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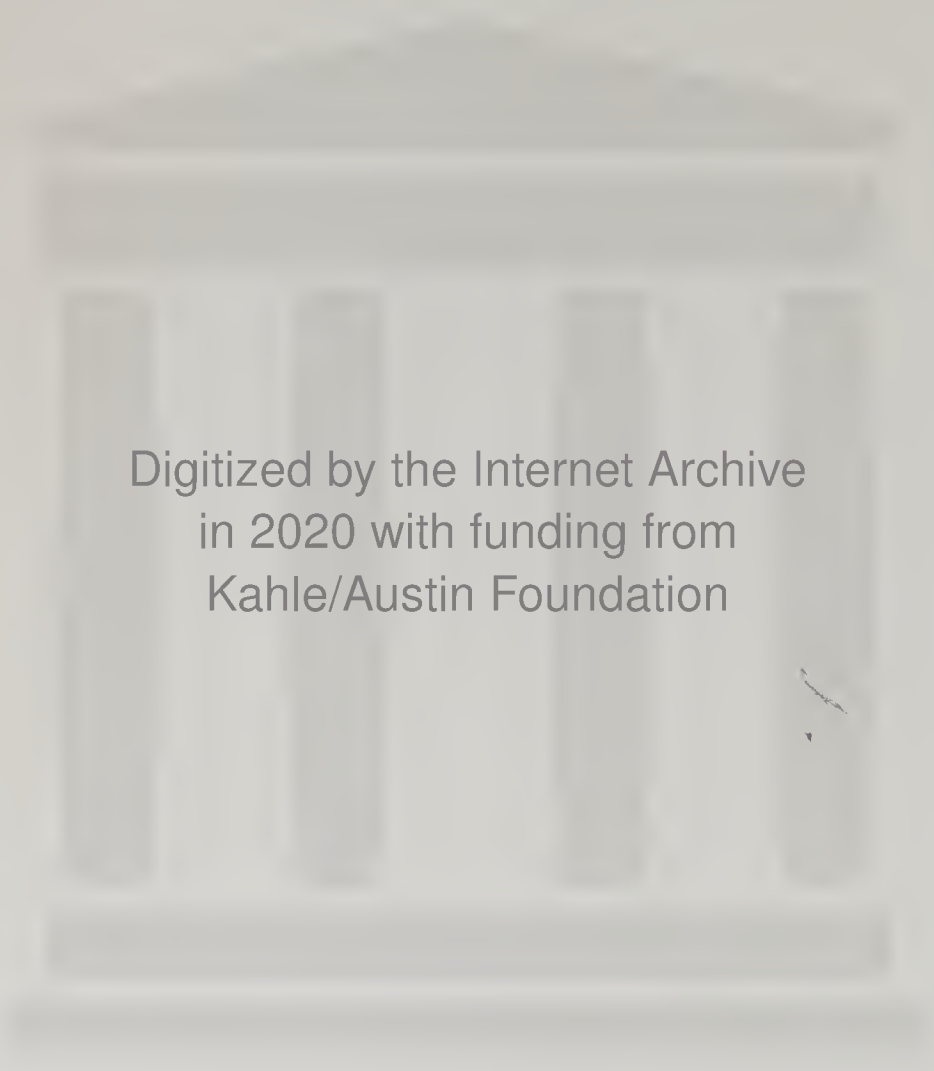
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HALONIUM IONS

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REACTIVE INTERMEDIATES IN ORGANIC CHEMISTRY

Edited by **GEORGE A. OLAH**
Case Western Reserve University

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HALONIUM IONS

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Department of Chemistry
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To the memory of Hans Meerwein who more than anybody
helped to open the door to the new frontiers of the
chemistry of cationic organic intermediates

11

With valuable contribution by my former coworkers, Dr. Yoke K. Mo (Raychem Corp., Menlo Park, California) and Dr. Yoronobu Yamada (Tokyo Institute of Technology) without which this book would not have been realized.

Introduction to the Series

Reactive intermediates have always occupied a place of importance in the spectrum of organic chemistry. They were, however, long considered only as transient species of short life-time. With the increase in chemical sophistication many reactive intermediates have been directly observed, characterized, and even isolated. While the importance of reactive intermediates has never been disputed, they are usually considered from other points of view, primarily relative to possible reaction mechanism pathways based on kinetic, stereochemical, and synthetic chemical evidence. It was felt that it would be of value to initiate a series that would be primarily concerned with the reactive intermediates themselves and their impact and importance in organic chemistry. In each volume, critical, but not necessarily exhaustive coverage is anticipated. The reactive intermediates will be discussed from the points of view of: formation, isolation, physical characterization, and reactions.

The aim, therefore, is to create a forum wherein all the resources at the disposal of experts in the field could be brought together to enable the reader to become acquainted with the reactive intermediates in organic chemistry and their importance.

As the need arises, it is anticipated that supplementary volumes will be published to present new data in this rapidly developing field.

GEORGE A. OLAH



Jim our cocker spaniel may again enlighten for other dog-lovers too this otherwise wasted page.

Preface

Onium ions are well-recognized ionic organic intermediates. They include not only such traditionally established and thoroughly studied classes as ammonium, phosphonium, oxonium, and sulfonium ions, but also higher-valence-state cations of other elements such as carbon and silicon (e.g., carbonium and siliconium ions). Organic halogen cations, that is, halonium

ions of an acyclic ($\text{R}\overset{+}{\text{X}}\text{R}$, $\text{Ar}\overset{+}{\text{X}}\text{R}$, and $\text{Ar}\overset{+}{\text{X}}\text{Ar}$) or cyclic ()

nature, in recent years have gained increasing significance, both as reaction intermediates and as preparative reagents. They are related to oxonium ions in reactivity but offering greater selectivity.

This review has been formulated over several years in connection with the actively pursued research work in our laboratory under the auspices of the National Science Foundation, to whom we are most grateful for support. It concentrates primarily on data relating to halonium ion intermediates as directly observed or isolated species, their structural study, and their chemistry.

It has become increasingly apparent that the field has achieved sufficient significance to warrant a coherent review. Limitations imposed to keep the size of this review to a reasonable length indicated the necessity for dealing only with halonium ions reported as bona fide species and not with the substantial literature concerning the possible involvement of halonium ion intermediates without, however, direct study of the species themselves. In other words, this review is restricted to long-lived organic halonium ions in solution chemistry of as isolated salts. Neither are halogenated carbocations (frequently in equilibrium with bridged halonium ions) discussed, because they are reviewed in the monograph "Carbonium Ions" vol. V. of this series.

It was a pleasure to utilize a quiet and most pleasant stay in the summer of 1974 at the Université Louis Pasteur in Strasbourg, where part of the writing of this book was accomplished. I would like to express my gratitude to my friends in Strasbourg, particularly Professors Guy Ourisson and Jean Sommer, for their outstanding hospitality, and to the university and the Centre National de la Recherche Scientifique for their support. Dr. G. Liang and Mr. S. Prakash are thanked for preparing the indexes, Mrs. M. Hoicourtz and E. Green for typing the manuscript.

GEORGE A. OLAH

Cleveland
June 1975

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HALONIUM IONS

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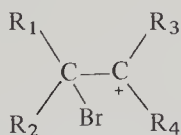
Introduction

1.1 GENERAL ASPECTS

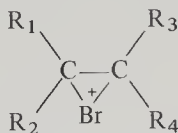
Organic halonium ions, as we now recognize them, were first prepared in case of some remarkable stable diaryliodonium compounds. In 1894, Hartmann and Meyer¹ were the first to prepare a diphenyliodonium ion salt when they reacted iodosobenzene in concentrated H_2SO_4 and obtained *p*-iodophenyl, phenyliodonium bisulfate. Diphenyliodonium ions have since been studied by various research groups, most notably since 1950 by Nesmeyanov² by Beringer. Diarylbromonium and -chloronium ions, although considerably less stable and much less investigated, were also prepared in the 1950s by Nesmeyanov and coworkers². As in the case of triarylcarbenium ions, these aryl-substituted ions were considered to be of exceptional stability and the only existing type of organic halonium ion; thus they were thought to have no particular significance or relevance otherwise in organic chemistry.

Open-chain dialkylhalonium ions of the type R_2X^+ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) were unknown until recently, as were alkylarylhalonium ions ($\text{Ar}\overset{+}{\text{X}}\text{R}$). Realization of their possible role as intermediates in alkylation reactions of haloalkanes and -arenes has followed their recent preparation and study.³

One of the most daring proposals of a organic reaction mechanism of its time was made in 1937 by Roberts and Kimball⁴ who suggested that the observed trans stereospecificity of the bromine addition to alkenes is a consequence of intermediate bridged bromonium ion formation. The brief original publication suggested the the actual structure of the ion is undoubtedly intermediate between 1 and 2. Structure 1 was not intended to represent a conventional free carbenium ion, however. Since the two carbons in either



1



2

structure are joined by a single bond and by a halogen bridge, free rotation is not to be expected. A clear description of the difference in binding between carbon and bromine in 1 and 2 was not given.

The bromonium ion concept was quickly used by other investigators to account for stereospecific transformation of olefins,⁵ notably by Winstein and Lucas,⁶ but was not unanimously accepted.⁷ For example, in discussing the

mechanistic concepts of bromonium ion formation, Gould,⁸ in his still popular text, wrote in 1959, "Although a number of additions are discussed in terms of the halogenonium-ion mechanism, the reader should bear in mind that few organic mechanisms have been accepted so widely while supported with such limited data."

In 1967, Olah and Bollinger⁹ reported the first preparation and spectroscopic characterization of stable, long-lived bridged alkylenehalonium ions. This was followed by Olah and DeMember's³ preparation in 1969 of the first dialkylhalonium ions. Since then the field of organic halonium ions has undergone rapid development through substantial contributions from an increasing number of investigators, notably by Peterson.¹⁰

The study of organic halonium ions has clearly reached a point where a comprehensive survey was needed. This review considers halonium ions reported as intermediate, directly observed, or isolated species, but does not discuss in detail halogen additions and related reactions in which halonium ion intermediates could have been involved but were not directly studied. Organic halonium ions can be defined as organic ligand substituted halogen cations (generally divalent, as no examples of higher-valence ions, although possible, have been reported) and are recognized as an important class of onium ions. The halogen atom in organic halonium ions is generally bound to two carbon atoms [although in the case of acidic halonium ions, that is, protonated alkyl and aryl halides (RX^+H) one ligand may be hydrogen].

1.2 CLASSES OF ORGANIC HALONIUM IONS

Organic halonium ions can be divided into two main categories: (1) acyclic (open-chain) halonium ions and (2) cyclic halonium ions.

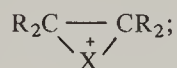
In the first class, diarylhalonium (ArX^+Ar),¹¹ alkylarylhalonium (RX^+Ar),¹² and dialkylhalonium (R_2X^+)³ ions are known. Recently, open-chain di- and trihalonium ions have also been prepared.¹³



In the second class, three-membered-ring ethylenehalonium,^{9,14} five-membered-ring tetramethylene halonium,¹⁵ and six-membered-ring pentamethylenehalonium¹⁶ ions are best known, although some four-membered-ring ions have also been reported.^{17,18} Substantial interest¹⁹ has also been shown in heteroaromatic halophenium ions.

1.3 NOMENCLATURE

The naming of organic cations is not yet governed by definite rules of the International Union of Pure and Applied Chemistry (IUPAC). In most publications in the field, and in this review, the trivial naming system adopted by analogy with other onium ions is used: alkylenehalonium ions for cyclic, three-membered-ring ions of the type






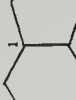

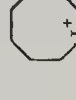


















tri-, tetra-, and pentamethylenehalonium ions for four-, five-, and six-membered-ring cyclic halonium ions; dialkyl-, alkylaryl-, and diarylhalonium ions for open-chain halonium ions of the R_2X^+ , RArX^+ , and Ar_2X^+ type, respectively. Acidic halonium ions of the RXH^+ or ArXH^+ type are named as hydrido alkyl- or arylhalonium ions or as protonated haloalkanes or -arenes, respectively.

With the proliferation of ring sizes among cyclic halonium ions, and the isolation of recrystallized salts, Peterson¹⁶ felt it appropriate to discuss nomenclature systems for this new class of heterocycle. He consulted with the Chemical Abstracts Service and came to the following conclusions. The names for polymethylenehalonium ions used by Olah and by Peterson are approved IUPAC names. However, an extension of the Hantsch-Widman²⁰ names for heterocycles (see Table 1) often leads to shorter names and has already been the basis for names appearing in *Chemical Abstracts*. A third system of nomenclature is based on the substitution of the positive halogen for CH_2 in the appropriate cycloalkane (replacement names).²¹ Such names are used for complex heterocycles (such as bicyclic compounds), of which at least two examples have been reported in the case of halonium ions: 3-chloronia[4.3.2.] bicyclononane²² and 2-bromonia[3.1.0] bicyclohexane.²³

Unfortunately, different numbering systems apply for the different nomenclatures. In the Hantsch-Widman and replacement systems for monocyclic rings, the halogen is numbered 1. (Note that for polycyclic systems the halogen is not necessarily numbered 1 in the replacement system.) In the polymethylene system, carbon was numbered 1 in the early papers on ethylenebromonium ions, while halogen was numbered 1 for tetramethylenehalonium ions. It now seems reasonable that nomenclature and numbering should be made uniform. In the present review, we use exclusively the polymethylene system with halogen numbered 1, with the exception of bicyclic halonium ions in which the systematic replacement nomenclature is used.

TABLE 1
Nomenclature of Cyclic Halonium Ions

Compound	Polymethylene or heteroarene name ^a	Hantzsch-Widman name ^b	Replacement name ^c
	a		
	b		
	c		
	d		
	e		
	f		
	g		
	h		

^aIUPAC, *Definitive Rules for Nomenclature of Organic Chemistry*, Section C, Butterworths, London, 1965, Rules C-82, C-107.

^bIUPAC, *Definitive Rules for Nomenclature of Organic Chemistry*, Section A and B, Butterworths, London, 1966, Rule D; see also *The Naming and Indexing of Chemical Compounds from Chemical Abstracts*, American Chemical Society, Washington, D.C., 1957, Rule 375.

^cGlossary section of IUPAC publication referred to in footnotes a and b, Rules B-4 and C-82.3.

^dName appearing in *Chem. Abstr.*, *Subject Index*, 69, (1968).

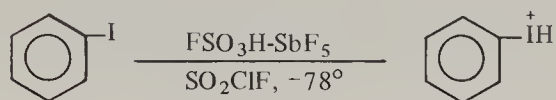
^eKurt L. Loening, director of nomenclature of the Chemical Abstracts Service, has suggested that the name might be misleading, but Peterson has chosen the shorter name for the sake of simplicity (see ref. 16).

PART A

Acyclic Halonium Ions

11

Halobenzenes do not form diphenylhelenium ions under conditions which



quantitatively yield the corresponding 4-halobenzenium ions on protonation with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ at -78° . Iodobenzene under the same conditions yields a single ion with deshielded pmr and cmr resonances similar to those of the methyl phenyliodonium ion (Table 1). The iodine-protonated hydridohalonium ion structure is therefore assigned to this ion; the shielding of C_{ipso} and the deshielding of C_{ortho} in CH_5IH^+ compared to $\text{C}_6\text{H}_5\text{I}^+\text{CH}_3$ is consistent with the removal of a β - and a γ - CH_3 group, respectively. In the case of CH_3IH , the proton in $\text{C}_6\text{H}_5\text{IH}$ evidently exchanges rapidly (on the nmr scale) with the excess acid. $\text{C}_6\text{H}_5\text{IH}$ does not, however, rearrange to ring-protonated $\text{C}_6\text{H}_6\text{I}^+$, even when the temperature is raised to -20° .

TABLE 2
Cmr Data for Alkyl- and Arylhydridohalonium Ions, Their Precursors,
and Related Model Ions

Compound	Cmr data ^a
$\text{CH}_3\text{I}^{\text{b}}$	CH_3 , -21.5 ; $J_{\text{CH}} = 150.3$
$\text{CH}_3\text{I}^+\text{CH}_3^{\text{c}}$	CH_3 , 8.7 ; $J_{\text{CH}} = 158.1$
$\text{CH}_3\text{I}^+\text{H}^{\text{c}}$	CH_3 , 2.7 ; $J_{\text{CH}} = 155.2$
$\text{CH}_3\text{Br}^{\text{b}}$	CH_3 , 10.8
$\text{CH}_3\text{Br}^+\text{CH}_3^{\text{c}}$	CH_3 , 37.5
$\text{CH}_3\text{Br}^+\text{H}^{\text{c}}$	CH_3 , 32.6
$\text{C}_6\text{H}_5\text{I}^{\text{b}}$	C_{ipso} , 95.1 ; C_{ortho} , 137.9 ; C_{meta} , 130.8 ; C_{para} , 128.0
$\text{C}_6\text{H}_5\text{I}^+\text{H}^{\text{c}}$	C_{ipso} , 100.0 ; C_{ortho} , 138.6 ; C_{meta} , 132.8 ; C_{para} , 132.8
$\text{C}_6\text{H}_5\text{I}^+\text{CH}_3^{\text{b}}$	C_{ipso} , 105.2 ; C_{ortho} , 137.6 ; C_{meta} , 133.7 ; C_{para} , 133.7

^aChemical shifts are in parts per million from external capillary trimethylsilane (TMS). Coupling constants are in hertz.

^bIn SO_2ClF at -70° .

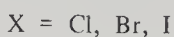
^cIn $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ at -70° .

Dialkylhalonium Ions

Dialkylhalonium ions were first obtained as stable fluoroantimonates and characterized by Olah and DeMamber³ in 1969. Subsequently, the isolation and carbon-13 nmr, Raman, and ir spectroscopic study of a series of dialkylhalonium ions, including the parent dimethylhalonium ions, was reported.²⁶ The alkylating ability²⁶ as well as the intermolecular exchange reactions²⁷ of dialkylhalonium ions were also studied.

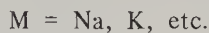
3.1 PREPARATION AND ISOLATION

There are two general methods for the preparation of dialkylhalonium ions: (1) the reaction of excess primary and secondary alkyl halides with $\text{SbF}_5\text{-SO}_2$, anhydrous fluoroantimonic acid (HF-SbF_5), or anhydrous silver hexafluoroantimonate (or related complex fluoro silver salts) in SO_2 solution, and (2) the alkylation of alkyl halides with methyl or ethyl fluoroantimonate (or alkylcarbenium fluoroantimonates) in SO_2 solution.^{3,26} The first method is

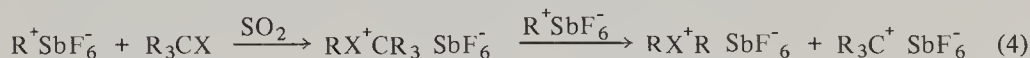


only suitable for the preparation of symmetric dialkylhalonium ions, while the second method can be used for both symmetric and unsymmetric dialkylhalonium ions.

Additional methods for the preparation of dialkylhalonium ions [equations (3) to (7)] were also found. However, these methods generally have less practical value because they usually yield products contaminated by other ions in the same solution. (3) The reaction of alkyl fluoroantimonates with metal halides in SO_2 solution gives the corresponding dialkylhalonium ions.



(4) Tertiary alkyl halides react with alkyl fluoroantimonates to give the corresponding tertiary alkylcarbenium ions and the symmetric dialkylhalonium



ions. (5) When an excess of alkyl fluoroantimonate was treated with dihalides such as 1,4-dihaloalkanes, the initially formed dialkylalkylenedihalonium ions were cleaved to give five-membered-ring halonium ions and dialkylhalonium



ions.²⁸ (6) When haloalkylcarbenium ions, such as dimethylchlorocarbonium ions, were treated with the analogous alkanes, rapidly exchanging diisopropyl-



chloronium ions were obtained²⁷ (see Section 3.5). (7) Dialkylhalonium ions can also be directly obtained from alkanes and $SbF_5 \cdot Cl_2 \cdot SO_2 \cdot ClF$ solution at -78° .²⁹ For example, ethane reacted with this powerful chlorinating reagent to give the dimethylchloronium ion.



The details of the preparation of a series of dialkylhalonium ions are summarized in Table 3. Generally, the preparation of symmetric dialkylhalonium ions is more simple and the reactions are clean. Unsymmetric dialkylhalonium ions undergo disproportionation and alkylation (self-condensation) reactions, even at low temperatures (ca. -30°). Data in Table 2 (see remarks) also suggest a qualitative measure of the decreasing stability of unsymmetric halonium ions in the order $\text{---}\overset{+}{I}\text{---} > \text{---}\overset{+}{Br}\text{---} > \text{---}\overset{+}{Cl}\text{---}$ and an increasing tendency for disproportionation according to $\text{---}\overset{+}{Cl}\text{---} > \text{---}\overset{+}{Br}\text{---} > \text{---}\overset{+}{I}\text{---}$.

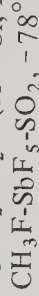
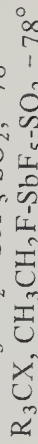
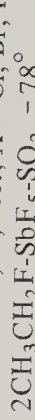
Dimethylhalonium fluoroantimonates such as dimethylbromonium and -iodonium fluoroantimonates can be isolated as crystalline salts. They are stable in a dry atmosphere at room temperature, and some are now commercially available. Dimethylhalonium fluoroantimonate salts are very hygroscopic, and exposure to atmospheric moisture leads to immediate hydrolysis.

TABLE 3

Preparation of Dialkylhalonium Ions

Reagents and temperature (°C)	Method of preparation	Dialkylhalonium ion formed	Remarks
2CH ₃ X (X = Cl, Br, I), SbF ₅ -SO ₂ , -60°	(1)		Preferred preparative method
CH ₃ X, (X = Cl, Br, I) CH ₃ F-SbF ₅ -SO ₂ , -60°	(2)	CH ₃ X ⁺ CH ₃ SbF ₅ X ⁻	Preparative method
MX, (M = Na, K, etc.; X = Cl, Br, I) 2CH ₃ F-SbF ₅ -SO ₂ , -60°	(3)		Less practical
R ₃ CX, CH ₃ F-SbF ₅ -SO ₂ , -60°	(4)		Formation of R ₃ C ⁺
X(CH ₂) _n X (X = Cl, Br; n = 4, 5) CH ₃ F-SbF ₅ SO ₂	(5)		Formation of five-membered-ring halonium ions
CH ₄ or C ₂ H ₆ , SbF ₅ -Cl ₂ -SO ₂ ClF, -78°	(7)		Poor yield
CH ₃ CH ₂ X, (X = Cl, Br, I) CH ₃ F-SbF ₅ -SO ₂ , -78°	(2)	$\text{CH}_3\text{X}^+\text{CH}_2\text{CH}_3 \text{ SbF}_5\text{X}^- \xrightarrow[\text{Br (90\%), I (100\%)}]{\text{X = Cl (50\%)}}$	Preferred method
CH ₃ X, (X = Cl, Br, I) CH ₃ CH ₂ F-SbF ₅ SO ₂ , -78°	(2)	$\text{CH}_3\text{X}^+\text{CH}_3 + (\text{CH}_3\text{CH}_2)_2\text{X}^+ \text{ SbF}_5\text{X}^-$	
		X = Cl (50%), Br (10%), I (0%)	
2CH ₃ CH ₂ X, (X = Cl, Br, I) SbF ₅ -SO ₂ , -78°	(1)		Preferred preparative method
CH ₃ CH ₂ X, (X = Cl, Br, I) CH ₃ CH ₂ F-SbF ₅ -SO ₂	(2)	(CH ₃ CH ₂) ₂ X ⁺ SbF ₅ X ⁻	Preparative method

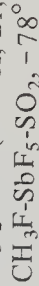
MX (M = Na, K, etc.; X = Cl, Br, I),



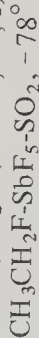
(3)

(4)

(2)



(2)



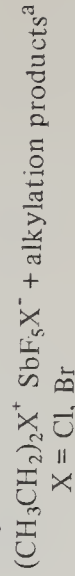
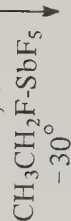
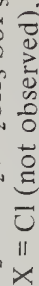
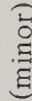
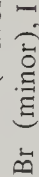
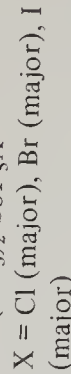
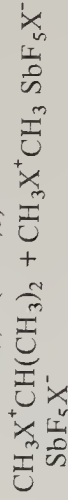
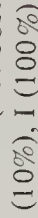
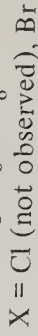
(2)

Less practical

Formation of R_3C^+

These halonium ions are not stable at -30° and disproportionate to dimethylhalonium ions and some alkylation products.^a Iodonium ion is stable at -40°

These ions are not stable at -30° and decompose to alkylation products



Iodonium ion is stable at -20°

TABLE 3
Preparation of Dialkylhalonium Ions (Continued)

Reagents and temperature (°C)	Method of preparation	Dialkylhalonium ion formed	Remarks
$(\text{CH}_3)_2\text{CHX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\text{CH}_3\text{CH}_2\text{F}\cdot\text{SbF}_5\text{-SO}_2$, -78°	(2)	$\text{CH}_3\text{CH}_2\text{X}^+\text{CH}(\text{CH}_3)_2\text{SbF}_5\text{X}^-$ $\text{X} = \text{Cl}, \text{Br}, \text{I}$ $\downarrow -20^\circ$ $(\text{CH}_3\text{CH}_2)_2\text{X}^+ + \text{alkylation products}^a$ $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{X}^+\text{SbF}_5\text{X}^-$ $\text{X} = \text{Cl}$ (0%), Br (15%), I (15%), $[(\text{CH}_3)_2\text{CH}]_2\text{X}^+\text{SbF}_5\text{X}^-$ $\text{X} = \text{Cl}$, (100%), Br (85%), I (15%)	Exchanging dialkylhalonium ions Exchanging dialkylhalonium ions
$2(\text{CH}_3)_2\text{CHX}$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) $\text{SbF}_5\text{-SO}_2$, -78°	(1)	$[(\text{CH}_3)_2\text{CH}]_2\text{X}^+\text{SbF}_5\text{X}^-$	Exchanging dialkylhalonium ions
$2(\text{CH}_3)_3\text{CX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\text{SbF}_5\text{-SO}_2$, -78°	(1)	$[(\text{CH}_3)_3\text{C}]_2\text{X}^+\text{SbF}_5\text{X}^-$	Exchanging dialkylhalonium ions

^aFor example, formation of *tert*-hexyl cation.

