taining 0.33 ml of 70% perchloric acid catalyst. The reaction mixture was allowed to reflux (101°) for 3 hr after which most of the solvent was removed by distillation at 44° (93 mm). The remaining acid was neutralized, and the mixture extracted with ether. The ethereal extracts were dried ($MgSO_4$), concentrated, and distilled to give 11.4 g of a mixture containing 12.9% 4-chloro-4-penten-1-yl formate, 35.5% 5-chloro-2-pentanone, and 51.6% 5-formoxy-2-pentanone. The mixture was analyzed by nmr, and the three products formed were isolated and identified in separate runs. 4-Chloro-4-penten-1-yl formate was isolated by preparative gas chromatography (Dow Corning 550); nmr (CCl_4) δ 8.03 (s, 1, OC*H*O), 5.21 (s, 2, $H_2C{=}C$), and 4.18 ppm (t, 2, CH_2O_2CH).

Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.11. Found: C, 48.87; H, 6.22.

5-Chloro-2-pentanone was isolated as the DNP derivative, mp 122.5–124.5°. A mixture melting point with an authentic sample (Columbia Organic Chemical Co.) was also taken. 5-Formoxy-2-pentanone was isolated as the DNP derivative of 5-hydroxy-2-pentanone, mp 145–147°. The formate grouping was hydrolyzed by the acidic reagent. The mixture melting point with an authentic sample showed no depression, mp 145–147°.

Basic Hydrolysis of 4-Chloro-4-hexen-1-yl Trifluoroacetate. 4-Chloro-4-hexen-1-yl trifluoroacetate (15.0 g, 0.0654 mole) was added to 50 ml of 2.5 *M* sodium hydroxide and stirred for 12 hr. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled giving 5.03 g (57%) of 4-chloro-4-hexen-1-ol: bp 99° (17 mm); ir (CCl_4) 3322 (OH) and 1052 cm^{-1} (CO); nmr (neat) δ 5.55 (t of q, 1, J = 6.5 Hz, J = 0.9 Hz, $HC{=}CCl$), 3.57 (t, 2, J = 6 Hz, CH_2OH), and 1.68 ppm (t of d, 3, J = 6.5 Hz, J = 1.1 Hz, $CH_3C{=}C$).

Reduction of 4-Chloro-4-hexen-1-ol. A solution of 2.21 g (0.10 mole) of 4-chloro-4-hexen-1-ol in 4.5 ml of methylcyclohexane was added dropwise with stirring to 33 ml of a 3 *M* solution of sodium metal in liquid ammonia, and stirred for 30 min. The excess sodium and sodium amide formed during the reaction were neutralized with solid ammonium chloride. The mixture was dissolved in water and extracted three times with one-third the volume of ether. The ethereal extract was washed (5% HCl, saturated $NaHCO_3$, and saturated NaCl), dried ($MgSO_4$), and distilled to give 0.636 g (38%) of 4-hexen-1-ol: bp 155–158° (lit.[28] bp 158°). Analysis for per cent *cis* isomer in the predominantly *trans*-alkene (*cf.* Table II) was accomplished by gas chromatography on a 12 ft, $^1/_8$ in. tris-(cyanoethoxy)propane column at 65°.

Basic Hydrolysis of 4-Iodo-4-hexen-1-yl Trifluoroacetate. 4-Iodo-4-hexen-1-yl trifluoroacetate (10 g, 0.031 mole) was hydrolyzed with 23 ml of 2.5 *M* sodium hydroxide (using the same procedure as for 4-chloro-4-hexen-1-yl trifluoroacetate) to yield 5.4 g (69.5%) of 4-iodo-4-hexen-1-ol: bp 105° (4.5 mm); nmr (CCl_4) δ 1.78 (m, 3, $CH_3CH{=}C$), 3.56 (t, 2, CH_2OH), and 5.60 ppm (q, 1, CH_3-$CH{=}C$).

Anal. Calcd for $C_6H_{11}IO$: C, 31.88; H, 4.90. Found: C, 32.13; H, 4.86.

Reduction of 4-Iodo-4-hexen-1-ol. 4-Iodo-4-hexen-1-ol (3.71 g, 0.016 mole) was reduced (using the same procedure as for 4-chloro-4-hexen-1-ol) to yield 0.4 g (24%) of 4-hexen-1-ol: bp 156–158° (lit.[28] bp 158.4°); nmr (CCl_4) δ 5.37 (m, 2, $CH_3CH{=}CH$), 3.5 (t, 2, CH_2OH), and 1.62 ppm (m, 3, $CH_3CH{=}CH$).

