Onium Ions. V.[1] Di- and Trihalonium Ions

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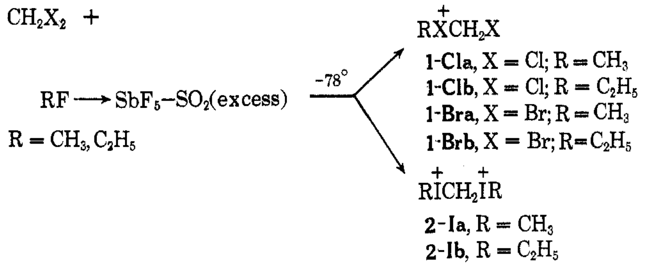
Alkylation of dihaloalkanes and dihalobenzenes with methyl and ethyl fluoroantimonate in SO_2 solution was carried out and products were studied by pmr spectroscopy. Monoalkylation giving alkyl- and haloalkyl(aryl)-halonium ions, as well as dialkylation leading to the formation of the corresponding dialkylalkylene(phenylene)-dihalonium ions, were observed. Alkylation of triiodobenzene and triiodomesitylene resulted in formation of the corresponding trialkylphenylene trihalonium ions.

In our previous studies we have reported the preparation of a variety of dialkylhalonium ions by alkylating alkyl halides.[2] More recently, we have also prepared alkylarylhalonium ions and studied their behavior in Friedel-Crafts alkylation reactions.[1] In order to gain further insight into the nature of halonium ions and the donor ability of halogens toward electrophiles, we have now undertaken the preparation of dihalonium and trihalonium ions by alkylating dihaloalkanes, dihalobenzenes, and trihalobenzene with methyl and ethyl fluoroantimonate in SO_2 solution at low temperatures.

Results and Discussion

A. Dialkylalkylenedihalonium Ions. Alkylation of Dihalomethanes.—When excess methyl or ethyl fluoroantimonate in SO_2 solution[3] was treated with dichloro(bromo)methane (CH_2X_2, X = Cl and Br) at −78°, monoalkylated dihalomethanes **1-Cl** and **1-Br** were formed. In the case of diiodomethane, dimethyl- and diethylmethylenediiodonium ions **2-Ia,b** were formed. However, when equal molar diiodomethane was used, monoalkylated iodonium ions **1-Ia,b** were obtained. The pmr spectra of all halonium ions **1-Xa** shows two sharp singlet absorptions in a ratio of 2:3 for the methylene and methyl protons, respectively (Table I). The pmr spectrum of dihalonium ion **2-Ia** shows two deshielded singlet absorptions at δ 4.10 (CH_3) and 5.80 (CH_2) in a ratio of 3:1. The pmr spectra of halonium ions **1-Xb** and **2-Ib** all show a set of triplet (CH_3), quartet (CH_2), and singlet absorptions. It is of interest to note that the CH_3 proton shifts of halonium ions **1-Xb** are deshielded in the order I > Br > Cl (δ 2.40 > 2.22 > 2.01) while the methylene proton shifts show an opposite trend, Br > Cl > I (See Table I).

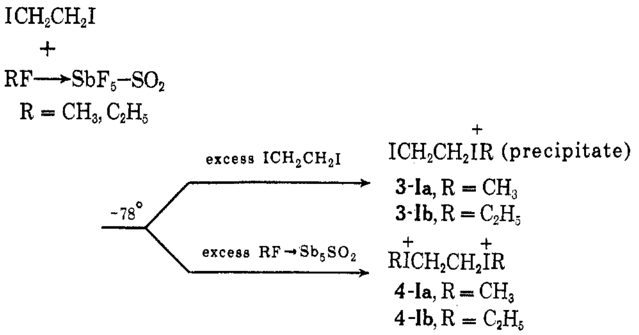


$$CH_2I_2\ (1\ \text{mol}) + RF \rightarrow SbF_5\ (1\ \text{mol}) \xrightarrow[-78^\circ]{SO_2} R\overset{+}{I}CH_2ISbF_6$$