TABLE 4

Pmr Parameters of Dialkylhalonium Ions^a

Ion	Method of preparation	CH ₃ X ⁺	-CH ₂ X ⁺ -	-CHX ⁺ -	CH ₃ CX ⁺ -	-CH ₂ CX ⁺ -	CH ₃ CCX ⁺
CH ₃ Cl ⁺ CH ₃	(1)	4.20 (s)					
CH ₃ Br ⁺ CH ₃	(1)	4.13 (s)					
CH ₃ I ⁺ CH ₃	(1)	3.60 (s)					
CH ₃ Cl ⁺ CH ₂ CH ₃	(2)	4.41 (s)	5.23 (q, J = 7)		1.98 (t, J = 7)		
CH ₃ Br ⁺ CH ₂ CH ₃	(2)	4.09 (s)	5.10 (q, J = 7)		2.14 (t, J = 7)		
CH ₃ I ⁺ CH ₂ CH ₃	(2)	3.57 (s)	4.60 (q, J = 7)		2.17 (t, J = 7)		
(CH ₃ CH ₂) ₂ Cl ⁺	(1)		5.20 (q, J = 7)		1.93 (t, J = 7)		
(CH ₃ CH ₂) ₂ Br ⁺	(1)		5.20 (q, J = 7)		2.20 (t, J = 7)		
(CH ₃ CH ₂) ₂ I ⁺	(1)		4.74 (q, J = 7.5)		2.30 (t, J = 7.5)		
CH ₃ Br ⁺ CH ₂ CH ₂ CH ₃	(2)	4.21 (s)	5.11 (t, J = 7)			2.3 (m)	1.34 (t, J = 7)
CH ₃ I ⁺ CH ₂ CH ₂ CH ₃	(2)	3.60 (s)	4.70 (t, J = 7)			2.33 (sex, J = 7)	1.33 (t, J = 7)
CH ₃ Cl ⁺ CH(CH ₃) ₂	(2)	4.48 (s)		6.20 (hep, J = 6)	2.18 (d, J = 6)		
CH ₃ Br ⁺ CH(CH ₃) ₂	(2)	4.18 (s)		6.21 (hep, J = 6)	2.23 (d, J = 6)		
CH ₃ I ⁺ CH(CH ₃) ₂	(2)	3.69 (s)		5.90 (hep, J = 6.5)	2.40 (d, J = 6.5)		
CH ₃ CH ₂ Br ⁺ CH ₂ CH ₂ CH ₃	(2)		5.13 (q, J = 7)		2.30 (t, J = 7)		
			5.13 (t, J = 7)			2.32 (m)	1.30 (t, J = 7)
CH ₃ CH ₂ I ⁺ CH ₂ CH ₂ CH ₃	(2)		4.67 (q, J = 7)		2.24 (t, J = 7)		
			4.70 (t, J = 7)			2.38 (sex, J = 7)	1.30 (t, J = 7)
CH ₃ CH ₂ Cl ⁺ CH(CH ₃) ₂	(2)		5.10 (q, J = 7.5)	6.23 (hep, J = 6)	2.03 (t, J = 7.5)		
					2.19 (d, J = 6)		
CH ₃ CH ₂ Br ⁺ CH(CH ₃) ₂	(2)		4.94 (q, J = 7)	6.21 (hep, J = 7)	2.09 (t, J = 7)		
					2.25 (d, J = 7)		

TABLE 4
Pmr Parameters of Dialkylhalonium Ions^a (continued)

Ion	Method of preparation	CH ₃ X ⁺	-CH ₂ X ⁺ -	-CHX ⁺ -	CH ₃ CX ⁺ -	-CH ₂ CX ⁺ -	CH ₃ CCX ⁺
CH ₃ CH ₂ I ⁺ CH(CH ₃) ₂	(2)		4.70 (q, J = 7.5)	5.90 (hep, J = 7)	2.30 (t, J = 7) 2.37 (d, J = 7)		
(CH ₃ CH ₂ CH ₂) ₂ Br ⁺	(1)		5.23 (t, J = 7)			2.3 (m)	1.31 (t, J = 7)
(CH ₃ CH ₂ CH ₂) ₂ I ⁺	(1)		4.61 (t, J = 7)			2.4 (m)	1.18 (t, J = 7)
[(CH ₃) ₂ CH] ₂ Br ⁺	(1)			6.30 (hep, J = 7)	2.30 (d, J = 7)		
[(CH ₃) ₂ CH] ₂ I ⁺	(1)			5.84 (hep, J = 7)	2.10 (d, J = 7)		

^aFrom external capillary TMS. Spectra were recorded in SO₂ solution at 60 MHz. Some of the pmr shifts of dialkylhalonium ions differ uniformly by 0.4-0.6 ppm from those reported in ref. 31. s, Singlet; d, doublet; t, triplet; q, quartet; sex, sextet; hep, heptet; m multiplet.

3.2 NMR SPECTROSCOPIC STUDIES

3.2.1 Pmr

The pmr parameters of studied dialkylhalonium ions are summarized in Table 4. The methyl proton shifts of all the methylated halonium ions are deshielded in the order $-\overset{+}{\text{Cl}}\text{--} > -\overset{+}{\text{Br}}\text{--} > -\overset{+}{\text{I}}\text{--}$, indicating the inductive effective of the halogen atoms. Chlorine, being the smallest halogen atom in halonium ions (fluoronium ions are not known in solution) can accommodate the least the charge, whereas iodine, the largest of the halogen atoms, can accept essentially most of the charge. The deshielding effect of the methyl protons in dimethylhalonium ions is also related to the inductive order of the halogen atoms. The α -methylene ($-\text{CH}_2\text{X}^+-$) and α -methine ($-\text{CHX}^+-$) protons of homologous dialkylhalonium ions show a similar order of deshielding ($-\overset{+}{\text{Cl}}\text{--} > -\overset{+}{\text{Br}}\text{--} > -\overset{+}{\text{I}}\text{--}$). However, the β -methyl protons of related homologous dialkylhalonium ions show an opposite deshielding order ($-\overset{+}{\text{I}}\text{--} > -\overset{+}{\text{Br}}\text{--} > -\overset{+}{\text{Cl}}\text{--}$), indicating that the inductive effect of the positively charged halogen atoms is diminishing and the anisotropy effect of the halogen atoms is causing an opposite trend ($-\overset{+}{\text{I}}\text{--} > -\overset{+}{\text{Br}}\text{--} > -\overset{+}{\text{Cl}}\text{--}$).

3.2.2 Carbon-13 Nmr

Olah and DeMember^{26a} reported the first carbon-13 nmr study of dimethylhalonium ions. Later Fourier-transform carbon-13 nmr allowed a more thorough study of dialkylhalonium ions.^{26c,d}

The carbon-13 chemical shifts of dialkylhalonium ions obtained by the Fourier-transform method are summarized in Table 5. The assignments were

TABLE 5
Carbon-13 Chemical Shifts of Dialkylhalonium Ions ($\text{RX}^+\text{R}'$)^a

R	R'	X	R'			R	
			α -C	β -C	γ -C	α -C	β -C
CH ₃	CH ₃	Cl	48.9			48.9	
CH ₃	CH ₃	Br	37.6			37.6	
CH ₃	CH ₃	I	9.5			9.5	
CH ₃	C ₂ H ₅	Cl	73.5	16.9		48.0	
CH ₃	C ₂ H ₅	Br	66.9	16.7		36.1	
CH ₃	C ₂ H ₅	I	37.9	17.3		8.0	
C ₂ H ₅	C ₂ H ₅	Cl	73.1	20.5		73.1	20.5
C ₂ H ₅	C ₂ H ₅	Br	64.4	18.1		64.4	18.1
C ₂ H ₅	C ₂ H ₅	I	36.9	18.1		35.9	18.1
CH ₃	<i>n</i> -C ₃ H ₇	I	48.9	26.3	17.1	9.5	

^aIn parts per million from TMS. In SO₂ at -30 to -40°.

made by the usual procedures of Grant and coworkers.³⁰ These include the use of "off-resonance" proton decoupling, as well as considerations of relative signal intensities and molecular symmetry. Also, the observation that polar groups exert a large inductive effect on the shifts of directly attached carbons was taken into consideration.

A comparison of the carbon shifts in dialkylhalonium ions and alkanes (Table 6) shows the effect of the RX^+ group on carbon shieldings along a hydrocarbon chain. It can be seen from the available data that RX^+ has an appreciable deshielding effect at the α and β carbons. The α effect correlates with the electronegativities of the halogens in that chlorine shows the largest deshielding effect. The β effects are nearly the same for all halogens, the least electronegative atom, iodine, as in the case of the alkylhalides,³¹ exhibiting the largest effect.

TABLE 6
Substituent Effects of RX^+ Groups in Dialkylhalonium Ions
Compared with Parent Alkanes

Carbon position	$\Delta\delta$ for ions from hydrocarbons (ppm) ^a		
	X = Cl	X = Br	X = I
R = Methyl			
Alpha			
CH ₃ ^c	50.9	39.6	11.5
CH ₂ ^d	67.5	60.9	31.9
Beta	10.9	10.7	11.3
R = Ethyl			
Alpha			
CH ₃ ^c	50.0	38.1	10.0
CH ₂ ^d	67.1	58.4	30.9
Beta	11.5	12.1	12.7

^aThe differences were calculated by subtracting the chemical shifts in a dialkylhalonium ion from the shifts in the corresponding unsubstituted hydrocarbon.

^bA positive sign indicates deshielding.

^cChemical shift difference between CH_4 and CH_3R , where $R = CH_3X^+$ or $CH_3CH_2X^+$.

^dChemical shift difference between CH_3CH_3 and CH_3CH_2R , where $R = CH_3X^+$ or $CH_3CH_2X^+$.

Differences in the α -substituent effects between alkyl halides³¹ and dialkylhalonium ions are shown in Table 7. α -Substituent effects have been found to correlate roughly with substituent electronegativity. The larger deshielding for RX^+ is consistent with its greater electronegativity compared with X.

The data in Table 7 show that the β -carbon shift in dialkylhalonium ions is shielded from the corresponding carbon in the parent alkyl halides. A similar

result was observed for carbon shielding in protonated and parent carboxylic acid esters.³²

TABLE 7
Differences in Substituent Effects between Haloalkanes and
Dialkylhalonium Ions (RX^+CH_3)

Carbon position	$\Delta\delta$ for ions from haloalkenes given in parentheses (ppm) ^a		
	X = Cl	X = Br	X = I
R = Methyl			
Alpha			
CH ₃	23.7 (CH ₃ Cl)	27.3 (CH ₃ Br)	29.9 (CH ₃ I)
CH ₂	33.5 (EtCl)	38.5 (EtBr)	36.6 (EtI)
Beta	-1.9 (EtCl)	-3.7 (EtBr)	-3.4 (EtI)
Gamma			0.5 (PrI)
R = Ethyl			
Alpha			
CH ₃	22.8 (CH ₃ Cl)	25.8 (CH ₃ Br)	28.4 (CH ₃ I)
CH ₂	33.1 (EtCl)	36.0 (EtBr)	37.6 (EtI)
Beta	-1.3 (EtCl)	-2.3 (EtBr)	-3.0 (EtI)

^aPositive values indicate a deshielding in the dialkylhalonium ion.

The cmr shifts of the methyl carbons of dimethylhalonium ions indicate that little charge is introduced into these carbons. The deshielding from their precursors (methyl chloride, bromide, and iodide) is 29.0, 25.8, and 23.0 ppm, respectively. The methyl carbons thus clearly remain sp^3 -hybridized. Most of the positive charge on dialkylhalonium ions is therefore located at the halogen centers.

It is interesting to note that carbons attached to chlorine are consistently more deshielded than those attached to bromine and iodine in the homologous dialkylhalonium ions. This is probably due to the fact that the larger halogen (e.g., iodine) can accommodate more charge than the smaller (e.g., chlorine), and also to related magnetic shielding effects (see Section 0.0). The relative stability of dialkylhalonium ions was observed to be in the order $\text{~}\overset{+}{\text{I}}\text{~} > \text{~}\overset{+}{\text{Br}}\text{~} > \text{~}\overset{+}{\text{Cl}}\text{~}$, whereas their relative chemical reactivity had an opposite sequence $\text{~}\overset{+}{\text{Cl}}\text{~} > \text{~}\overset{+}{\text{Br}}\text{~} > \text{~}\overset{+}{\text{I}}\text{~}$ (as observed in their alkylation reactions; see Section 5.4). These observations and the nmr data are thus in good accordance. Stability and reactivity of the ions are thus opposite, and similar, properties.

3.3 RAMAN AND IR SPECTROSCOPIC STUDIES

Olah and DeMember^{26b,c} reported Raman and ir spectroscopic studies of dimethylhalonium ions. Raman data for the dimethylhalonium ions studied are summarized in Table 8, along with data observed for isoelectronic model compounds.³³ Dimethylhalonium ions ($\text{CH}_3\text{X}^+\text{CH}_3$) could exist in either a

TABLE 8
Raman Frequencies of Dialkylhalonium Ions, Their Isoelectronic Models, and Methyl Halides^a

Compound	ν C—X—C deformation	$\nu_6 [\nu_{17}]$ C—X stretching	C—H stretching
$\text{CH}_3\text{ClCH}_3(\text{SO}_2)$	392 (0.31)	610 (0.36)	2865, 2950, 2980, 3080
$\text{CH}_3\text{BrCH}_3(\text{SO}_2)$	282 (0.46)	544 (0.31)[561 (dp)]	2865(0.70), 2950, 2978(0.23), 3100
$\text{CH}_3\text{ICH}_3(\text{SO}_2)$?	511 (0.33)	2872, 2952, 2973
$\text{CH}_3\text{CH}_2\text{ClCH}_2\text{CH}_3(\text{SO}_2)$	390 (0.27)	610 (0.35), 545 (0.36), 527 (dp)	2860(0.70), 2945 (0.24), 2987 (0.65), 3060
CH_3SCH_3 (neat)	282 (p)	691 (p)[742(dp)]	2832(p), 2910(p), 2966(p), 2982 (dp)
CH_3SeCH_3 (neat)	236 (dp)	587 (p)[602(dp)]	2823(p), 2919(p), 2996(dp)
CH_3TeCH_3 (neat)	198	526 (dp)	2810, 2923(p), 3000(dp)
$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3(\text{SO}_2)$	340 (0.54)	693(0.82), 656 (0.34), 638(0.82)	2946
CH_3Cl (neat) (SO_2)		731.2 706 [$\delta(\Delta\nu)=25\text{cm}^{-1}$]	1878.8, 2966.2, 3041.8, 2869, 2969
CH_3Br (neat) (SO_2)		611 595 [$\delta(\Delta\nu)=15\text{cm}^{-1}$]	2861, 2972, 3055.8, 2869, 2969, ?
CH_3I (neat) (SO_2)		532.8 527 [$\delta(\Delta\nu)=6\text{cm}^{-1}$]	2861, 2969.8, 3060.6, 2867, 2968, ?

^aSpectra reported were recorded at -40° . For detailed experimental conditions see G. A. Olah and A. Commeyras, *J. Am. Chem. Soc.*, 91, 2929 (1969). Values in parentheses are the depolarization factors taken as an average for three runs and are uncorrected. p, Polarized; dp, depolarized.

linear or bent conformation. On the basis of energetic considerations and the well-established geometry of the isoelectronic dimethyl chalcides, it is expected that dialkylhalonium ions contain sp^3 -hybridized halogen atoms, resulting in approximately tetrahedral geometry. Such an arrangement would lead to three skeletal vibrations which are both ir- and Raman-active. Two of the vibrations are totally symmetric (A_1 in character) and one asymmetric (of the B_1 type). Thus two polarized and one depolarized Raman-active, and three ir-active modes, are theoretically predicted for the fundamental skeletal vibrations of C_{2v} dimethylhalonium ions.

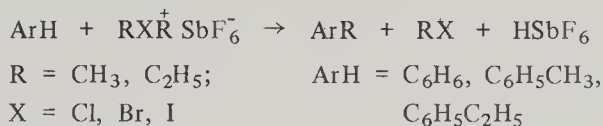
The observation of three Raman- and three ir-active skeletal vibrations for the dimethylhalonium ion, with two totally symmetric and one asymmetric, in accordance with the selection rules for the C_{2v} point group, and the correlation with the skeletal frequencies of dimethyl selenide, indicate that the methyl groups maintain preferred conformations with torsional minima in a C_{2v} arrangement. The Raman spectrum of the dimethylchloronium ion does not parallel that observed for dimethyl sulfide well enough to suggest a significant correlation between their molecular symmetry.

3.4 CHEMICAL REACTIVITY

Dialkylhalonium ions are reactive alkylating reagents. The alkylation of π -donor (aromatic and olefins) and n -donor bases with dialkylhalonium ions was studied.^{26c} Alkylation of aromatics with dialkylhalonium ions was found to be not significantly different from conventional Friedel-Crafts alkylations, showing particular similarities in the case of alkylation with alkyl iodides. Alkylation of n -donor bases with dialkylhalonium salts provides a simple synthetic route to a wide variety of onium ions.

3.4.1 Alkylation of Aromatics

The alkylation of aromatic hydrocarbons, such as benzene, toluene, and ethylbenzene, was studied with dimethyl- and diethylhalonium hexafluoroantimonates in SO_2ClF solution.^{26c} Data for alkylations are summarized in Table



9. Dimethyldihalonium ions give similar methylation results and are quite reactive even at temperatures as low as -50° . The dimethyliodonium ion is less reactive and alkylate benzene and toluene in SO_2ClF solution only when allowed to react (if necessary under pressure) at or above 0° .

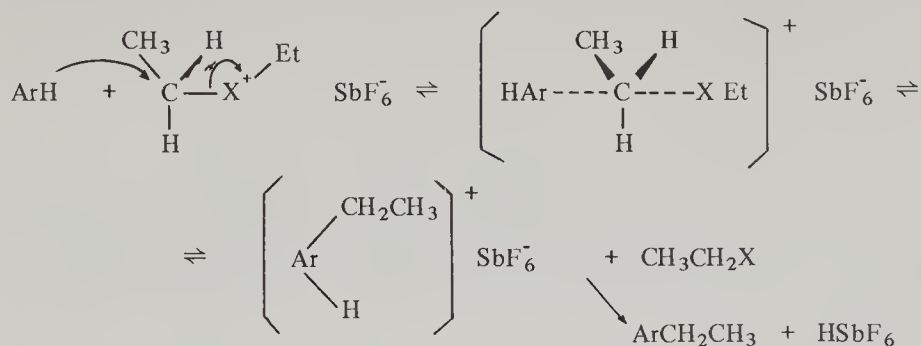
TABLE 9

Alkylation of Benzene, Toluene, and Ethylbenzene with Dimethyl- and Diethylhalonium Fluoroantimonates in SO_2ClF^a

Halonium ion	Aromatic substrate	Temp. ($^{\circ}\text{C}$)	Time (min)	k_T/k_B	Isomer distribution (%)			
					Ortho	Meta	Para	Ortho/para ratio
$(\text{CH}_3)_2\text{Cl}^+$	Toluene	25	10		46.6	27.2	26.7	1.75
		0	1		51.8	16.2	32.1	1.61
		-50	5		52.3	15.7	32.0	1.63
$(\text{CH}_3)_2\text{Br}^+$	Toluene	-50	2		58.6	13.0	28.4	2.06
		-50	5		57.8	9.5	32.7	1.76
		-50	2		59.0	8.6	32.4	1.82
$(\text{CH}_3)_2\text{I}^+$	Toluene	25	10		46.2	15.6	38.1	1.27
		0	10		53.9	11.8	34.3	1.57
		-20	60		No reaction			
$(\text{CH}_3\text{CH}_2)_2\text{Cl}^+$	Benzene-	-78	1	4.9	33.4	28.1	38.5	0.86
	Toluene	-78	2.5	4.8	31.4	24.6	44.0	0.72
	Ethylbenzene-toluene	-78	2.5	1.10	31.9	19.3	48.8	0.65
$(\text{CH}_3\text{CH}_2)_2\text{Br}^+$	Benzene-	-78	1	4.0	38.7	19.3	42.0	0.92
	Toluene	-78	5	4.5	36.0	18.2	45.8	0.78
	Ethylbenzene-toluene	-78	5	1.2	32.8	14.5	52.8	0.62
					(25.2)	(19.4)	(55.4)	(0.45)
$(\text{CH}_3\text{CH}_2)_2\text{I}^+$		-45	5	4.1	44.0	10.2	45.8	0.96

^a All data are average of at least three parallel experiments.

The ethylation of toluene by diethylhalonium ions gives ethyltoluenes with ortho/para isomer ratios between 0.60 and 0.96. The ortho/para isomer ratios obtained for the alkylation of toluene in conventional Friedel-Crafts ethylations range from 1.17 to 1.84 (average ca. 1.60). Furthermore, an approximate twofold increase in the k_T/k_B rate ratios for ethylation of toluene (*T*)-benzene (*B*) mixtures relative to usual competitive Friedel-Crafts ethylation reactions is also observed. Such differences are considered to be due to the steric ortho effect caused by diethylhalonium ions, and are in accordance with the most probable displacement reaction by the aromatic on the bulky diethylhalonium ions. This can be envisioned to proceed through an S_N2 -type transition state.



The alkylation data obtained from the reaction of dimethyl- and diethylhalonium ions provide evidence for direct alkylation of aromatics by dialkylhalonium ions. In addition, the data indicate that dialkylhalonium ions are not necessarily involved as active alkylating agents in general Friedel-Crafts systems, although some of the reported anomalous alkylation results, particularly with alkyl iodides, could be attributed to reaction conditions favoring dialkylhalonium ion formation.

3.4.2 Alkylation of Heteroorganic Compounds

Dimethyl- and diethylhalonium ions are particularly effective alkylating agents for heteroorganic compounds.^{26c} Table 10 summarizes the pmr data for onium ions obtained by alkylation of ethers, alcohols, water, ketones, aldehydes, and carboxylic acids, as well as nitro, sulfur, and amino compounds with dimethyl-, and diethyldihalonium ions. Alkylation of *O*-, *S*- and *N*- *n*-donor bases by dialkylchloronium and -bromonium ions appears to be practically quantitative, even under mild conditions. Dialkyliodonium ions generally do not react with the same *n*-donor bases in SO_2 or SO_2ClF solution at temperatures between -78 and 0° (although they can undergo alkylation under more forceful conditions).

In comparison with Meerwein's trialkyloxonium ions,³⁴ the advantage of alkylation with dialkylhalonium ions lies in their greater alkylating

TABLE 10
Onium Ions Obtained by Methylation and Ethylation of Heteroatom *n*-Donor
Bases with Dimethyl(diethyl)halonium Fluoroantimonates

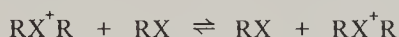
Heteroorganic substrate	Methylated onium ion	CH ₃ ⁺ CH ₃	CH ₂	CH	Pmr shifts (δ)	Aro- HY	Ethylated onium ion	CH ₂ ⁺ CH ₂ ⁺ CH ₃	CH ₃ ⁺ CH ₃	Pmr shifts (δ)	CH ₂	CH	Aro- HY	matic
(CH ₃) ₂ O	(CH ₃) ₃ O ⁺	4.30					(CH ₃) ₂ O ⁺ C ₂ H ₅	4.12	1.27	3.98				
(C ₂ H ₅) ₂ O	(C ₂ H ₅) ₂ O ⁺ CH ₃	4.23	1.58	4.62			(C ₂ H ₅) ₃ O ⁺	4.33	1.41					
CH ₃ OH	CH ₃ O ⁺ (CH ₃)H	3.68				9.42	CH ₃ OH(C ₂ H ₅) ⁺	4.27	1.39	3.88			9.38	
H ₂ O	CH ₃ OH ⁺	4.13				9.50	C ₂ H ₅ OH ⁺	4.86	1.60				9.2	
(CH ₃) ₂ C=O	(CH ₃) ₂ C=O ⁺ OCH ₃	4.80	3.94				(CH ₃) ₂ C=O ⁺ OC ₂ H ₅	5.02	2.05	3.92				
(C ₂ H ₅) ₂ C=O	(C ₂ H ₅) ₂ C=O ⁺ OCH ₃	4.63	1.44	3.82			(C ₂ H ₅) ₂ C=O ⁺ OC ₂ H ₅	5.13	1.98	1.41	3.80			
c-C ₃ H ₈ O	c-C ₃ H ₈ OCH ₃ ⁺	4.86			3.18, 2.24		c-C ₃ H ₈ OCH ₂ H ₅ ⁺	5.25	1.98					
(C ₆ H ₅) ₂ C=O	(C ₆ H ₅) ₂ C=O ⁺ OCH ₃	3.83			9.62		(C ₆ H ₅) ₂ C=O ⁺ OC ₂ H ₅	4.38	1.08					7.7-8.0
CH ₃ CHO	CH ₃ CH=O ⁺ OCH ₃	5.80	3.51		9.62		CH ₃ CH=O ⁺ OC ₂ H ₅	5.21	1.86	3.46			9.60	
C ₆ H ₅ CHO	C ₆ H ₅ CH=O ⁺ OCH ₃	4.12			9.42		C ₆ H ₅ CH=O ⁺ OC ₂ H ₅	5.58	1.92				9.95	7.7-8.0
HCOOH	HC(OCH ₃)OH syn	4.25			8.76	12.54	HC(OC ₂ H ₅)OH syn	4.54	1.92				8.62	13.06
	anti	4.18			8.70	12.54		5.00	2.06				8.42	13.06
CH ₃ COOH	CH ₃ C(OCH ₃)OH	4.32	2.64			12.84	CH ₃ C(OC ₂ H ₅)OH	4.95	1.48	2.75			12.47	
CH ₃ NO ₂	CH ₃ NO ⁺ CH ₃	4.67	5.04				CH ₃ NO ⁺ C ₂ H ₅	5.15	1.70	5.02				
CH ₃ CH ₂ CH ₂ NO ₂	CH ₃ CH ₂ CH ₂ NO ₂ ⁺ CH ₃	4.67	0.98	5.23, 2.18			CH ₃ CH ₂ CH ₂ NO ₂ ⁺ C ₂ H ₅	5.14	1.70	0.99	5.20, 2.16			
C ₆ H ₅ NO ₂	C ₆ H ₅ NO ₂ ⁺ CH ₃	4.65					C ₆ H ₅ NO ₂ ⁺ C ₂ H ₅	5.12	1.69					7.6-8.2
[(CH ₃) ₂ CH] ₂ S	[(CH ₃) ₂ CH] ₂ S ⁺ CH ₃	2.52	1.38	3.53			[(CH ₃) ₂ CH] ₂ S ⁺ C ₂ H ₅	3.03	1.45	1.33		3.57		
(C ₂ H ₅) ₂ S	(C ₂ H ₅) ₂ S ⁺ CH ₃	2.76	1.38	3.18			(C ₂ H ₅) ₃ S ⁺	3.26	1.40					
<i>t</i> -BuSH	<i>t</i> -BuS ⁺ HCH ₃	2.99	1.62		6.16		<i>t</i> -BuS ⁺ C ₂ H ₅	3.58	1.54	1.63			6.08	
(C ₂ H ₅) ₃ N	(C ₂ H ₅) ₃ N ⁺ CH ₃	2.97	1.23	3.21			(C ₂ H ₅) ₄ N ⁺	4.81	1.05					

ability (in case of chloronium and bromonium ions) and in the possibility of increased selectivity when the halogen center is being changed (iodonium ions are generally the most stable but the least reactive).