Reaction of 5-Halo-1-pentynes with Deuterated Trifluoroacetic Acid. 5-Chloro-, 5-bromo-, and 5-iodo-1-pentyne (2.5, 2.0, and 2.0 g, respectively) were allowed to react at 60.0° in deuterated trifluoroacetic acid (50, 40, and 40 ml, respectively) for approximately two, three, and three half-lives, respectively ($t_{1/2} \cong 11.5$, 8, and 4 hr, respectively). Nmr analyses of isolated products (20% in benzene, neat, and neat, respectively) indicated that peaks at δ 4.97, 5.63, and 6.17, respectively, were present to the extents of less than 8, 8, and 5%, respectively, compared to those of the hydrogen analogs. Boiling points for 4-bromo- and 4-iodo-4-penten-1-yl-5-*d* trifluoroacetates were, respectively, 40–60° (7 mm) and 45–50° (1.5 mm).

Reactions of Tetramethylenehalonium Ions[1]

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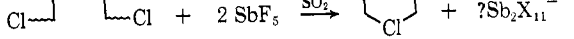
Contribution from the Department of Chemistry, St. Louis University,
St. Louis, Missouri 63156. *Received June 30, 1969*

Abstract: Tetramethylenechloronium ion was formed by treating 1 mol of 1,4-dichlorobutane with approximately 2 mol of antimony pentafluoride in SO_2. These conditions ensured complete ion formation. This ion was used to alkylate methanol, acetonitrile, dimethyl ether, acetone, and acetic acid. The synthetic utility of the alkylation was demonstrated. The nmr spectra of the initially formed intermediates in these alkylations were observed at −60°. 1,2,5-Trichloropentane and 1,2,5-tribromopentane gave five-membered ring halonium ions containing 2-halomethyl substituents upon treatment with antimony pentafluoride–sulfur dioxide. On treatment with methanol, SN2-like ring opening of the latter halonium ions predominated.

The recently reported tetramethylenehalonium ions (*e.g.*, **2**, eq 1)[3] are expected to resemble the earlier reported ethylenehalonium ions[4] and the very recently reported dialkylhalonium ions[5] in a number of their properties, particularly in their high reactivity as alkylating agents. Accordingly, as a step toward the further characterization of tetramethylenehalonium ions we have defined in more detail the conditions for their preparation and verified the synthetic utility of their use in alkylations of some common aliphatic functional groups. We also report the first results of a program of structural elaboration of tetramethylenehalonium ions *via* attachment of substituents compatible with the reactive halonium ion structure.

Results and Discussion

In the first phase of our work, studies on the stoichiometry of tetramethylenehalonium ion formation (eq 1)



(1)

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2, X = F or Cl

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(1) This research was supported by grants from the National Science Foundation (GP 6638) and the Petroleum Research Fund of the American Chemical Society (7904-A). We also acknowledge partial support of the purchase of a Varian HA-100D nmr spectrometer through National Science Foundation Grant No. GP-8510.