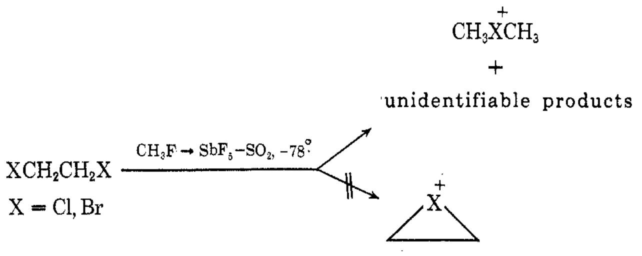
1-Ia, R = CH_3
1-Ib, R = C_2H_5

Attempted preparation of dialkylmethylenedichloronium (bromonium) ions by treating even a large excess of methyl (ethyl) fluoroantimonate in SO_2 with CH_2Cl_2 or CH_2Br_2 at −78° was unsuccessful, and only the monoalkylated ions **1X-a,b** were observed to formed. At the same time the preparation of *gem*-dihalonium ions **2-Ia,b** shows that iodine has unusual ability to delocalize positive charge and thus allows formation of dialkylmethylenedihalonium ions **2-Ia,b**, the two positive iodonium cations separated by a single methylene group.

Alkylation of Dihaloethanes.—When 1,2-diiodoethane was treated with methyl and ethyl fluoroantimonate, respectively, in sulfur dioxide solution, dialkylethylenedihalonium ions **4-1a,b** were formed. When equal or excess 1,2-diiodoethane was used, an insoluble iodonium salt precipitated, which is assumed to be monoalkylated 1,2-diiodoethane, **3-I** (low solubility prevented so far its identification).



When 1,2-dihaloethanes, XCH_2CH_2X (X = Cl or Br), were treated with methyl fluoroantimonate in SO_2 at −78°, the only identifiable products were dimethylhalonium ions, $CH_3XCH_3^+$ (X = Cl or Br), indicating that ionization cleavage of XCH_2CH_2X occurred *via* the formation of $XCH_2CH_2X^+CH_3$. No ethylenehalonium ions **5-X** were formed under these reaction



5-Cl, X = Cl
5-Br, X = Br

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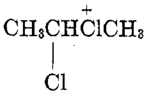
(1) Part III: G. A. Olah and E. G. Melby, *J. Amer. Chem. Soc.*, **94**, 6220 (1972). Part IV: G. A. Olah and E. G. Melby, *ibid.*, submitted for publication.

(2) G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969); **92**, 718 (1970).

(3) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *ibid.*, **91**, 2112 (1969).

TABLE I

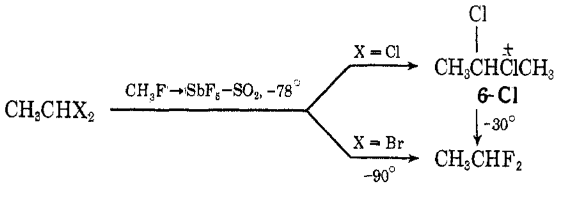
PMR PARAMETERS OF MONO- AND DIALKYLATED DIHALOALKANES[a]

