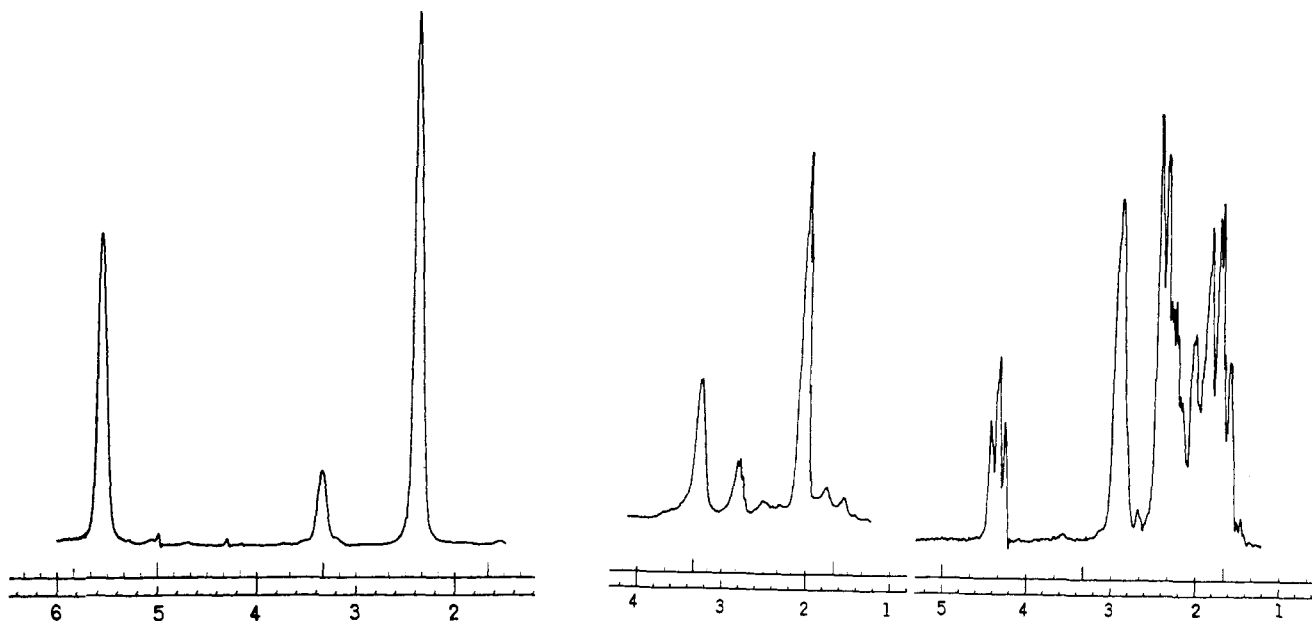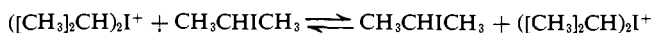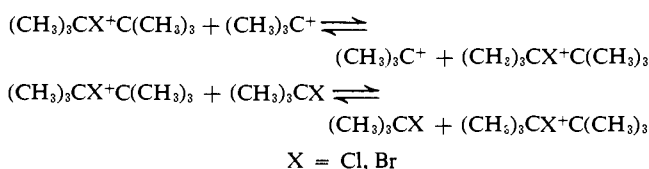
Figure 1. Pmr spectra of norbornyl cation (left), exchanging dinorbornylchloronium ion (center), and 2-*exo*-norbornyl chloride (right) at −78°.

donium ion with isopropyl iodide has a higher energy of activation.

$$([CH_3]_2CH)_2I^+ + CH_3CHICH_3 \rightleftharpoons CH_3CHICH_3 + ([CH_3]_2CH)_2I^+$$

Isopropyl cation was not formed when isopropyl iodide was treated with 4 or more equiv of SbF_5 in SO_2 solution at −40°. The pmr spectrum of the solution showed only the formation of the diisopropyliodonium ion. This result reflects the unusual stability of the diisopropyliodonium ion.