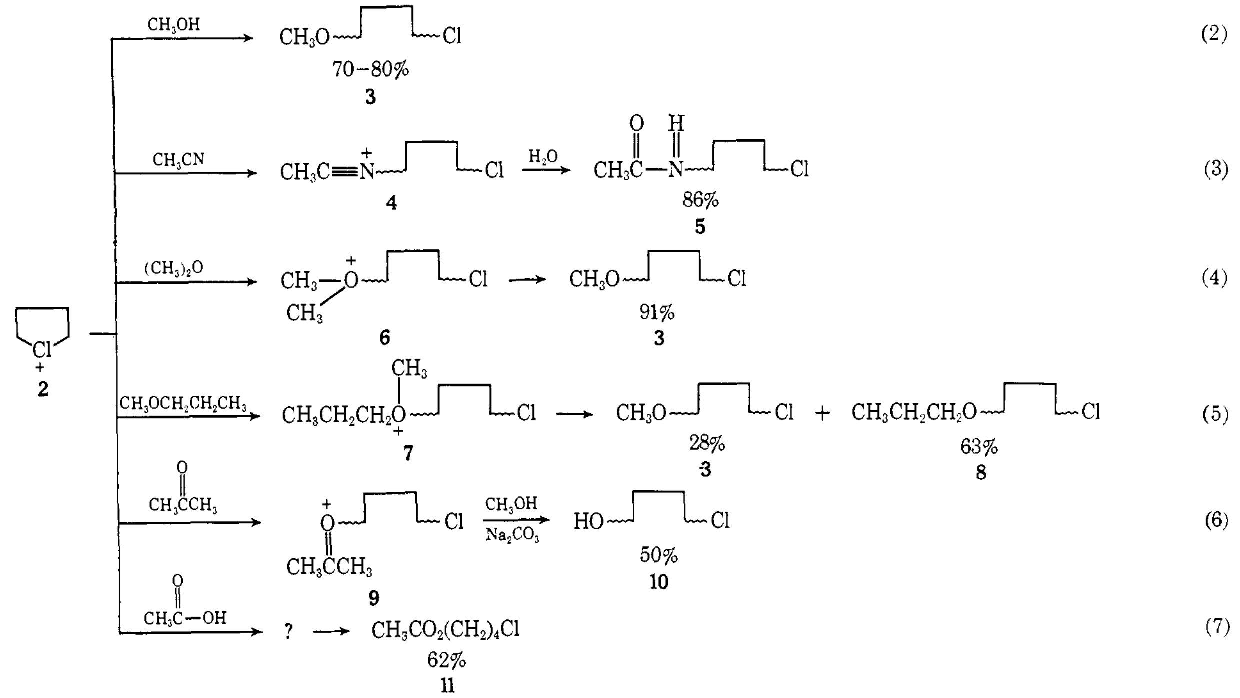
(2) (a) Postdoctoral Research Investigator; (b) NDEA Predoctoral Fellow, 1966–1969.

(3) (a) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968), and later papers from Olah's group quoted herein. (b) Bonds to electronegative substituents are shown as wavy lines to aid in visualizing the carbon chain.

(4) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967), and later papers in the series.

(5) G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969).

Scheme I. Products Formed from Tetramethylenechloronium Ion (**2**)



showed that the minimum number of moles of antimony pentafluoride per mole of 1,4-dichlorobutane (**1**) needed to ensure complete ion formation was approximately two. In a typical experiment, a solution made equimolar in SbF_5 and dihalide showed equal amounts of chloronium ion **2** and dihalide **1** by nmr analysis for each species at −60°. Warming to −40° for 20 min did not affect the spectrum. After treatment with a large excess of methanol (Scheme I, eq 2), gas chromatographic analysis indicated that equal amounts of dihalide and 4-chlorobutyl methyl ether (**3**) were present. Assuming, therefore, that any dihalide observed by gas chromatography was the result of incomplete ion formation, we treated solutions of SbF_5 in SO_2 with various amounts of dihalide, added methanol, and analyzed the products by gas chromatography. Nmr and gas chromatographic studies agreed in showing that no dihalide remained unreacted when at least 2 mol of SbF_5 per mole of dihalide was used. Although the concentration of dihalide in these solutions varied between 0.27 and 0.66 *M*, the yield of ether (**3**) observed by gas chromatographic analysis was between 70 and 80% and showed no correlation with overall concentration levels.

Recently published studies[6] rather strongly suggest that the requirement for 2 mol of SbF_5 per mole of dihalide which we observed results from reaction according to eq 1 to give anions containing two antimony atoms. In the reported studies the anion $Sb_2F_{11}^-$ was rather clearly indicated to be present in solutions prepared in several ways, based on the fluorine nmr spectra of the solutions. Somewhat surprisingly it was reported that ionization of *t*-butyl chloride in a reaction analogous to that shown in eq 1 gave a spectrum not differing appreciably from that of the ion $Sb_2F_{11}^-$,[6a] prompting us to represent the counterion as $Sb_2X_{11}^-$ (halogen not specified) in eq 1.

In our alkylation studies tetramethylenechloronium ion (**2**) (prepared using a 2:1 ratio of SbF_5 to dihalide) was treated with methanol, water, acetonitrile, dimethyl ether, methyl propyl ether, acetone, and acetic acid. In contrast with many studies in Olah's group, the nucleophile usually was added directly to the solution of halonium ion in sulfur dioxide in order to observe the nmr spectrum of the initial product of the alkylation. The products obtained by further reaction (quenching) during work-up were then identified by their nmr spectra. Yields of the latter products, reported in Scheme I, were determined by gas chromatography by comparison of peak areas with those obtained from solutions of known concentration.

