Solvents of Low Nucleophilicity. XIII. Stereospecific Additions to Triple Bonds in 1,4-Halogen Shift Reactions¹

Paul E. Peterson, Ronald J. Bopp,² and Manuel M. Ajo

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

Abstract: 1,4-Halogen shifts have been demonstrated in the reactions of 5-bromo- and 5-iodo-1-pentyne and 6-chloro- and 6-iodo-2-hexyne with trifluoroacetic acid. The products were 4-bromo- and 4-iodo-4-penten-1-yl trifluoroacetate and 4-chloro- and 4-iodo-4-hexen-1-yl trifluoroacetate, respectively. 5-Fluoro-1-pentyne appeared to undergo an analogous reaction to the extent of 15%, followed by addition of trifluoroacetic acid to the first-formed vinyl fluoride. The reaction of 5-fluoro-1-pentyne and the solvolysis of 5-fluoro-2-pentyl tosylate (which we reported elsewhere) may represent the first examples of fluorine participation. The addition of hydrogen and halogen to the triple bond during 1,4-halogen shifts occurred predominantly in *trans* fashion.

Ther studies from our laboratories and from others³ have provided extensive evidence for 1,4-halogen participation, including observation of tetramethylenehalonium ions in antimony pentafluoride-sulfur dioxide,⁴ and 2-methylenetetramethyleneiodonium ion in fluorosulfonic acid-antimony pentafluoride-sulfur dioxide. Although an early paper in this series provided evidence that chlorine, bromine, and iodine may participate to approximately equal extents,⁵ actual halogen shifts of bromine and iodine, and also fluorine, had not been observed before the presently reported study was undertaken, although examples discovered subsequently have now been reported.^{3c,d} Accordingly, we decided to compare the reactions of the various haloalkynes with trifluoroacetic acid, since halogen shift might occur (eq 1),⁶ and since the potential availability of clean addition reactions (of H and X) to the triple bond (eq 1) would permit determinations of the stereochemistry of addition. The few modern studies of the stereochemistry of electrophilic additions to alkynes are mentioned in the discussion section. The possibility of observing fluorine participation was of

 $R = H, CH_{3}$ X = halogen $CF_{3}CO_{2}H \rightarrow H_{A} \xrightarrow{3}{2} 1 \longrightarrow OCOCF_{3}$ $R = H_{A} \xrightarrow{3}{2} 1 \longrightarrow OCOCF_{3}$ $R = H_{B}, CH_{3}$ $R = H_{B}, CH_{3}$ $R = H_{B}, CH_{3}$ $R = H_{B}, CH_{3}$ $R = H_{B}, CH_{3}$

unique interest, and we have reported our result

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(2) NASA Trainee, 1966-1967.
(3) (a) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, J. Am. Chem. Soc., 87, 5163 (1965); (b) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, 89, 5902 (1967); (c) P. E. Peterson and J. F. Coffey, *Tetrahedron Lett.*, 3131 (1968); (d) P. E. Peterson and F. J. Slama, J. Am. Chem. Soc., 90, 6516 (1968); (e) W. S. Trahanovsky, G. L. Smyser, and M. D. Doyle, *Tetrahedron Lett.*, 3127 (1968).
(4) (a) G. A. Olah and P. E. Peterson, J. Am. Chem. Soc., 90, 4675

(4) (a) G. A. Olah and P. E. Peterson, J. Am. Chem. Soc., 90, 4675 (1968);
(b) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, 90, 6988 (1968).

(5) P. E. Peterson and G. Allen, ibid., 85, 3608 (1963).

(6) A wavy line indicates a bond between carbon and an electronegative substituent. This convention is used to indicate unambiguously the length of the carbon chain in "broken line" formulas. (possible observation of fluorine participation) in a preliminary communication.⁷

Description and Results

The 5-halo-1-alkynes and 6-halo-2-alkynes were prepared as described in the Experimental Section, and the rates of reaction with trifluoroacetic acid were measured by either the nmr method described in the Experimental Section or a gas chromatographic method, involving the use of a basic forecolumn to remove the acidic solvent.⁸ The observed first-order rate constants are given in Table I along with values for other alkynes, reported previously.⁹ Also given are values of $k_{\rm H}/k_{\rm X}$, the rates relative to that of 1-hexyne, the per cent of 1,4-halogen shift, based on analysis of the products of reaction (last columns), and other data involving k_{Δ} , to be defined in the Discussion.

As anticipated, 5-bromo-1-pentyne, 5-iodo-1-pentyne, 6-chloro-2-hexyne, and 6-iodo-2-hexyne reacted to give predominantly the 1,4-halogen shifted products. The "normal" addition product of trifluoroacetic acid to 5-iodo-1-pentyne was independently prepared (by mercury catalyzed addition of trifluoroacetic acid to 5-iodo-1-pentyne) and shown to be almost unreactive under the conditions of the halogen shift reactions. In the case of the pentynes the spectra of the halogen shifted products strongly resembled those of the 2halopropenes in the vinyl region. The separation of the peaks corresponding to $H_{\rm A}$ and $H_{\rm B}$ in our vinyl bromide and iodide (eq 1) (and in the vinyl chloride when the spectrum was determined in benzene) encouraged us to determine the stereospecificity of the addition to the triple bond by nmr analysis of the products obtained from the reaction of 5-halo-1pentynes with deuterated trifluoroacetic acid. Based on nmr assignments from the literature, 10 the additions of halogen and deuterium to the triple bond in the "halogen shift" reactions of 5-halo-1-pentynes occurred predominantly or exclusively in trans fashion¹⁰ (cf. Figure 1). In the case of the hexynes, the stereochemistry was determined by hydrolysis of the tri-

⁽⁷⁾ P. E. Peterson and R. J. Bopp, J. Am. Chem. Soc., 89, 1283 (1967).