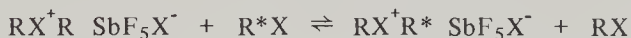
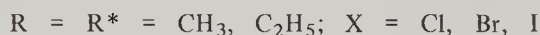
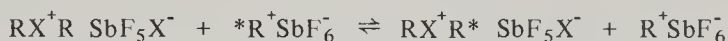
3.5 INTERMOLECULAR EXCHANGE REACTIONS OF DIALKYLHALONIUM IONS WITH ALKYL HALIDES AND ALKYL CARBENIUM IONS

We have so far discussed the alkylation of a variety of *n*-donor bases, other than halogen donors, by dimethyl- and diethylhalonium ions. If the *n*-donor base is an excess of alkyl halide, intermolecular exchange reactions via transalkylation take place.²⁷ The intermolecular exchange reaction of dialkylhalonium ions with alkyl halides and alkylcarbenium ions³⁵ was studied in detail.

1"



Dimethyl- and diethylhalonium ions, prepared from methyl and ethyl halides with SbF_5 in SO_2 solution, do not undergo intermolecular exchange reactions with excess methyl and ethyl halides. Similarly, dimethyl- and diethylhalonium ions, prepared by methylation of methyl halides and ethylation of ethyl halides with methyl and ethyl fluoroantimonates,³⁶ do not undergo intermolecular exchange reactions with an excess of methyl and ethyl fluorantimonate, respectively.

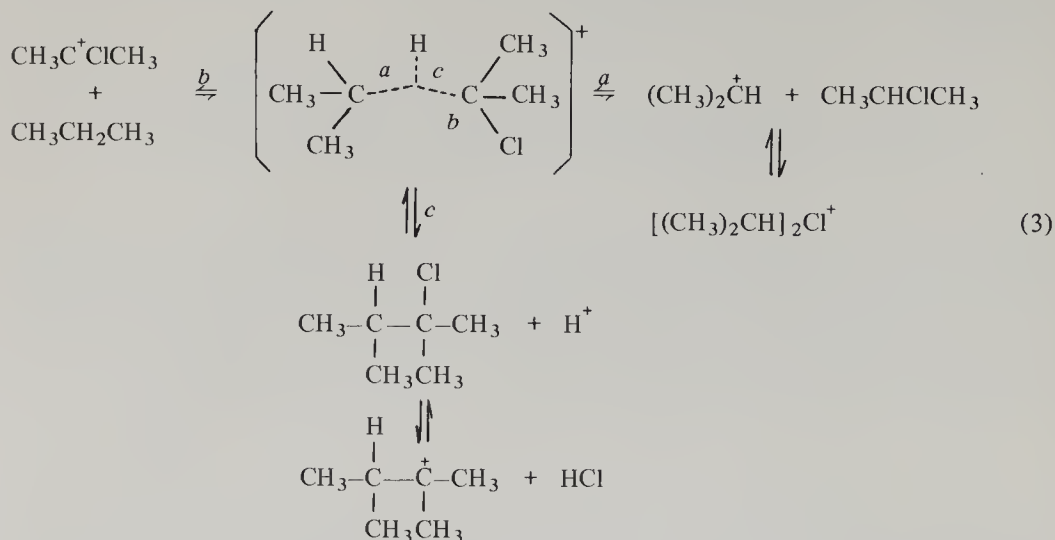


Diisopropylchloronium ion undergoes intermolecular exchange with both isopropyl cation and isopropyl chloride. The exchange reactions depend on the experimental conditions and can be divided into three types: (1) exchange with isopropyl chloride when 2 equivalents or more of isopropyl chloride are treated with SbF_5 in SO_2 solution, (2) exchange with isopropyl cation when



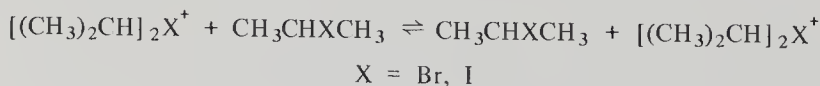
isopropyl chloride is treated with 2-4 equivalents of SbF_5 (isopropyl cation is formed when 4 equivalents or more of SbF_5 are used), and (3) when 0.5-2.0 equivalents of isopropyl chloride are treated with SbF_5 in SO_2 solution; three

different intermolecular exchange reactions, proceeding through carbonium ion transition states, occur in addition to the exchange reactions (1) and (2).



The last type [equation (3)] of intermolecular exchange reaction is particularly significant, because it shows the competing σ - versus n -donor ability toward an electrophile. The isopropyl cation alkylates the n -donor chlorine atom of isopropyl chloride to give the diisopropylchloronium ion. At the same time it is also capable of alkylating the σ -donor C—H single bond³⁵ of isopropyl chloride, forming a carbonium ion-type transition state. There are three possible types of cleavage (a , b , and c). The carbonium ion can return to isopropyl chloride and isopropyl cation via a . Protolytic cleavage via b could give dimethylchlorocarbenium ion and propane. This has been experimentally proved by mixing an appropriate amount of dimethylchlorocarbenium ion and propane and obtaining the same reaction mixture, as shown by pmr spectroscopy. Deprotonation could generate the alkylation product 2,3-dimethyl-2-chlorobutane, which is further ionized to *tert*-hexyl cation. The formation of *tert*-hexyl cation is an irreversible process.

Diisopropylbromonium and diisopropyliodonium ions also exchange with excess isopropyl bromide and iodide, respectively. Such exchange reactions



have been studied by temperature-dependent pmr spectra. Diisopropylbromonium ions also exchange with excess isopropyl cations, similarly to the exchange of diisopropylchloronium ions. Diisopropyliodonium ion, however, does not exchange with isopropyl cation even when 4 equivalents or more of

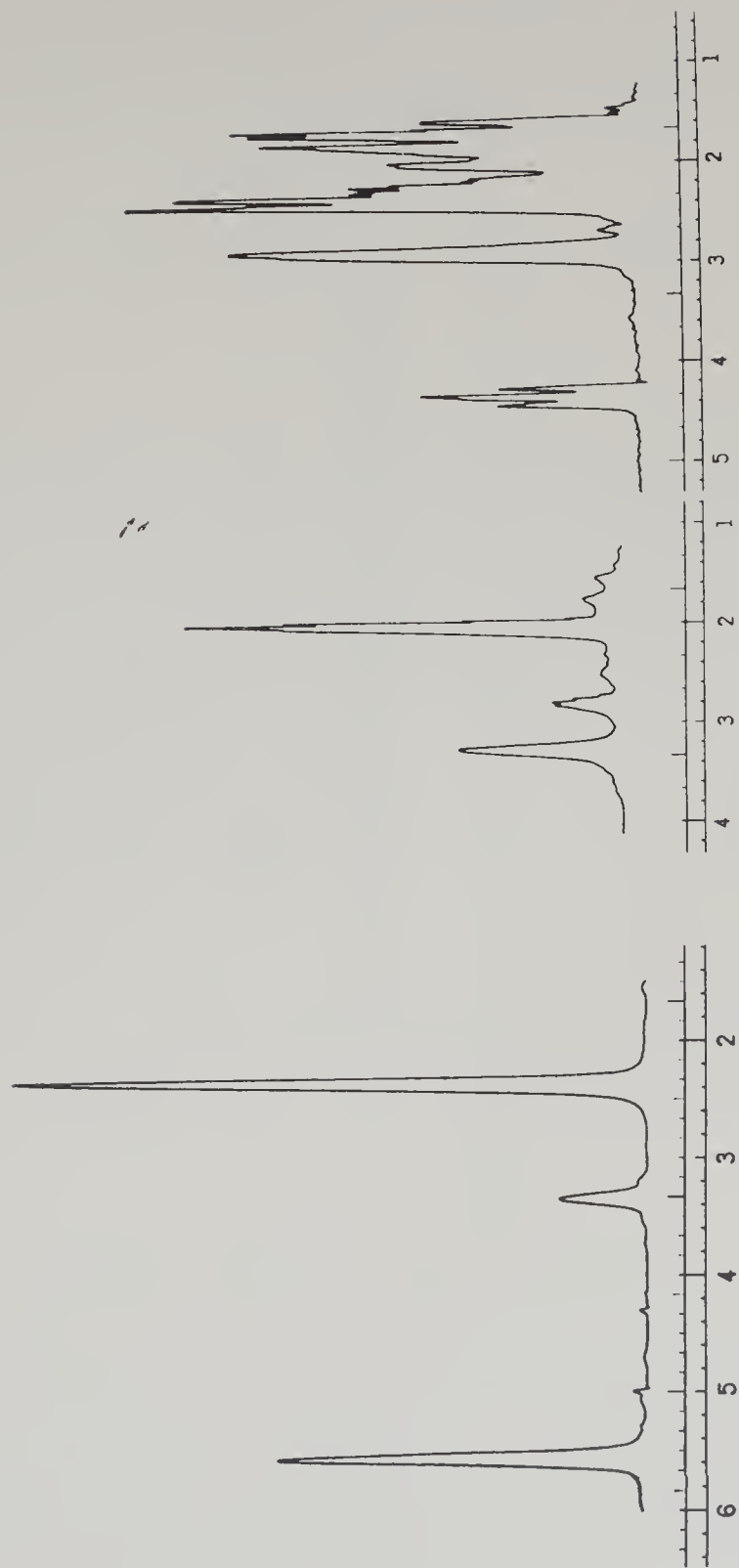


Figure 1. PMR spectra of norbornyl cation (left), exchanging dinorbornylchloronium ion (center), and 2-exo-norbornyl chloride (right) at -78° .

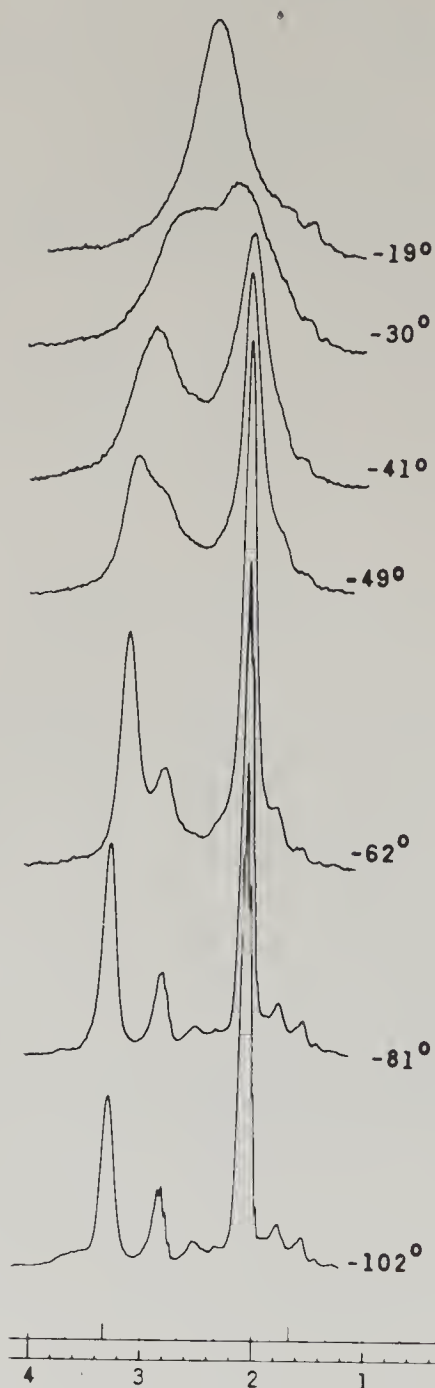
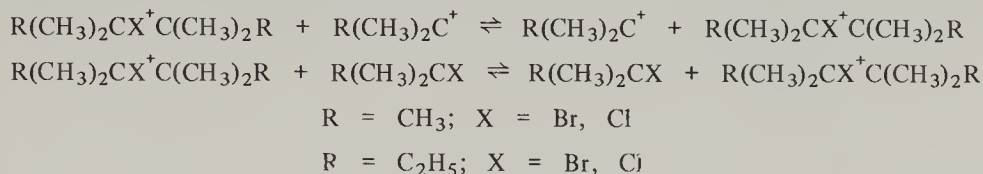


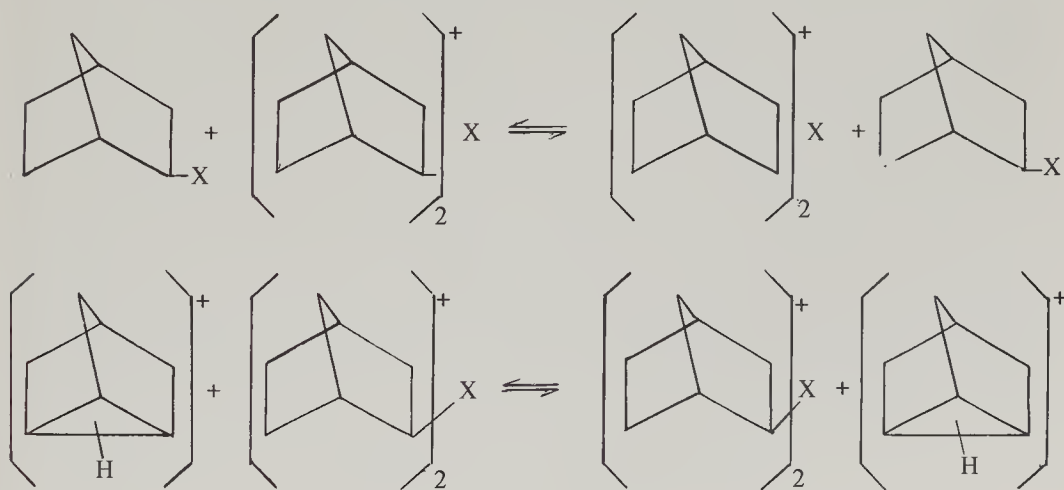
Figure 2. Temperature-dependent pmr spectra of the dinorbornylchloronium ion.

SbF_5 is treated with isopropyl iodide. Only diisopropyliodonium ion was observed under these experimental conditions. Isopropyl cation could not be generated from isopropyl iodide under any stable ion conditions utilized. These data reflect the unusual stability of the diisopropyliodonium ion.

The intermolecular exchange reaction of di-*tert*-butylhalonium ions and di-*tert*-amylhalonium ions with their corresponding halides or/and alkylcarbenium ions was also studied. These exchange reactions have been demonstrated by the concentration-dependent pmr spectra of the systems.



The intermolecular exchange reactions of dinorbornylhalonium ions are interesting. These ions exchange with either excess norbornyl cation or excess 2-*exo*-norbornyl halide, depending on the experimental conditions. The pmr spectra of all the systems are similar to that of the norbornyl cation,³⁷ regardless of which component is in excess, and are temperature-dependent (Figures 1 and 2). The pmr absorptions are deshielded when more SbF_5 is added and are shielded when more 2-*exo*-norbornyl halide is added. The



temperature-dependent nature of the systems indicates that 6,1,2-hydrogen shifts, as well as the Wagner-Meerwein rearrangement, are still taking place in the involved unassociated norbornyl cations at the temperatures studied ($> -100^\circ$), in accordance with studies of the norbornyl cation itself.

The 1-adamantyl cation prepared from adamantyl halides with $\text{SbF}_5\text{-SO}_2\text{SO}_2\text{ClF}$ solution³⁸ displays three pmr absorptions at δ 5.40, 4.52, and 2.67. Diadamantylhalonium ions were formed as yellowish-orange precipitates when equimolar amounts of adamantyl halides were added to a solution of adamantyl cations in $\text{SbF}_5\text{-SO}_2$ (SO_2ClF). The precipitates were redissolved when methylene chloride was added as a cosolvent. The pmr spectrum of each of the resulting

solution showed three absorptions similar to those of the adamantyl cation but slightly shielded. The shielding effect is proportional to the amount of adamantyl chloride or bromide added to the solution of the adamantyl cation. For example, Figure 3 (left) shows the change in proton chemical shifts when adamantyl chloride was added to a solution of the 1-adamantyl cation. Further addition of

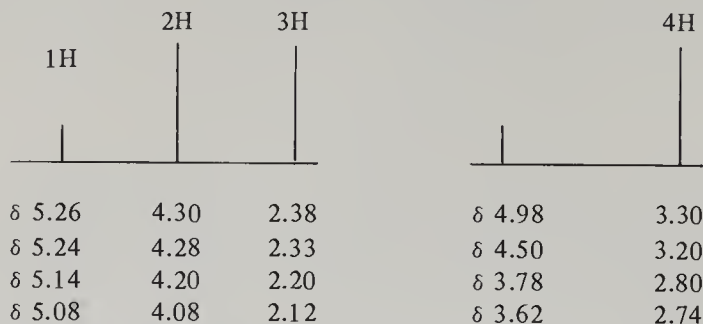
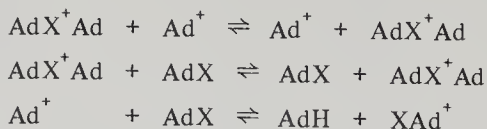


Figure 3. Pmr data of diadamantylchloronium ion exchanging with 1-adamantyl chloride and/or 1-adamantyl cation.

adamantyl chloride to the above solution caused the collapse of the two methylene absorptions into a singlet. The new singlet and the methine absorption both became shielded when the concentration of adamantyl chloride was increased (Figure 3, right). The ratio of the two proton absorptions is 4:1. The pmr spectrum is temperature-independent from -80 to -10° . These data again suggest intermolecular exchange of diadamantylchloronium ion with adamantyl chloride and/or adamantyl cation. In this case the 1-adamantyl cation can also undergoes intermolecular hydrogen exchange with a tertiary C—H bond of 1-haloadamantanes (the σ -donor site competing with the n -donor halogen atoms).



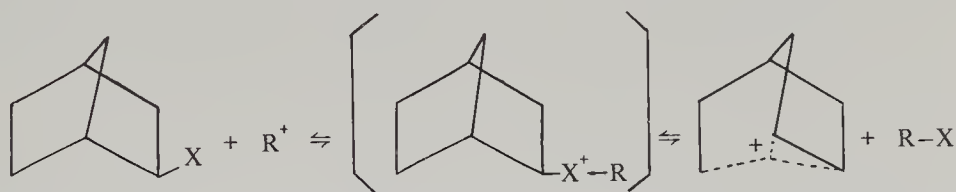
Ad = adamantyl; X = Br, Cl

3.5.1 Determination of Relative Carbocation Stabilities through Competitive Exchange

The intermolecular exchange reaction of alkyl halides with alkylcarbenium ions through dialkylhalonium ions can be advantageously used to determine directly, by competitive comparison, the relative stabilities of the ions.³⁹

Tertiary carbenium ions are uniformly accepted to be considerably more stable than secondary ions.³⁵ Should a secondary ion exhibit extraordinary stability, a specific reason, such as nonclassical σ -delocalization, would be

required to explain its behavior. The much-studied 2-norbornyl cation³⁷ indeed possesses such unusual stability as compared with other secondary or even tertiary ions. This conclusion is based on the direct observation of the preferred equilibria formed between a series of secondary and tertiary carbenium ions and 2-norbornyl chloride and bromide, respectively, in SO_2ClF solution at -70° (as determined by pmr spectroscopic study of the ions present).



$\text{R}^+ = (\text{CH}_3)_3\text{C}^+, (\text{CH}_3)_2\text{CH}^+$, cyclopentyl, 1-methyl-1-cyclopentyl, and 1-adamantyl cations
 $\text{X} = \text{Cl}$ and Br

The equilibria shown in Table 11 were also determined from the other direction, that is, by the addition of solutions of alkyl or cycloalkyl chlorides and bromides in SO_2ClF to a solution of the norbornyl cation (also in a SO_2ClF solution without excess SbF_5) at -70° and followed by pmr. The interchange reaction is considered to involve formation of the corresponding alkylnorbornylhalonium ions which then disproportionate in the direction of the thermodynamically more stable 2-norbornyl or alkyl cations.

When the secondary 2-norbornyl cation was allowed to compete in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution with tertiary carbenium ions, such as *tert*-butyl, methylcyclopentyl, and 1-adamantyl cations, the equilibria formed show the former to exist as the predominant ion, or at least comparable in concentration to the latter ions, indicating that the 2-norbornyl cation is more or at least as stable as the compared tertiary carbocations. When the 2-norbornyl cation was allowed to compete with secondary carbocations, such as isopropyl and cyclopentyl cations, the former appear as the sole detectable ion in the solution (see Table 11).

TABLE 11
Equilibrium Concentration of Competing Carbocations
at -70° in SO_2ClF Solution

R^+	$\text{R}^+ + \text{exo-2-norbornyl bromide} \rightleftharpoons$	$\text{R bromide} + \text{2-norbornyl cation}$
<i>tert</i> -Butyl	30%	70%
1-Methyl-1-cyclopentyl	20%	80%
1-Adamantyl	45%	55%
Isopropyl	(<2%)	>98%
Cyclopentyl	(<2%)	>98%

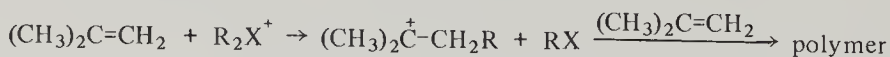
The 2-norbornyl cation thus possesses not only comparable or greater stability than tertiary alkyl or cycloalkyl cations, but also greater stability than the degenerate, rapidly equilibrating secondary cyclopentyl cation.³⁵ Rapid equilibration thus provides no substantial stabilization in itself. When competing with the *tert*-butyl cation, the cyclopentyl cation was also found to be considerably less stable.

The results are in good accord with recent gas-phase ion stability measurements by Beauchamp⁴⁰ using competitive ICR techniques (with which of course no structure for the ions involved can be assured). Both in solution and in the gas phase the norbornyl ion thus shows exceptional stability when compared to usual secondary carbocations, and is similar or more stable than tertiary ions. Only the σ -delocalized nonclassical structure of the ion can account for these findings, in complete agreement with all other structural and chemical studies.

Direct competitive comparison of carbocation stability through exchange equilibria of alkyl or cycloalkyl halides and alkyl- or cycloalkylcarbenium ions is also applicable to other systems and should gain extended use. As the exchange proceeds through dialkyl- or cycloalkylhalonium ions utilizing the nonbonded electron pairs of halogens, steric hindrance should not much affect the reactions, which could be a major consideration in exchange reactions of carbocations with the corresponding hydrocarbons (σ donors).

3.6 ALKYLATION AND POLYMERIZATION OF ALKENES

Dialkylhalonium ions, as discussed, are effective alkylating agents for aromatics and various *n*-donor bases. A study of the reaction of alkenes such as 1-butene, 2-butene, and 2-methylpropene (isobutylene) with dimethylbromonium fluoroantimonate in SO₂ solution has also been carried out.^{26a,41} Ready alkylation takes place but under the reaction conditions, the initially formed alkylcarbenium ions are not sufficiently stable to be observed. In the presence of excess alkenes, the reaction proceeds rapidly, yielding polymers.⁴¹



Dialkylhalonium ions thus are effective cationic polymerization initiators. The possible involvement of dialkylhalonium ions in Friedel-Crafts polymerization of alkenes with systems such as AlCl₃-CH₃Cl and AlBr₃-CH₃Br must therefore also be considered.

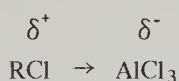
The aluminum halide-catalyzed polymerization of isobutylene (the most extensively studied cationic polymerization) is frequently carried out in methyl chloride solution. The same reaction in methyl bromide is much slower, and methyl iodide practically stops the polymerization. Plesch⁴² used the slowness

of the reaction in methyl bromide to develop his concept that the catalytic activity of aluminum bromide in the system is due to the AlBr_2^+ ion. The real reason, however, probably is formation of dialkylhalonium ions not considered before, with exception of some of Kennedy's⁴³ recent work in a somewhat different context. It was indeed shown that n -donor alkyl halides can compete with π -donor alkenes for alkylcarbenium ions and slow down polymerization parallel with the stability of the corresponding dimethylhalonium ions, and follow the order of decreasing deactivating trend: $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$.

3.7 ROLE OF DIALKYLHALONIUM IONS IN FRIEDEL-CRAFTS REACTIONS

The observation of dialkylhalonium ion formation in alkyl halide-antimony pentafluoride systems raises the question of their involvement in Friedel-Crafts reactions (alkylation and polymerizations). Alkyl halide-Lewis acid halide complexes (as well as the related alkylcarbenium ions) can obviously alkylate not only aromatic and aliphatic hydrocarbons but also excess alkyl halides (other than fluorides) to form dialkylhalonium ions. The 1:1 or 1:2 alkyl halide-Lewis acid complexes therefore could be expected to contain dialkylhalonium ion complexes.

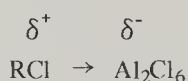
DeHaan and Brown⁴⁴ showed, based on kinetic evidence, that in methyl bromide-gallium bromide (and related chloride systems) the dimethylbromonium (or -chloronium) ion is involved.



1:1



2:1



1:2

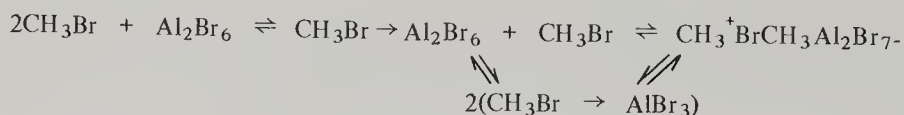


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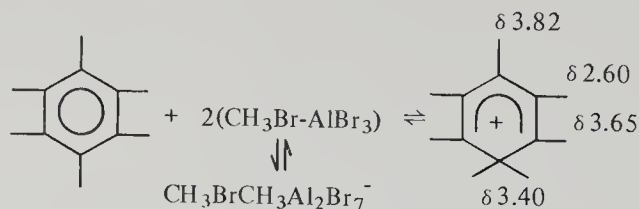
The preparation and study of a series of dialkylhalonium complexes allowed a direct comparison with common Friedel-Crafts alkylation systems, such as methyl halide-aluminum halide complexes, in order to determine directly the possible contribution of dimethylhalonium ions.

AlBr_3 dissolves in CH_3Br and gives a clear solution which is stable at room temperature. Walker,⁴⁵ from vapor pressure measurements, found the composition of the liquid phase to be $\text{CH}_3\text{Br}-\text{AlBr}_3/\text{CH}_3\text{Br}-\text{Al}_2\text{Br}_6 = 0.678:0.288 = 0.033$ (at 23.8°). By the same technique Brown and Wallace⁴⁶ established the 1:1 complex at -78° . Ir spectra of this complex were recorded by Perkampus and Baumgarten⁴⁷ at -196° , and by Kinsella and Coward⁴⁸ at room temperature. Raman investigations were carried out by Rice and Bold.⁴⁹ However, no clear conclusions were reached from these studies.