We also determined the amount of the nucleophilic reactant needed to ensure complete reaction of the ion. For example, when 2 mol of acetonitrile for each mole of dihalide used in ion formation was added to a solution of the halonium ion, the nmr spectrum showed only the nitrilium ion (**4**) (Scheme I) to be present. However, if less than this amount of acetonitrile were used, the nmr spectrum also showed the presence of unreacted halonium ion. This result suggests that the excess antimony pentafluoride used may form a Lewis acid-base complex with acetonitrile, making the latter unavailable for alkylation. The postulated counterion, $Sb_2X_{11}^-$, may of course be regarded as a source of SbX_5 in reactions with acetonitrile or other Lewis bases. Dimethyl ether (2 mol) also was required to ensure complete reaction of our tetramethylenechloronium ion solutions, and approximately 3 of acetone and acetic acid were required.

No special precautions were taken in our experiments to exclude atmospheric water. Indeed, addition of small amounts of water to the SbF_5–SO_2 solution prior to addition of the dihalide seemed to have little effect on the yield of product. Furthermore, when the chloronium ion **2** was treated with water by allowing ice to dissolve slowly at −75° in an SO_2 solution of **2**, the nmr spectrum at −60° showed the presence of

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(6) (a) J. Bacon, A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **47**, 1655 (1969); (b) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

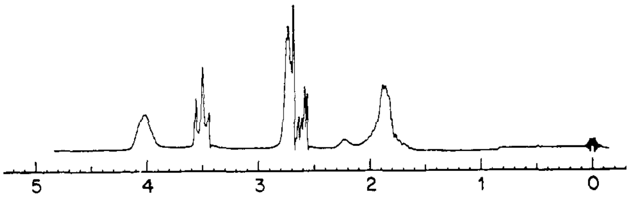


Figure 1. Nmr spectrum (SO_2, −60°) from the addition of acetonitrile to tetramethylenechloronium ion; molar ratio, SbF_5:tetramethylene dichloride:acetonitrile 2:1:2.

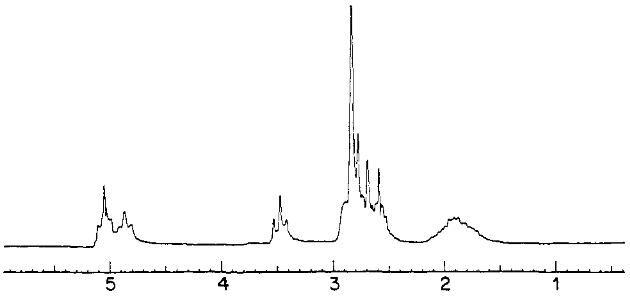
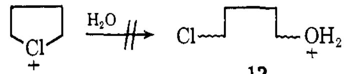


Figure 2. Nmr spectrum (SO_2, −60°) from the addition of acetone to tetramethylenechloronium ion; molar ratio, SbF_5:tetramethylene dichloride:acetone 2:1:1. Peaks of unreacted chloronium ion appear at δ 2.10 and 5.15.

water complexed with SbF_5 and chloronium ion but none of the reaction product **12**. On warming and work-up, no 4-chloro-1-butanol or other organic material soluble in CCl_4 was observed by gas chromatography.



2 **12** (8)

Identification of the nitrilium ion **4** (Scheme I) depends in part on the agreement of the chemical shifts (*cf.* Figure 1) with those obtained by Olah and Kiovsky[7] for N-ethylacetonitrilium ion. Also analogous to the spectrum of N-ethylacetonitrilium ion was the long-range coupling observed (*cf.* Figure 1) between the CH_3-C and the $C{\equiv}N^+$-CH_2 hydrogens. The complex region, δ 2.5–2.8 (Figure 1), presumably includes peaks attributable to the methyl group of the nitrilium ion **4** and to the methyl group of acetonitrile complexed with antimony pentafluoride. Similar complexities were observed in this region when the chloronium ion **2** was treated with acetone and acetic acid. For the various nucleophiles, the amount of reactant had a marked effect on this region of the spectrum.

On warming and treatment with water, the nitrilium ion **4** was converted to the amide **5** which was isolated in 40% yield by distillation. The overall yield as determined by gas chromatography was 86%.[8]

When the chloronium ion **2** was treated with excess dimethyl ether, 4-chlorobutyl methyl ether (**3**) was obtained in 91% yield. This product could have been formed from the oxonium ion **6** either by attack of water or by attack of excess dimethyl ether. Since the product was formed even when water was excluded on work-up, the latter mode of product formation probably occurs.