⁽⁸⁾ P. E. Peterson and E. V. P. Tao, J. Org. Chem., 29, 2322 (1964).

⁽⁹⁾ P. E. Peterson and J. E. Duddey, J. Am. Chem. Soc., 88, 4990 (1966).

^{(10) (}a) R. J. Bopp, Ph.D. Thesis, St. Louis University, St. Louis, Mo., 1967; (b) S. W. Tobey, J. Org. Chem., 34, 1281 (1969).

Table I. Rates of Reaction of Trifluoroacetic Acid with 5-Substituted 1-Pentynes and 6-Substituted 2-Hexynes at 60.0°

Alkyne	$k \times 10^{6},$ sec ⁻¹	$k_{ m H}/k_{ m X}$	$k_{\Delta}/k_{ m B}$	$100k_{\Delta}/k_{\rm T}$ calcd from rates	100k∆/k _T from product analyses
2-Hexyne	297ª				
1-Hexyne	269ª	1			
5-Fluoro-1-pentyne	15.90	16.9	0.25	20	15
5-Chloro-2-pentyne	77.6ª	3.47	3.4	77	85,ª 91.0–91.5 ^b
5-Bromo-1-pentyne	114 ^b	2.36	4.3	81	95,95
5-Iodo-1-pentyne	217 ^b	1.24	6.1	86	96.4–96.7 ^b
5-Methoxy-1-pentyne	106ª	2.54	6.5		
5-Cyano-1-pentyne	3.60ª	74.7			
5-Trifluoroacetoxy-1-pentyne	4.48ª	60.0			
6-Chloro-2-hexyne	258 ^b		5.8	86	86 ⁵
6-Iodo-2-hexyne	826 ^b		14	93	

^a From ref 9. ^b This study.

fluoroacetate group followed by stereospecific reduction of the halogen (with retention of configuration) with sodium in liquid ammonia¹¹ to the 4-hexen-1-ol (eq 2). The infrared spectrum of this 4-hexen-1-ol



in carbon disulfide showed a strong band at 965 cm⁻¹ characteristic of the CH out-of-plane vibration in *trans*-disubstituted alkenes, and a very weak absorption in the region (730-675 cm⁻¹) where *cis*-disubstituted alkenes absorb.¹² The predominance of the *trans* isomer was confirmed by gas chromatographic comparison with reference samples of *cis*- and *trans*-4-hexen-1-ol. The quantitative results of the various stereochemical experiments are shown in Table II.

 Table II.
 Per Cent cis Isomer in the Predominantly trans-Vinyl

 Halides from Halogen Shift Reactions

Reactant	cis, %
5-Chloro-1-pentyne	8
5-Bromo-1-pentyne	8
5-Iodo-1-pentyne	5
6-Chloro-2-hexyne	9.6
6-Chloro-2-hexyne ^a	9.0
6-Iodo-2-hexyne	16.6

^a Addition carried to one half-life.

5-Chloro-1-pentyne was allowed to react with formic acid containing perchloric acid, since 1,4-halogen shifts had not been observed in solvents other than trifluoroacetic acid, although examples discovered subsequently have now been reported.^{3c} The products and their relative mole per cents as determined by analytical and preparative gas chromatography and nmr analysis are shown in eq 3. The presence of 5 indicates that some chlorine shift occurred.

The previous preliminary description⁷ of the somewhat complex mixture of reaction products derived

(11) M. C. Hoff, K. W. Greenlee, and C. E. Boord, J. Am. Chem. Soc., 73, 3329 (1951).
(12) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-

(12) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., Japan, 1964, p 24.



from 5-fluoro-1-pentyne will not be repeated here although appropriate details are given in the Experimental Section. The key result was the formation of 15% 4-fluoro-1,4-pentanediol bistrifluoroacetate (6)



Figure 1. The nmr spectrum of 4-iodo-4-penten-1-yl trifluoroacetate (bottom) and of the corresponding deuterated compound obtained from the reaction of 5-iodo-1-pentyne with deuterated trifluoroacetic acid (top).

which, on the basis of control experiments, may have been derived by addition of trifluoroacetic acid to the vinyl fluoride 2 (eq 1, X = F), the primary product of 1,4-fluorine shift. The major product of reaction (55% yield) was the fluorine-free ketone 7. Among the "control" experiments was a determination of the



rates of reaction of trifluoroacetic acid with 2-halo-

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propenes (see Table III), the results of which helped us to explain the ready formation of 6. That relatively stabile addition products were formed from the 2halopropenes was shown by the nmr spectra, taken as reaction proceeded (cf. Experimental Section).

Table III. First-Order Rate Constants for Reaction of Trifluoroacetic Acid with Propenes at 25.0°

Compound	$10^{5}k$, sec ⁻¹	$k_{\rm X}/k_{\rm H}$		
\sim	4.81	1		
F	340	71		
CL	1.70	0.35		
Br	0.395	0.082		