Registry no.	Ion	δ_{CH}	δ_{CH_2}	δ_{CH_2X}	$\delta_{CH_2X^+}$	$\delta_{X^+CH_2}$	δ_{CH_3}	$\delta_{X^+CH_3}$
37160-90-0	$ClCH_2\overset{+}{Cl}CH_3$				5.56 (s)			4.51 (s)
37160-91-1	$ClCH_2\overset{+}{Cl}CH_2CH_3$				5.50 (s)	5.52 (q) $J = 7$	2.01 (t) $J = 7$	
37160-92-2	$BrCH_2\overset{+}{Br}CH_3$				6.33 (s)			4.30 (s)
37160-93-3	$BrCH_2\overset{+}{Br}CH_2CH_3$				6.32 (s)	5.46 (q) $J = 7$	2.22 (t) $J = 7$	
37160-94-4	$ICH_2\overset{+}{I}CH_3$				5.17 (s)			3.58 (s)
37160-95-5	$ICH_2\overset{+}{I}CH_2CH_3$				5.40 (s)	4.90 (q) $J = 7$	2.40 (t) $J = 7$	
37160-96-6	$(CH_3\overset{+}{I})_2CH_2$				5.80 (s)			4.10 (s)
37160-97-7	$(CH_3CH_2\overset{+}{I})_2CH_2$				5.88 (s)	5.33 (q) $J = 7$	2.44 (t) $J = 7$	
37160-98-8	$(CH_3\overset{+}{I}CH_2)_2$				5.06 (s)			4.00 (s)
37160-99-9	$(CH_3CH_2\overset{+}{I}CH_2)_2$				4.90 (s)	4.93 (q) $J = 7.5$	2.20 (t) $J = 7.5$	
24400-25-7	 $CH_3\underset{\underset{Cl}{\vert}}{CH}\overset{+}{Cl}CH_3$	6.23 (q) $J = 6$					2.17 (d) $J = 6$	4.50 (s)
37161-01-6	$Cl(CH_2)_3\overset{+}{Cl}CH_3$		2.90 (qu) $J = 5$	4.00 (t) $J = 5$	5.47 (t) $J = 5$			4.52 (s)
37161-02-7	$Cl(CH_2)_3\overset{+}{Cl}CH_2CH_3$		2.74 (m)	3.91 (t) $J = 6$	5.3 (m)[b]	5.3 (m)[b]	2.00 (t) $J = 7$	
37161-03-8	$Cl(CH_2)_3\overset{+}{Br}CH_3$		2.70 (qu) $J = 5$	3.84 (t) $J = 5$	5.10 (t) $J = 5.5$			4.08 (s)
37161-04-9	$Cl(CH_2)_3\overset{+}{Br}CH_2CH_3$		2.83 (m)	3.94 (t) $J = 6$	5.2 (m)[b]	5.2 (m)[b]	2.20 (t) $J = 6.5$	
37161-05-0	$Br(CH_2)_3\overset{+}{Br}CH_3$		2.82 (qu) $J = 7$	3.70 (t) $J = 7$	5.20 (t) $J = 6$			4.10 (s)
37161-06-1	$Br(CH_2)_3\overset{+}{Br}CH_2CH_3$		2.93 (m)	3.80 (t) $J = 7$	5.1 (m)[b]	5.1 (m)[b]	2.17 (t) $J = 7$	
37161-07-2	$I(CH_2)_3\overset{+}{I}CH_3$		2.70 (qu) $J = 7$	3.58 (t) $J = 7$	4.57 (t) $J = 7$			3.58 (s)
37161-08-3	$I(CH_2)_3\overset{+}{I}CH_2CH_3$		2.90 (m)	3.92 (t) $J = 7$	4.7 (m)[b]	4.7 (m)[b]	2.28 (t) $J = 7$	
37161-09-4	$CH_2(CH_2\overset{+}{Br}CH_3)_2$		3.24 (qu) $J = 7$		5.03 (t) $J = 7$	5.03 (t) $J = 7$		4.26 (s)
37161-10-7	$CH_2(CH_2\overset{+}{Br}CH_2CH_3)_2$		3.2 (m)		4.93 (t) $J = 7$	5.28 (q) $J = 7$	2.16 (t) $J = 7$	
37161-11-8	$CH_2(CH_2\overset{+}{I}CH_3)_2$		3.2 (m)		4.60 (t) $J = 8$			3.80 (s)
37161-12-9	$CH_2(CH_2\overset{+}{I}CH_2CH_3)_3$		3.2 (m)		4.60 (t) $J = 8$	4.83 (q) $J = 7$	2.30 (t) $J = 7$	

[a] Proton chemical shifts are referred to external capillary TMS. Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; qu = quintet; m = multiplet. *J* values are in hertz. [b] Overlapping multiplet.

conditions, although the ethylenebromonium ion **5-Br** was known to form from 1,2-dibromoethane in SbF_5–SO_2 solution.

Methylation of 1,1-dichloroethane in CH_3F–SbF_5–SO_2 solution at −78° gave the methyl α-chloroethylchloronium ion **6-Cl**. Halonium **6-Cl** decomposed and gave the halogen-exchanged cleavage product CH_3CHF_2 at higher temperature (*ca.* −30°). In the case of 1,1-dibromoethane, no methyl α-bromoethylbromonium ion **6-Br** could be observed even at −90°,



as halogen-exchanged decomposition product CH_3CHF_2 formed immediately.

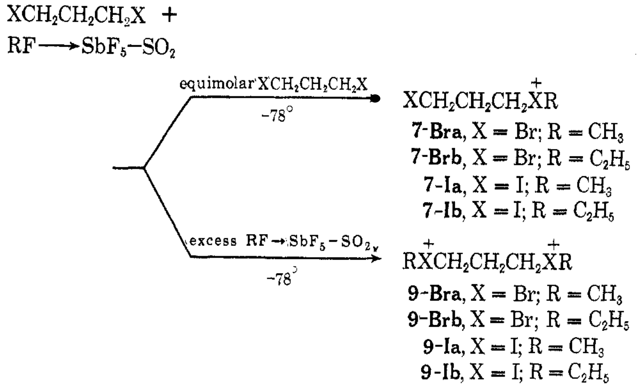
Alkylation of Dihalopropanes.—1,3-Dichloro- and 1-bromo-3-chloropropanes were monoalkylated in excess $RF–SbF_5–SO_2$ ($R = CH_3, C_2H_5$) solutions at −78° to give halonium ions **7-Cl** and **8-Br**, respectively. The

$$ClCH_2CH_2CH_2X \xrightarrow{RF\rightarrow SbF_5–SO_2,\ -78°} ClCH_2CH_2CH_2X^+R$$

