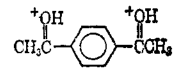
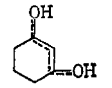
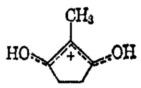
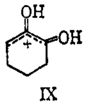
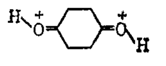
Table II. Pmr Data of Protonated Cyclic Diketones[a]

Ion	δ, ppm CH$_3$	CH$_2$	CH	$=\overset{+}{O}H$
 VI	−3.8 (−2.6) (d) J = 1.2	...	−9.1	−14.9 (qu) J=1.2
 VII		α −3.22 (tr) J = 5.9 β −2.64 (qu) J = 5.9	−6.52 (s)	*b*
 VIII	−2.08	−3.34		*b*
 IX		β −3.65 (m) δ −3.26 (m) γ −2.92 (p) J = 6.0	−9.02 (tr) J = 6.0	−14.0 (br)
 X	...	−4.0 (−2.7)	...	−15.7

[a] J values in hertz. Abbreviations used are: s, singlet; d, doublet; tr, triplet; qu, quadruplet; p, pentuplet; m, multiplet. [b] Not observable even at −100°.

Preparation of Protonated Diketones. Samples of protonated diketones were prepared by dissolving approximately 1.5 ml of FSO_3H-SbF_5 (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling to −76°. The diketone (approximately 0.2 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −76°, and with vigorous agitation slowly added to the acid solution. Samples prepared in this manner gave nmr spectra (generally taken at −60°) which showed no appreciable chemical shift differences with temperature or small concentration variations. The acid was always in excess of the aldehyde as indicated by the large acid peak at about −10.9 ppm.

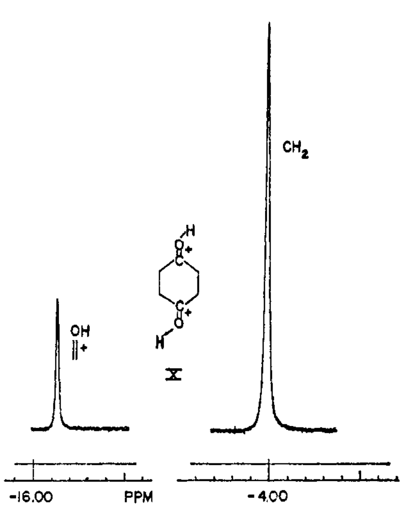


Figure 8. Diprotonated 1,4-cyclohexanedione.

Acknowledgment. Support of this research by grants of the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Halonium Ion Formation *via* 1,4-Halogen Participation. Five-Membered-Ring Tetramethylenehalonium, 2-Methyltetramethylenehalonium, and 2,5-Dimethyltetramethylenehalonium Ions[1]

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156. *Received February 8, 1968*

Abstract: Tetramethylene- and 2-methyltetramethylenechloronium, -bromonium, and -iodonium ions were formed by ionization of 1,4-dihalobutanes and 1,4-dihalopentanes, respectively, in antimony pentafluoride–sulfur dioxide solution at −60°. 2,5-Dimethyltetramethylenehalonium ions were formed by protonation of 5-halo-1-hexenes in fluorosulfonic acid–antimony pentafluoride–sulfur dioxide. Selected five-membered-ring halonium ions were shown by nmr observation to be stable for brief periods of time even at temperatures in the range −30–0°, depending on the structure.

Three-membered-ring ethyleniodonium, -bromonium, and -chloronium ions, long postulated as intermediates in reactions involving 1,2-halogen participation or in additions of halogen to alkenes, have recently been observed by nmr spectroscopy in antimony pentafluoride–sulfur dioxide solutions.[2] We now report the observation of the analogous five-membered-ring ions which are formed by 1,4-halogen participation from 1,4-dihalobutanes in SbF_5–SO_2 solution.

1,4-Halogen participation was postulated to occur in 4-iodo- and 4-bromo-1-butyl tosylate acetolysis,[3] but the indications for participation, enhanced reaction rates and special salt effects, were not very pronounced. As outlined below, examples of 1,4-halogen partic-

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[1] Stable Carbonium Ions. LXVII. Part LXVI: G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 4672 (1968).