Discussion

Comparison of the Halogens in Reactions Involving 1,4 Shifts. As noted previously in connection with the reaction of 5-chloro-1-pentyne,9 if the halogen shifts observed in the present study occur in the rate-determining step, the rate constant (Table I) in each instance represents a composite of the rate constant (designated k_{Δ} according to Winstein's usage) for the reaction proceeding with halogen shift and that for the "normal" Markovnikov addition of trifluoroacetic acid to the triple bond (designated k_s). The latter rate constant is expected to be decreased by electron-attracting substituents. Based on the deviations from the line defined by "nonparticipating" substituents in a Hammett-Taft plot of log $k_{\rm H}/k_{\rm X}$ vs. $\sigma_{\rm I}$, $k_{\Delta}/k_{\rm s}$ values (Table I) were obtained for the reaction of 5-bromo-, 5-iodo-, and (nominally) 5-fluoro-1-pentyne for comparison with the previously determined value for the reaction of 5-chloro-1-pentyne.⁹ The k_s values for the additions of trifluoroacetic acid to 6-chloro- and 6-iodo-2-hexyne were obtained by dividing the rate for 2-hexyne by two, and correcting this $k_{\rm H}$ value for the inductive effect of chlorine at C-4 and C-5 (formula 2, eq 1). The inductive effect at C-4 was assumed to be the same as that for 5-chloro-1-pentyne, and the inductive effect at C-5 was corrected for the additional distance using the attenuation factor $0.62.^{3b}$ The k_s value listed in Table I is the sum of these k_s values which are applicable to the cation formation at C-4 and C-5.

The per cents of halogen shift, $100k_{\Delta}/k_{T}$, estimated from the deviations from the Hammett-Taft plot for 5-halo-1-pentynes, are somewhat smaller than the amounts of participation found from the ratios of "participation" and "normal" products. These discrepancies could be caused by a low ρ value obtained from the Hammett-Taft plot (as a consequence of the perhaps unjustified assumption that the cyano and trifluoroacetoxy substituents do not participate), to the halogen shift occurring after the rate-determining step, or to the approximations inherent in the Hammett-Taft treatment. Use of a ρ value of -4.04 instead of the previously used value of -2.50 leads to the calculated values of $100k_{\Delta}/k_{T}$, 95.5, 96.0, and 96.6, respectively, for 5-chloro-, 5-bromo-, and 5-iodo-1-pentyne. In view

of this better agreement with observed per cents of halogen shift, the old ρ value is suspect, but it has been retained in Table I because the precise magnitude of any new value remains undetermined. Clearly the closely similar 1,4-participation tendencies of chlorine, bromine, and iodine, previously found for alkene reactions,⁵ has been now confirmed for the analogous alkyne reactivities, as shown by the respective k_{Δ}/k_{s} values (3.5, 4.3, and 6.1). The strikingly different result found in the case of 2-halocyclohexyl tosylate solvolysis (where the relative participation tendency is $I \gg Br \gg$ Cl)¹³ has been explained^{3b} on the basis that 1,4-participation is "weak" in that most of the charge in the transition state is on carbon whereas in 1,2-participation the charge in the transition state is forced to reside to a greater extent on the halogen as a consequence of the large inductive destabilization of a $\hat{\beta}$ -halocarbonium ion. Accordingly, 1,2-participation, "strong participation," exhibits the expected halonium ion stability order, whereas 1,4-participation (involving $C \cdots X-R$ bond formation) might tend to exhibit the $H \cdots X-R$ (hydrogen bonding) stability order characteristic of weak electrostatic bonds. This analogy accounts reasonably well for the similar 1,4-participation tendencies of chlorine, bromine, and iodine, since it is known that the corresponding alkyl halides form hydrogen bonds of only slightly differing strengths with phenol,¹⁴ the relative stability order being $F \gg$ Cl > Br > I.

Based on the analogy with hydrogen bonding, fluorine could conceivably be the best 1,4-participating halogen, contrary to traditional expectations. Based on the trend shown by the other halogens (slightly the inverse of the hydrogen bonding order), fluorine might still be expected to show more than 15% (based on the yield of 6) or $20 \pm 20\%$ (based on kinetic data) of participation. Although a number of factors could uniquely influence the participation tendency of fluorine, a particularly clear one is provided by the geometry of fluoropentyne, in comparison with that of chloropentyne. The short C-F bond distance prevents fluorine (alone among the halogens) from approaching within covalent bonding distance of the potential cationic carbon in the 5-halo-1-alkyne.

Finally, in view of the special interest attached to fluorine participation, an assessment of the possibility that 6 arises from side reactions not involving fluorine participation is in order. The formation of 7 (presumably from 5-fluoro-2-pentanone via a reaction involving ketone participation)7 with concomitant liberation of fluoride ion raises the suspicion that the fluorine in 6 was derived from fluoride ions in solution. However 7 is the most obvious precursor of 6 available which contains a terminal trifluoroacetoxy group, and we were unable to convert 7 to 6 under carefully simulated conditions. Furthermore it seems doubtful that the hypothetical intermediate 8 would be converted pre-



⁽¹³⁾ For a reinterpretation of the original data, see A. Streitwieser, J. Am. Chem. Soc., 78, 4935 (1956).
(14) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *ibid.*, 84, 3221 (1962).

dominantly to 6, since 1-fluorohexane gave only secondary triffuoroacetates (presumably via 1-hexene) upon reaction with trifluoroacetic acid. Furthermore, 1-fluorohexane did not react with trifluoroacetic acid when sodium trifluoroacetate was present (as was the case in our reaction of 5-fluoro-1-pentyne). Nevertheless, the conversion of 8 to 6 by a process involving loss of primary fluorine via neighboring group participation by the trifluoroacetoxyl group is conceivable. Similarly the first formed normal addition product of trifluoroacetic acid to 5-fluoro-1-pentyne could lose fluorine via trifluoroacetoxyl participation, and in additional steps yield 6. Since our other studies have not yielded evidence for trifluoroacetoxyl participation, we conclude that the formation of 6 from these side reactions is unlikely but deserving of further study. If 1,4-fluorine participation occurs in the reaction of 5-fluoro-1pentyne, as seems likely also from our tosylate solvolysis data,^{3b} it is probable that the discovery of more definitive examples of fluorine participation will eventually resolve any uncertainty.^{14a} In this connection it may be noted that attempts to observe tetramethylenefluoronium ions at low temperature were unsuccessful,^{4a} although rapid rearrangements probably proceeding via ethylenefluoronium ion transition states have been postulated. 15