A comparative study with nmr spectroscopy of the 1:1 $\text{CH}_3\text{Br}-\text{AlBr}_3$ complex and the related 1:1 $\text{AlI}_3-\text{CH}_3\text{I}$ complex (the $\text{AlCl}_3-\text{CH}_3\text{Cl}$ complex is less suitable, because of the lower boiling point of methyl chloride and the difficulties in handling the 1:1 complex at atmospheric pressure) showed in the 1:1 $\text{CH}_3\text{Br}-\text{AlBr}_3$ complex (neat) a singlet pmr absorption at δ 4.0 (in SO_2ClF solution at -40° , δ 3.40). The corresponding 1:1 $\text{CH}_3\text{I}-\text{AlI}_3$ complex showed a singlet absorption at δ 3.65. The chemical shifts of both complexes closely resemble those observed for the dimethylbromonium and -iodonium ions, respectively, and are different from the well-defined $\text{CH}_3\text{F} \rightarrow \text{SbF}_5$ donor-acceptor complex³⁶ (δ 5.56 in SO_2), in which case no dimethylfluoronium ion formation is involved. These data seem to indicate that 1:1 $\text{CH}_3\text{Br}-\text{AlBr}_3$ or $\text{CH}_3\text{I}-\text{AlI}_3$ complexes contain at least a substantial contribution from the corresponding dimethylbromonium or -iodonium ions in the equilibrating systems.

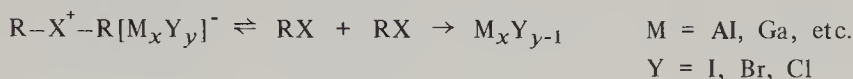


The chemical behavior of the methyl halide-aluminum halide complex is indicative of the equilibrium system. When treated with typical *n*-donors such as nitromethane, acetone, methyl benzoate, or propionaldehyde, which have been *n*-alkylated with dimethylhalonium ions, the methyl halide complexes in sharp contrast give no alkylation products but form the corresponding AlBr_3 or AlI_3 donor-acceptor complexes. This is in accordance with the transfer of aluminum halide from the methyl halide donor-acceptor complexes to the stronger *n*-donor bases, thus shifting the equilibrium in this direction. At the same time, the methyl halide-aluminum halide complexes readily alkylate aromatics or olefins. Hexamethylbenzene, for example, forms heptamethylbenzenium bromoaluminate.⁵⁰



Preparation as well as spectroscopic study and investigation of the alkylating ability of dialkylhalonium ions established their structure and relative stability, as well as their chemical reactivity. In general, the relative stability of dialkylhalonium ions follows the order $\text{RI}^+\text{R} > \text{RBr}^+\text{R} > \text{RCl}^+\text{R}$, indicating that a larger halogen atom is more capable of accommodating charge. Alkylating ability, however, is generally inversely proportional to the stability of the ion.

Dialkylhalonium ions are also formed under regular Friedel-Crafts conditions as rapidly exchanging systems with excess alkyl halides, according to the equilibria



Whereas this observation helps to explain the generally very complex kinetic order of Friedel-Crafts alkylation systems, dialkylhalonium ions are not necessarily the de facto reactive alkylating agents. It is clear, however, that even in competition with reactive π -donor systems (olefins, aromatics) an excess of alkyl halide (over the alkyl halide alkylating agent) must be considered an n -donor system capable of forming dialkylhalonium ions. This is not the case, however, for alkyl fluorides. What is interesting, as shown in the case of CH_3F (excess) with SbF_5 , is that alkylation of the C-H bond (σ donor) takes place (giving ethyl and subsequently higher alkyl products), as the corresponding dimethylfluoronium ion ($CH_3F^+CH_3$) seems incapable of forming in solution density.

3.8 DIALKYL AKYLENEDIHALONIUM IONS

Alkylation of alkylene dihalides with methyl and ethyl fluoroantimonate ($CH_3F-SbF_5-SO_2$ and $C_2H_5F-SbF_5-SO_2$) gives monoalkylated halonium ions and/or dialkylated dihalonium ions, depending on the reaction conditions.¹³ Ions prepared are summarized in Table 12. Iodine shows an unusual ability to stabilize positive charge, as demonstrated by the formation of dialkyl alkylene-diiodonium ions $RI^+(CH_2)_nI^+R$, $n = 1$ to 6, $R = CH_3, C_2H_5$. In the extreme case ($n = 1$) the two positive iodonium cation sites are separated by only a single methylene group. However, dialkyl alkylene-dibromonium ions were formed only when the two positive bromines were separated by three methylene groups. In the case of four methylene groups, rearrangement to the more stable five-membered-ring tetramethylenebromonium ion took place. Dialkyl alkylene-dichloronium ions have not yet been directly observed. Consequently, the ease of formation of dialkyl alkylene-dihalonium ions is similar to that of dialkylhalonium ions, that is, $>\dot{I} > >\dot{Br} > >\dot{Cl}$.

The pmr data of mono- and dihalonium ions, formed by alkylation of the corresponding dihaloalkanes under various conditions, are summarized in Table 13. Representative spectra are shown in Figure 4. It is interesting to note that the methyl protons ($-X^+CH_3$) and the methylene protons of ethyl groups ($-X^+CH_2-C$) in all these halonium ions show a deshielding order of $>\dot{Cl} > >\dot{Br} > >\dot{I}$, while the methyl protons of the same ethyl group show an opposite trend $>\dot{I} > >\dot{Br} > >\dot{Cl}$. The structure of dialkyl alkylene-dihalonium ions was also studied by carbon-13 nmr spectroscopy (Table 14).

TABLE 12

Alkylation of Dihaloalkanes with Methyl and Ethyl Fluoroantimonate

Dihaloalkane	Alkylating reagent, RF-SbF ₅ -SO ₂	Halonium ion formation	Remarks
CH ₂ Cl ₂	CH ₃ (excess)	CH ₃ Cl ⁺ CH ₂ Cl	
CH ₂ Br ₂	C ₂ H ₅ (excess)	CH ₃ CH ₂ Cl ⁺ CH ₂ Cl	
	CH ₃ (excess)	CH ₃ Br ⁺ CH ₂ Br	
	C ₂ H ₅ (excess)	CH ₃ CH ₂ Br ⁺ CH ₂ Br	
CH ₂ I ₂	CH ₃ (1 mole)	CH ₃ I ⁺ CH ₂ I	
	C ₂ H ₅ (1 mole)	CH ₃ CH ₂ I ⁺ CH ₂ I	
	CH ₃ (excess)	CH ₃ I ⁺ CH ₂ I ⁺ CH ₃	
	C ₂ H ₅ (excess)	CH ₃ CH ₂ I ⁺ CH ₂ I ⁺ CH ₂ CH ₃	
ClCH ₂ CH ₂ Cl	CH ₃ (excess)	CH ₃ Cl ⁺ CH ₃ and unidentified products	
BrCH ₂ CH ₂ Br	CH ₃ (excess)	CH ₃ Br ⁺ CH ₃ and unidentified products	
ICH ₂ CH ₂ I	CH ₃ (1 mole)	CH ₃ I ⁺ CH ₂ CH ₂ I	Forms as a precipitate; structure not yet confirmed
	C ₂ H ₅ (1 mole)	CH ₃ CH ₂ I ⁺ CH ₂ CH ₂ I	Forms as a precipitate; structure not yet confirmed
CH ₃ CHCl ₂	CH ₃ (excess)	CH ₃ I ⁺ CH ₂ CH ₂ I ⁺ CH ₃	
	C ₂ H ₅ (excess)	CH ₃ CH ₂ I ⁺ CH ₂ CH ₂ I ⁺ CH ₂ CH ₃	
	CH ₃ (excess)	CH ₃ Cl ⁺ CHCH ₃ Cl	Halogen exchanges to CH ₃ CHF ₂ + (CH ₃) ₂ C ⁺ at -30°
CH ₃ CHBr ₂	CH ₃ (excess)	CH ₃ CHF ₂ + CH ₃ Br ⁺ CH ₃	Halogen exchanges to CH ₃ CHF ₂ + (CH ₃) ₂ Br at -78°
ClCH ₂ CH ₂ CH ₂ Cl	CH ₃ (excess)	CH ₃ Cl ⁺ CH ₂ CH ₂ CH ₂ Cl	
	C ₂ H ₅ (excess)	CH ₃ CH ₂ Cl ⁺ CH ₂ CH ₂ CH ₂ Cl	
BrCH ₂ CH ₂ CH ₂ Cl	CH ₃ (excess)	CH ₃ Br ⁺ CH ₂ CH ₂ CH ₂ Cl	
	C ₂ H ₅ (excess)	CH ₃ CH ₂ Br ⁺ CH ₂ CH ₂ CH ₂ Cl	






Br(CH ₂) ₃ Br	CH ₃ (1 mole) C ₂ H ₅ (1 mole) CH ₃ (excess) C ₂ H ₅ (excess) CH ₃ (1 mole) C ₂ H ₅ (1 mole) CH ₃ (excess) C ₂ H ₅ (excess) CH ₃ (1 mole)	CH ₃ Br ⁺ (CH ₂) ₃ Br CH ₃ CH ₂ Br ⁺ (CH ₂) ₃ Br (CH ₃ Br ⁺ CH ₂) ₂ CH ₂ (CH ₃ CH ₂ Br ⁺ CH ₂) ₂ CH ₂ CH ₃ I ⁺ (CH ₂) ₃ I CH ₃ CH ₂ I ⁺ (CH ₂) ₃ I (CH ₃ I ⁺ CH ₂) ₂ CH ₂ (CH ₃ CH ₂ I ⁺ CH ₂) ₂ CH ₂ CH ₃ CHBr ⁺ CH ₂ Br ⁺ CH ₂ Br ⁺ CH ₂ Br ⁺ CH ₃	
I(CH ₂) ₃ I			
CH ₃ CHBrCH ₂ Br	CH ₃ (excess)	CH ₃ CHBr ⁺ CH ₂ Br ⁺ CH ₃	
CH ₃ CHClCH ₂ Cl	CH ₃ (excess)	CH ₃ CHCl ⁺ CH ₂ Cl ⁺ CH ₃ CH ₃	Rearranges to (CH ₃) ₂ Cl ⁺ and CH ₃ CHCH ₂ Cl ⁺ ⇌ CH ₃ CH ⁺ -CH ₂ ⇌ CH ₃ CH ₂ CHCl ⁺ at -10°
ClCH ₂ CHClCH ₂ CH ₂ CH ₃ or ClCH ₂ CH ₂ CHClCH ₃ or ClCH ₂ CH ₂ CH ₂ CH ₂ Cl	CH ₃ (excess)	 + (CH ₃) ₂ Cl ⁺	Initially formed halonium ions were not observed at -78°
BrCH ₂ CHBrCH ₂ CH ₃ or BrCH ₂ CH ₂ CHBrCH ₃ or BrCH ₂ CH ₂ CH ₂ CH ₂ Br	CH ₃ (excess)	 + (CH ₃) ₂ Br ⁺	Initially formed halonium ions were not observed at -78°
ICH ₂ CH ₂ CH ₂ CH ₂ I	CH ₃ (excess)	CH ₃ I ⁺ CH ₂ CH ₂ CH ₂ CH ₂ I ⁺ CH ₃	Rearranges to  and (CH ₃) ₂ I ⁺ at -40°
CH ₃ CHBrCHBrCH ₂ (meso and dl/)	CH ₃ (excess)	(CH ₃) ₂ Br ⁺ +  + 	Initially formed halonium ions were not observed at -78°
Br(CH ₂) ₅ Br	CH ₃ (excess)	CH ₃ Br ⁺ (CH ₂) ₅ Br ⁺ CH ₃	
I(CH ₂) ₅ I	CH ₃ (excess)	CH ₃ I ⁺ (CH ₂) ₅ I ⁺ CH ₃	
I(CH ₂) ₆ I	CH ₃ (excess)	CH ₃ I ⁺ (CH ₂) ₆ I ⁺ CH ₃	

TABLE 13

Pmr Parameters of Mono- and Dialkylated Dihaloalkanes^a

Ion	δ_{CH}	δ_{CH_2}	$\delta_{\text{CH}_2\text{X}}$	$\delta_{\text{CH}_2\text{X}}$	$\delta_{\text{XCH}_2}^+$	δ_{CH_3}	$\delta_{\text{XCH}_3}^+$
$\text{ClCH}_2\text{ClCH}_3$ $\text{ClCH}_2\text{ClCH}_2\text{CH}_3$				5.56 (s) 5.50 (s)	5.52 (q), $J = 7$	2.01 (t), $J = 7$	4.51 (s)
$\text{BrCH}_2\text{BrCH}_3$ $\text{BrCH}_2\text{BrCH}_2\text{CH}_3$				6.33 (s) 6.32 (s)	5.46 (q), $J = 7$	2.22 (t), $J = 7$	4.30 (s)
ICH_2ICH_3 $\text{ICH}_2\text{ICH}_2\text{CH}_3$				5.17 (s) 5.40 (s)	4.90 (q), $J = 7$	2.40 (t), $J = 7$	3.58 (s)
$(\text{CH}_3\text{I})_2\text{CH}_2$ $(\text{CH}_3\text{CH}_2\text{I})_2\text{CH}_2$				5.80 (s) 5.88 (s)	5.33 (q), $J = 7$	2.44 (t), $J = 7$	4.10 (s)
$(\text{CH}_3\text{ICH}_2)_2$ $(\text{CH}_3\text{CH}_2\text{ICH}_2)_2$				5.06 (s) 4.90 (s)	4.93 (q), $J = 7.5$	2.20 (t), $J = 7.5$ 2.17 (d), $J = 6$	4.00 (s) 4.50 (s)
$\text{CH}_3\text{CHClCH}_3$ $\text{Cl}(\text{CH}_2)_3\text{ClCH}_3$	6.23 (q), $J = 6$	2.90 (qu), $J = 5$ 2.74 (m)	4.00 (t), $J = 5$ 3.91 (t), $J = 6$	5.47 (t), $J = 5$ 5.3 (m) ^b	5.3 (m) ^b	2.00 (t), $J = 7$	4.52 (s)
$\text{Cl}(\text{CH}_2)_3\text{BrCH}_3$ $\text{Cl}(\text{CH}_2)_3\text{BrCH}_2\text{CH}_3$		2.70 (qu), $J = 5$ 2.83 (m)	3.84 (t), $J = 5$ 3.94 (t), $J = 6$	5.10 (t), $J = 5.5$ 5.2 (m) ^b	5.2 (m) ^b	2.20 (t), $J = 6.5$	4.08 (s)

$\text{Br}(\text{CH}_2)_3\overset{+}{\text{Br}}\text{CH}_3$	2.82 (qu), $J = 7$	3.70 (t), $J = 7$	5.20 (t), $J = 6$		4.10 (s)
$\text{Br}(\text{CH}_2)_3\overset{+}{\text{Br}}\text{CH}_2\text{CH}_3$	2.93 (m)	3.80 (t), $J = 7$	5.1 (m) ^b	2.17 (t), $J = 7$	
$\text{I}(\text{CH}_2)_3\overset{+}{\text{I}}\text{CH}_3$	2.70 (qu), $J = 7$	3.58 (t), $J = 7$	4.57 (t), $J = 7$		3.58 (s)
$\text{I}(\text{CH}_2)_3\overset{+}{\text{I}}\text{CH}_2\text{CH}_3$	2.90 (m)	3.92 (t), $J = 7$	4.7 (m) ^b	2.28 (t), $J = 7$	
$\text{CH}_2(\text{CH}_2)_2\overset{+}{\text{Br}}\text{CH}_3$	3.24 (qu), $J = 7$	5.03 (t), $J = 7$			4.26 (s)
$\text{CH}_2(\text{CH}_2)_2\overset{+}{\text{Br}}\text{CH}_2\text{CH}_3$	3.2 (m)	4.93 (t), $J = 7$	5.28 (q), $J = 7$	2.16 (t), $J = 7$	
$\text{CH}_2(\text{CH}_2)_2\overset{+}{\text{I}}\text{CH}_3$	3.2 (m)	4.60 (t), $J = 8$			3.80 (s)
$\text{CH}_2(\text{CH}_2)_2\overset{+}{\text{I}}\text{CH}_2\text{CH}_3$	3.2 (m)	4.60 (t), $J = 8$	4.83 (q), $J = 7$	2.30 (t), $J = 7$	

^aProton chemical shifts are referred to external capillary TMS. s, Singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet. *J* values are in hertz.

^bOverlapping multiplet.

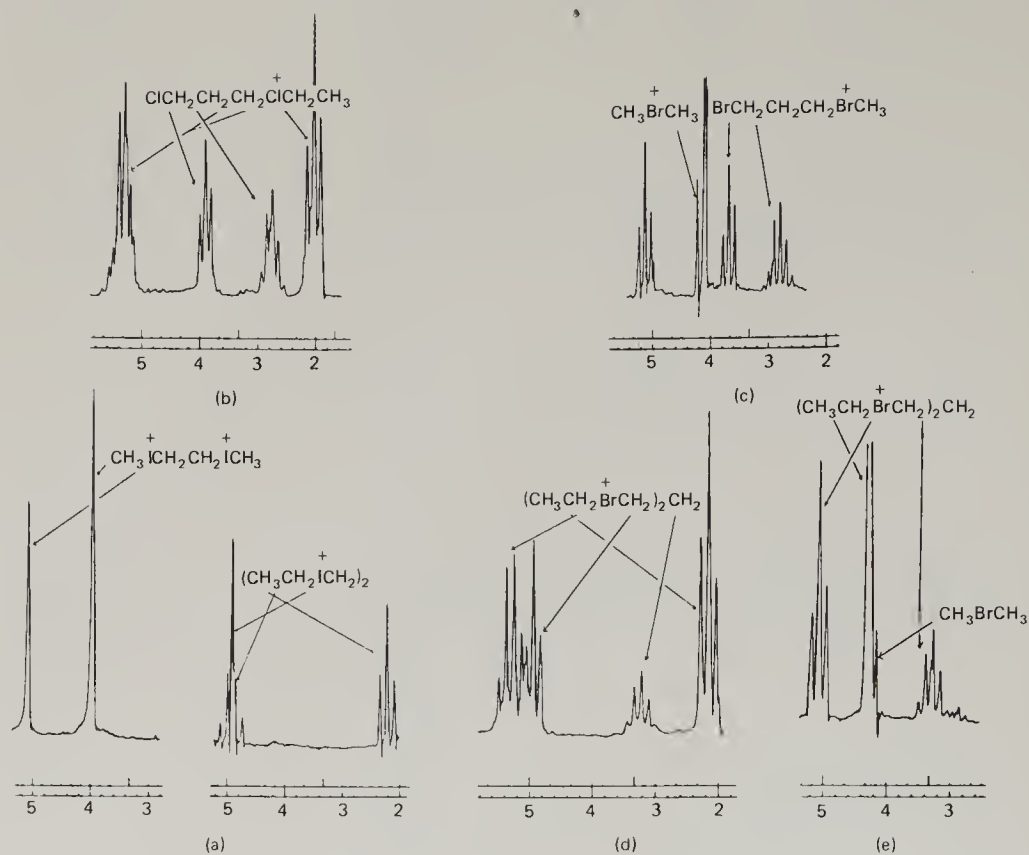


Figure 4. Pmr spectra of dialkyl alkylenedihalonium ions.

TABLE 14
Carbon-13 Nmr Data of Mono- and Dialkylated Diehaloalkanes^a

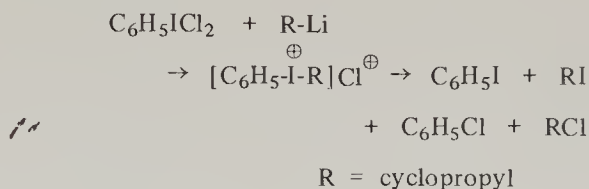
Ion	δ_{13C}			
	$CH_3\overset{+}{X}-$	$-CH_2\overset{+}{X}-$	$-CH_2C\overset{+}{X}-$	$-CH_2CC\overset{+}{X}-$
$CH_3\overset{+}{I}CH_2\overset{+}{I}CH_3$	19.9 (160)	0.2 (183)		
$CH_3\overset{+}{I}CH_2I$	17.2 (159)	-24.1 (180)		
$CH_3\overset{+}{I}(CH_2)_3\overset{+}{I}CH_3$	11.1 (159)	33.4 (158)	30.1 (136)	
$CH_3\overset{+}{I}(CH_2)_3I$	10.3 (158)	41.3 (158)	33.0 (131)	6.2 (153) ^c
CH_3BrCH_2Br	40.4 (162)	50.7 (190)		
$CH_3\overset{+}{Br}(CH_2)_3\overset{+}{Br}CH_3$	39.9 (162)	60.2 (164)	28.7 (136)	
$CH_3\overset{+}{Br}(CH_2)_3Br$	38.4 (163)	67.4 (163)	32.0 (133)	31.6 (155) ^d

^aSpectra were recorded on a Varian XL100FT spectrometer at -65° . The chemical shifts are referred to external TMS in SO_2 at -55° . J_{CH} values (in hertz) are given in parentheses.^bAssignments may be reversed.^cFor CH_2I .^dFor CH_2Br .

Alkylarylhalonium Ions

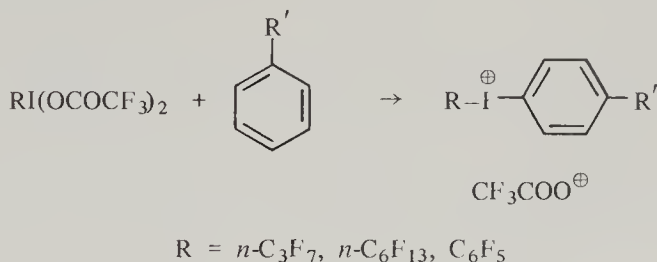
4.1 PREPARATION AND NMR STUDY

Dence and Roberts⁵¹ attempted to prepare the cyclopropylphenyliodonium ion from phenyliodoso chloride and cyclopropyllithium. However, they were unable to isolate the corresponding iodonium ion or any cyclopropylbenzene from



the reaction products. Thus the iodonium ion was not formed, even as an unstable reaction intermediate.

Perfluoroalkyliodoso trifluoroacetate reacts with aromatic compounds to give perfluoroalkylaryl iodonium ions⁵²



Anion-exchange reactions of these iodonium ions were carried out easily by using inorganic halides.

Alkylarylhalonium ions (other than perfluorinated derivatives) were first prepared by Olah and Melby.⁵³

When a SO_2 solution of iodobenzene was added to a SO_2 solution of the $\text{CH}_3\text{F-SbF}_5$ complex (methyl fluoroantimonate) at -78° , a clear slightly colored solution resulted. The pmr spectrum of this solution at -80° showed in addition to the excess methyl fluoroantimonate a methyl singlet at δ 3.80 and a multiplet aromatic region (7.7-8.3) with a peak area ratio of 3:5. The aromatic signals showed the same coupling pattern as that of iodobenzene in SO_2 but were deshielded by approximately 0.5 ppm. The fluorine-19 nmr spectrum of the solution showed only a very broad absorption centered at ϕ 112 (from CF_3CCl_3), which is characteristic of the SbF_6^- counterion. The species that

TABLE 15
Pmr Parameters of Alkylarylhalonium Ions^a

Ion	CH ₃ X ⁺ --	CH ₃	--CH ₂ --	CH ₃ CX ⁺	Aromatic	Fluorine-19 ^b
C ₆ H ₅ Br ⁺ CH ₃	4.45				7.5-7.9	
C ₆ H ₅ I ⁺ CH ₃	3.80				7.7-8.3	
4-FC ₆ H ₄ I ⁺ CH ₃	3.80				7.0-8.1	103.4
4-FC ₆ H ₄ Br ⁺ CH ₃	4.40				7.3-8.1	103.7
4-CH ₃ C ₆ H ₄ I ⁺ CH ₃	3.75	2.40			7.3-8.0	
4-CH ₃ C ₆ H ₄ --Br ⁺ CH ₃	4.35	2.40			7.4-7.9	
C ₆ H ₅ I ⁺ C ₂ H ₅			4.70	1.95	7.6-8.1	
4-FC ₆ H ₄ I ⁺ C ₂ H ₅			4.75	1.92	7.2-8.2	104.2
C ₆ H ₅ Br ⁺ C ₂ H ₅			5.30	1.90	7.7-8.2	
4-FC ₆ H ₄ Br ⁺ C ₂ H ₅			5.35	1.90	7.3-8.1	104.1

^aProton chemical shifts are from TMS in an external capillary tube. Spectra were recorded at -70° in SO₂ solution at 60 MHz. Relative peak areas were in agreement with expectation.

^bFluorine chemical shifts are from CF₃CCl₃ in an external capillary tube. The chemical shifts of 4-fluorobromobenzene and 4-fluoroiodobenzene in SO₂ solution are 114.8 and 113.9 ppm, respectively.