7-Cla, $X = Cl$; $R = CH_3$
7-Clb, $X = Cl_3$; $R = C_2H_5$
8-Bra, $X = Br$; $R = CH_3$
8-Brb, $X = Br$; $R = C_2H_5$

pmr spectra of halonium ion **7Cla** and **8-Bra** are very similar. Monoalkylation was evidenced by the observed nonequivalent terminal methylene groups of **7-Cl**. Thus, the $-CH_2Cl^+$ protons show a more deshielded triplet (δ 5.47) than that of $-CH_2Cl$ (δ 4.00). Alkylation of 1-bromo-3-chloropropane occurs at the bromine atom rather than chlorine to give **8-Br**. This is based on the fact that bromine has better ability to delocalize charge, and also the methyl and methylene proton shift (of the ethyl group) in **8-Br** are too shielded for $BrCH_2CH_2CH_2Cl^+R$ ($R = CH_3, C_2H_5$). Ions **8-Cl** were not stable above −20° and decomposed to yet unidentified products. On the other hand, ions **8-Br** were stable to −10°.

Alkylation of 1,3-dibromo(iodo)propane in $RF \rightarrow SbF_5–SO_2$ solution gave mono- or dihalonium ions **7-X** and **9-X** (X = Br, I), respectively, dependent on the reaction conditions. The pmr spectra of **9-Bra**



and **9-Brb** are shown in Figure 1. Similar pmr characteristics are observed for ions **7-X** (X = Cl, Br, I) and ions **9-X** (X = Br and I) (Table I). The formation of dihalonium ions **9-X** is evidenced from the observation of the two equivalent terminal methylene pmr absorptions (4 H) and a quintet absorption for the center methylene protons (2 H).

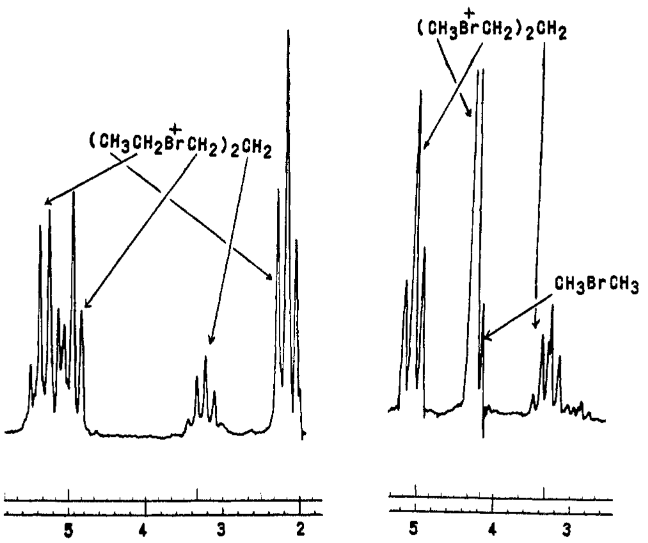
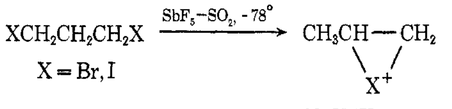


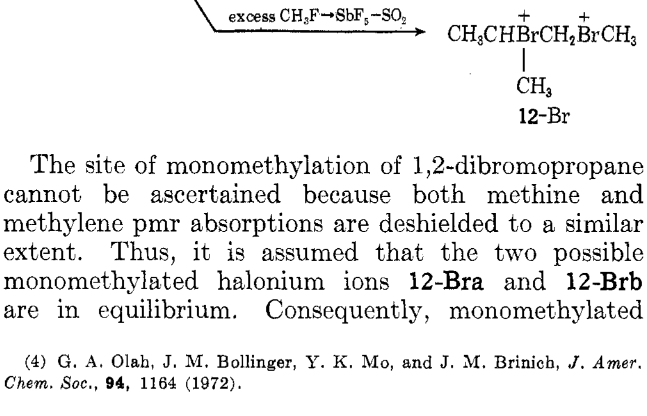
Figure 1.—Pmr spectra of dimethylated (right) and diethylated (left) 1,3-dibromopropane (**9-Bra** and **9-Brb**).