Di-*tert*-butylhalonium Ions. The pmr spectrum of the *tert*-butyl cation (generated from *tert*-butyl chloride in SbF_5–SO_2 solution) displays a singlet absorption at δ 4.02. This singlet absorption is shielded when more *tert*-butyl chloride is added to the solution. The shielding effect is proportional to the amount of *tert*-butyl chloride added. On the other hand, the pmr singlet absorption (at δ 1.90) of *tert*-butyl chloride in SO_2 is deshielded when SbF_5–SO_2 solution is added. Thus, this singlet absorption can be observed between δ 1.90 and 4.02 dependent on the relative concentration of *tert*-butyl chloride and SbF_5 in SO_2 solution. It should be noted that some polymeric products ($\sim$10%) were also formed under the experimental conditions. Consequently, the static di-*tert*-butylchloronium ion was not observed even at −90°, and underwent intermolecular exchange with either *tert*-butyl cation or/and *tert*-butyl chloride. Similar results were also obtained in the case of the di-*tert*-butylbromonium ion.

$$(CH_3)_3CX^+C(CH_3)_3 + (CH_3)_3C^+ \rightleftharpoons$$
$$(CH_3)_3C^+ + (CH_3)_3CX^+C(CH_3)_3$$
$$(CH_3)_3CX^+C(CH_3)_3 + (CH_3)_3CX \rightleftharpoons$$
$$(CH_3)_3CX + (CH_3)_3CX^+C(CH_3)_3$$
$$X = Cl, Br$$

Di-*tert*-amylhalonium Ions. *tert*-Amyl chloride in SO_2 solution displays three pmr absorptions at δ 1.05 (CH_3C, 3 H, t, $J = 7$ Hz), 1.61 (CH_3CCl, 6 H, s), and 1.90 (CH_2, 2 H, q, $J = 7$ Hz). These absorptions were deshielded when antimony pentafluoride in $SO_2(SO_2$–

ClF) solution was added. The deshielding effect was proportional to the amount of antimony pentafluoride added. In the case when more than 1 equiv of antimony pentafluoride was added, the *tert*-amyl cation was formed. On the other hand, the shielding of the absorptions of the *tert*-amyl cation was also observed when *tert*-amyl chloride was added to the solution of *tert*-amyl cation. Thus, the process is reversible. These data suggest that intermolecular exchange reactions of di-*tert*-amylchloronium ion with *tert*-amyl chloride or with *tert*-amyl cation have taken place. It should be noted that a small amount (5%) of unidentified product ions were also formed besides the exchange reactions. Similar results were also obtained with *tert*-amyl bromide in SbF_5–SO_2 solution.

Dinorbornylhalonium Ions. When 2-*exo*-norbornyl chloride was treated with 0.5 equiv of antimony pentafluoride in SO_2, at −70°, an organic precipitate was formed. The precipitate was redissolved when an equal volume of methylene chloride was added. The pmr spectrum of the resulting solution (Figure 1, center) displayed three absorptions at δ 3.28 (4 H), 2.83 (1 H), and 2.07 (6 H). The pmr spectrum is very similar to that of the norbornyl cation at the same temperature, Figure 1 (left). For comparison, the pmr spectrum of 2-*exo*-norbornyl chloride is also shown in Figure 1 (right). The proton chemical shift of each absorption is shielded from that of the norbornyl cation. In addition, the separation of the three absorptions is smaller than that in the case of the norbornyl cation. These data do not agree with the formation of a "static" dinorbornylchloronium ion. Furthermore, when more 2-*exo*-norbornyl chloride was added to the solution, the pmr spectrum again displayed three absorptions in a ratio of 4:1:6 and each absorption is further shielded. The shielding effect is proportional to the amount of 2-*exo*-norbornyl chloride added. On the other hand, when antimony pentafluoride was added to the above solution, the pmr spectrum again showed three absorptions (ratio 4:1:6), but each absorption is deshielded.

Figure 3.