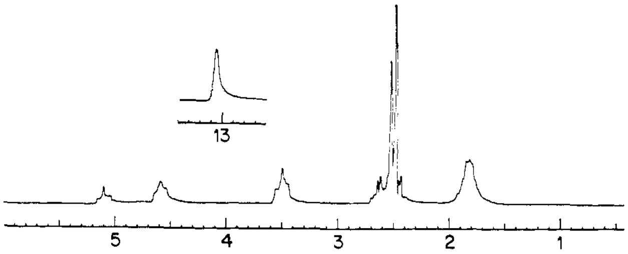


Figure 3. Nmr spectrum (SO_2, −60°) from the addition of acetic acid to tetramethylenechloronium ion; molar ratio, SbF_5:tetramethylene dichloride:acetic acid 2:1:3. Peak of unreacted halonium ion appears at δ 5.11.

The salient features of the spectrum of the oxonium ion **6** (Scheme I) are a triplet at δ 4.58 due to CH_2O^+ and a singlet at δ 4.23 due to $(CH_3)_2O^+$. These shifts may be compared with the shift of δ 4.49 for the CH_3 groups of $(CH_3)_2OH^+$ observed by Olah and O'Brien.[9] That no trimethyloxonium ion was present was demonstrated by the addition of trimethyloxonium fluoroborate to the solution. A new singlet at δ 4.29 appeared. Thus the oxonium ion **6** did not form trimethyloxonium ion by alkylation of excess dimethyl ether under the reaction conditions at −60° (*cf.* ref 10). It was also observed that a solution of the ether **3** and trimethyloxonium fluoroborate at −60° in SO_2 was apparently unchanged after standing at that temperature for over 0.5 hr. These results, of course, do not exclude the above mentioned possibility of reaction of oxonium ions with dimethyl ether in the presence of a large excess of ether at a temperature near room temperature.

On treatment with methyl propyl ether, the chloronium ion **2** gave 4-chlorobutyl methyl ether (**3**) and 4-chlorobutyl propyl ether (**8**). From the yields shown in eq 5 it is seen that attack on the intermediate oxonium ion **7**, probably by excess methyl propyl ether, occurred predominantly at the less hindered methyl group.

The spectrum of the ion that resulted from treatment of the chloronium ion **2** with acetone (Figure 2) is attributable to a mixture of the oxonium ion **9** and excess acetone complexed with SbF_5. Peaks in the region δ 2.6–2.9 presumably arise from the dimethyl group of oxonium ion **9** as well as from acetone complexed with SbF_5. By analogy with alkylated and protonated ethers, the ion **9** and protonated acetone might be expected to show similar chemical shifts. In agreement with this expectation, acetone, protonated by 1:1 SbF_5–FSO_3H in SO_2, showed δ 2.97, which may be compared with the reported[11] value, δ 3.45, possibly obtained under different conditions.

When the solution resulting from treatment of chloronium ion **2** with acetone was treated with cold methanol, followed by work-up involving washing with water, three products were obtained, including 4-chloro-1-butanol (eq 6). Other products were mesityl oxide (the aldol condensation product of acetone) and 4-me-

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[7] G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968).

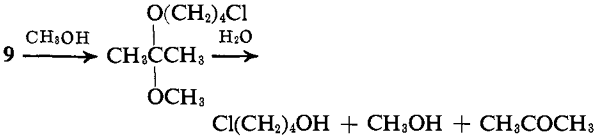
[8] Nitrilium ions, generated by treating nitriles with oxonium ions, have recently been used in the synthesis of amines by R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).

[9] G. A. Olah and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 1725 (1967).

[10] P. E. Peterson and F. Slama, *ibid.*, **90**, 6516 (1968).

[11] G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

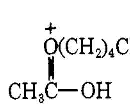
thoxy-4-methyl-2-pentanone, which may result from attack of methanol on mesityl oxide. 4-Chloro-1-butanol (**10**) was probably formed as shown below (eq 9). The amounts of the three products depended



$$9 \xrightarrow{CH_3OH} CH_3\overset{O(CH_2)_4Cl}{\underset{OCH_3}{C}}CH_3 \xrightarrow{H_2O} Cl(CH_2)_4OH + CH_3OH + CH_3COCH_3 \quad (9)$$

on whether or not Na_2CO_3 was added along with the methanol. The yield of 4-chloro-1-butanol increased from 22 to 50% when Na_2CO_3 was present. In the absence of Na_2CO_3, the relative amount of mesityl oxide to 4-chloro-1-butanol increased sharply.