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

[3] R. E. Glick, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1954.

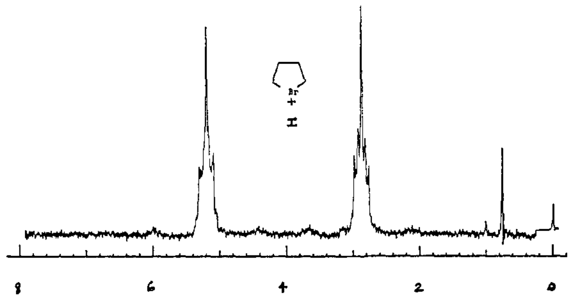


Figure 1. Nmr spectrum of the tetramethylenebromonium ion.

ipation were independently recognized when carbonium ion reactions in trifluoroacetic acid were investigated. In this weakly nucleophilic solvent, halogen participation is expected to be more pronounced than in other commonly used solvents since the halogen, as an internal nucleophile, competes effectively with solvent molecules in solvating the developing carbonium ion. Following the initial observation of anomalous rates in the addition of trifluoroacetic acid to 5-halo-1-hexenes,[4] examples of 1,4-halogen shifts were encountered in the addition of trifluoroacetic acid to 5-chloro-1-hexene-5-*d*,[5] to 5-chloro-1-pentyne,[6] and to 5-bromo- and 5-iodo-1-pentynes,[7] and, surprisingly, 5-fluoro-1-pentyne.[8] A comprehensive analysis of inductive and participation effects in the addition of trifluoroacetic acid to 5-halo-1-alkenes[9] has recently been followed by a similar study of the solvolysis of ω-chloro- and ω-fluoro-2-alkyl tosylates which revealed rate-accelerating 1,4-chlorine participation effects up to 99-fold, although inductive effects partially masked the acceleration.[10] In the present study in which the five-membered-ring ions were observed by nmr, we obtained evidence that the five-membered-ring ions are more stable than their three-membered-ring counterparts, as might have been predicted.

Results and Discussion

In view of kinetic data of Peterson, *et al.*,[10] indicating 1,4-halogen participation in the solvolysis of ω-halo-2-alkyl tosylates, it was of interest to extend the previous investigations of Olah and Bollinger[2] to the study of the ionization of 1,4-dihalobutanes and related 1,4-dihaloalkanes in order to obtain the expected five-membered-ring halonium ions.

Diprimary Ions. Ionization of 1,4-dihalobutanes in antimony pentafluoride–sulfur dioxide gave the parent tetramethylenehalonium ions, in which the positive halogen is diprimary (eq 1). The nmr spectrum of the tetramethylenebromonium ion I obtained in this way is shown in Figure 1 and the data of the ions are summarized in Table I. The downfield position of the α-methylene hydrogens given in Table I is suggestive of the halonium structure, as is the large difference in chemical shift between the α- and β-methylene protons. The observed nmr data could *a priori* also be accommodated by a reaction of the dihalide with the Lewis acid antimony pentafluoride to give an adduct. Reaction of 1-fluoro-4-iodobutane, however, gave the same species, II, obtained from 1,4-diiodobutane, along with a second unexpected species, III, identified from nmr analysis as the 2-ethylethyleniodonium ion (Figure 2). The structure III was confirmed by an independent preparation (eq 2). The formation of ion III from 1-fluoro-4-iodobutane but not from 1,4-diiodobutane is an effect of varying the leaving group which may give insight into the mechanism of the formation of III, which is chemically (and, we presume, thermodynamically) less stable than II. Presumably ion III comes from an initial 1,2-hydrogen shift following the