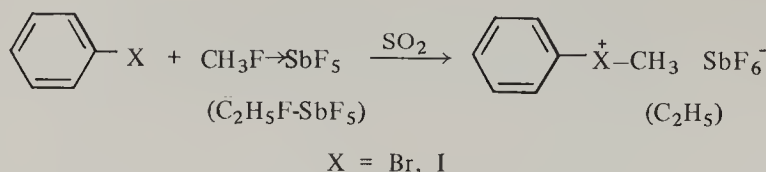
TABLE 16

Carbon-13 Chemical Shifts of Alkylarylhalonium Ions^a

Ion	R ₂	R ₃	R ₄	X	δ C-1	δ C-2	δ C-3	δ C-4	δ C-5	δ C-6	δ XCH ₃	δ CH ₃
C ₆ H ₅ Br ⁺ CH ₃	H	H	H	Br	127.6	134.6	132.7	135.5	132.7	134.6	50.0	
<i>o</i> -CH ₃ C ₆ H ₄ Br ⁺ CH ₃	CH ₃	H	H	Br	128.9	142.2	135.0 ^b	137.4 ^b	133.8 ^b	136.8 ^b	49.2	23.4
<i>m</i> -CH ₃ C ₆ H ₄ Br ⁺ CH ₃	H	CH ₃	H	Br	129.0	135.6	147.7	137.8	134.1	130.8	50.5	23.4
<i>p</i> -CH ₃ C ₆ H ₄ Br ⁺ CH ₃	H	H	CH ₃	Br	125.4	136.6	153.7	148.8	133.7	136.6	50.7	23.4
<i>o</i> -FC ₆ H ₄ Br ⁺ CH ₃	F	H	H	Br	112.0 (22)	164.9 (25.4)	120.6 (19)	158.7 (7)	134.4	129.6	50.8	
<i>m</i> -FC ₆ H ₄ Br ⁺ CH ₃	H	F	H	Br	125.8 (10)	120.4 (26)	164.1 (25.4)	123.4 (19)	135.8 (10)	129.0	50.9	
<i>p</i> -FC ₆ H ₄ Br ⁺ CH ₃	H	H	F	Br	124.0	135.6 (9)	122.0 (22)	166.8	122.0 (22)	135.6 (9)	51.1	
C ₆ H ₅ I ⁺ CH ₃	H	H	H	I	106.4	137.8	133.9	133.9	133.9	137.8	20.5	
<i>o</i> -CH ₃ C ₆ H ₄ I ⁺ CH ₃	CH ₃	H	H	I	112.7	144.4	134.7 ^b	136.1 ^c	131.8	140.0 ^c	19.3	27.8
<i>m</i> -CH ₃ C ₆ H ₄ I ⁺ CH ₃	H	CH ₃	H	I	106.7	138.5	145.4	135.3	133.9	136.1	20.3	23.0
<i>p</i> -CH ₃ C ₆ H ₄ I ⁺ CH ₃	H	H	CH ₃	I	102.8	138.2	135.1	146.8	135.1	138.2	20.3	23.0
<i>o</i> -C ₆ H ₄ I ⁺ CH ₃	F	H	H	I	92.1 (22)	166.6 (25.0)	119.2 (22)	138.7 (10)	129.6	139.4	20.9	
<i>m</i> -C ₆ H ₄ I ⁺ CH ₃	H	F	H	I	104.6 (10)	125.5 (26)	163.8 (25.0)	123.1 (19)	135.8 (10)	154.6	21.1	
<i>p</i> -C ₆ H ₄ I ⁺ CH ₃	H	H	F	I	99.8	141.2 (10)	121.9 (22)	166.7 (25.7)	121.9 (22)	141.2 (10)	21.1	
CH ₃ I ⁺ C ₆ H ₄ I ⁺ CH ₃	H	H	⁺ ICH ₃	I	110.7	141.5	141.5	110.7	141.5	141.5	20.9	

^aIn parts per million from TMS. Hexafluoroantimonate salts in SO₂ at -60°, unless otherwise indicated. *J*_{13C} and *F* values (in hertz) are given in parenthesis.^bAssignment tentative and would be reversed with respect to the ring positions.

accounts for the nmr data is the methylphenyliodonium ion ($\text{CH}_3\text{I}^+\text{C}_6\text{H}_5$). When bromobenzene and other aryl bromides or iodides were added in the same manner to methyl fluoroantimonate in SO_2 , analogous spectra were obtained, indicating the formation of the corresponding methylarylhalonium ions.



Likewise, the reaction of aryl bromides and iodides with ethyl fluoroantimonate in SO_2 gave the corresponding ethylarylhalonium ions. The structure of all alkylarylhalonium ions prepared was studied by nmr (hydrogen-1, carbon-13, and fluorine-19) spectroscopy. The proton and fluorine nmr data are summarized in Table 15. The proton chemical shifts of the methyl and ethyl protons are in good agreement with those of dialkylhalonium ions (Table 4). The aromatic protons are generally deshielded by approximately 0.5 ppm, corresponding to their halonium precursors. The fluorine chemical shifts of fluorinated alkylarylhalonium ions are slightly deshielded by ≈ 10 ppm from those of the corresponding precursors.

In order to study the trend of distribution of the positive charge and its delocalization into the aromatic ring, the Fourier-transform carbon-13 nmr shifts of a series of alkylarylhalonium ions (Table 16) were also determined.^{26d}

In monosubstituted benzenes the carbon shieldings of most interest are the C-1 (ipso) carbon shielding because it occurs over the widest range of shifts,

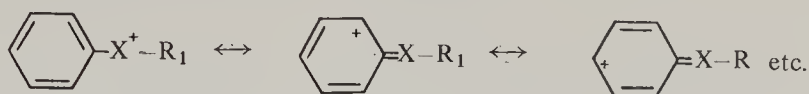
TABLE 17
Aryl Carbon Shieldings in Phenylmethylhalonium Ions ($\text{C}_6\text{H}_5\text{X}^+\text{CH}_3$)
and in Monosubstituted Benzenes ($\text{C}_6\text{H}_5\text{X}$)

X	δ_{C} (ppm) ^a			
	C-1	Ortho	Meta	Para
Br	123.4	132.1	131.0	127.8
$^+\text{BrCH}_3$	127.6	134.6	132.7	135.5
Δ	4.2	2.5	1.7	7.7
I	96.8	139.0	131.7	129.8
$^+\text{ICH}_3$	106.4	137.8	133.9	133.9
Δ	9.6	-1.2	2.2	4.1

^aReferred to TMS.

and the C-4 (para) carbon shielding because, apart from a few exceptions, it reflects the electron-withdrawing or electron-donating ability of the substituent. These shifts in bromo- and iodobenzene for the methylphenylbromonium and iodonium ions are shown in Table 17).

The data show that upon methylation of the ring halogen, the largest downfield shifts occur for the ipso and para carbons. This suggests the following resonance structures for alkylarylhalonium ions:



The charge delocalization into the ortho and para positions is reflected by the deshielding effect on these carbons (Table 17).

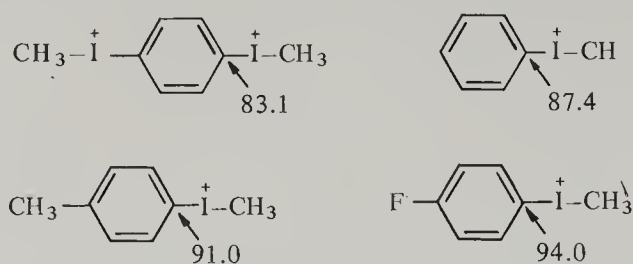
These changes are too large to be solvent effects alone, and suggest that the CH_3X^+ group is somewhat electron-withdrawing compared with X. The smaller change in the para-carbon shift for iodine reflects the lesser ability of its lone-pair electrons, compared with those of bromine, to interact with the π electrons of the benzene ring. The para-carbon shift change in both cases is smaller than that observed (10-15 ppm) on protonation of monosubstituted benzenes (e.g., benzoic acid, benzaldehyde, nitrobenzene) and shows the lesser ability of the halogen lone pairs to interact with the π electrons of the benzene ring.

Comparison of the relevant values in Table 16 and those of haloalkanes and -arenes shows that the α -substituent effects in alkyl and aryl halides are significantly different. This is true for many substituents other than halogens and most likely is attributable to the greater polarizability of the phenyl ring system. A similar difference, only larger, is observed for the α -carbon shifts of aryl- and alkylmethylhalonium ions ($\delta_{\text{C}_{\text{ipso}}}$ and δ_{CH_3}). The larger difference results from a much larger deshielding of the methyl resonance on methylation of methyl iodide (29.9 ppm for iodine and 27.3 ppm for bromine) than of the ipso-carbon resonance on methylation of aryl halides (6 ppm for iodine and 4.2 ppm for bromine).

The β -substituent effect is approximately the same for alkyl and aryl iodides (10-11 ppm) and is unaffected by methylation of the iodine atom. The situation is slightly different in bromobenzene, where this effect is 5.8 ppm, or about one-half that in alkyl bromides. Placing a positive charge on the bromine by methylation results slight in deshielding from aryl bromides and slight shielding from alkyl bromides.

The effect of individual substituents in many disubstituted benzenes appears to be additive, provided that substituents are meta or para to each other. This

is shown by the ipso-carbon shielding of $p\text{-CH}_3\text{I}^+$, $p\text{-CH}_3-$, and p -fluoromethylphenyliodonium ions, which increase to higher field in that order, in agreement with the observed para-substituent effects of CH_3I^+ , methyl, and fluorine (+5.1, -3.4, and -4.4 ppm, respectively). The same trend is found in para-substituted methylphenylbromonium ions.

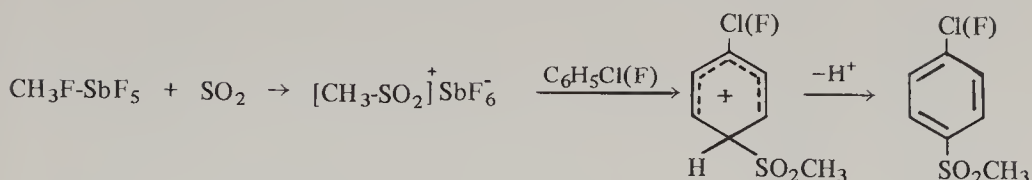


Consistent with the much smaller meta-substituent effects found in monosubstituted benzenes, the ipso-carbon shielding in meta-substituted methylphenylhalonium ions is almost constant. Trends similar to those mentioned above have been observed in m - and $p\text{-CH}_3$, fluorine-, and $\text{C}=\text{O}$ -substituted benzoyl cations.

It has been noted that methyl carbon shielding in substituted toluenes is essentially independent of the nature of the meta and para substituents, but that ortho substituents produce upfield shifts, except in the case of iodine. Data for CH_3I^+ and CH_3Br^+ substituents are consistent with these observations, since in the meta and para derivatives of toluene, δ_{CH_3} is 170.6 ± 0.3 ppm [δ_{CH_3} (toluene) = 172.6] and δ_{CH_3} in the $o\text{-CH}_3\text{I}^+$ derivative of toluene is 166.0. The methyl resonance in the corresponding ortho-bromo compound, unlike iodine, is essentially unchanged from that in the meta and para derivatives.

The shielding of a methyl group bonded directly to halogen in arylalkylhalonium ions is unaffected by meta or para ring substituents but is affected slightly by an ortho ring substituent. It is of interest that these methyl group shifts in methylarylhalonium ions are deshielded by 11-13 ppm from the corresponding signals in alkylmethylhalonium ions, implying that ArX^+ is more electronegative than CH_3X^+ , since this difference is too large to be accounted for by anisotropy contributions from the phenyl ring. Perhaps this may be regarded as additional evidence for charge delocalization into the phenyl ring, except that the deshielding is of the same magnitude for both iodine and bromine.

The reaction of chlorobenzene and fluorobenzene with methyl fluoroantimonate in SO_2 does not result in the formation of alkylarylhalonium ions, but instead ring-methylated and sulfonylmethylated products are found (the latter preferably in the para position). Methyl fluoroantimonate apparently also methylates SO_2 , forming an effective sulfonylating agent. When chlorobenzene



is added to methyl fluoroantimonate in SO_2ClF , sulfonylmethylation does not occur, while methylation occurs on the aromatic ring to give chlorotoluenes and chloroxylenes.

4.2 RELATIVE STABILITY, ALKYLATING ABILITY, AND ROLE IN FRIEDEL-CRAFTS REACTIONS

All the studied alkylarylhalonium ions are stable up to -20° . When a SO_2 solution of methylphenylbromonium ions is heated in a sealed tube to 0° , transformation readily occurs to give a mixture of bromoxylenes. The SO_2 solution of methylphenyliodonium ions is considerable more stable. However, after 15 hr at room temperature in a sealed tube, transformation to C-methylated products occurs. Transformation of ethylphenylbromonium ions occurs readily at -70° to give C-methylated products.¹²

Transformation of alkylarylhalonium ions (at higher temperatures) to the C-methylated products may play a role in Friedel-Crafts alkylation of halobenzenes. However, studies have shown that the transformation of alkylarylhalonium ions to C-alkylated haloaromatics is intermolecular rather than intramolecular.

Alkylarylhalonium ion were shown to be good general alkylating agents not only for π -donor aromatic systems, but also for n bases. They alkylate ethers, amines, and methyl halides to give the corresponding onium ions. The fact that alkylarylhalonium ions irreversibly react with methyl halides to give dimethylhalonium ions shows that methyl halides have a greater affinity for incipient methyl cations than halobenzenes.

4.3 DIALKYL PHENYLENEDIHALONIUM IONS

The alkylation of dihaloarenes with methyl and ethyl fluoroantimonate in SO_2 solution at low temperature was studied. Mono- or dihalonium ion formation takes place under various conditions, depending on the nature of the substrates as well as the alkylating reagents.¹³ Data are summarized in Table 18. The unusually strong donor ability of iodine leads to formation of three diiodonium ions from the corresponding isomeric diiodobenzenes (Figure 5). However, only *p*-dibromobenzene (of the three isomeric dibromobenzenes) was dialkylated to give a dibromonium ion with methyl fluoroantimonate in

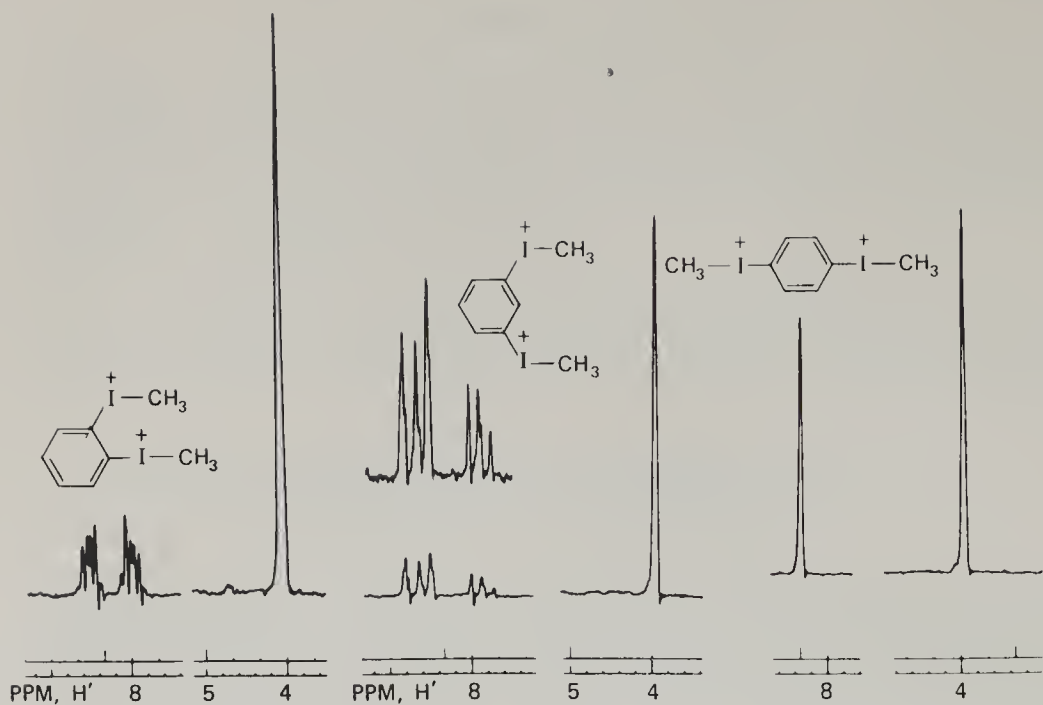


Figure 5. Pmr spectra of dimethylated *o*-diiodobenzene (left), *m*-diiodobenzene (middle), and *p*-diiodobenzene (right).

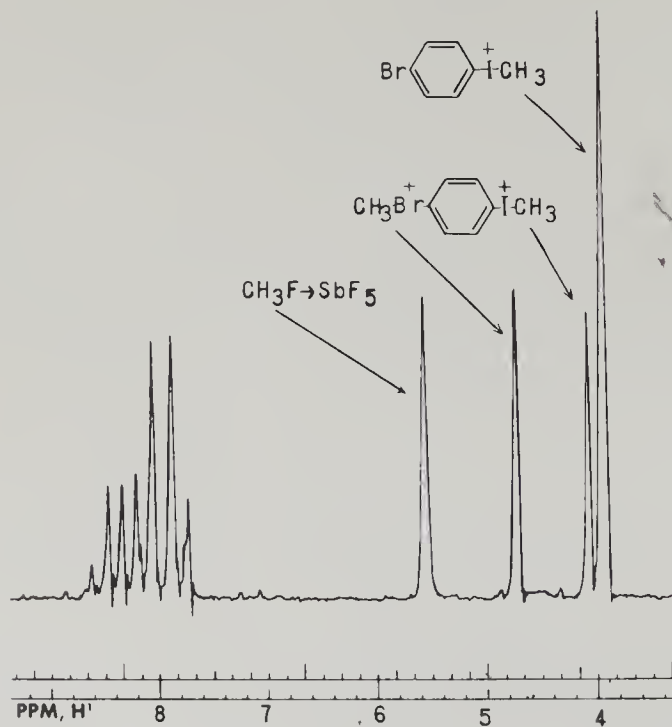


Figure 6. Pmr spectrum of mono- and dimethylated *p*-bromoiodobenzene.

TABLE 18

Alkylation of Di- and Trihaloarenes with Methyl and Ethyl Fluoroantimonate

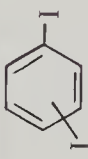
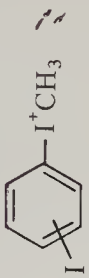
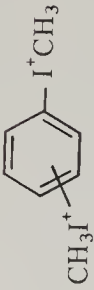
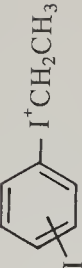
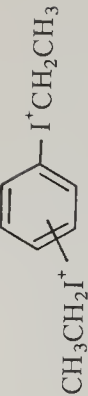
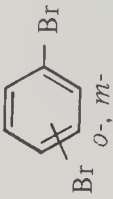
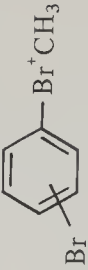
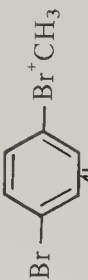
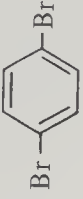
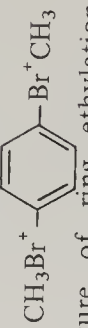
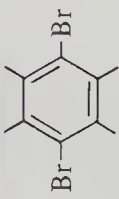
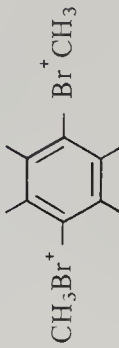
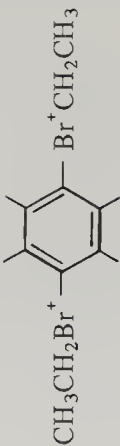
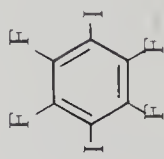
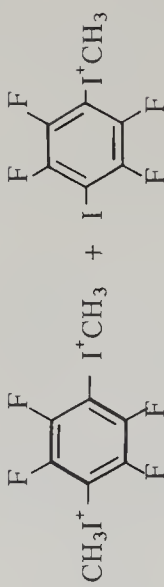
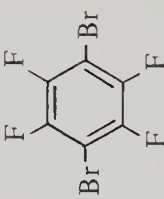
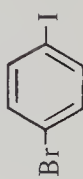
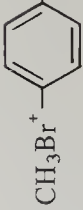
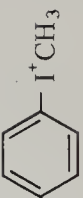
Di- and tri-haloarene	Alkylating reagent, RF-SbF ₅ -SO ₂	Halonium ion formed	Remarks
	CH ₃ F-SbF ₅ -SO ₂ (1 mole)		
<i>o</i> -, <i>m</i> -, <i>p</i> -	CH ₃ F-SbF ₅ -SO ₂ (excess)		
	C ₂ H ₅ F-SbF ₅ -SO ₂ (1 mole)		
	C ₂ H ₅ F-SbF ₅ -SO ₂ (excess)		
	CH ₃ F-SbF ₅ -SO ₂ (excess)		
<i>o</i> -, <i>m</i> -	CH ₃ F-SbF ₅ -SO ₂ (excess)		
	C ₂ H ₅ F-SbF ₅ -SO ₂ (excess)		
<i>o</i> -, <i>m</i> -, <i>p</i> -	C ₂ H ₅ F-SbF ₅ -SO ₂ (excess)	Mixture of ring ethylation products	Only monohalonium ion observed at -10°

TABLE 18 (continued)

Di- and tri-haloarene	Alkylating reagent, RF-SbF ₅ -SO ₂	Halonium ion formed	Remarks
	CH ₃ F-SbF ₅ -SO ₂ (excess)		
	C ₂ H ₅ F-SbF ₅ -SO ₂ (excess)		
	CH ₃ F-SbF ₅ -SO ₂ (excess)		
	C ₂ H ₅ F-SbF ₅ -SO ₂ (excess)		Halonium ions formed are not soluble enough to be identified
	CH ₃ F-SbF ₅ -SO ₂ (excess) or C ₂ H ₅ F-SbF ₅ -SO ₂ (excess)	No reaction	
	CH ₃ F-SbF ₅ -SO ₂ (excess)	 + 	

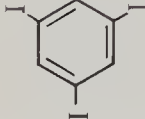
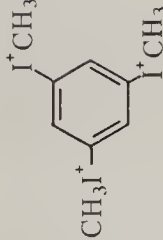
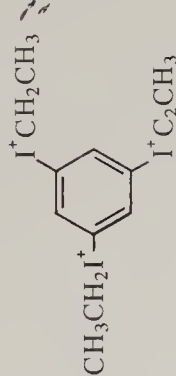
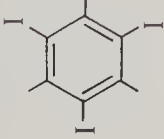
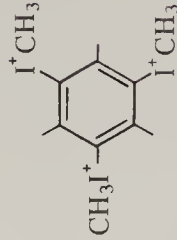
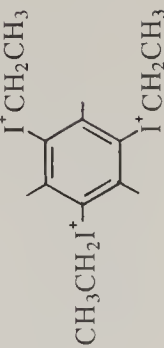
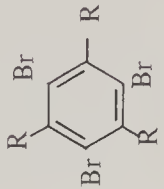
	$C_2H_5F-SbF_5-SO_2$ (excess)	Mixture of ring ethylation products		
	$CH_3F-SbF_5-SO_2$ (excess)			
	$C_2H_5F-SbF_5-SO_2$ (excess)			
	$CH_3F-SbF_5-SO_2$ (1 mole) or $C_2H_5F-SbF_5-SO_2$ (1 mole)	No reaction		1,3,5-Triiodobenzene does not dissolve in the alkylating reagents
	$CH_3F-SbF_5-SO_2ClF-SO_2$ (excess)			
	$CH_3CH_2F-SbF_5-SO_2$ (excess)			
	$CH_3F-SbF_5-SO_2$ (excess)	No reaction		1,3,5-Tribromoben- zene does not dis- solve in the alkyl- ating reagent
R = H, F, CH_3				

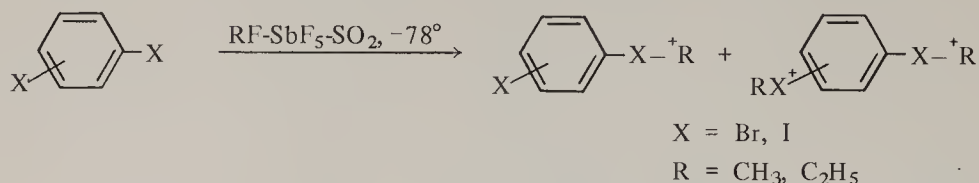
TABLE 19
Pmr Parameters of Mono-, Di-, and Trialkylated Halobenzenes^a

Ion	δ XCH ₃	δ CH ₃	δ CH ₃ CX	δ CH ₂ X	δ Aromatic
$o-(\text{CH}_3\text{I})_2\text{C}_6\text{H}_4$	4.10 (s)				8.0-8.8 (m)
$o-(\text{C}_2\text{H}_5\text{I})\text{C}_6\text{H}_4$			2.23 (t), $J = 7$	5.23 (q), $J = 7$	8.1-8.7 (m)
$m-(\text{CH}_3\text{I})_2\text{C}_6\text{H}_4$	3.97 (s)				7.7-8.9 (m)
$m-(\text{C}_2\text{H}_5\text{I})_2\text{C}_6\text{H}_4$			2.15 (t), $J = 7.5$	5.06 (q), $J = 7.5$	7.8-8.7 (m)
$p-(\text{CH}_3\text{I})_2\text{C}_6\text{H}_4$	3.95 (s)				8.35 (s)
$p-(\text{C}_2\text{H}_5\text{I})_2\text{C}_6\text{H}_4$			2.14 (t), $J = 7.5$	5.02 (q), $J = 7.5$	8.35 (s)
$o\text{-BrC}_6\text{H}_4\text{BrCH}_3$	4.55 (s)				7.6-8.3 (m)
$m\text{-BrC}_6\text{H}_4\text{BrCH}_3$	4.48 (s)				7.5-8.2 (m)
$p\text{-BrC}_6\text{H}_4\text{BrCH}_3$	4.53 (s)				7.95 (s)
$p-(\text{CH}_3\text{Br})_2\text{C}_6\text{H}_4$	4.56 (s)				8.38 (s)
$p\text{-CH}_3\text{Br})_2\text{C}_6(\text{CH}_3)_4$	4.40 (s)	2.85 (s)			
$p-(\text{C}_2\text{H}_5\text{Br})_2\text{C}_6(\text{CH}_3)_4$		2.80 (s)	2.05 (t), $J = 7$	5.30 (q), $J = 7$	

$p\text{-IC}_6\text{H}_4\text{ICH}_3^+$	4.20 (s)				7.7-8.2 (m)
$p\text{-(CH}_3\text{I)}_2\text{C}_6\text{F}_4^+$	4.31 (s)				7.7-8.2 (m)
$p\text{-BrC}_6\text{H}_4\text{ICH}_3^+$	3.90 (s)				8.2-8.7 (m)
$p\text{-CH}_3\text{BrC}_6\text{H}_4\text{ICH}_3^+$	4.05 (s)				
	4.65 (s)				
$1,3,5\text{-(CH}_3\text{I)}_3\text{C}_6\text{(CH}_3\text{)}_3^+$	4.00 (s)	3.65 (s)			
$1,3,5\text{(C}_2\text{H}_5\text{I)}_3\text{C}_6\text{(C}_2\text{H}_5\text{)}_3^+$		3.60 (s)	2.18 (t), $J = 7$	5.20 (q), $J = 7$	
$1,3,5\text{(CH}_3\text{I)}_3\text{C}_6\text{H}_3^+$					8.38 (s)
$1,3,5\text{(C}_2\text{H}_5\text{I)}_3\text{C}_6\text{H}_3^+$	4.00 (s)		2.12 (t), $J = 7$	5.02 (t), $J = 7$	8.30 (s)

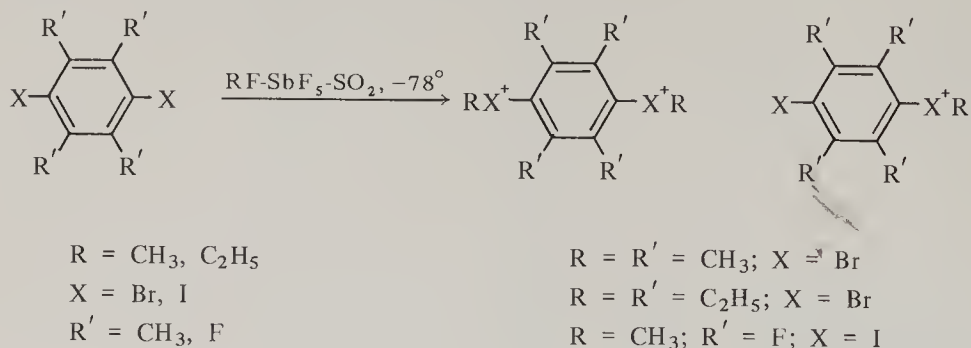
^aFrom TMS in external capillary tube. Spectra were recorded at -70° in SO_2 solution at 60 MHz. s, Singlet; t, triplet; q, quartet; m, multiplet.