Treatment of ion **2** with acetic acid led to the formation of 4-chloro-1-butyl acetate (**11**). The nmr spectrum obtained at −60° is shown in Figure 3. This spectrum is attributable to a mixture of unreacted chloronium ion, monoalkylated acetic acid **13**, and acetic acid complexed with antimony pentafluoride. Alternatively, dialkylated acetic acid **14** might be present.



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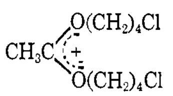

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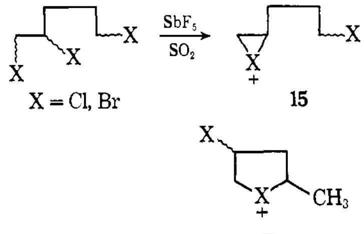
We attempted, unsuccessfully, to obtain the spectrum of dialkylated acetic acid by treating the chloronium ion **2** with 4-chloro-1-butyl acetate (**11**). Some evidence against dialkylated acetic acid **14** being the initially formed intermediate in this reaction may be found in the fact that work-up involves treatment with cold methanol. If such a species were present, one might expect to isolate some 4-chloro-1-butanol on work-up (*cf.* the reaction of **9** with methanol). However, no 4-chloro-1-butanol was found.

As a first step in a program of determining the compatibility of substituents with halonium ions and assessing the effects of compatible substituents upon reactions of the ions, 1,2,5-trichloropentane and 1,2,5-tribromopentane were treated with antimony pentafluoride in SO_2 at −60°. We were interested in which of the possible halonium ions, **15**, **16**, or **17**, would be formed, provided the substituents present in these ions proved to be compatible. Although the possibility of forming ion **17** may not be immediately apparent, it may be recalled that 1,5-dibromopentane has been shown to give 2-methyltetramethylenebromonium ion on treatment with antimony pentafluoride.[3] We have now found that upon treatment with antimony pentafluoride, the corresponding chloride, 1,5-dichloropentane, gives the analogous 2-methyltetramethylenechloronium ion (eq 11). More notably, 1,6-dichlorohexane gave the previously reported[12] 2,2-dimethyltetramethylenechloronium ion (eq 12). Accordingly, if the neighboring halogen suppressed the expected ionization of the secondary halogen in the 1,2,5-trihalopentanes, one might expect to obtain the ion **17**. Previous attempts to prepare ethylenechloronium ions have failed,[13] suggesting that for X = Cl, ion **15** would, if formed at all, rearrange or polymerize. On the other hand ions **16** and **17** might also be expected to be difficult to prepare, since they are destabilized by the inductive substituents present.



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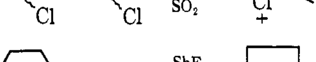
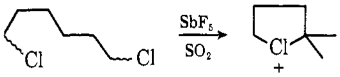


(11)



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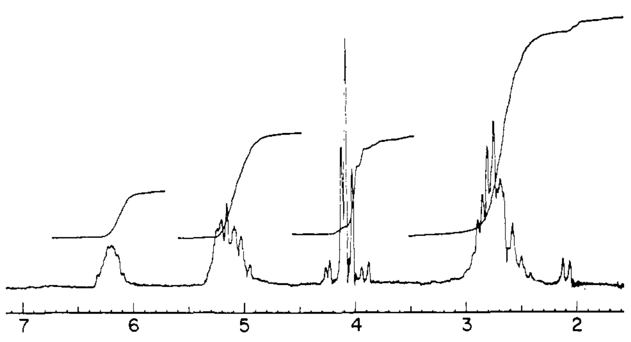

Figure 4. Nmr spectrum (SO_2, −60°) of the 2-chloromethyltetramethylenechloronium ion; molar ratio, SbF_5:1,4,5-trichloropentane 2:0.8.

In fact, 1,2,5-trichloropentane reacted readily to give the product whose nmr spectrum is shown in Figure 4. The peaks near δ 6.2 (methine hydrogen) and 5.1 (methylene hydrogens neighboring to positive chlorine), as well as the observed coupling, were those expected for the five-membered ring ion **16** rather than those expected for either ions **15** or **17**.[14] Reaction of 1,2,5-tribromopentane gave a similar result.