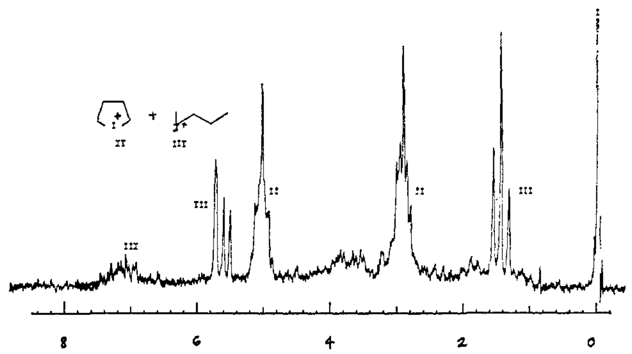
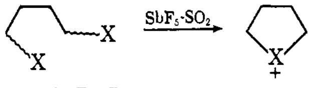


Figure 2. Ions obtained from the reaction of 1-fluoro-4-iodobutane with antimony pentafluoride.

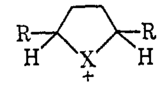


X = Cl, Br, I

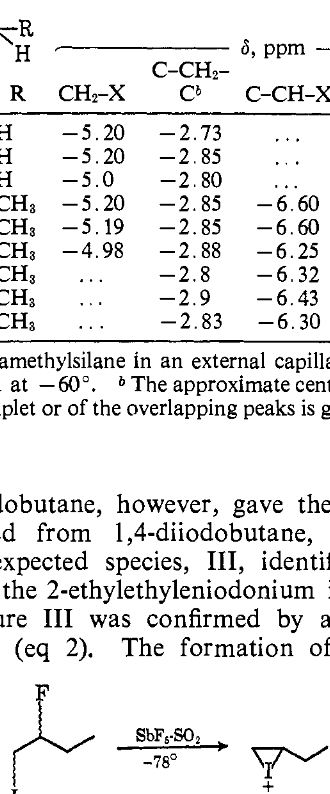
I, X = Br
II, X = I

(1)

Table I. Proton Magnetic Resonance Data of Tetramethylenehalonium Ions[a]

 R	X	R	CH₂–X	C–CH₂–C[b]	C–CH–X	CH₃[c]
			δ, ppm			
H	Cl	H	−5.20	−2.73	...	...
H	Br	H	−5.20	−2.85	...	...
H	I	H	−5.0	−2.80	...	...
H	Cl	CH_3	−5.20	−2.85	−6.60	−2.10
H	Br	CH_3	−5.19	−2.85	−6.60	−2.10
H	I	CH_3	−4.98	−2.88	−6.25	−2.12
CH_3	Cl	CH_3	...	−2.8	−6.32	−2.08, −2.08
CH_3	Br	CH_3	...	−2.9	−6.43	−2.15, −2.16
CH_3	I	CH_3	...	−2.83	−6.30	−2.12, −2.22

[a] From tetramethylsilane in an external capillary tube. Spectra were recorded at −60°. [b] The approximate central position of the complex multiplet or of the overlapping peaks is given. [c] Doublets, $J \cong 2.5$ Hz.



III

(2)

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[4] P. E. Peterson and G. Allen, *J. Amer. Chem. Soc.*, **85**, 3608 (1963).

[5] P. E. Peterson and E. V. P. Tao, *ibid.*, 86, 4503 (1964).

[6] P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

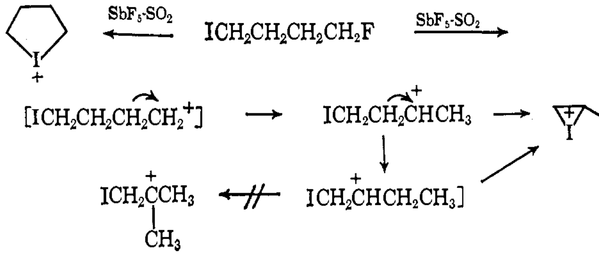
[7] P. E. Peterson and R. J. Bopp, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966, Paper S3.

[8] P. E. Peterson and R. J. Bopp, *J. Amer. Chem. Soc.*, **89**, 1283 (1967).

[9] P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *ibid.*, 87, 5163 (1965).