SO₂ solution at -78° . *p*-Bromiodobenzene^{*} was both mono- and dimethylated under the same conditions (Figure 6). The structural proof of mono- and



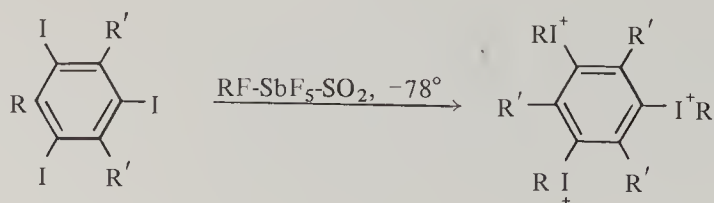
dialkylated halobenzenes as real dialkyl phenylenedihalonium ions was based on pmr studies (Table 19). Dichlorobenzenes, however, showed only ring alkylation with methyl and ethyl fluoroantimonates without giving observable mono- or dihalonium ions. Dialkyl phenylenedihalonium ions prepared at higher temperature decompose, again apparently by intermolecular processes, to give ring-alkylated haloarenes.

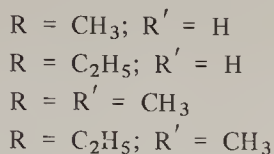
The substituents on the aromatic ring also affect the ease of formation of dihalonium ions. For example, 2,3,5,6-tetramethyldibromobenzene was dialkylated with methyl and ethyl fluoroantimonate in SO₂ solution at -78° , while 2,3,5,6-tetrafluorodibromobenzene was inert to the same alkylating reagents. In contrast, 2,3,5,6-tetrafluorodiiodobenzene was found to be dimethylated with excess methyl fluoroantimonate in SO₂ solution at -78° .



4.4 TRIALKYL PHENYLENETRIHALONIUM IONS

1,3,5-Triiodobenzene and 2,4,6-triiodomesitylene were trialkylated with excess methyl and ethyl fluoroantimonates in SO₂ (SO₂ClF) solution to the corresponding trihalonium ions.¹³ However, alkylation of 1,3,5-tribromobenzene, 2,4,6-





tribromomesitylene, and 1,3,5-tribromotrifluorobenzene under similar conditions failed, since the starting materials were insoluble in the alkylating reagents. A study of the alkylation of trihaloarenes with methyl and ethyl fluoroantimonates is summarized in Table 17. The structure of the trihalonium ions is in agreement with pmr and cmr data (Tables 18 and 19).

The unusual donor ability of iodine toward electrophiles is reflected in the formation of dihalonium ions, even in the case of diiodomethane and *o*-diiodobenzene. The formation of trimethyl phenylenetriiodonium ions further reveals the ability of iodine to accommodate positive charge. Dialkyl alkylene-dibromonium ions were formed only when dibromopropanes were treated with methyl (or 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. Dialkyl phenylenedichloronium ions have so far not been observed. These results reveal that the ease of halonium ion or dihalonium ion formation in alkylarylhalonium ions also decreases in the order $\text{I}^+ < \text{Br}^+ < \text{Cl}^+$.

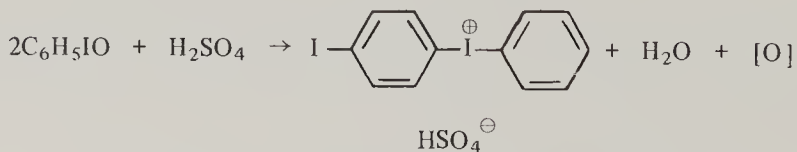
Diarylhalonium Ions

In contrast to dialkylhalonium ions and alkylarylhalonium ions, diarylhalonium ions are considerably more stable. This is particularly the case for diaryliodonium ions, which have been known for 80 years.¹ It is interesting, however, to compare the discovery and assumed significance of these ions with that of the related carbocations, that is, triarylcarenium ions (triarylmethyl cations). The latter were also discovered at about the turn of the century, but were considered only a specific class of organic cations limited exclusively to the highly stabilized triarylmethyl systems. The general significance of carbocations as intermediates in electrophilic reactions was not recognized until many years later, when it became evident that they are intermediates in all electrophilic organic reactions. Subsequently, methods were developed to prepare practically any conceivable type of carbocations under stable ion conditions. Halonium ions represent a somewhat similar case. Diaryliodonium (or to a lesser extent diarylbromonium and -chloronium ions) were at first considered a specific class of highly stabilized halonium ions. No relationship or significance was attached to these ions until many years later, when it was realized that many other types of halonium ions (such as dialkyl-, alkylaryl-, and alkylenehalonium ions) can exist, and the general significance of halonium ions in electrophilic halogenation reactions of organic compounds was pointed out.

5.1 DIARYLIODONIUM IONS

5.1.1 Preparation and Isolation

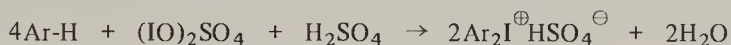
A variety of synthetic methods for diaryliodonium ions has been developed since Hartman and Meyer discovered them by preparing *p*-iododiphenyliodonium bisulfate salts from iodosobenzene in concentrated H_2SO_4 in 1894¹.



The synthetic methods for preparation of diaryliodonium ions can be divided into those for symmetric and unsymmetric diaryliodonium ions.¹¹

Symmetric Diaryliodonium Ions

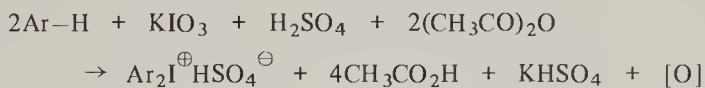
In concentrated H_2SO_4 diaryliodonium ions are obtained from iodyl sulfate, which is synthesized by decomposing iodic acid by heating in concentrated H_2SO_4 , and aromatic compounds in good yield.⁵⁴



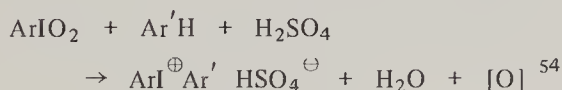
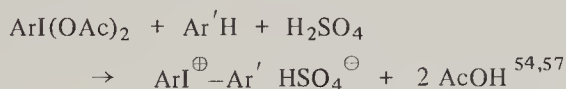
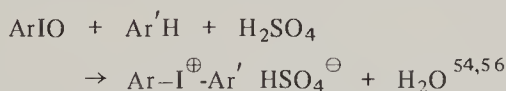
By using iodine(III) trifluoroacetate, prepared from iodine,⁵⁵ trifluoroacetic acid, and fuming nitric acid, diaryliodonium ions are obtained from aromatic compounds and trifluoroacetic acid in acetic anhydride. The yields are, however, generally not too high.



Aromatics react with alkali iodates in acetic acid-acetic anhydride- H_2SO_4 solution to give diaryliodonium ions.⁵⁴ This method is very useful for the isolation of soluble salts such as diaryliodonium chlorides, nitrates, and bisulfates.

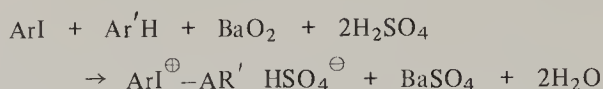
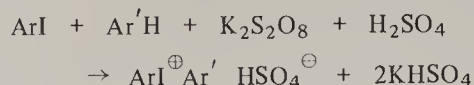
*Unsymmetric Diaryliodonium Ions*

The most convenient preparation involves the condensation of iodosoarenes or iodoxyarenes with aromatics in the presence of H_2SO_4 . In the case of an

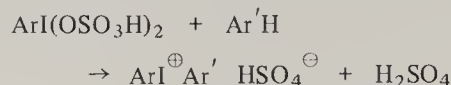
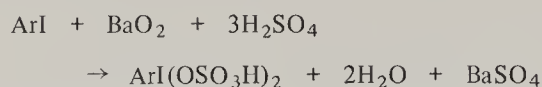
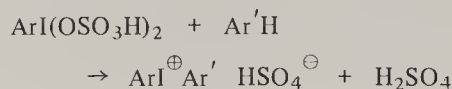
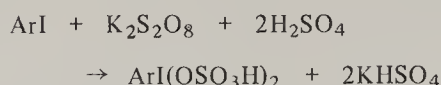


iodosoarene bearing an electron-withdrawing group, such as a nitro group, the reaction is carried out in H_2SO_4 to give diaryliodonium ions in good yield. In the case of electron-releasing groups, the reaction proceeds in acetic anhydride, giving good yield.

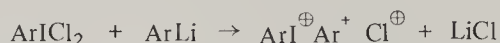
Iodoarenes can be reacted with arenes by *in situ* oxidation of the iodoarene to iodosoarenes which, without isolation, can be coupled to form diaryliodonium ions.^{54,58} Potassium persulfate and barium oxide are most useful as oxidants



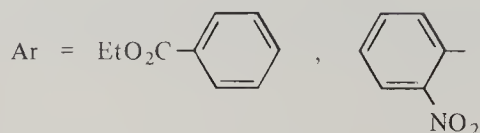
of iodoarenes. This method is suitable for iodoarenes bearing electron-withdrawing groups.

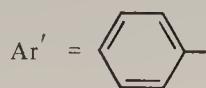


Aryllithium compounds react with arylidoso chloride at low temperatures to give diaryliodonium ions.⁵⁹ However, the yields are not good. Usually,

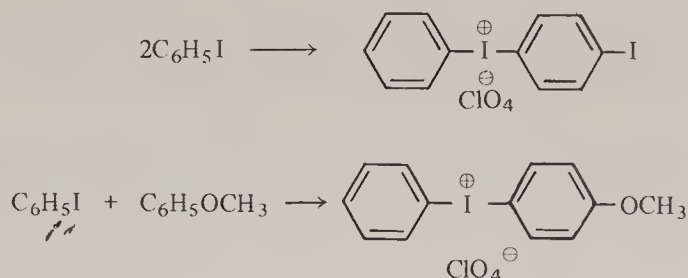


trivalent iodine compounds such as phenyliodoso chloride and iodosobenzene are used in the synthesis of diaryliodonium ions. However, Nesmeyanov et al.⁶⁰ have also reported the synthesis of diaryliodonium ions from aryldiazonium salts and iodoarenes. In this reaction aryl cations can be formed by decomposition of the aryldiazonium salt, which react with the iodoarene to give the corresponding diaryliodonium ions. Except for cyclic iodonium ions, however,

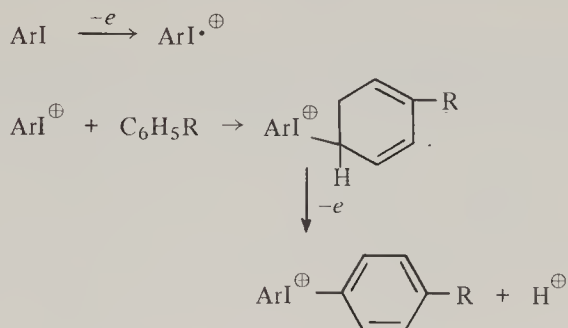




diaryliodonium ions have not been prepared from iodoarenes and aryl cations, formed via the decomposition of diazonium salts, in satisfactory yields. Interestingly, Miller and Hoffman⁶¹ have reported the electrochemical synthesis



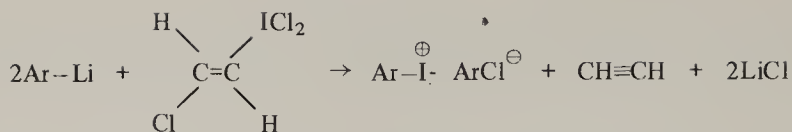
of diaryliodonium ions. The cation radical of iodobenzene is first formed and reacts with the aromatic compound to give the corresponding diaryliodonium



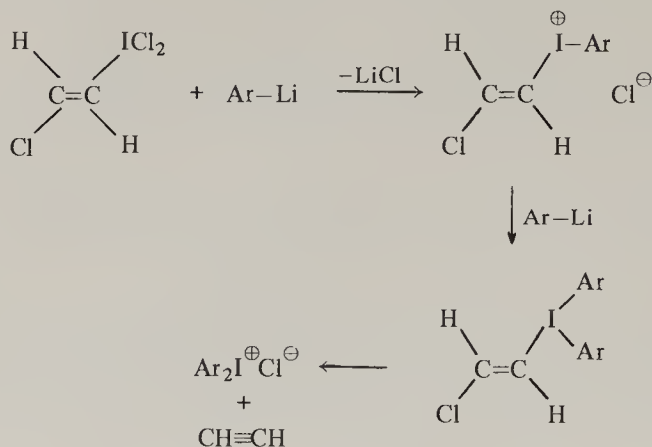
ion. Beringer et al.⁶² have reported the synthesis of diaryliodonium ions from aryllithiums and *trans*-chlorovinylidoso dichloride. Ions prepared are summarized in Table 20. Concerning the mechanism of the reaction they suggested

TABLE 20
Preparation of Diaryliodonium Ions from Aryllithiums
and *trans*-Chlorovinylidoso Dichloride

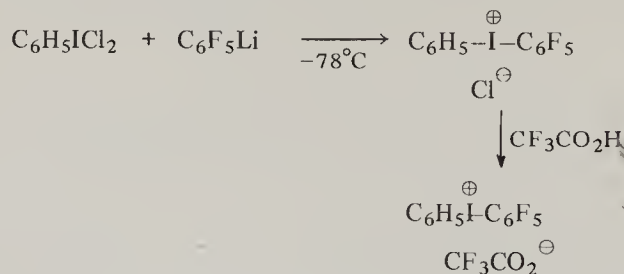
Diaryliodonium ion	Yield (%)
$\text{Ph}_2\text{I}^+\text{I}^-$	100
$(p\text{-Tolyl})_2\text{I}^+\text{I}^-$	73
$(2\text{-Naphtlyl})_2\text{I}^+\text{Cl}^-$	55
$(9\text{-Anthranyl})_2\text{I}^+\text{Cl}^-$	32
Dibenziodophenium Cl^-	39



the formation of diaryl-*trans*- β -chloroethenyliodine as the intermediate, which decomposes to give the corresponding diaryliodonium ion and acetylene.

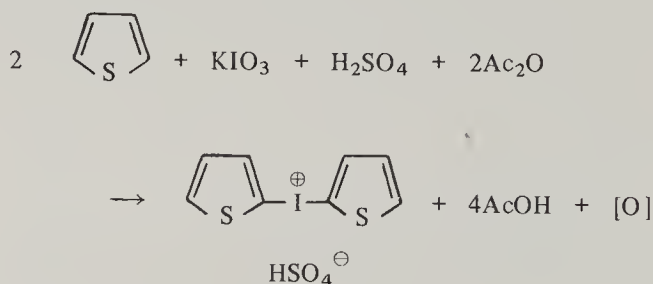


Phenylpentafluorophenyliodonium ions were prepared from phenyliodoso dichloride and pentafluorophenyllithium in good yield.⁶³

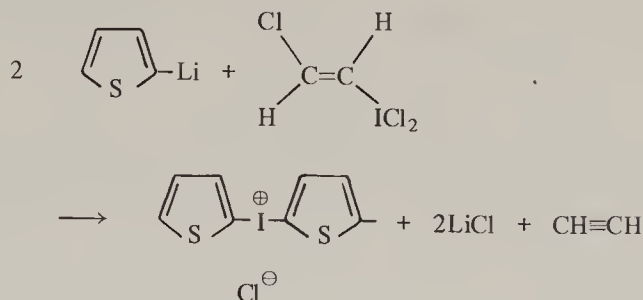


Heteroaryliodonium Ions

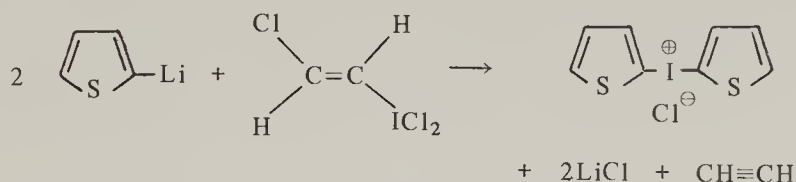
Beringer et al.⁵⁷ synthesized 2,2'-dithienyliodonium ions from thiophene and potassium iodate in acetic acid-acetic anhydride-concentrated H_2SO_4



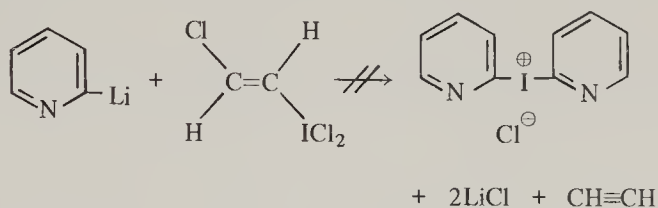
solution. Subsequently, they also synthesized these iodonium ions from 2-thienyl lithium and *trans*- β -chloroidosochloroethylene in good yield.⁶⁴



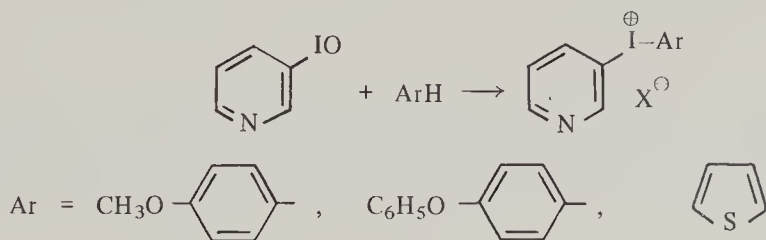
The 2,2'-difurfuryliodonium ion has also been synthesized from 2-furfuryl lithium and *trans*- β -chloroidosochloroethylene by the same method.



From 2-pyridyllithium and *trans*- β -chloroidosochloroethylene, the corresponding iodonium ion could not be obtained.



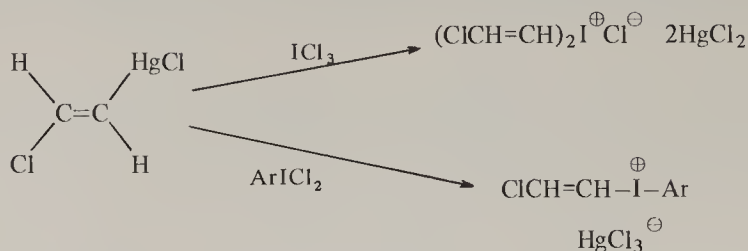
3-Iodosopyridine was allowed to react with an aryl compound to give 3-pyridylaryliodonium ions.⁶⁵



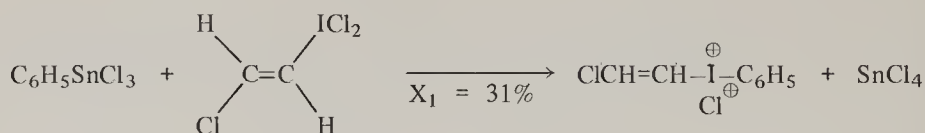
Iodonium Ions Bearing Olefinic or Acetylenic Ligands

trans-Chlorovinylmercuric chloride reacts with iodine trichloride to give the double salt of bis(*trans*-2-chlorovinyl)iodonium chloride in 6.0% yield, which is

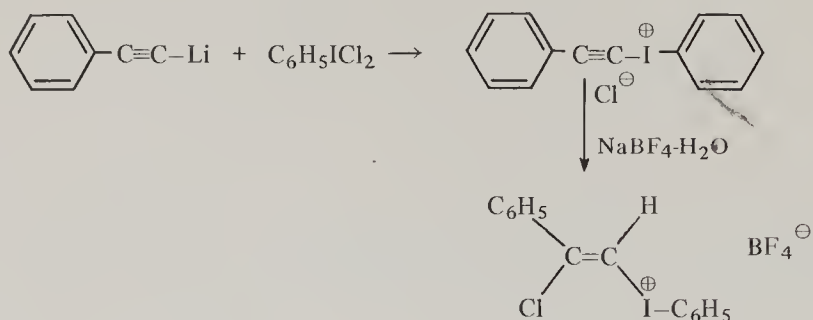
treated with hydrogen sulfide to give a free iodonium ion.⁶⁶ By treating



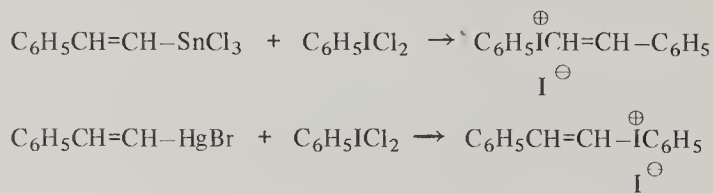
trans-chlorovinylmercuric chloride with ariylodose chloride, ariyl(*trans*-chlorovinyl)iodonium ion was formed in 31% yield,⁶⁷ which eliminated acetylene on treatment with alkali solution. This iodonium ion was synthesized also in the reaction of *trans*- β -chloriodosochloroethylene with phenyltin trichloride.

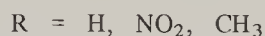


Phenylethynyllithium reacts with phenyliodoso chloride to give phenylethynyl, phenyliodonium chloride which is treated with sodium fluoroborate to give the β,β -phenylchlorovinyl, phenyliodonium ion.⁶⁸ Nesmeyanov et al.⁶⁹ have report-



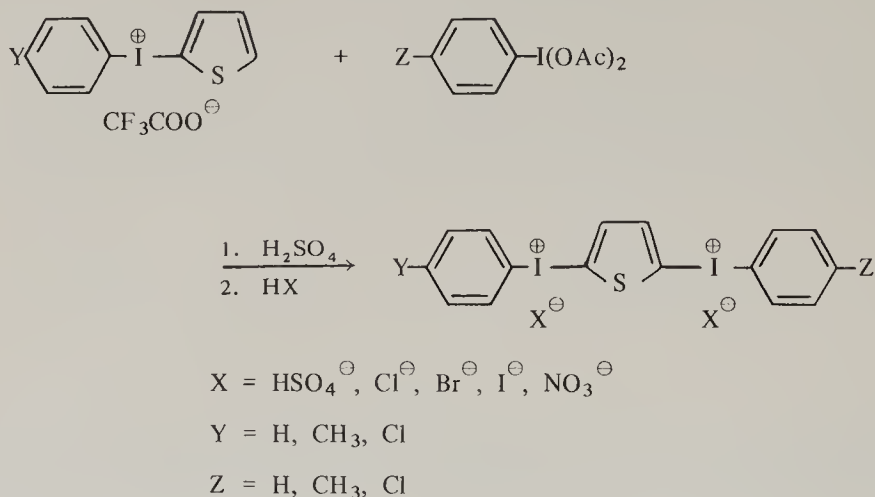
ed the synthesis of the iodonium ion bearing a β -styryl group as a ligand from β -phenylvinyltin trichloride or β -phenylvinylmercuric bromide and phenyliodoso chloride, although in very low yield. The reactivity of the vinyl groups to



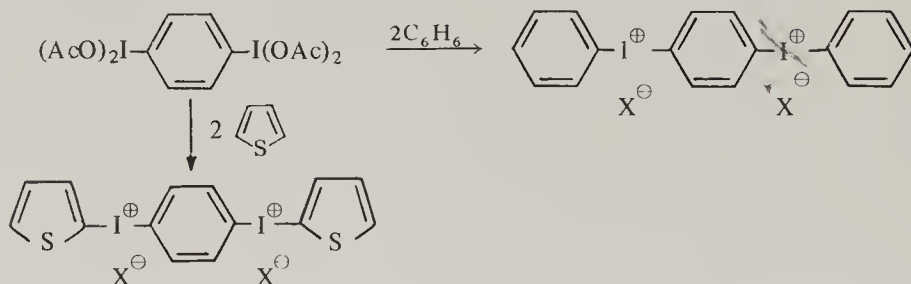
$$\text{CH}_2=\text{CH}-\overset{\oplus}{\underset{\text{X}}{\text{I}}}-\text{C}_6\text{H}_5 \rightarrow \text{CH}_2=\text{CH}-\text{X} + \text{C}_6\text{H}_5\text{I}$$
$$\begin{array}{c} \text{X} \\ | \\ \text{C}_6\text{H}_4 - \text{I}^+ \\ | \\ \text{C}_6\text{H}_4 - \text{O}^- \end{array} + \text{HX} \longrightarrow \begin{array}{c} \text{X} \\ | \\ \text{C}_6\text{H}_4 - \text{I}^+ \text{X}^- \\ | \\ \text{C}_6\text{H}_4 - \text{OH} \end{array}$$

$$\text{Ph}_3\text{P}=\text{CHCOR} + \text{C}_6\text{H}_5\text{I}(\text{OAc})_2 \xrightarrow{\text{HBF}_4} \text{Ph}_3\text{P} = \begin{array}{c} \text{C}-\text{COR} \\ | \\ \text{I}^{\oplus} \text{BF}_4^{\ominus} \\ | \\ \text{C}_6\text{H}_5 \end{array} \leftrightarrow \text{Ph}_3\text{P}^{\oplus} - \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C}-\text{R} \\ | \quad | \\ \text{I}^{\oplus} \text{BF}_4^{\ominus} \\ | \\ \text{C}_6\text{H}_5 \end{array} \quad \text{R} = \text{OEt, Ph}$$
$$\text{Ph}-\overset{\oplus}{\text{I}}-\overset{\text{CO}_2\text{Et}}{\underset{\text{BF}_4^{\ominus} \quad \text{PPh}_3^{\oplus}}{\text{C}}} + \text{HBr} \xrightarrow{-\text{Ph}} \text{Ph}_3\text{P}^{\oplus}-\overset{\text{Br}}{\underset{\text{CO}_2\text{Et}}{\text{CH}}}-\text{BF}_4^{\ominus}$$
$$\text{PhI}^{\oplus}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{CPh} \\ \text{PPh}_3 \end{array} + \text{HCl} \xrightarrow{-\text{PhI}} \text{Ph}_3\text{P} = \text{C} \begin{array}{l} \text{Cl} \\ \text{COPh} \end{array} + \text{HBF}_4$$

Di- and Polyiodonium Ions

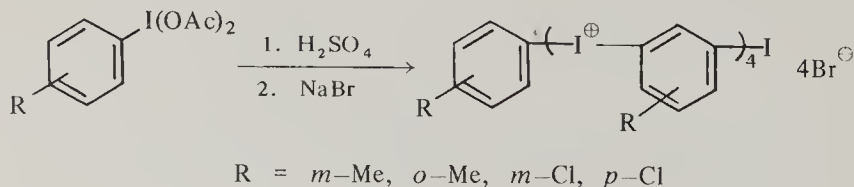
The first synthesis of a diiodonium ion was that of the 2,5-thiophenediyl-bis(phenyliodonium) ion prepared from phenyl-2-thienyliodonium ions and arylidoso acetate by Jezic.⁷³ This reaction has been proposed to be an electrophilic substitution reaction of arylidoso acetate at the 4-position of the thienyl group of the iodonium ion.