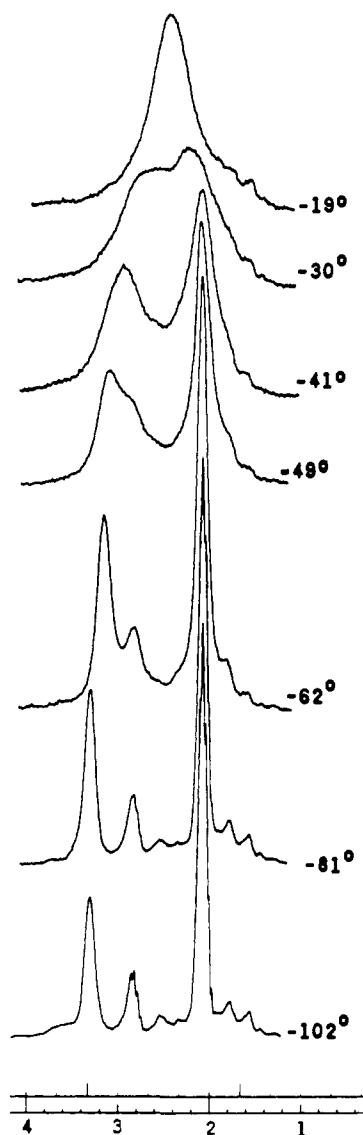| 1H	2H	2H	1H	4H
5.26	4.30	2.38	4.98	3.30
5.24	4.28	2.33	4.50	3.20
5.14	4.20	2.20	3.78	2.80
5.08	4.08	2.12	3.62	2.74

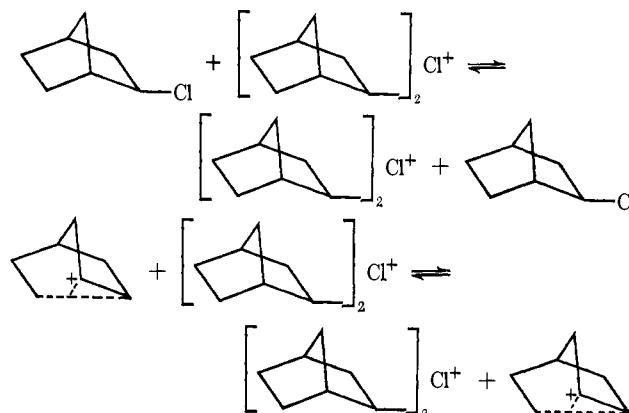Figure 2. Temperature-dependent pmr spectra of exchanging dinorbornylchloronium ion.

The pmr spectra of the solutions were temperature dependent and similar to that of the norbornyl cation.[13] Figure 2 shows the temperature-dependent pmr spectra of 2-exo-norbornyl chloride when treated with 0.5 equiv of SbF$_5$ in SO$_2$-CH$_2$Cl$_2$ solution. All data suggest that intermolecular exchange reactions of the dinorbornyl-chloronium ion take place with either 2-exo-norbornyl chloride or/and norbornyl cation. The temperature-dependent nature of the solutions indicate that 6,1,2-hydrogen shifts as well as the Wagner–Meerwein rearrangement are still taking place in the involved unassociated norbornyl cation in the studied temperature range. These data are in accordance with our previous studies on the long-lived norbornyl cation and its intramolecular rearrangement processes.

Similar results were also obtained in the case of 2-exo-norbornyl bromide with antimony pentafluoride in SO$_2$-CH$_2$Cl$_2$ solution. The intermolecular exchange process involves the dinorbornylbromonium ion.
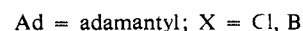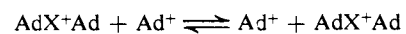
Diadamantylhalonium Ions. The 1-adamantyl cat-