It should be noted that halonium ions **7-X** (except **7-Cl**) and dihalonium ions **9-X** are stable to −10° although 1,3-dihalopropanes are known to generate methylethylenehalonium ions **10-X** when treated with $SbF_5–SO_2$ solution.[4]



10-X (X = Br, I)

When 1,2-dibromopropane was added to excess methyl fluoroantimonate in SO_2 solution at −78°, dihalonium ion **12-Br** was formed. On the other hand, monomethylated 1,2-dibromopropane **11-Br** was obtained when equal molar methyl fluoroantimonate was used.



The site of monomethylation of 1,2-dibromopropane cannot be ascertained because both methine and methylene pmr absorptions are deshielded to a similar extent. Thus, it is assumed that the two possible monomethylated halonium ions **12-Bra** and **12-Brb** are in equilibrium. Consequently, monomethylated

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[4] G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972).

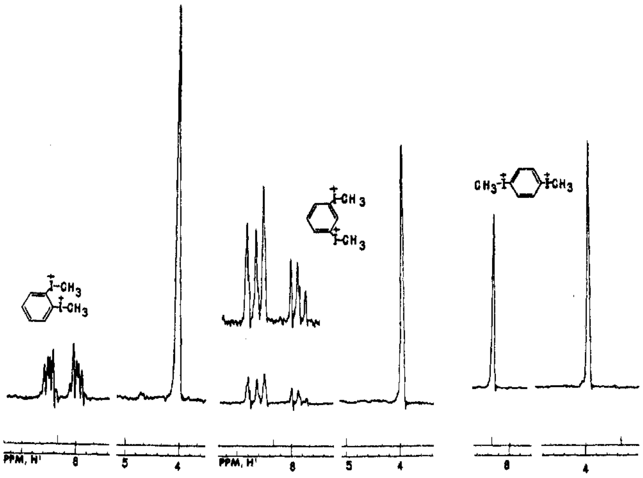
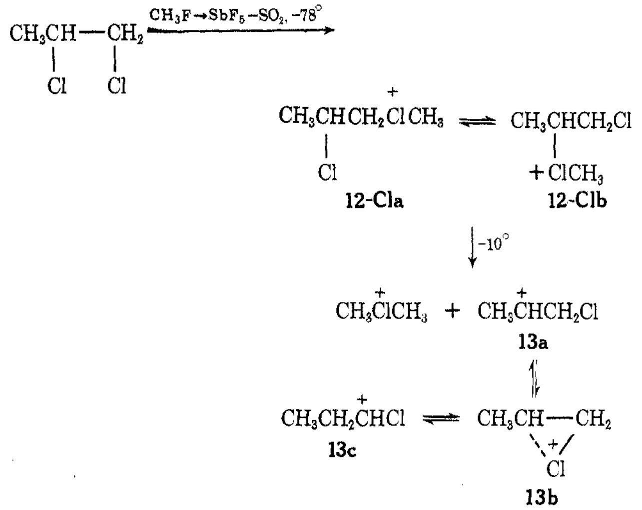
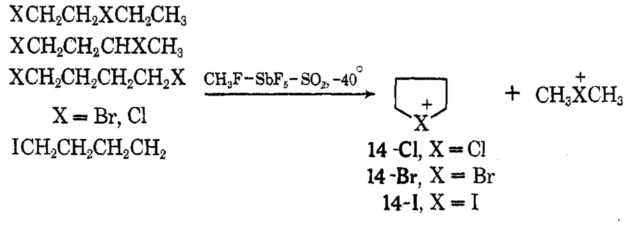


Figure 2.—Pmr spectra of dimethylated *o*-diiodobenzene, **16a** (left), *m*-diiodobenzene, **16b** (middle), and *p*-diiodobenzene, **16c** (right).

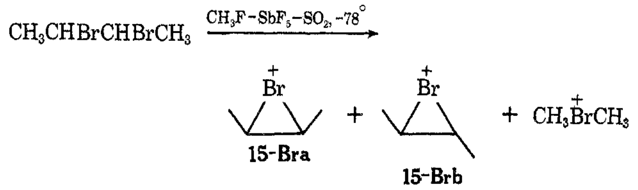
1,2-dichloropropane obtained under similar conditions may also exist in equilibrium (**12-Cla** ⇌ **12-Clb**). Dimethylated 1,2-chloropropane was not formed even in the presence of a large excess of methyl fluoroantimonate. When the solution was warmed to −10°, dimethylchloronium ion and ions **13a** ⇌ **13b** ⇌ **13c**, together with some yet unidentified products, were formed.