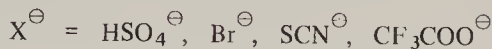
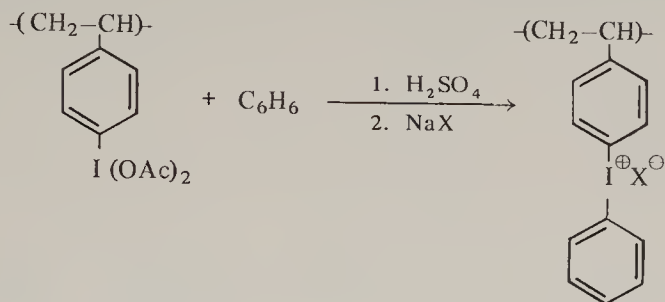
p-Phenylenediidoso acetate reacts with benzene or thiophene to give the corresponding bisiodonium ions.⁷⁴



Substituted phenyliidoso acetates were treated in concentrated H_2SO_4 to give tetraiodonium ions in a self-condensation reaction of arylidoso acetate.⁷⁴ These polyiodonium ions contain the cationic iodine in the

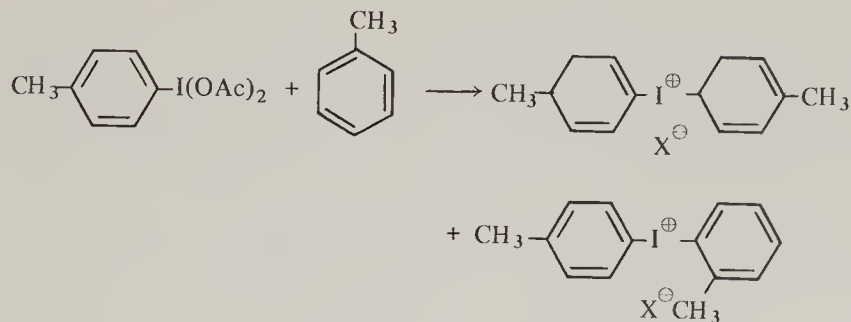


main chain. Yamada and Okawava⁷⁵ synthesized a polyiodonium ion from polystyryliodoso acetate and benzene containing the cationic iodine in the side chain.



5.1.2 Kinetics of Formation

In the reaction of substituted phenyliodoso acetate with toluene, the reaction is first-order in both components under pseudo-first-order conditions.⁷⁶ H_2SO_4 has a very marked catalytic effect (a 30-fold change in acid concentration corresponds to a 5000-fold change in rate). The products are about 90%



para isomer and 10% ortho isomer. Meta isomers are generally not formed. LeCount et al.⁷⁷ have also reported studies of the isomer distributions.

5.1.3 Structural Aspects

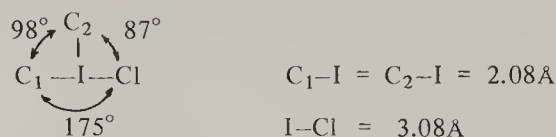
Diaryliodonium halides are generally ionic substances; the interaction between cationic iodine and the counteranions depends on the nature of the counteranions. Depending on the counterion, not only ionic, but also covalent character can be involved, such as in diaryliodonium chlorides.

X-Ray Studies

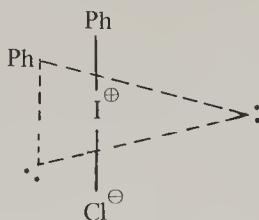
Medin⁷⁸ first showed by X-ray studies that in diphenyliodonium iodide the distance between the two iodine atoms is incompatible with a covalent link,

and that the compound is a true iodonium salt.

Khotsyanova studied the crystal structure of diphenyliodonium chloride.⁷⁹ The molecule is T-shaped, containing a linear C-I_{Ar}-I-Cl group perpendicular to the other C-2_{Ar}-I group as shown. If the two nonbonded pairs of electrons



on iodine are taken into account, the molecule should have a trigonal bipyramidal structure.



Ir Spectra

Many substituted diphenyliodonium ions were investigated by ir spectroscopy. In the case of diphenyliodonium iodide, the following major absorptions were found.⁸⁰ (The corresponding data for iodobenzene are shown in paren-

C-C stretching	1563 cm ⁻¹ (1473 cm ⁻¹)
Ring breathing	992 cm ⁻¹ (987 cm ⁻¹)
Out-of-plane C-H	742 cm ⁻¹ 736 cm ⁻¹

thesis.) Arshad et al.⁸¹ concluded the presence of interaction of the non-bonded pairs of electrons with the ring π electrons from the appearance of the weak absorption at 1590 cm⁻¹.

Uv Spectra

The uv spectra of a series of substituted diphenyliodonium ion have been studied⁸² (Table 21). The wavelength of B bands shifts to the longer wavelength when the substituent group is changed to a strongly electron-withdrawing group. However, in the meta isomer such a shift is not observed. This indicates the presence of $p\pi-d\pi$ resonance between the phenyl ring and the cationic iodine center as shown. In the uv spectra of diaryliodonium iodide in ethanol,

TABLE 21
Uv Absorption Maxima of Diphenyliodonium Ions

Iodonium ion	Wavelength (nm) ^a	
	A band	B band
$\left(\text{C}_6\text{H}_5-\text{I}^+ \right)$	207 (3.86)	226 (4.12)
$\text{C}_6\text{H}_5-\text{I}^+-\text{C}_6\text{H}_5$	209 (4.23)	226 (4.19)
$\text{C}_6\text{H}_5-\text{I}^+-\text{C}_6\text{H}_4\text{OCH}_3$	210 (4.28)	245 (4.16)
$\text{C}_6\text{H}_5-\text{I}^+-\text{C}_6\text{H}_4\text{OH}$	211 (4.32)	246 (4.12)
$\text{C}_6\text{H}_5-\text{I}^+-\text{C}_6\text{H}_4\text{NH}_2$	211 (3.79)	285 (4.03)
$\text{C}_6\text{H}_5-\text{I}^+-\text{C}_6\text{H}_4\text{O}^-$	222 (4.19)	292 (4.21)
$\text{C}_6\text{H}_5-\text{I}^+-\text{C}_6\text{H}_3(\text{OCH}_3)_2$	210 (4.39)	218 (4.38)

^aLog ϵ is given in parentheses.



a shoulder absorption appears at 300-350 nm.⁸³ In methylene chloride, however, a new absorption maximum appears at 340-360 nm, which undergoes a bathochromic shift in passing to solvents with lesser polarity, along with increasing intensity of the band. Thus the iodide anions form a charge transfer complex with diaryliodonium ions. When the counteranion is tetrafluoroborate, chloride, or bromide, this is not observed.

Nmr Spectra

Based on pmr data for diphenyliodonium ions (Table 22), the π -resonance interaction between the $5d$ orbital of iodine and the phenyl ring has been

TABLE 22
Proton Nmr Shifts of Diphenyliodonium Ion Salts

Solvent	Anion	Aromatic proton		
		δ Ortho	δ Meta	δ Para
CH ₂ Cl ₂	Cl ⁻	7.99	7.35	7.51
	NO ₃ ⁻	7.97	7.42	7.58
	AcO ⁻	7.91	7.33	7.48
CH ₃ OH	Cl ⁻	8.16	7.48	7.64
	NO ₃ ⁻	8.16	7.48	7.66
	AcO ⁻	8.15	7.48	7.66
D ₂ O	Cl ⁻	8.04	7.40	7.58
	NO ₃ ⁻	8.03	7.41	7.57
	AcO ⁻	8.06	7.42	7.58
Average shift difference		-0.63 ± 0.05 -0.16 ± 0.02		

discussed.⁸⁴ The differences between the ortho, para, and meta protons depend not only on the inductive effect of the positive iodine center, but also on the $d\pi$ - $p\pi$ resonance between the cationic iodine and the phenyl rings. Petrosyan et al.⁸⁵ have also discussed the interaction between the diphenyliodonium ions and counteranions, based on nmr data (Table 23). In the case of the tetra-

TABLE 23
Proton Chemical Shifts of Diphenyliodonium Ion Salts in Dimethyl Sulfoxide

Counteranion	δ Ring protons (δ) ^a		
	Ortho	Meta	Para
BF ₄ ⁻	8.37 (8.17)	7.63	(7.62)
I ⁻	8.30	7.62	
Br ⁻	8.27	7.59	
Cl ⁻	8.22 (8.17)	7.51	(7.62)
CH ₃ COO ⁻	8.17 (8.16)	7.53	(7.61)

^aValues obtained in methanol are given in parentheses.

fluoroborate anion, the iodonium ion is quite free. However, in the case of other more nucleophilic counteranions, increasing interaction is present between

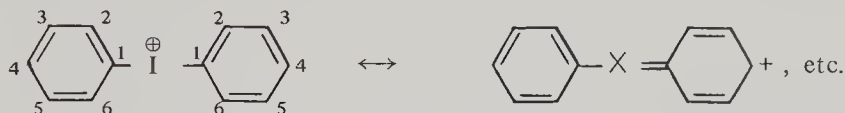
the iodonium ion and its counteranion. In methanol, the chemical shifts show no variation and are all similar to those of the BF_4^- salts. They suggest that no significant interaction between iodonium ions and counteranions exists in this solvent.

Nesmeyanov et al.⁸⁶ have calculated from the nmr data the effective charge at the para-carbon atom in onium compounds relative to their neutral molecular analogs (Table 24).

TABLE 24
Effective Charge at Para Carbons of Phenyl-Substituted Onium Ions
Relative to Their Neutral Analogs

$\text{C}_6\text{H}_5\text{X}^+\text{C}_6\text{H}_5\text{BF}_4^-$				$(\text{C}_6\text{H}_5)_3\text{X}^+\text{BF}_4^-$		
X	I^+	Br^+	Cl^+	S^+	O^+	C^+
Charge	0.027	0.047	0.063	0.053	0.086	0.106

Olah et al.⁸⁷ studied the carbon-13 spectra of diphenyliodonium and -bromonium ions in SO_2 solution at -40° (Table 25). Charge delocalization into the phenyl rings indicates the contribution of resonance forms of a quinoidal structure.



X = I, Br

TABLE 25
Carbon-13 Chemical Shifts of Diarylhalonium Ions^a

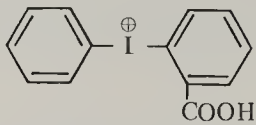
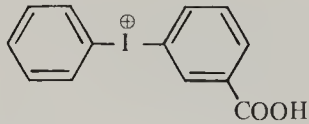
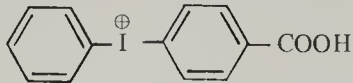
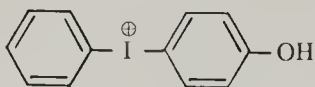
X^+	C-1	C-2	C-3	C-4	C-5	C-6
Br^+	133.3	131.1	134.4	135.0	134.4	141.1
I^+	111.1	131.5	128.7	129.2	128.7	131.5

^aIn parts per million from TMS.

Substituent Effect of the Phenyliodonio Group

Beringer et al.⁸⁸ determined the acidity of various benzoic acids and phenols bearing a phenyliodonio group (Table 26). The phenyliodonio benzoic acids ($\text{C}_6\text{H}_5\text{I}^+\text{C}_6\text{H}_4\text{COOH}$) are stronger acids than 4-nitrobenzoic acid ($\text{p}K_a = 5.83$ in $\text{CH}_3\text{CN-H}_2\text{O}$) (15:1). This is based on the electrostatic effect of the phenyliodonio group.

TABLE 26
 pK_a Values of Acidic Diaryliodonium Ions

Acid	Apparent ionization constant, pK_a^a
	3.5 ^b (6.24)
	5.55 ^b (6.45)
	4.60 ^b (6.47)
	8.33 ^c (9.66)

^aValues for the corresponding iodide compound are given in parentheses.

^bIn $\text{CH}_3\text{CN-H}_2\text{O}$ (15:1).

^cIn $\text{EtOH-H}_2\text{O}$ (3:7).

Degree of Dissociation

From conductivity data of diphenyliodonium salts at 5° in methanol and water, the degree of dissociation was calculated⁸⁹ (Table 27). In both water and methanol the degree of dissociation of diphenyliodonium fluoroborate is higher than that of other iodonium salts.

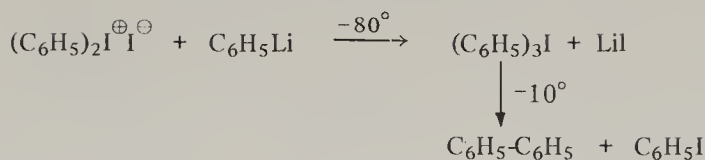
TABLE 27
Degree of Dissociation of Diphenyliodonium Salts

Solvent	Counterion			
	BF_4^-	Cl^-	Br^-	OAc^-
H_2O	97.8	90.8	88.2	86.3
CH_3OH	98.4	89.2	85.2	80.9

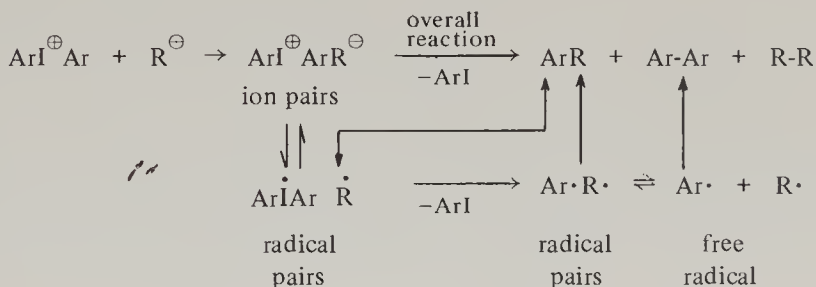
5.1.4 Chemical Reactivity

Reactions with Anionic Reagents

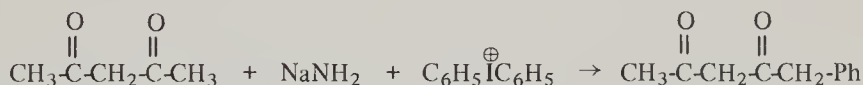
Diphenyliodonium iodide reacts with phenyllithium at -80° to give triphenyliodine which decomposes at -10° to biphenyl and iodobenzene.⁹⁰ The phenyla-



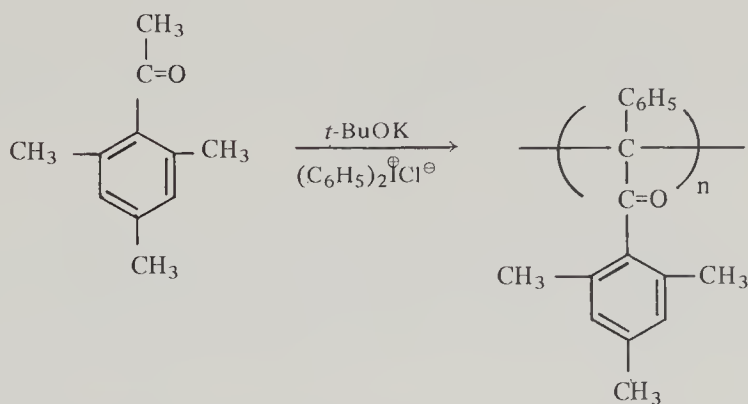
tion of β -diketones, such as dimedone, and malonic esters by diphenyliodonium ion was studied.⁹¹ It has been demonstrated, on the basis of products, that the reaction proceeds by a radical mechanism. Hauser et al.⁹² have reported



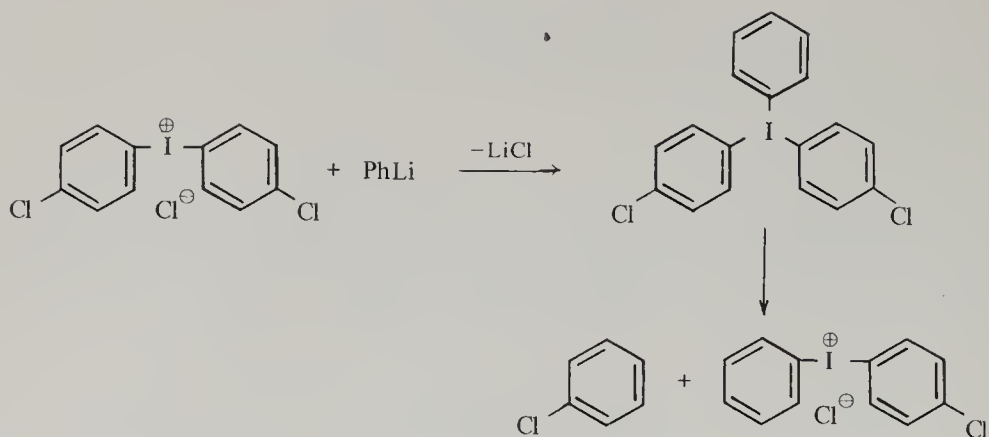
many examples of the phenylation of active methylene groups by using diphenyliodonium ions. However, in an attempted phenylation of 2,4,6-



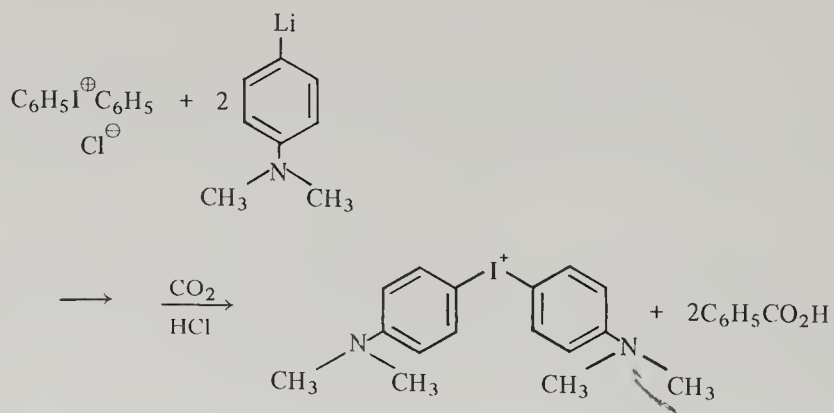
trimethylacetophenone, no phenylated product was obtained; only polymer formation took place.⁹³



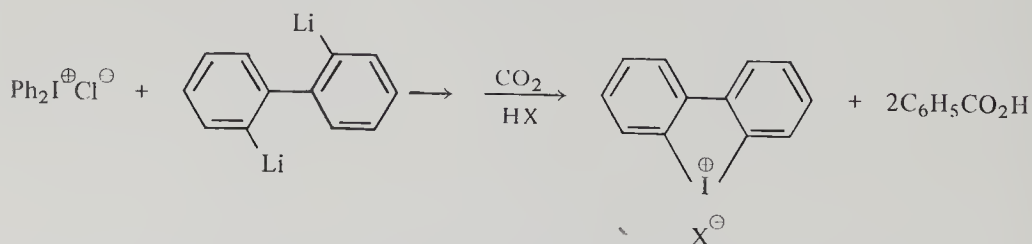
4,4'-Dichlorodiphenyliodonium chloride reacts with phenyllithium to give bis(4-chlorophenyl)phenyliodine which on cleavage with hydrogen chloride gives chlorobenzene and phenyl,*p*-chlorophenyliodonium chloride.⁹⁴



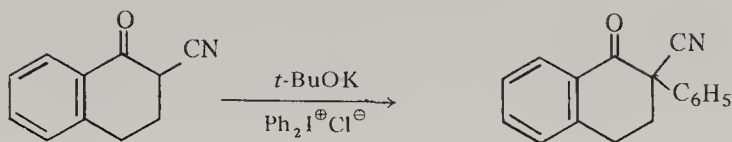
In the reaction of diphenyliodonium chloride with an excess of 4-dimethylaminophenyllithium, 4,4'-bis(dimethylamino)diphenyliodonium chloride was obtained (formed in a ligand exchange reaction). Diphenyliodonium chloride,



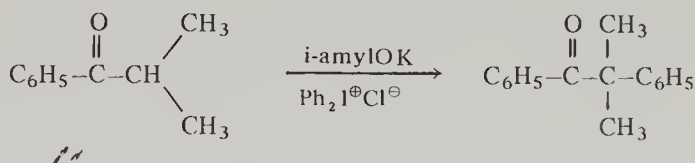
when treated with 2,2'-dilithiobiphenyl, gave after carbonation and acidification dibenziodophenium ion and benzoic acid.



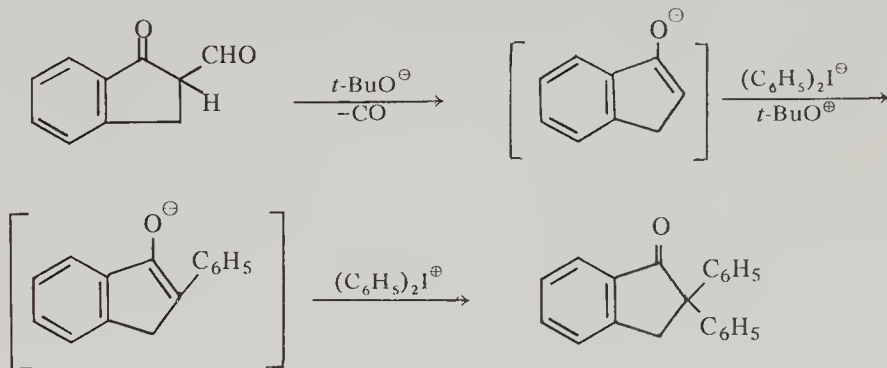
Active methylene groups are easily phenylated to give the corresponding phenyl compounds.⁹³



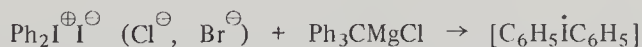
In the reaction of isopropyl phenyl ketone with diphenyliodonium ion, on treatment with potassium isoamyloxide, the phenylated compound was obtained



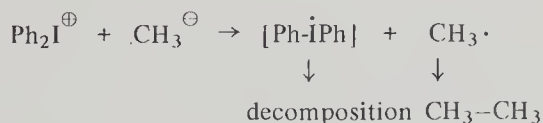
in 57% yield. In the phenylation of 2-formyl-1-indanone, decarbonylation occurs and the diphenylated product is obtained in 74% yield.



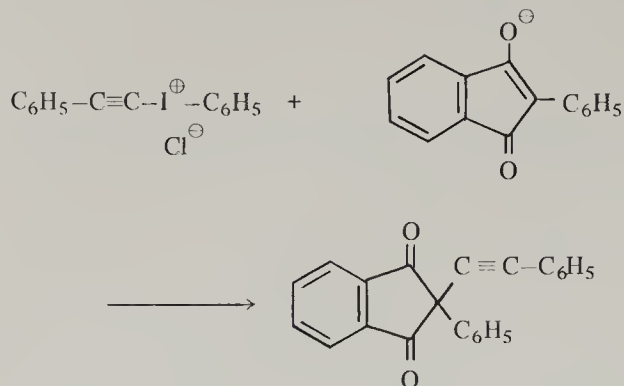
Diphenyliodonium ions react with tritylmagnesium chloride in tetrahydrofuran to give diphenyliodine radicals which were directly observed by esr spectroscopy.⁴⁵



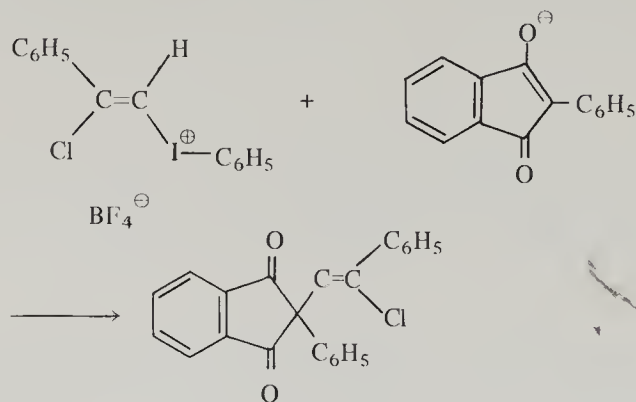
In the reaction with methylmagnesium iodide, methane and ethane are formed. The formation of ethane indicates that the methyl radical is an intermediate, which in turn must also mean that the diphenyliodine radical is an intermediate.



Phenyl(β -phenylethynyl)iodonium chloride reacts with the carbanion of 2-phenyl-1,3-indandione to give 2-phenyl-2-phenylethynyl-1,3-indandione in 73% yield.⁴⁶ Likewise, in the reaction with phenyl(α -chlorostyryl)iodonium

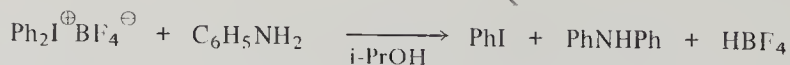


fluoroborate, 2-phenyl-2-(α -chlorostyryl)-1,3-indandione was obtained in 67% yield by cleavage of the bond between iodine and the vinyl group.

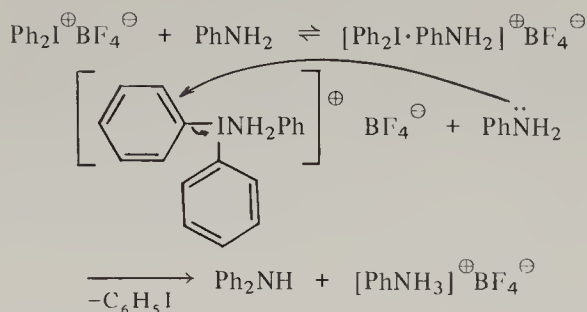


Reactions with Amines

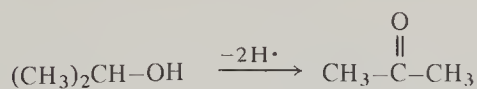
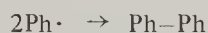
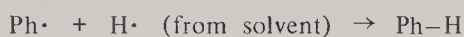
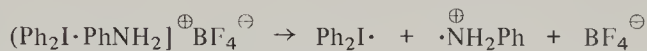
Aromatic Amines. The reaction of diphenyliodonium ion with aniline is not a conventional $\text{S}_{\text{N}}2$ displacement.⁹⁷ Diphenyliodonium fluoroborate and aniline form a relatively stable complex (a charge transfer complex absorption appears at 320 nm). The use of an excess of aniline increases, whereas an excess of iodonium salt decreases, the yield of diphenylamine formed.