ion has been prepared from adamantyl halide with SbF$_5$-SO$_2$(SO$_2$ClF) solution.[14] The pmr spectrum of adamantyl cation displays three absorptions at δ 5.40, 4.52, and 2.67. Diadamantylhalonium ions were, however, not previously prepared and studied. A yellowish organic precipitate was formed when equimolar adamantyl chloride was added to the solution of the adamantyl cation in SbF$_5$-SO$_2$ (or SO$_2$ClF). The precipitate was redissolved when methylene chloride was added as a cosolvent. The pmr spectrum of the resulting solution shows three absorptions similar to those of the adamantyl cation, but slightly shielded. The shielding effect is proportional to the amount of adamantyl chloride added to the solution of the adamantyl cation. Figure 3 (left) shows the change of proton chemical shifts when adamantyl chloride was added to a solution of the adamantyl cation. Further addition of adamantyl chloride to the above solution caused the collapse of the two methylene absorptions into a singlet. The new singlet and the methine singlet absorption were shielded when the concentration of adamantyl chloride was increased (Figure 3, right). The ratio of the two proton absorptions is 4:1. The pmr spectra of all of these solutions are temperature independent from −80 to −10°. These data again suggest intermolecular exchange of the diadamantyl-chloronium ion with either adamantyl chloride or/and the adamantyl cation. In this case the 1-adamantyl cation can also undergo intermolecular hydrogen exchange with a tertiary C–H bond of 1-chloroadamantane (the σ-donor site competing with the n-donor chlorine atom).

$$AdX^+Ad + Ad^+ \rightleftharpoons Ad^+ + AdX^+Ad$$
$$AdX^+Ad + Ad^{\cdot} \rightleftharpoons AdX + AdX^+Ad$$
$$Ad^+ + AdX \rightleftharpoons AdH + XAd^+$$
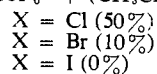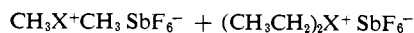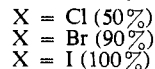$$Ad = adamantyl; \quad X = Cl, B$$

Similar results were also obtained for the diadamantylbromonium ion.

(13) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, J. Amer. Chem. Soc., 92, 4627 (1970), and references therein.

(14) P. v. R. Schleyer, W. E. Watts, R. C. For, Jr., M. B. Comisarow, and G. A. Olah, J. Amer. Chem. Soc., 86, 4195 (1964).

Disproportionation of symmetrical dialkylhalonium ions has been observed during preparation and nmr study of these species.[3] The degree of disproportionation of unsymmetrical dialkylhalonium ions is dependent on the nature of the halogen atom and alkyl groups. For example, methylethylhalonium ions disproportionate to give different ratios of dimethyl- and diethylhalonium ions.

$$2CH_3X^+CH_2CH_3\ SbF_6^- \rightleftharpoons$$
$$X = Cl\ (50\%)$$
$$X = Br\ (90\%)$$
$$X = I\ (100\%)$$

$$CH_3X^+CH_3\ SbF_6^- + (CH_3CH_2)_2X^+\ SbF_6^-$$
$$X = Cl\ (50\%)$$
$$X = Br\ (10\%)$$
$$X = I\ (0\%)$$

In the case of methylisopropylhalonium ions, complete disproportionation is observed at $-30°$.

$$i\text{-}C_3H_7X^+CH_3\ SbF_5X^- \xrightarrow{-30°}$$
$$CH_3X^+CH_3\ SbF_5X^- + (i\text{-}C_3H_7)_2X^+\ SbF_5X^-$$
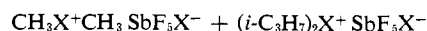
Attempts to prepare methylbutyl-, methyladamantyl-, or methylnorbornylhalonium ions were unsuccessful. The formed halonium ions completely disproportionated to dimethylhalonium ions and the stable *tert*-butyl,

$$RX + CH_3F \rightarrow SbF_5 \longrightarrow CH_3X^+CH_3SbF_5X^- + R^+SbF_5X^-$$
$$R = tert\text{-butyl, adamantyl, norbornyl}$$
$$X = Cl, Br$$

adamantyl, and norbornyl cations, respectively, or the rapidly exchanging di-*tert*-butyl-, adamantyl-, and norbornylhalonium ions.