Addition of trifluoroacetic acid to 6-chloro- and 6-iodo-2-hexyne occurs 3.6 and 3.8 times faster than addition to 5-chloro- and 5-iodo-1-pentyne, respectively. In contrast, 2-hexyne adds trifluoroacetic acid 1.1 times faster than 1-hexyne. Accordingly the halogen participation process is facilitated more by replacing hydrogen with an alkyl group than is the addition of solvent to the triple bond. The complex factors involved in alkyl group substituent effects when the hybridization of the bond to the substituent must be taken into account have been discussed.¹⁶

Stereochemistry of Additions to the Triple Bond. Turning to stereochemical considerations, we note that hydrogen chloride in acetic acid was recently reported to add in *trans* fashion to 3-hexyne,¹⁷ whereas it reacts with 1-phenylpropyne to give a mixture in which the *cis* adduct predominates.¹⁸ Kinetic evidence for synchronous formation of C-H and C-X bonds was obtained for the reaction of 3-hexyne.¹⁷ The addition of trifluoroacetic acid to 3-hexyne has been shown previously to occur nonstereospecifically to give similar amounts of *cis*- and *trans*-3-hexen-3-yl trifluoroacetate.⁹ As mentioned earlier in this paper our additions of halogen and deuterium, or halogen and hydrogen, to the triple bond occurred predominantly in *trans* fashion.

Like the *trans* additions of Fahey and Lee,^{17, 18} our reactions of 5-halo-1-pentynes and 6-halo-2-hexynes must involve synchronous C-H and C-X bond formation, in view of the observed rate accelerations (after allowing for the inductive effect) which indicate the occurrence of C-X bond formation in the transition

states. In regard to the degree of C-H bond formation in the transition state, we note here that reactions of deuterated trifluoroacetic acid with 5-halo-1-pentynes proceeded roughly three to five times more slowly than the corresponding reactions of the hydrogen acid, based on nmr observations of reacting solutions. Similar solvent isotope effects have been observed in the additions of aqueous sulfuric acid to phenylacetylenes,^{16a} in which C-H bond formation is postulated to occur in the rate-determining step. In the addition reactions carried out in deuterated solvent, the per cent hydrogen trans to halogen was taken to be equal to the per cent cis addition. However, this hydrogen could have originated in part from selective uptake of hydrogen (compared to deuterium) from the solvent, if the isotope effects observed in isotopically "pure" solvents are applicable to the reaction of a small amount of one isotopic reactant dissolved in the other. Our solvent contained initially 0.5 mole % of acidic hydrogen, and at the end of the preparative additions approximately 1%, the additional hydrogen presumably resulting from double bond isomerization in the vinyl halide products. The stereospecificity of the 1,4-halogen shift reactions of 6-chloro- and 6-iodo-2-hexyne was determined as outlined in eq 2. The per cent *cis*-vinyl halide in the reaction is equal to the per cent cis-4-hexen-1-ol after reduction, provided the liquid ammonia reduction is 100% stereospecific. Isomerization of trans- to cis-vinyl halide was ruled out on the basis of experiments which showed that regardless of whether the reaction was carried out for one or seven half-lives, the same percentage of cis-4-hexen-1-ol was found in the addition of trifluoroacetic acid to 6-chloro-2-hexyne. Although the stereochemical results of our study are in agreement with the observation that synchronous formation of bonds in addition reactions occurs in trans fashion, the problem of predicting which addition reactions will proceed nonstereospecifically remains unsolved.

A New Synthesis of *trans*-Vinyl Halides. A stereospecific synthesis of trisubstituted double bonds from *trans* "unsymmetrical" vinyl halides has been developed by Corey and coworkers in connection with the synthesis of farnesol and the juvenile hormone.¹⁹ The 1,4-halogen shift reactions of 6-chloro- and 6-iodo-2hexyne open a new route to the synthesis of *trans* "unsymmetrical" vinyl halides (having the R groups nonidentical; *cf.* Figure 2). Corey's synthesis²⁰ leads

$$\mathbf{RC} = \mathbf{CH}_{2}\mathbf{OH} \quad \underbrace{\begin{array}{c} \mathbf{THF 3 \ hr \ reflux} \\ (1) \ 0.1 \ M \ \mathrm{LiAlH_{4}-AlCl_{3}, \ 60:1} \\ (2) \ I_{3}(-78^{\circ}) \end{array}}_{\mathbf{R}} \quad \begin{array}{c} \mathbf{H} \quad \mathbf{CH}_{2}\mathbf{OH} \\ \mathbf{R} \quad \mathbf{I} \end{array}$$
(4)

to a *trans*-vinyl halide where one of the R groups must be CH_2OH (eq 4). The synthesis *via* a 1,4-halogen shift reaction leads to a *trans*-vinyl halide where one of the R groups is $CH_2CH_2CH_2OH$ or, presumably, an alkylated derivative of this group.

Other pertinent literature is scarce. A synthesis of vinyl halides proceeding *via* bromination of allylic bromides is possibly a general method for synthesis of

⁽¹⁴a) NOTE ADDED IN PROOF. In our laboratory Joseph M. Indelicato has now shown that 4-fluoro-1-butyl-1- d_2 trifluoromethanesulfonate trifluoroacetolyzes without fluorine shift.

⁽¹⁵⁾ G. A. Olah and J. M. Bollinger, J. Am. Chem. Soc., 90, 947 (1968).

^{(16) (}a) D. S. Noyce, M. A. Matesich, O. P., M. D. Shiavelli, and P. E. Peterson, *ibid.*, 87, 2295 (1965); (b) D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, 89, 6225 (1967).