[10] P. E. Peterson, R. J. Bopp, D. M. Chevli, E. Curran, D. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967).

ionization step to give the intermediate 4-iodo-2-butyl cation which undergoes a second hydrogen shift (eq 3).

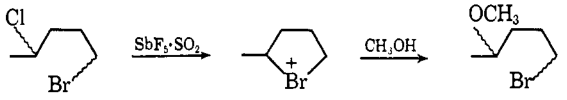


(3)

It may be assumed that fluorine ionizes more rapidly than conformational interconversions occur to give a species having the geometry favorable for iodine participation. Slower ionization of iodine from 1,4-iodobutane, then, could account for the different reaction course which is followed in this instance in which iodine is the leaving group. It is to be noted that conformational changes are expected to be relatively slow at the reaction temperatures employed, near −78°, whereas ionization of fluorine at this temperature occurs at a rate too fast to observe in the time required to take an nmr spectrum.

1,4-Difluorobutane was also dissolved in both antimony pentafluoride–sulfur dioxide and antimony pentafluoride–fluorosulfonic acid–sulfur dioxide solutions but gave only unidentifiable species.[11] There were no absorptions which one could interpret as arising from the tetramethylenefluoronium ion. The possibility existed that the failure to generate the tetramethylenefluoronium ion was due to unfavorable ring size, and for that reason 1,5-difluoropentane was treated in the same way. Once again the species arising from this compound were not identifiable. They did not give the absorptions expected for the pentamethylenefluoronium ion.

Primary–Secondary Ions. Reaction of a primary–secondary 1,4-dihalopentane with antimony pentafluoride results in the breaking of the secondary C–X bond with participation of the primary halogen, as shown for 1-bromo-4-chloropentane (eq 4) and formation of the 2-methyltetramethylenebromonium ion IV. Quenching of the 2-methyltetramethylenebromonium ion in methanol give 1-bromo-4-methoxypentane. The tendency of primary halonium ions to undergo SN1-like opening has been postulated previously based on the products of reactions thought to involve halogen participation.[9] It was desirable to prove further the preferential ionization of the secondary chlorine atom with 1,4-bromine participation leading to the 2-methyltetramethylenebromonium ion (eq 4) by preparing independently the 2-methyltetramethylenechloronium ion V by two other alternative routes.



IV

(4)

In the first of these alternative reactions, the trifluoroacetate group in 5-chloro-2-pentyl trifluoroacetate was found to ionize in sulfur dioxide–antimony pentafluoride–fluorosulfonic acid (eq 5). The nmr spectrum of the resulting 2-methyltetramethylenechloronium ion is shown in Figure 3.

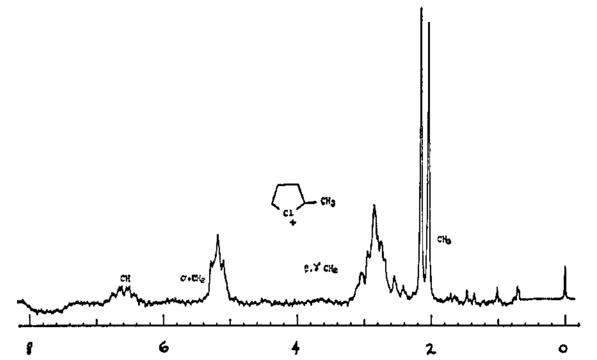
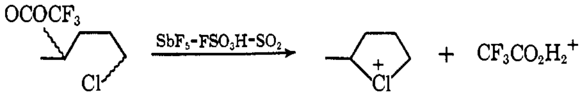


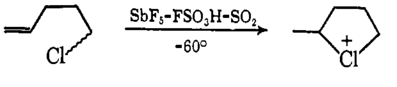
Figure 3. Nmr spectrum of the 2-methyltetramethylenechloronium ion.