Mechanisms. The mechanism of intermolecular exchange of dialkylhalonium ions with alkyl halides or with alkylcarbenium ions can be considered as either of SN1 or SN2 type. A limiting SN1 type mechanism is indicated in the case of diadamantylhalonium ions. The most likely SN2 type mechanism would be the exchange reaction of the dimethyl (ethyl) halonium ions. However, it has been shown that these halonium ions do not undergo intermolecular exchange with either alkyl halides or alkylcarbenium ions. In the case of diisopropylhalonium ions it was demonstrated that isopropyl cation is involved in the intermolecular exchange reactions (SN1) although the overall reaction may still be mixed in nature. *tert*-Butyl and *tert*-amyl cations may also be involved in the exchange reactions of di-*tert*-butylhalonium ions and di-*tert*-amylhalonium ions, respectively.

The nonexchanging dialkylhalonium ions of tertiary alkyl and norbornyl systems could, however, not be directly observed by nmr spectroscopy. Consequently, as a referee suggested, "an alternative direct exchange reaction between alkylcarbenium ions and alkyl halides could also explain the experimental data." However,

$$RX + R^+ \rightleftharpoons R^+ + RX$$

we feel such an exchange reaction always must involve the electrophilic attack at the n-donor halogen atom by the alkylcarbenium ion, thus forming the corresponding dialkylhalonium ion. Dissociation of the dialkyl-

$$RX + R^+ \rightleftharpoons [RX^+R] \rightleftharpoons R^+ + RX$$
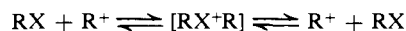
halonium ion into alkylcarbenium ion and alkyl halide results in the observed exchange.

The present study of the intermolecular exchange reactions of dialkylhalonium ions can also be related to the structure of cyclic halonium ions (ethylenehalonium,[4] and tetramethylenehalonium ions[5]), and gives further useful information. The absence of intermolecular exchange of dimethyl- and diethylhalonium ions indicates that the dissociation of the ions is unlikely to take place, or in other words, methyl or ethyl cation is not present even in very low concentration, in these systems. Earlier proton and carbon-13 nmr studies of ethylene- and tetramethylethylenehalonium ions could not fully distinguish between static cyclic and potentially rapidly equilibrating open-chain ions such as II and III. Indeed the equilibration between open chain β-halocarbenium ions and cyclic alkylenehalonium ions was observed (see subsequent paper[15]) in some tertiary
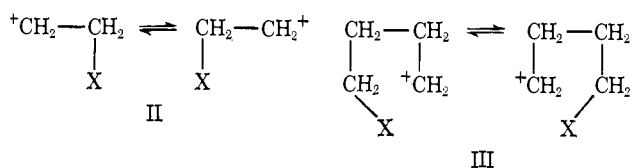
and secondary systems by temperature-dependent nmr studies. Primary systems, however, seem to prefer bridging.

The intermolecular exchange reactions of dialkylhalonium ions are also of importance in further understanding the complex Friedel–Crafts alkylation systems.

Experimental Section

Materials. All the alkyl halides were commercially available in high purity and were used without further purification. Antimony pentafluoride (Allied Chemical Co.) was refluxed overnight while passing a stream of dry nitrogen through it. It was then distilled twice (bp 150°). Sulfur dioxide was obtained from J. T. Baker Chemical Co.

Preparation of Dialkylhalonium Ions and Their Exchange Reactions. Solutions of dialkylhalonium ions were prepared by adding the desired amount of alkyl halide in SO_2 at $-78°$ to antimony pentafluoride in SO_2 (in specified concentration). The solution was stirred generally for 5 min, giving clear solutions suitable for nmr study.

Nmr Spectra. A Varian Associate Model A56/60A nmr spectrometer equipped with a variable-temperature probe was used for ^{1}H nmr spectra. Proton chemical shifts (δ) in SO_2 solvent are from external capillary TMS.

(15) G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *J. Amer. Chem. Soc.*, **96**, 3565 (1974).