In addition to providing an indication of structure, the spectrum of Figure 4 has some bearing on the question of whether halonium ions are in equilibrium with the corresponding carbonium ions.[4,12,13] The absence of large percentages of carbonium ions in solutions of various halonium ions has been inferred from the absence of certain rearrangements,[15,16] from chemical shift data,[17] and from the absence of long-range coupling.[15,16,18] The observation of *cis* and *trans* isomers of 2,5-dimethylhalonium ions shows that these ions do not interconvert rapidly *via* opening to planar carbonium ions.[3] Similarly, the spectrum (Figure 4) of the chloronium ion **16** and that of the bromine analog (X = Br; spectrum not shown) show that rapid equilibration of the configuration of the asymmetric methine carbon *via* a ring-opening reaction to a car-

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(12) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 6988(1968).

(13) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 947 (1968).

(14) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968).

(15) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. G. Bastion, *ibid.*, **86**, 1360 (1964).

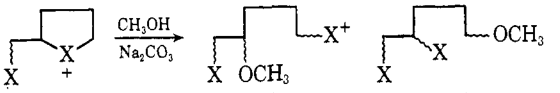
(16) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *ibid.*, **89**, 2692 (1967).

(17) G. A. Olah and J. Lukas, *ibid.*, **89**, 2277 (1967).

(18) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *ibid.*, **89**, 156 (1967).

bonium ion does not occur. This statement is based on the observation that the $-CH_2X$ group of ion **16** ($X = Cl$, Br) appears (δ 4.1 for $X = Cl$) as the AB part of an ABX spectrum, owing to the nonequivalence of the hydrogens "induced" by the asymmetric center.

It has been reported that methylethylene-[12] and 2-methyltetramethylene-[3] halonium ions gave SN1-like ring opening to form secondary ethers on treatment with methanol. On the contrary, when, in the present study, the 2-halomethyltetramethylenehalonium ions **16** were allowed to react with methanol, both SN1-like and SN2-like cleavage resulted, with SN2-like opening predominating. In the methanolysis of 2-chloromethyltetramethylenechloronium ion (**16**, X = Cl) the gas-chromatographically measured ratio of 4,5-dichloro-1-pentyl methyl ether to 1,5-dichloro-2-pentyl methyl ether was 9.6 in one experiment and 6.5 in another. In the analogous reaction where X = Br (eq 13) the ratio of 4,5-dibromo-1-pentyl methyl ether to 1,5-dibromo-2-pentyl methyl ether was 2.8. These results presumably indicate that the inductive effect of the XCH_2 group greatly slows the SN1-like ring opening of the ions, **16**, permitting SN2-like opening to predominate.



(13)

16 minor major

The chemical shifts of methyl compounds in SO_2 and CCl_4 are given in Table I for comparison with those of our alkylated derivatives. The absence of strong interactions of the solvent with common functional groups is implied by the parallelism, also noted for other compounds,[17] of chemical shifts in sulfur dioxide and carbon tetrachloride.

Table I. Chemical Shifts of C–H Groups in SO_2 at $-60°$ and in CCl_4 at Room Temperature

Compd	Chemical shift in SO_2[a] (CCl_4)[b] δ, ppm
CH_3COCH_3	1.82 (2.05)[c]
CH_3CN	1.68 (1.95)[c]
$Cl(CH_2)_4Cl$	3.29, 1.56 (3.52, 1.93)
$(CH_3)_3O^+BF_4^-$	4.17
$(CH_3)_2O$	2.84 (3.29)[d]
CH_3OH	2.94 (3.32)[c]
CH_3CO_2H	1.71 (2.03)[c]

[a] With respect to a capillary of TMS (*cf.* Experimental Section). [b] With respect to internal TMS. [c] P. E. Peterson, *J. Org. Chem.*, **31**, 439 (1966). [d] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, p 55.

Experimental Section

1,4-Dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, and antimony pentafluoride are commercially available compounds. The preparation of the 4,5-dihalo-1-pentyl methyl ethers and the 1,5-dihalo-2-pentyl methyl ethers will be reported elsewhere. The antimony pentafluoride was distilled after warming under a stream of nitrogen to remove the hydrofluoric acid present. After distillation at atmospheric pressure (bp 149°), the antimony pentafluoride was kept in Teflon bottles until used.