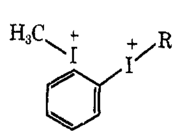
Dihalobutanes.—Methylation of 1,2-, 1,3-, and 1,4-dibromo(chloro)butanes and 1,4-diiodobutane with methyl fluoroantimonate in SO_2 solution at −40° results in cyclization to a mixture of dimethylhalonium ions $CH_3XCH_3^+$ and tetramethylenehalonium ions **14-X**.[5] The driving force for this cyclization is assumed to be the formation of the very stable five-membered ring ion.



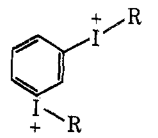
In addition, treating *meso*- and *dl*-2,3-dibromobutane with CH_3F–SbF_5–SO_2 solution at −78° results in the formation of dimethylbromonium ion and *cis*- and *trans*-1,2-dimethylethylenebromonium ions **15-Br** (giving identical pmr spectra with those reported).[6]



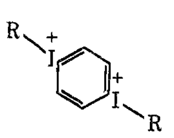
B. Dialkylphenylenedihalonium Ions.—Dialkylation of *o*-, *m*-, and *p*-diiodobenzene with excess methyl and ethyl fluoroantimonate at −78° in SO_2 solution results in the formation of the corresponding dialkylphenylenediiodonium ins, **16**, **17**, and **18**.



16a, R = CH_3
b, R = C_2H_5



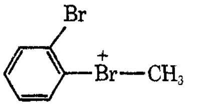
17a, R = CH_3
b, R = C_2H_5



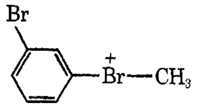
18a, R = CH_3
b, R = C_2H_5

The pmr spectra of **16a**, **17a**, and **18a** are shown in Figure 2. The dialkylphenylenediiodonium ions are all stable to −10°. Attempts to prepare monomethylated diiodobenzenes by reaction of equimolar methyl fluoroantimonate with *o*-, *m*-, or *p*-diiodobenzene were unsuccessful because under these conditions, owing to low solubility of monomethylated products, formation of precipitates prevented identification.

Methylation of *o*- and *m*-dibromobenzene with excess methyl fluoroantimonate resulted in the formation of the monomethylated ions, **19** and **20**.

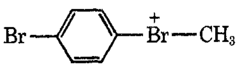


19

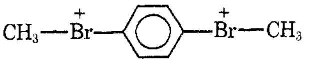


20

p-Dibromobenzene forms under similar conditions a mixture of monomethylated ion **21a** and dimethylated ion **21b** at −80° (as indicated by the pmr spectrum of the solution). Upon heating to −20°, dimethylated **21a** begins to disappear and an increasing amount of monomethylated **21b** is formed. Cooling the solution back to −80° reverses the process, giving the same ratio of ions **21a** and **21b**. Ethylation of *o*-, *m*-, and *p*-dibromobenzene with ethyl fluoroantimonate resulted in a complex mixture, consisting of aromatic ring ethylated products. Alkylation of 2,3,5,6-tetramethyldibromobenzene with methyl and ethyl fluoroanti-



21a



21b

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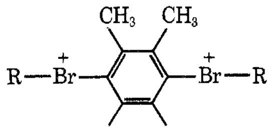
[5] G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968).

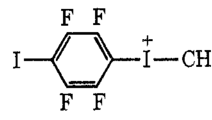
[6] G. A. Olah, J. M. Bollinger, and J. M. Brinich, *ibid.*, **90**, 2587 (1968).

monate resulted in complete formation of the corresponding dihalonium ions, **22a**,**b**.

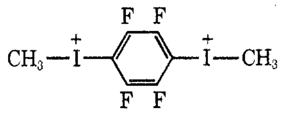


22a, R = CH_3
b, R = C_2H_5

Methylation of 2,3,5,6-tetrafluorodiiodobenzene in CH_3F–SbF_5–SO_2 solution at −78° results in a mixture of monomethylated and dimethylated ions **23a**,**b**.



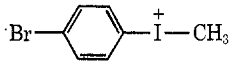
23a



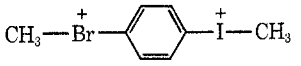
23b

The fluorine-19 spectrum of ion **23a** shows multiplets centered at ϕ 119.6 and 126.9 (relative to CCl_3F), while the ^{19}F nmr spectrum of **23b** is a singlet at ϕ 113.4. Attempts to form the corresponding ethylated ions failed owing to the insolubility of the starting material in the reagent. Likewise, 2,3,5,6-tetrafluorodibromobenzene was insoluble in both methyl and ethyl fluoroantimonate in SO_2 solution.