⁽¹⁷⁾ R. C. Fahey and D. J. Lee, *ibid.*, **89**, 2780 (1967).

⁽¹⁸⁾ R. C. Fahey and D. J. Lee, *ibid.*, 88, 5555 (1966).

^{(19) (}a) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *ibid.*, **89**, 4245 (1967); (b) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *ibid.*, **90**, 5618 (1968); (c) E. J. Corey and G. H. Posner, *ibid.*, **90**, 5616 (1968).

⁽²⁰⁾ M. M. Lespiau and Wieman, Bull. Soc. Chim. Fr., 45, 627 (1929).



Figure 2. trans-Vinyl halides, X = Cl, Br, I.

trans "unsymmetrical" vinyl bromides, but its stereospecificity is not yet assured.²⁰ "Symmetrical" transvinyl halides (having identical R groups) are available from the corresponding alkenes via halogenation and elimination,¹¹ by addition of hydrochloric acid to alkynes,¹⁷ and from alkynes via vinylalanes.²¹ In view of the few methods available, we conclude that our 1,4-halogen shift reactions of haloalkynes represent a potentially useful synthesis of vinyl halides, as well as an interesting example of neighboring halogen participation.

Experimental Section

Compounds. 5-Chloro-1-pentyne was purchased from Farchan Research Laboratories. 6-Chloro-2-hexyne was prepared by the reaction of 1-bromo-3-chloropropane with methylacetylene and sodium in liquid ammonia.²² Standard methods for the preparation of primary iodides from primary chlorides²³ and primary fluorides from primary iodides²⁴ were used for preparation of 5iodo-1-pentyne²⁵ and 5-fluoro-1-pentyne.²⁶ 5-Bromo-1-pentyne was prepared from the corresponding tosylate.26 The authentic sample of *cis*-4-hexen-1-ol was prepared from 4-hexyn-1-ol.²⁷ The authentic trans-4-hexen-1-ol was obtained from Dr. N. A. LeBel.28 The ir and nmr spectra of the above mentioned compounds were those expected.

Equipment. The gas chromatographic analyses were done using an F & M Model 609 or a Hewlett-Packard Model 5750 flame ionization gas chromatograph. The nmr spectra were taken on a Varian Associates Model A-60 spectrometer or a Varian Associates Model HA-100d spectrometer equipped with a time-averaging computer Model C-1024. The ir spectra were taken on a Beckmann Model IR-5A or a Perkin-Elmer Model 21 spectrophotometer. Most of the distillations were done on a Nester and Faust spinning band column Model 190 or Model 195. The C & H analyses were done by Scandinavian Microanalytical Laboratories, Box 25, Herlev, Denmark.

6-Chloro-2-hexyne. Liquid propyne (128.0 g, 3.2 moles) was added to a solution of 74.0 g (3.2 g-atoms) of sodium metal in 2.51 l. of liquid ammonia containing 600 mg of ferric nitrate catalyst. The mixture was stirred for 4 hr, 473.0 g (3.0 moles) of 1-bromo-3chloropropane was added, and the mixture was stirred for 4 additional hr. Ether (500 ml) was added, and the mixture was slowly brought to room temperature (overnight) in order to evaporate most of the ammonia. Addition of 300 ml of 5% hydrochloric acid neutralized the remaining ammonia. The reaction mixture was extracted with one-third the volume of ether, and the combined ether extracts were dried (MgSO₄). Removal of the ether and distillation through a spinning band column gave 53.0 g (15.1%) of gas chromatographically pure (Dow Corning 550 silicone oil) 6-chloro-2-hexyne, bp 86-88° (90 mm) [lit.²² bp 146-158° (760 mm)].

6-Iodo-2-hexyne. A 37-g sample (84%) of gas chromatographically pure (Dow Corning 550 silicone oil) 6-iodo-2-hexyne, bp 99-104° (35 mm) [lit.26 bp 97-103° (35 mm)], was obtained from the reaction²³ of 6-chloro-2-hexyne with sodium iodide in acetone.

(1963). (27) L. Crombie and S. H. Harper, J. Chem. Soc., 1707 (1950).

4-Hexyn-1-ol. 6-Chloro-2-hexyne (5.83 g, 0.050 mole) was added to a solution of sodium benzoate (5.76 g, 0.100 mole) in 125 ml of dimethylformamide and 25 ml of water. After refluxing for 50 hr the mixture was cooled, and 125 ml of water was added. The mixture was extracted with ether and the ethereal extracts were washed with water. Removal of the ether gave a yellow crystalline solid (the benzoate ester), which was dissolved in 60 ml of 95% ethanol and added to a solution of sodium hydroxide (4.0 g, 0.100 mole) in 20 ml of water. After 1 hr of reflux the solution was cooled, neutralized, concentrated, and extracted with ether. The ethereal extracts were washed, dried (MgSO₄), and distilled through a spinning band column to give 1.52 g (31%) of 4-hexyn-1-ol, bp 92° (150 mm) [lit.²⁷ for the compound prepared by another method, bp 165-168° (760 mm)].

5-Iodo-1-penten-2-yl Trifluoroacetate. 5-Iodo-1-pentyne (9.70 g, 0.050 mole) was added to a solution of mercuric acetate (1.00 g, 0.003 mole) in 50 ml of trifluoroacetic acid. The mixture was stirred at room temperature for 3 hr, and the solvent removed under vacuum. The remaining solution was neutralized with sodium bicarbonate and extracted with ether. The ethereal extracts were washed, dried (MgSO₄), and distilled through a spinning band column to give 10.2 g (66%) of 5-iodo-1-penten-2-yl trifluoroacetate: bp 83-86° (25 mm); nmr (CCl₄) δ 5.00 (m, 2, H₂C=C), 3.19 (t, 2, CH₂I), 2.45 (t, 2, CH₂C=C), and 1.98 (q, 2, CH₂CH₂-CH₂I). The reactivity of the compound in trifluoroacetic acid was determined and found to be almost negligible under the conditions of addition of trifluoroacetic acid to haloalkynes reported in this paper.