1,2,5-Trichloropentane. A flask containing 25.5 g (0.25 mol) of 5-chloro-1-pentene in 100 ml of carbon tetrachloride was cooled in an ice bath, while chlorine (17.1 g, 0.24 mol) was carried into it by a stream of oxygen under subdued light. Distillation gave a small amount of lower boiling product and 34.9 g (83%) of 1,2,5-trichloropentane, pb 94° (12 Torr); nmr (CCl_4) δ 3.9–4.2 (m, 1), 3.4–3.9 (m, including a triplet at 3.56, 4), 1.5–2.5 (m, 4).

Anal. Calcd for $C_5H_9Cl_3$: C, 34.21; H, 5.18. Found: C, 34.31; H, 5.17.

1,2,5-Tribromopentane. A flask containing 15.0 g of 5-bromo-1-pentene in 25 g of CCl_4 was cooled in an ice bath while bromine (15.0 g, 0.094 mol) was added in subdued light. Removal of the carbon tetrachloride and distillation afforded 1,2,5-tribromopentane (28.2 g, 97%) pb, 120° (0.5 Torr).

Preparation of the Ions and the Nmr Spectra. Tetramethylenechloronium ion was prepared by weighing out antimony pentafluoride and adding sufficient SO_2 at $-75°$ to make the solution 0.8 *M* in antimony pentafluoride, followed by the addition of sufficient 1,4-dichlorobutane to make the solution 0.4 *M* in 1,4-dichlorobutane. 2-Chloromethyltetramethylenechloronium ion and 2-bromomethyltetramethylenebromonium ion were prepared by analogous procedures. The reactions with nucleophiles were carried out by direct addition of the quenching agent to the solution of the ion in SO_2 at $-60°$. The spectra of the resulting products were obtained immediately at $-60°$, using a Varian HA-100D spectrometer. All chemical shifts in SO_2 are reported relative to external (capillary) TMS. The capillaries had an inner diameter of approximately 0.5 mm. No special measures were taken to make sure that the capillaries were centered in the nmr tube. Centered capillaries with inner diameters of 1.6–1.8 mm led to chemical shifts 0.02–0.04 ppm downfield from those observed with noncentered capillaries. The larger capillaries however gave large spinning side bands when not centered and small spinning side bands even when centered and therefore were not used.

Preparative Reactions of Tetramethylenechloronium Ion. Solutions whose concentrations ranged from 0.25 to 0.8 *M* in 1,4-dichlorobutane were prepared as described above. In all cases the molar concentration of the antimony pentafluoride was twice that of the 1,4-dichlorobutane. The solution was allowed to stand for 0.5 hr, excess nucleophile was added, and the solution was allowed to warm to room temperature. The solution was diluted with water, extracted with carbon tetrachloride, and dried over magnesium sulfate. Yields were determined on a Hewlett-Packard Model 5750 flame ionization gas chromatograph by comparison with standard solutions of known concentration. Specific variations from this procedure are listed below.

a. Reaction with Acetonitrile. Water was added when the solution reached 0°, and the solution was extracted with chloroform. From 1.03 g of 1,4-dichlorobutane was obtained 0.45 g (37%) of 4-chlorobutylacetamide, bp 120° (1 mm) on distillation through a short-path distillation column; nmr ($CDCl_3$) δ 6.48 (s, 1), 3.54 (t, 2), 3.26 (q, 2), 1.96 (s, 3), and 1.76 (m, 4). On shaking with D_2O, the broad peak at δ 6.48 disappeared and the quartet at δ 3.26 became a triplet.

Anal. Calcd for $C_6H_{12}ClNO$: C, 48.16; H, 8.03; N, 9.36. Found: C, 48.17; H, 8.09; N, 9.12.

b. Reaction with Dimethyl Ether. Water was added at 0°.

c. Reaction with Acetone. A mixture of sodium carbonate and cold methanol was added prior to warming. The solution was extracted with carbon tetrachloride without diluting with water. The carbon tetrachloride was washed with water.

d. Reaction with Acetic Acid. A mixture of cold methanol and sodium carbonate was added prior to allowing the mixture to warm to room temperature. The solution was extracted with carbon tetrachloride without diluting with water. The carbon tetrachloride extract was washed with water. 4-Chlorobutyl acetatew as isolated by preparative gas chromatography (Dow Corning 550 fluid, 6 ft, 130°); nmr (CCl_4) δ 4.05 (t, 2), 3.52 (t, 2), 1.98 (s, 3), and 2.81 (m, 4).

Anal. Calcd for $C_6H_{11}ClO_2$: C, 47.91; H, 7.31. Found: C, 47.76; H, 7.43.