Methylation of *p*-bromoiodobenzene with CH_3F–SbF_5–SO_2 at −78° also resulted in a mixture of monomethylated and dimethylated ions **24a** and **24b**.



24a



24b

The methyl group is attached to the iodine atom in ion **24a** instead of the bromine on the basis of the pmr chemical shift (δ 3.90) which agrees with all other methylphenyliodonium ions.[1] Ethylation of *p*-bromoiodobenzene with ethyl fluoroantimonate resulted in ring-ethylated products.

We have not yet succeeded in obtaining alkylarylchloronium ions under long-lived conditions, since reaction of chlorobenzenes with CH_3F–SbF_5 complex at −78° results in fast aromatic ring substitution. Likewise, alkylation of dibromo- and diiodobenzenes with methyl fluoroantimonate at temperatures higher than −78° results in irreversible ring substitution. As we observed previously,[1] all alkylarylhalonium ions are efficient alkylating agents. Therefore, solutions of alkylarylhalonium ions and dihalonium ions are unstable at higher temperatures since aromatic ring alkylation occurs *via* an intermolecular nucleophilic displacement mechanism. The pmr parameters of all dialkylphenylenedihalonium ions studied are summarized in Table II.

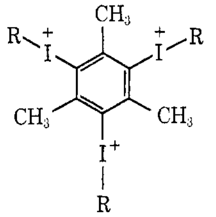
Table II

Pmr Parameters of Mono-, Di-, and Trialkylated Halobenzenes[a]

Ion	δ_{XCH_3}	δ_{CH_3}	δ_{CH_3CX}	δ_{CH_2X}	$\delta_{aromatic}$
16a	4.10 (s)				8.0–8.8 (m)
16b			2.23 (t) $J = 7$	5.23 (q) $J = 7$	8.1–8.7 (m)
17a	3.97 (s)				7.7–8.9 (m)
17b			2.15 (t) $J = 7.5$	5.06 (q) $J = 7.5$	7.8–8.7 (m)
18a	3.95 (s)				8.35 (s)
18b			2.14 (t) $J = 7.5$	5.02 (q) $J = 7.5$	8.35 (s)
19	4.55 (s)				7.6–8.3 (m)
20	4.48 (s)				7.5–8.2 (m)
21a	4.53 (s)				7.95 (s)
21b	4.56 (s)				8.38 (s)
22a	4.40 (s)	2.85 (s)			
22b		2.80 (s)	2.05 (t) $J = 7$	5.30 (q) $J = 7$	
23a	4.20 (s)				
23b	4.31 (s)				
24a	3.90 (s)				7.7–8.2 (m)
24b	4.05 (s)				7.7–8.2 (m)
	4.65 (s)				8.2–8.7 (m)
25a	4.00 (s)	3.65 (s)			
25b		3.60 (s)	2.18 (t) $J = 7$	5.20 (q) $J = 7$	
26a	4.00 (s)				8.38 (s)
26b			2.12 (t) $J = 7$	5.02 (t) $J = 7$	8.30 (s)

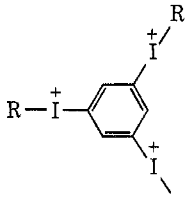
[a] From TMS in external capillary tube. Spectra were recorded at −70° in SO_2 solution at 60 MHz. Abbreviations: s = singlet, t = triplet, q = quartet, and m = multiplet. J values are in hertz.

C. Trialkylphenylenetriiodonium Ions.—When 2,4,6-triiodomesitylene is mixed with CH_3F–SbF_5–SO_2 at −78°, no reaction occurs (the starting material is insoluble in the reagent, which may account for lack of reactivity). Addition of 2,4,6-triiodomesitylene to methyl fluoroantimonate in SO_2ClF results in the formation of a dark-colored precipitate. When SO_2 is added to this mixture, the precipitate dissolves. The pmr of this solution shows two singlets with a peak area ratio of 1:1 at δ 3.65 and 4.00. The pmr data are consistent with the formation of the trimethyl 2,4,6-trimethylphenylenetriiodonium ion (**25a**). Ethylation of 2,4,6-triiodomesitylene with ethyl fluoroantimonate in SO_2 resulted in the formation of the corresponding triethylated halonium ion, **25b**.