Rate Determinations. Solutions of the alkynes (0.1 M except for 5-fluoro-1-pentyne which was 0.28 M) were prepared in trifluoroacetic acid, 0.125 M in sodium trifluoroacetate, and allowed to react at $60.0 \pm 0.05^{\circ}$. Samples of the reaction mixture were removed at intervals and stored in a dewar flask filled with powdered Dry Ice. On completion of a reaction, the samples were analyzed using a gas chromatograph or by nmr at 100 MHz.

In the gas chromatographic method a carefully measured 1- or 2- μ l aliquot was injected with a 10- μ l syringe on a column containing several inches of a basic packing in the front of the column. The columns used in determining the reaction rates were as follows: a 6-ft silicone oil column (20% Dow Corning 550 on 60-80 mesh firebrick) at 115 and 140° for 5-fluoro-1-pentyne and 6-chloro-2hexyne, respectively; a 1-ft silicone rubber column (20% SE 30 on 60-80 mesh firebrick) at 95 and 115° for 5-bromo-1-pentyne and 5iodo-1-pentyne, respectively. The basic fore column was made of potassium carbonate-Carbowax on 60-80 mesh firebrick. Firstorder rate constants were calculated in two ways: (1) from a plot of log (A) vs. time according to the formula $k = -2.303([\Delta \log$ (A)]/ Δt) where A is the integrated area of the gas chromatograph peak attributed to the reacting alkyne; (2) from a plot of log (A_{∞} A) vs. time according to the formula $k = -2.303([\Delta \log (A_{\infty}$ (-A)]/ Δt) where A is the integrated area of the gas chromatographic peak attributed to the main product and A_{∞} is the area due to the main product after the reaction proceeded seven half-lives. The rate constant for 6-chloro-2-hexyne was calculated by both methods and the average taken. The rate constants for all other alkynes except 6-iodo-2-hexyne (which was analyzed using the nmr method described below) were calculated using method 1. In the nmr method 1-ml aliquots were placed in an nmr tube and spectra were taken at 0.0° probe temperature. The first-order rate constant was obtained by plotting the logarithm of the per cent reaction vs. time. The fraction reaction was taken to be equal to R/(R + P)where R is the integrated area due to the CH_2I triplet of the reactant 6-iodo-2-hexyne and P is the integrated area of the triplet due to $CH_2O_2CCF_3$ of the product 4-iodo-4-hexen-1-yl trifluoroacetate.

Reaction of 5-Fluoro-1-pentyne with Trifluoroacetic Acid. 1 l. of trifluoroacetic acid containing sodium trifluoroacetate (37.7 g, 0.278 mole), 5-fluoro-1-pentyne (21.7 g, 0.252 mole) was added. The reaction mixture was placed in a 60° rate bath and allowed to react for 24 hr (2 half-lives), after which it was divided into five portions of approximately 200 ml. Each portion was placed on a spinning band column to remove as much solvent as possible (bp 35-40° (130-160 mm)). The resulting concentrates were combined (150 ml) and placed in a 1000-ml flask fitted with a condenser. Saturated sodium bicarbonate was added to the concentrate. The neutralized mixture was then extracted five times with 200-ml portions of ether. The ether extract was dried over molecular sieve and flash distilled to give 27.3 g of volatile material and 3.51 g of residue. An integration of the nmr spectrum as well as the gas chromatogram of the total distillable products was used to determine the ratio of products.

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The isolation and complete characterization of the main products of the reaction were obtained from an earlier study done on approximately one-third the scale. The procedure described above was followed. During the distillation four fractions were collected plus a fifth volatile component which collected in the Dry Iceacetone trap. Purification of the fractions was accomplished by preparative gas chromatography, as described below.

A. 5-Fluoro-2-penten-2-yl Trifluoroacetate. The first distillation fraction was shown to contain two components. Separation of the components was accomplished by using preparative gas chromatography (Dow Corning 550 fluid). Of the two elutants collected only the second one, one of the isomers of 5-fluoro-2-penten-2-yl trifluoroacetate, was pure: nmr (CCl₄) δ 5.39 (t, 1, CH=C), 4.42 (d of t, 2, $J_{H-F} = 47$ Hz, $J_{H-H} = 6$ Hz, CH_2F), and 1.95 ppm (t, 3, CH₃C=C); ir (CCl₄) 1790 (C=O) and 1700 cm⁻¹ (C=C). The yield of 5-fluoro-2-penten-2-yl trifluoroacetates, determined in a separate reaction, was 15%. Confirmation of the structure followed from the reaction with 2,4-dinitrophenylhydrazine reagent. Under the reaction conditions the vinyl trifluoroacetate is hydrolyzed to the ketone, 5-fluoro-2-pentanone, which forms the DNP derivative, mp 141.6-142.6°. The first impure elutant was a mixture of 5fluoro-2-pentanone and 5-fluoro-2-penten-2-yl trifluoroacetate. The DNP derivative was analyzed.

Anal. Calcd for $C_{11}H_{13}N_4O_4$: C, 46.48; H, 4.61. Found: C, 46.26; H, 4.66.