V

(5)

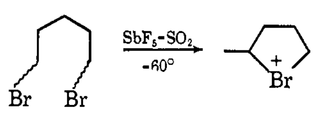
Protonation of 5-chloro-1-pentene (eq 6) in the same strong acid system also yielded the same ion. This reaction represents a new "π route" to halonium ions. 5-Iodo-1-pentene reacted similarly to give the 2-methyltetramethyleneiodonium ion VI. Quenching of the 2-methyltetramethylenechloronium ion in methanol gave 1-chloro-4-methoxypentane.



(6)

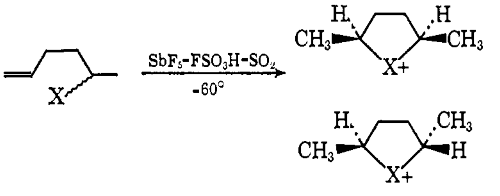
The π route to halonium ions in conjunction with the trifluoroacetate ionization and the results of methanolysis tends to further confirm the halonium ion structures formed *via* 1,4-halogen participation in the present study.

A further route to primary–secondary ions was found in the reaction of the *diprimary* halide, 1,5-dibromopentane, according to eq 7. The expected six-membered-ring halonium ion was not formed, or else (thought to be less likely) was formed as an intermediate which rearranged to give the five-membered-ring halonium ion as shown in eq 7. The analogy with the formation of a three-membered-ring halonium ion starting from 1-fluoro-4-iodobutane (eq 2) suggests that mechanistic considerations comparable to those already discussed in the case of 1-fluoro-4-iodobutane are involved.



(7)

Disecondary Ions. The π route of preparation through protonation of 5-halo-1-hexenes was used for the formation of disecondary ions as shown in eq 8.



(8)

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(11) Unpublished results of Dr. J. M. Bollinger.

Table II. Proton Magnetic Resonance Chemical Shifts[a] of Halonium Ion Precursors and Methanolysis Products

Compouund	δ, ppm			
	CH_2-X, O-CH_2[b]	C-CH_2-C[b]	C-CH-X[b]	CH_3
$Cl(CH_2)_4Cl$	−3.53	−1.94	...	...
$Br(CH_2)_4Br$	−3.50	−2.02	...	...
$I(CH_2)_4I$	−3.20	−1.95	...	...
$CH_3CHCl(CH_2)_2CH_2Br$	−3.40	−1.97	−3.98	−1.57[c]
$CH_2{=}CH(CH_2)_2CH_2Cl$	−3.50	...	...	...
$CH_2{=}CH(CH_2)_2CH_2I$	−3.15	...	...	...
$CH_2{=}CH(CH_2)_2CHClCH_3$	...	...	−3.95	−1.50[c]
$CH_2{=}CH(CH_2)_2CHBrCH_3$	...	...	−4.08	−1.71[c]
$CH_2{=}CH(CH_2)_2CHICH_3$	...	...	−4.08	−1.90[c]
$CH_3O(CH_2)_4Cl$	−3.30, −3.50	−1.75	...	−3.25[c]
$CH_3O(CH_2)_4Br$		−1.75	...	−3.75
$CH_3O(CH_2)_4I$	−3.35, −3.17	−1.75	...	−3.25[c]
$CH_3CH(OCH_3)(CH_2)_3Cl$	−3.50	−1.67	Obscured	−3.25,[c] −1.10[d]
$CH_3CH(OCH_3)(CH_2)_3Br$	−3.38	−1.7	Obscured	−3.25,[c] −1.12[d]
$CH_3CH(OCH_3)(CH_2)_2CHICH_3$	...	−1.65	−4.1	−3.25,[c] −1.12[d]

[a] From internal tetramethylsilane for 10% solutions in carbon tetrachloride. [b] The approximate central position of the complex multiplet or of the overlapping peaks is given. [c] Doublet, $J \cong 6.5$ Hz. [d] Methoxyl singlet.

The formation of *cis* and *trans* isomers was clearly shown by the appearance of a pair of methyl doublets in the case of the 2,5-dimethyltetramethyleniodonium ion (Figure 4).