25a, R = CH_3
b, R = C_2H_5

Alkylation of 1,3,5-triiodobenzene with methyl and ethyl fluoroantimonate in SO_2 solution resulted in the formation of the corresponding trialkylphenylenetriiodonium ions, **26a**,**b**. Attempts to prepare mono- or



26a, R = CH_3
b, R = C_2H_5

dialkylated triiodobenzenes failed, since the starting materials would dissolve only in excess CH_3F-SbF_5. The formation of these ions further illustrates the unusual donor ability of iodine toward electrophiles. Furthermore, based on nmr data, most of the positive charge must reside on iodine and not on the aromatic ring. Methylation of 1,3,5-tribromobenzene, 1,3,5-tribromomesitylene, and 1,3,5-tribromotrifluorobenzene was not achieved, since the starting materials were insoluble in the reagent CH_3F-SbF_5 complex under all conditions.

Conclusion

The unusual donor ability of iodine toward electrophiles is reflected in the formation of dihalonium ions even in the cases of diiodomethane and *o*-diiodobenzene. The formation of the trimethylphenylenetriiodonium ion further reveals the ability of iodine to accommodate a positive charge. Dialkylalkylenedibromonium ions were formed only when dibromopropanes were treated with methyl (ethyl) fluoroantimonate solution at low temperature. Methylation of dibromobenzenes results in the formation of either monomethylated species or a mixture of monomethylated and dimethylated species. It was not found possible to trimethylate tribromobenzenes. Dichloronium ions were never observed. These results reveal that the ease of halonium ion or dihalonium ion formation is the decreasing order $I < Br < Cl$.

Owing to the localization of charge on halogen, dihalonium ions need only one methylene group between the two electropositive iodines, *e.g.*, $^{+}RICH_2IR^{+}$ ($R = CH_3, C_2H_5$), in contrast to the formation of dicarbenium ions, which require at least two methylene groups to separate the two carbenium centers.

Experimental Section

Materials.—All of the dihaloalkanes used in this study were commercially available materials. All of the dihalo- and trihalobenzenes were commercially available except the following. Dibromodurene (mp 198.5–199.5°) was prepared by the method of Smith and Moyle.[7] 3,6-Dibromo-1,2,4,5-tetrafluorobenzene (mp 78.2–78.5°) and 2,4,6-tribromo-1,3,5-trifluorobenzene (mp 98.0–99.0°) were prepared by the method of Hellmann and Bilbo.[8] 3,6-Diiodo-1,2,4,5-tetrafluorobenzene (mp 89.5–90.5°) was prepared by the method of Nield, Stephens, and Tatlow,[9] modified by the use of excess iodine. 2,4,6-Triiodomesitylene (mp 208.0–209.0°) was prepared by the method of Varma and Sreenwasmurthyacher.[10] 2,4,6-Tribromomesitylene (mp 224.0–225.0°) was prepared by the method of Hennion and Anderson.[11] 1,3,5-Triiodobenzene was prepared by the method of Jackson and Behr.[12]

Preparation of Ions and Their Pmr Studies.—The preparation of methyl (ethyl) fluoroantimonate in SO_2 solution has been described previously.[8] (i) Monoalkylation of dihaloalkanes was achieved when equimolar dihaloalkanes in SO_2 solution (cooled at −78°) were mixed with methyl (ethyl) fluoroantimonate in SO_2 solution at −78°. The mixtures were stirred vigorously until clear solutions were formed. (ii) Dihalonium ions were prepared similarly to i except that excess methyl (ethyl) fluoroantimonate was used. (iii) Alkylation of 2,4,6-triiodomesitylene was achieved by addition of CH_3F-SbF_5 complex in SO_2ClF to solid triiodomesitylene at −78°. The dark precipitate that formed was dissolved in SO_2.

Monohalonium ions referred to (pmr spectra in this paper were already reported and characterized in our previously reported studies. Nmr spectra were obtained on a Varian Associates Model A-56/60A nmr spectrometer equipped with a variable-temperature probe. Proton chemical shifts are referred to external TMS. Fluorine chemical shifts are referred to external $CFCl_3$.

Registry No.—**16a**, 37406-81-8; **16b**, 37161-13-0; **17a**, 37161-14-1; **17b**, 37161-15-2; **18a**, 37161-16-3; **18b**, 37161-17-4; **19**, 37161-18-5; **20**, 37161-19-6; **21a**, 37161-20-9; **21b**, 37161-21-0; **22a**, 37161-22-1; **22b**, 37161-23-2; **23a**, 37161-24-3; **23b**, 37161-25-4; **24a**, 37161-26-5; **24b**, 37161-27-6; **25a**, 37161-28-7; **25b**, 37161-29-8; **26a**, 37161-30-1; **26b**, 37161-31-2.

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