B. 5-Trifluoroacetoxy-2-pentanone. Distillation fractions 2 and 3 contained mainly one compound, 5-trifluoroacetoxy-2-pentanone: bp 67° (5 mm); nmr (CF₃COOH) δ 4.35 (t, 2, CH₂O₂CCF₃) and 2.12 ppm (s, 3, CH₃C=O). The nmr and ir spectra, the boiling point, and the gas chromatographic retention times agreed with those of an authentic sample of 5-trifluoroacetoxy-2-pentanone prepared by esterification of 5-hydroxy-2-pentanone with trifluoro-acetic anhydride. The yield of ketone, determined in a separate reaction, was 52%. Only the DNP derivative of the somewhat unstable ketone was analyzed (see above).

C. 2-Fluoro-2,5-bis(trifluoroacetoxy)pentane. Distillation fraction four contained two components, 5-trifluoroacetoxy-2-pentanone and 2-fluoro-2,5-bis(trifluoroacetoxy)pentane. The latter compound was partially separated from the mixture by preparative gas chromatography on diethylene glycol succinate (8.97% of 5-trifluoroacetoxy-2-pentanone present): nmr (CCl₄) δ 4.38 (t, 2, CH₂O₂CF₈) and 1.90 ppm (d, 3, J = 18 Hz, CH₃CH(O₂CCF₈)). The yield, determined in a separate reaction, was 15%.

Anal. Calcd for $C_9H_9F_7O_2$ (containing 8.97% 5-trifluoroace-toxy-2-pentanone impurity): C, 35.13; H, 3.03. Found: C, 35.10; H, 3.14.

D. 5-Fluoro-2-pentanone. The volatile component collected in the trap was shown to be 5-fluoro-2-pentanone: nmr (CCl₄) δ 4.39 (t of d, 2, $J_{\rm H-F}$ = 46 Hz, $J_{\rm H-H}$ = 6 Hz, CH_2F) and 2.12 ppm (s, 3, CH_3C =O). The yield determined in a separate reaction was 12%. The sample was allowed to react with DNP reagent. After several recrystallizations a mp of 141-142° was obtained. A mixture melting point, 142-143°, was taken with the DNP of the product obtained from 5-fluoro-2-penten-2-yl trifluoroacetate. The nmr and ir spectra and gas chromatographic retention times were the same as those of an authentic sample of the ketone prepared from the hydrolysis of 5-fluoro-1-pentyne.

Other products indicated to be present in small amounts are the terminal double bonded compound 5-fluoro-1-penten-2-yl trifluoro-acetate and the other internal double bonded isomer of 5-fluoro-2-penten-2-yl trifluoroacetate.

5-Fluoro-2-penten-2-yl Trifluoroacetate (Other Isomer). A trace was isolated by preparative gas chromatography (neopentyl glycol succinate) in another experiment. The nmr (CCl₄) showed a vinyl triplet centered at δ 5.25 as compared to 5.39 for the other isomer, and a closely spaced triplet for the vinyl methyl at 2.03 as compared to 1.95 for the other isomer.

5-Fluoro-1-penten-2-yl Trifluoroacetate. There was only a slight indication of terminal double bond in the nmr spectrum of the flash-distilled products. However, reactions run for a much shorter time (2 hr), as compared to the above case of 24 hr, showed the terminal double bond to be present to a greater extent than the internal double bonded compounds.

Hydration of 5-Fluoro-1-pentyne. To 150 ml of a catalytic solution containing mercuric sulfate, concentrated sulfuric acid, and 60% acetic acid in the ratio 1:1:50 by weight was added 5-fluoro-1-pentyne (17.5 g, 0.2 mole). The reaction mixture was heated at 65° for 10 hr, after which it was neutralized with sodium carbonate and extracted with ether. The ether extracted was dried over mo-

lecular sieve and distilled to give 19 g (90%) of 5-fluoro-2-pentanone, bp 68° (64 mm).

Anal. Calcd for C_5H_9OF : C, 57.67; H, 8.71. Found: C, 57.33; H, 8.71

Studies of Reaction Products by Nmr. A solution of trifluoroacetic acid which was 0.28 M in added sodium trifluoroacetate and 0.28 M in 5-fluoro-2-pentanone was sealed in an nmr tube and reacted at 60° . The nmr tube was removed and spectra were taken at various time intervals, until the reaction was completed. The same procedure was followed for 2-fluoro-2,5-ditrifluoroacetoxypentane. The compound formed from both reactions as indicated by nmr is 5-trifluoroacetoxy-2-pentanone.

In another experiment, 10% solutions of 2-fluoropropene and 2-chloropropene in trifluoroacetic acid which was 0.125 M in added sodium trifluoroacetate were placed in nmr tubes at room temperature and spectra taken at various times during the reaction. The products formed, as indicated by nmr, were 2-fluoro-2-trifluoroacetoxypropane and 2-chloro-2-trifluoroacetoxypropane, respectively.

A 10% solution of 1-fluorohexane in trifluoroacetic acid containing 0.125 *M* added sodium trifluoroacetate was allowed to react at 60° in a sealed nmr tube. The nmr spectra taken with time showed no reaction after 60 hr. However, in a similar experiment without added sodium trifluoroacetate, 1-fluoro-hexane reacted completely within 24 hr to give 2- or 2- and 3-hexyl trifluoroacetate based on the nmr spectrum, which showed a sextuplet centered at δ 5.25 characteristic of a secondary trifluoroacetate and a doublet at δ 1.37 characteristic of a terminal methyl group next to a trifluoroacetate.

Reaction of 5-Bromo-1-pentyne with Trifluoroacetic Acid. A 10% solution of 5-bromo-1-pentyne in trifluoroacetic acid was sealed in an nmr tube and the reaction followed with time. After seven half-lives the nmr (CF₃CO₂H) spectra corresponded to that of 4-bromo-4-penten-1-yl-trifluoroacetate: δ 4.41 (t, 2, CH₂O₂-CCF₃), 5.48 (d, 1, HCH=CBr, H *cis* to Br), and 5.67 ppm (m, 1, HCH=CBr, H *trans* to Br).