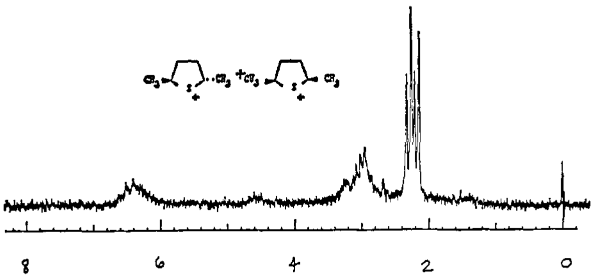

Figure 4. Nmr spectrum of *cis*- and *trans*-2,5-dimethyltetramethyleneiodonium ions.

Experimental Section

All dihalides were known from the literature and were commercially available materials or prepared by standard methods. 1,4-Difluorobutane and 1,5-difluoropentane were prepared by the method of Hoffmann[12] substituting the corresponding bromides for chlorides. The yields were comparable to those reported.

Preparation of Ions. The previously described methods for forming halonium ions from halides in SbF_5–SO_2 solution at 78° were employed,[2] subject to the following exceptions and supplementary comments. Formation of iodonium ions led to light brown solutions from which a dark solid precipitated if the concentration was high or if the solution was stored for several hours. In the case of 1-fluoro-4-iodobutane the proportion of the 2-ethylethyleniodonium ion increased when successive further additions of dihalide precursor were made, suggesting that the tetramethyleniodonium ion selectively precipitated. Solutions of bromonium ions were light red or orange, and solutions of chloronium ions were yellow. It was not established whether the colors were attributable to the ions themselves or to other substances (possibly free halogen) present as impurities in small quantities.

Reactions with 1:1 antimony pentafluoride–fluorosulfonic acid were accomplished by adding the organic reactant with active stirring directly into the solution of the 1:1 acid in sulfur dioxides at −78°. (The reactant was not premixed with sulfur dioxide as in previous work.)

It may be noted that impurity peaks were present in the nmr spectra of halonium ions derived from protonation of alkenes (eq 8). In Figure 4 this peak may be seen at δ −4.3. Other peaks between 0 and 1 ppm were shown to be side bands of tetramethylsilane.

Methanolysis of Halonium Ions. The previously published procedure for reaction of the solutions containing halonium ions with methanol was used, except that carbon tetrachloride was used as the extraction solvent instead of pentane in order to facilitate observation of the methyl esters by nmr without complete removal of the solvent. Identification of the reaction products is based on the clean nmr spectra obtained. Table II summarizes the pmr data of the halo methyl esters obtained in quenching experiments. P. E. P. is undertaking a separate study of the yield, purity, and synthetic applications of products derived from tetramethylenehalonium ions.

Stability Studies. Solutions of the tetramethyleniodonium ions and tetramethylenebromonium ions in antimony pentafluoride–sulfur dioxide darkened somewhat and appeared to precipitate some solid upon warming to 0° for 5 min. Reexamination of the nmr spectra at −60° indicated that most of the halonium ions remained intact, although the spectra were slightly broadened owing possibly to a viscosity effect. The presence of polymeric halonium ions, $[(CH_2)_4X\text{–}]_n^+$, cannot be excluded based on the nmr spectra alone. Solutions containing the 2-ethylethyleniodonium ion and the tetramethyleniodonium ion showed the slow disappearance of the former ion at −50° (and rapid disappearance at −30°) without any change in the spectrum of the latter. Solutions containing the 2,5-dimethyltetramethyleniodonium ion underwent darkening and a decrease in the intensity of the nmr spectrum after 20 min at −30°.

Acknowledgment. Support of this work at both Case Western Reserve University and St. Louis University by grants of the Petroleum Research Fund (administered by the American Chemical Society) and the National Science Foundation is gratefully acknowledged. Dr. J. Martin Bollinger is thanked for the nmr spectra of the tetramethylenechloronium and 5-methyltetramethyleniodonium ions, as well as useful discussions.

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(12) E. W. Hoffmann, *J. Org. Chem.*, **14**, 105 (1949).