Reaction of 5-Iodo-1-pentyne with Trifluoroacetic Acid. 5-Iodo-1-pentyne (4.0 g, 0.022 mole) was added to 75 ml of trifluoroacetic acid. The reaction mixture was placed in a 60° bath for 7 hr. Removal of the solvent and distillation through a spinning band column yielded 4.65 g (74%) of 4-iodo-4-penten-1-yl trifluoroacetate: bp 68-70° (4 mm); nmr (neat) δ 4.40 (t, 2, CH₂O₂CCF₃), 5.74 (d, 1, HCH=CI, H *cis* to I), and 6.12 ppm (q, 1, HCH=CI, H *trans* to I).

Anal. Calcd for $C_7H_8IO_2F_3$: C, 27.29; H, 2.61. Found: C, 27.32; H, 2.85.

Reaction of 6-Chloro-2-hexyne with Trifluoroacetic Acid. A solution of 6-chloro-2-hexyne (20 g, 0.17 mole) in 100 ml of trifluoro-acetic acid was heated at 60.0° for 13 hr. Removal of the solvent and distillation through a spinning band column yielded 27.1 g (68.5%) of 4-chloro-4-hexen-1-yl trifluoroacetate: bp 150° (3.5 mm); nmr (neat) δ 1.72 (t of d, 3, CH₃CH=C), 4.37 (t, 2, J = 6 Hz, CH₂O₂CCF₃), and 5.66 ppm (q, 1, CH₃CH=C).

Anal. Calcd for $C_8H_{10}OClF$: C, 41.67; H, 4.37. Found: C, 41.80; H, 4.42.

Reaction of 6-Iodo-2-hexyne with Trifluoroacetic Acid. A solution of 6-iodo-2-hexyne (15.0 g, 0.072 mole) in 42 ml of trifluoroacetic acid was heated in a constant-temperature bath at 60.0° for 5.6 hr. Removal of the solvent and distillation through a spinning band column yielded 16.1 g (69.2%) of 4-iodo-4-hexen-1-yl trifluoroacetate: bp 75-58° (3.5 mm); nmr (neat) δ 1.71 (t of d, 3, CH₃CH=C), 4.32 (t, 2, J = 6 Hz, CH₂O₂CCF₃), and 5.62 ppm (t of q, 1, CH₃CH=C).

Anal. Calcd for $C_8H_{10}O_2IF_8$: C, 29.83; H, 3.13. Found: C, 29.81; H, 3.12.

Per Cent 1,4-Halogen Shift. A direct measurement of the per cent of 1,4-halogen shift was obtained for the reactions of 5-chloro-, 5-bromo-, and 5-iodo-1-pentyne with trifluoroacetic acid. A 0.1 M solution of the alkyne was allowed to react for one half-life placed in an nmr tube, and its spectrum taken and time averaged at 0.0°. The ratio of the "participation" to "normal" products was obtained from the ratio of the integrated areas of the singlets at 5.03, 4.98, and 5.04 ppm (corresponding to the vinyl protons of 5-chloro-, 5-bromo-, and 5-iodo-1-penten-2-yl trifluoroacetate, respectively) to those of the multiplets centered at δ 5.17, 5.47, and 5.96 ppm (corresponding to the vinyl protons, and 4-iodo-4-penten-1-yl trifluoroacetate, respectively).

Reaction of 5-Chloro-1-pentyne with Formic Acid. 5-Chloro-1pentyne (15 g, 0.15 mole) was added to 267 ml of formic acid containing 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 (MgSO₄), 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 (CCl₄) δ 8.03 (s, 1, OCHO), 5 21 (s. 2 HC=C) and 4 18 npm (t. 2 CHO₂CH)

5.21 (s, 2, H₂C=C), and 4.18 ppm (t, 2, CH₂O₂CH). *Anal.* Calcd for C₆H₉ClO₂: 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 (MgSO₄), concentrated, and distilled giving 5.03 g (57%) of 4-chloro-4-hexen-1-ol: bp 99° (17 mm); ir (CCl₄) 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, CH₂OH), and 1.68 ppm (t of d, 3, *J* = 6.5 Hz, *J* = 1.1 Hz, CH₃C=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 NaHCO₃, and saturated NaCl), dried (MgSO₄), 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, $\frac{1}{8}$ 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 (CCl₄) δ 1.78 (m, 3, CH₃CH=C), 3.56 (t, 2, CH₂OH), and 5.60 ppm (q, 1, CH₃-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 (CCl₄) δ 5.37 (m, 2, CH₃CH=CH), 3.5 (t, 2, CH₂OH), and 1.62 ppm (m, 3, CH₃CH=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-4penten-1-yl-5-*d* trifluoroacetates were, respectively, 40-60° (7 mm) and 45-50° (1.5 mm).

Reactions of Tetramethylenehalonium Ions¹

Paul E. Peterson, Paul R. Clifford,^{2a} and Francis J. Slama^{2b}

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 SO₂. 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 $(e.g., 2, eq 1)^{s}$ are expected to resemble the earlier reported ethylenehalonium ions⁴ and the very recently reported dialkylhalonium ions⁵ in a number of their properties, particularly in their high reactivity as alkylating agents. Accordingly, as a step toward the further

(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).

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)

$$\begin{array}{ccccccc} Cl & + & 2 \operatorname{SbF}_5 & \xrightarrow{\operatorname{SO}_2} & & & \\ & & & \\ & & & & \\ &$$

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