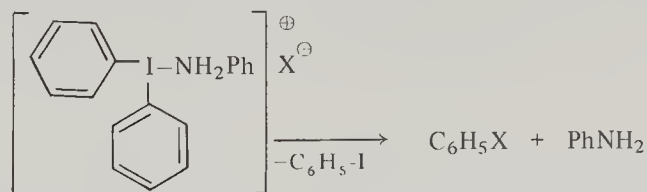
From the results, the following ionic reaction mechanism was proposed.



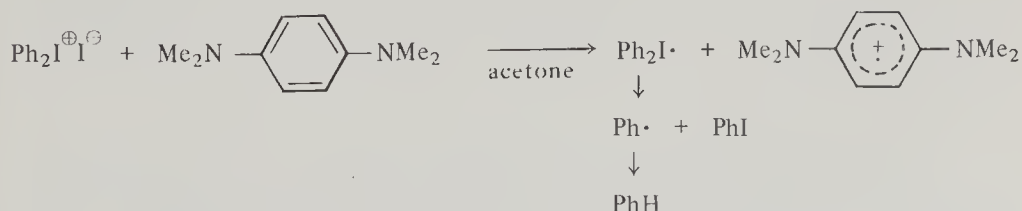
As in the reaction not only diphenylamine but also benzene, biphenyl, and acetone (from isopropyl alcohol used as the solvent) were formed,⁹⁸ a different radical mechanism was proposed, accounting also for the side reactions.



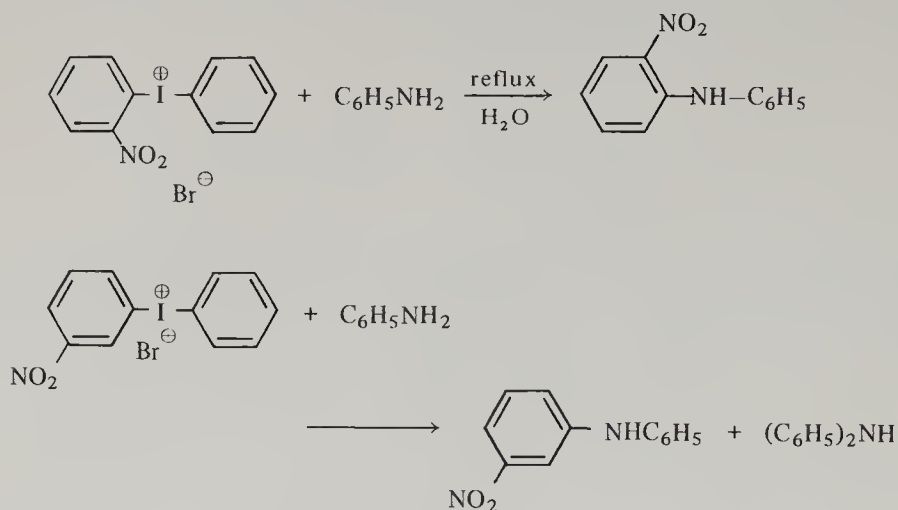
The homolytic nature of the reaction was also indicated by the substituent effects.⁹⁹ However, when the counterion is halide ion (e.g., Cl^{\ominus} , Br^{\ominus}), not only diphenylamine but also halobenzene was formed.¹⁰⁰ Thus the following competing ionic reaction also occurs. Diphenyliodonium iodide is easily reduced



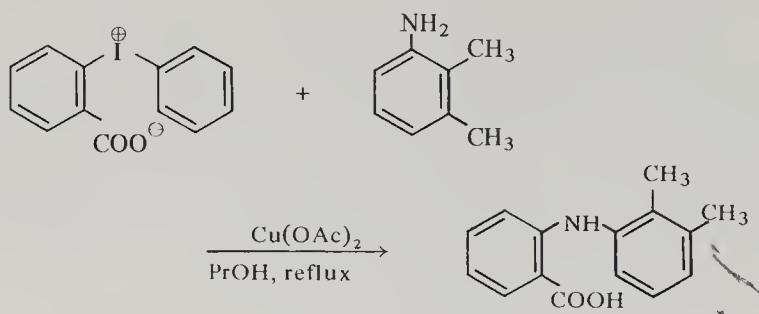
by bis(*N,N*-dimethyl)phenylenediamine at room temperature to give the diphenyliodonine radical and the radical cation of *p*-phenylenediamine, as shown by esr spectroscopy.¹⁰¹ In the reaction of unsymmetric diaryliodonium ions



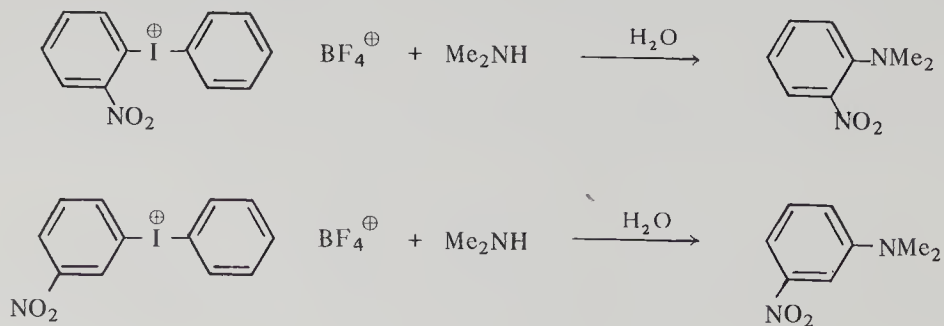
with aromatic amines, the more electropositive aryl group reacts with the amine to give the corresponding diarylamine.¹⁰² Diphenyliodonium-2-carboxyl-



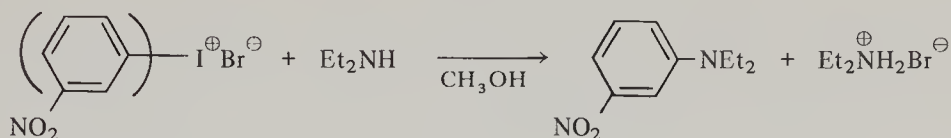
ate reacts with 2,3-dimethylaniline in isopropyl alcohol to give the corresponding diarylamine.¹⁰³



Aliphatic Amines. Beringer et al.¹⁰⁴ have reported the reaction of *o*- and *m*-nitrodiphenyliodonium tetrafluoroborates with dimethylamine to give the corresponding arylated amines in 83 and 43% yield, respectively. However,



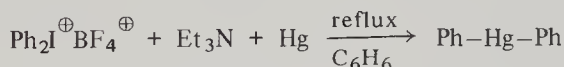
Reutov et al.¹⁰⁵ have reported the reaction of di-(*m*-nitrophenyl)iodonium ions with diethylamine to give only 4% a yield of *N,N*-diethyl-*m*-nitroaniline but a 100% yield of diethylammonium ions. In the reaction of the same iodonium ion with *n*-hexylamine, 9% *n*-hexyl-*m*-nitrophenylamine and 100% *n*-hexylammonium ion were obtained.



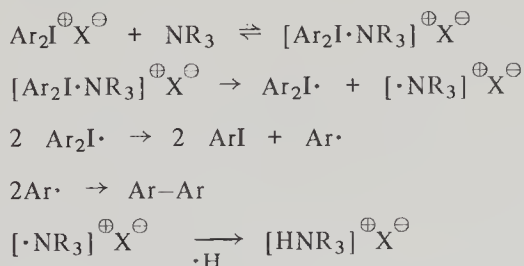
In the reaction of diphenyliodonium ions with diethylamine, only a trace of *N,N*-diethylaniline, and 69% diethylammonium ion were obtained in acetone solution.¹⁰⁶ Diphenyliodonium ions react with triethylamine to give triethylammonium ions as the major product.



Diphenyliodonium ions also react with triethylamine in the presence of mercury to give diphenylmercury, although only in low yield.¹⁰⁷



These results indicate formation of the diphenyliodine radical and the cation radical of triethylamine. Therefore the reaction of diaryliodonium ions with aliphatic amines is not a simple phenylation of an amine, but the following homolytic reaction sequence occurs.



Reactions With Aziridines

In the reaction with aziridines, diphenyliodonium iodide acts as catalyst to give the corresponding olefin and oxazole¹⁰⁸ (Table 28). In the reaction,

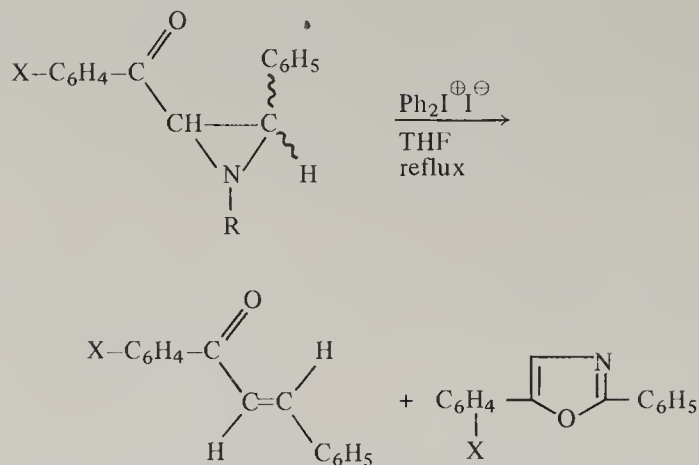
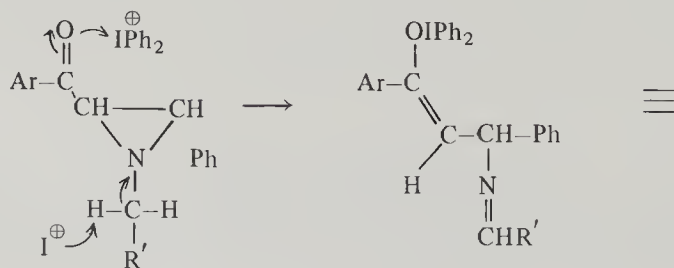


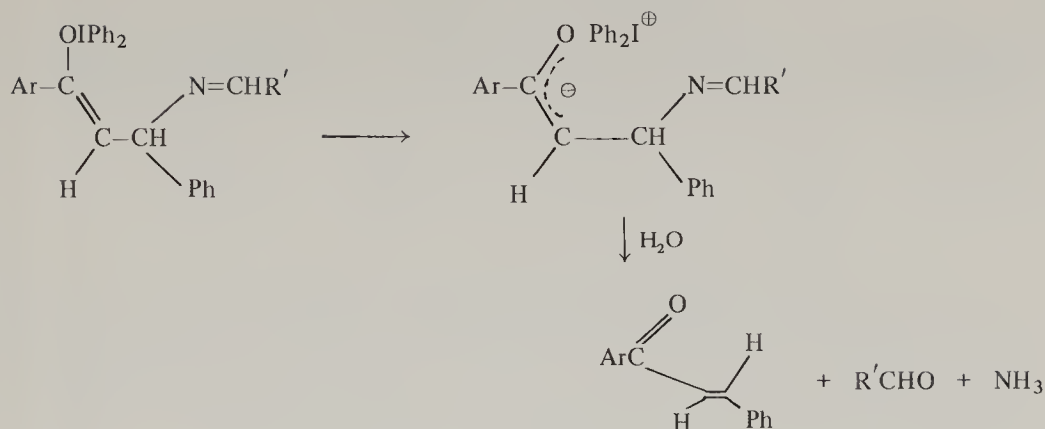
TABLE 28

Products of the Reaction of Diphenyliodonium Ions with Substituted Aziridines

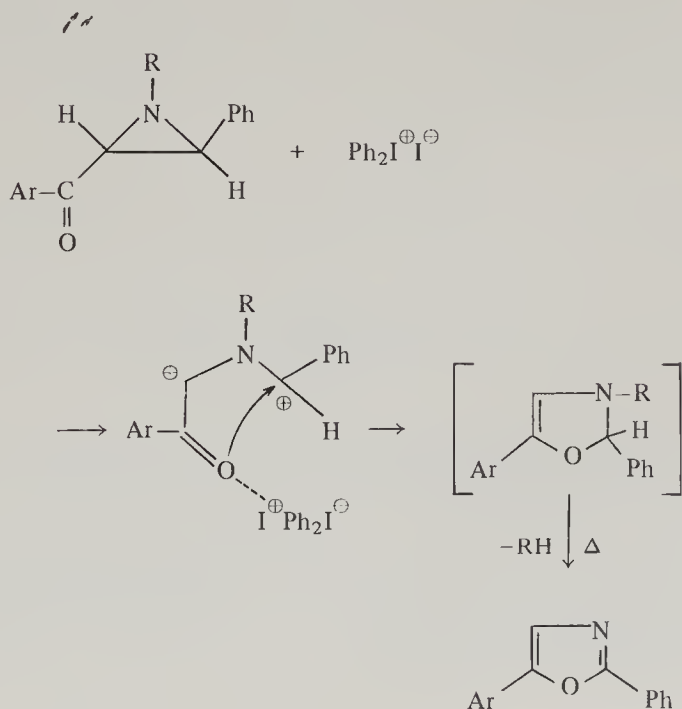
X	R	Yield (%)	
		<i>trans</i> -Benzalacetophenone	Oxazole
H	CH ₂ C ₆ H ₅ (trans)	73	7
H	CH ₂ C ₆ H ₅ (cis)	75	8
H	C ₆ H ₁₁ (trans)	76	
H	C ₆ H ₁₁ (cis)	72	
CH ₃	CH ₂ C ₆ H ₅ (trans)	52	44
CH ₃	CH ₂ C ₆ H ₅ (cis)	54	41
CH ₃	C ₆ H ₁₁ (trans)	67	
CH ₃	C ₆ H ₁₁ (cis)	65	

the diphenyliodonium ion attacks the carbonyl group, causing cleavage of the C-N bond.



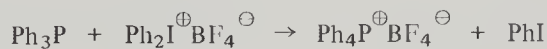


The oxazole is formed via C—C bond fission.



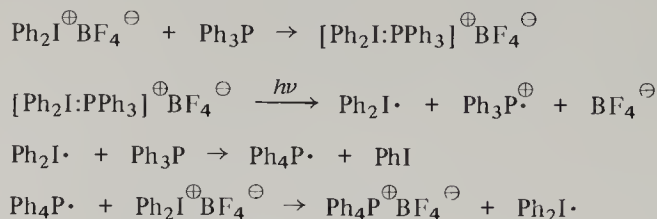
Reactions with Phosphines

Reactions with Triphenylphosphine. In the photolytic reaction of diphenyliodonium fluoroborate with triphenylphosphine, tetraphenylphosphonium fluoroborate was obtained in good yield.¹⁰⁹

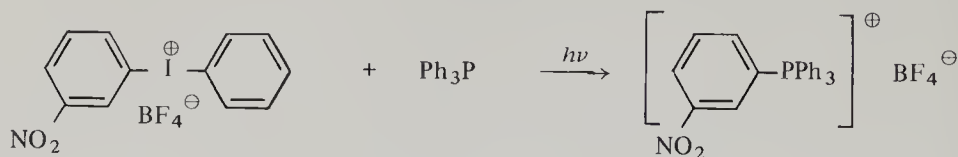


The presence of hydroquinone lowers the yield of phosphonium salt and, when ethanol was used as the solvent, benzene and acetaldehyde were formed

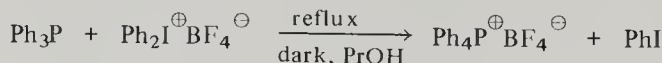
as by-products. A radical mechanism was proposed, and intermediate formation of $[\text{Ph}_2\text{I}^+\text{PPh}_3]^\oplus\text{BF}_4^\ominus$ (absorption maximum appears at 336 nm) was indicated.



In the photolytic reaction of unsymmetric iodonium ions with triphenylphosphine, phosphonium ions were obtained in a similar manner.¹¹⁰



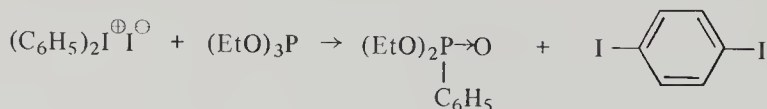
In the related thermal reaction, phosphonium ions are also formed.¹¹¹



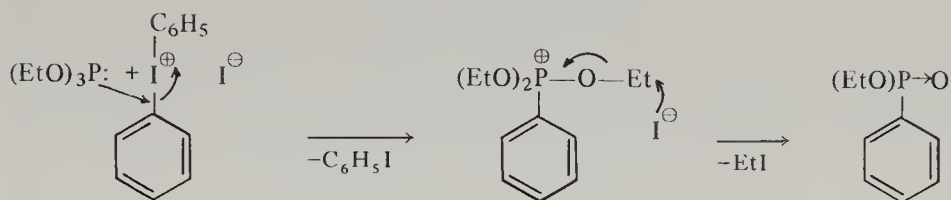
The presence of hydroquinone decreases the yield of phosphonium salt. Thus the thermal reaction also proceeds by the radical mechanism.

Reactions with Alkyl Phosphites and Alkyl Phosphates

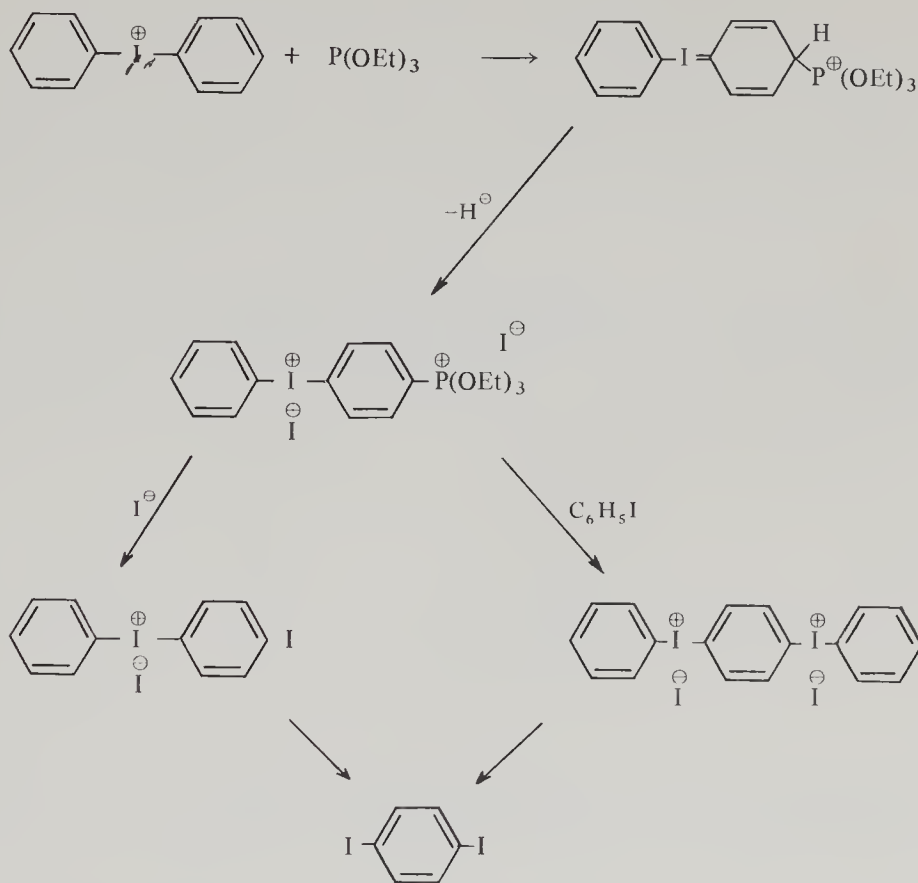
Diphenyliodonium iodide reacts with triethyl phosphite to give *p*-diiodobenzene and diethyl phenylphosphonate.¹¹²



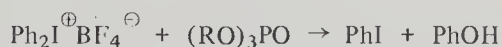
Apparently, two distinct reactions take place. In the first the nucleophilic attack by phosphorus of the triethyl phosphite occurs at the C-1 phenyl carbon of the diphenyliodonium ion to give a phosphonium ion which decomposes to give diethyl phenylphosphonate. In the second reaction nucleophilic attack



occurs at the C-4 position of the aromatic ring, leading to the formation of *p*-diiodobenzene. These reactions indicate the ambident nature and reactivity



of diaryliodonium ions. Diphenyliodonium fluoroborate reacts with trialkyl phosphate to give iodobenzene and phenol.¹¹³



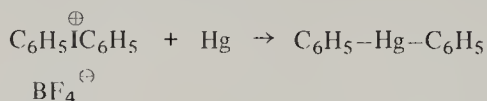
Reaction with Mercury

Diphenyliodonium halides react with mercury to give the corresponding phenylmercuric halide and iodobenzene.¹¹⁴ The reaction rate increases with



reduced polarity of the solvent,¹¹⁵ and the addition of a common ion effectively interferes with the reaction of mercury and diphenyliodonium halide.¹¹⁶

In the presence of iron or copper, diphenyliodonium fluoroborate reacts with mercury to give diphenylmercury.¹¹⁷

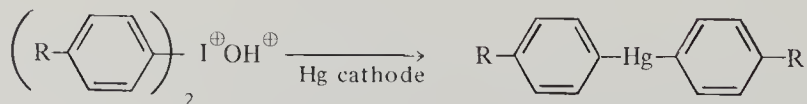


Protic solvents such as methanol and water are preferred for the preparation of diphenylmercury. The effect of solvent on the reaction is shown in Table 29.

TABLE 29
Solvent Dependence of the
Preparation of Diphenylmercury
from Diphenyliodonium Ion
and Mercury

Solvent	Yield (%)
CH ₃ OH	53
H ₂ O	27
Acetone	Trace
Dioxane	0
C ₆ H ₆	0

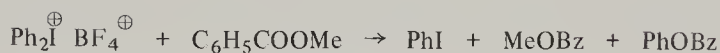
Diarylmercuries are also obtained electrochemically from diaryliodonium hydroxides by using a mercury cathode¹¹⁸ (Table 30).

*O-Phenylation Reactions*

The reaction of diphenyliodonium fluoroborate with methyl benzoate gives phenyl benzoate in low yield, formed by an ester exchange reaction.¹¹⁹

TABLE 30
Yield of the Electrochemical
Preparation of
Diphenylmercuries from Di-
phenyliodonium Ions (RAr)₂I⁺

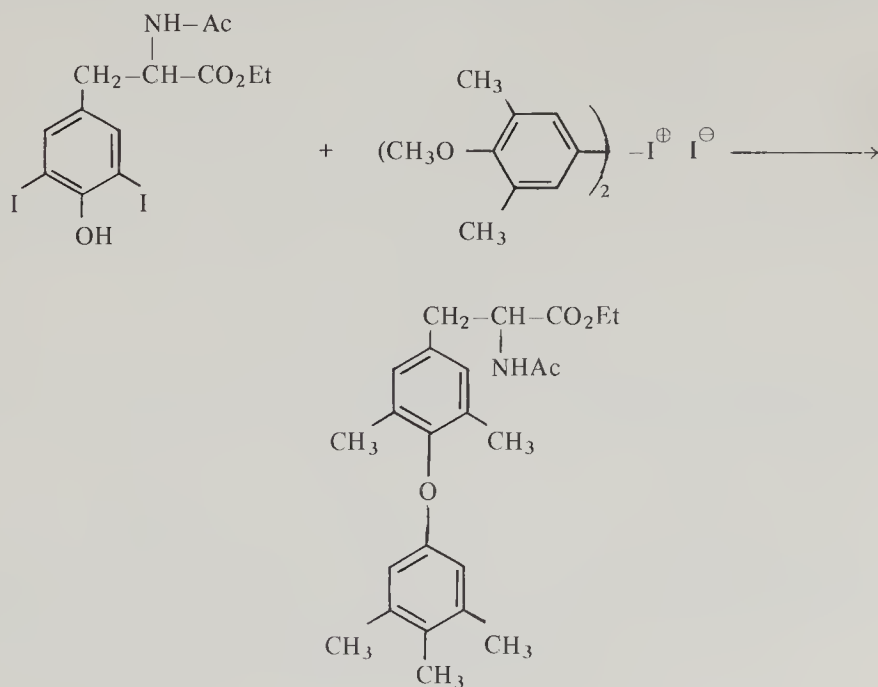
R	Yield (%)
H	51
CH ₃	41
CH ₃ O	58



In the reaction of diphenyliodonium fluoroborate with phosphonium ylide, *O*-phenylated phosphonium ions were obtained in 15% yield.¹²⁰

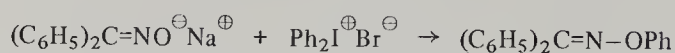


The reaction of di(4-methoxy-3,5-dimethylphenyl)iodonium iodide with *N*-acetyl-3,5-diiodo-*L*-phenylalanine ethyl ester proceeds in methanol (45°, 24 hr) in the presence of triethylamine and copper powder to give the arylated compound in 70% yield.¹²¹ However, the reaction of di(4-methoxy-3,5-dimethyl-

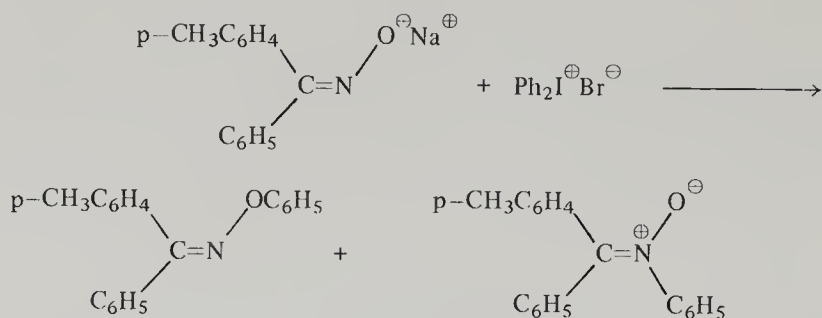


phenyl)iodonium trifluoroacetate with 4-bromo-2,6-dimethylphenol did not give the corresponding arylated compound; only poly-2,6-dimethylphenylene ether was obtained.¹²²

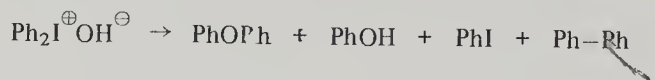
Phenylation of oxime anions has also been reported. The reaction of diphenyliodonium bromide with the anion of benzophenone oxime gives the *O*-phenylated compound in 79% yield.¹²³ However, in the case of *p*-methylben-



zophenone oxime not only *O*-phenylated but also *N*-phenylated products were obtained.

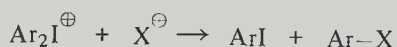


In the thermolytic reaction of diphenyliodonium hydroxide, diphenyl ether was obtained, which was formed in the reaction of diphenyliodonium ion and phenol, obtained from the thermolysis of diphenyliodonium hydroxide.¹²⁴



Reactions with Inorganic Nucleophiles

The reactions of diaryliodonium ions with inorganic nucleophiles such as nitrite ion, halide ions, and cyanide ion have been shown to give the correspond-



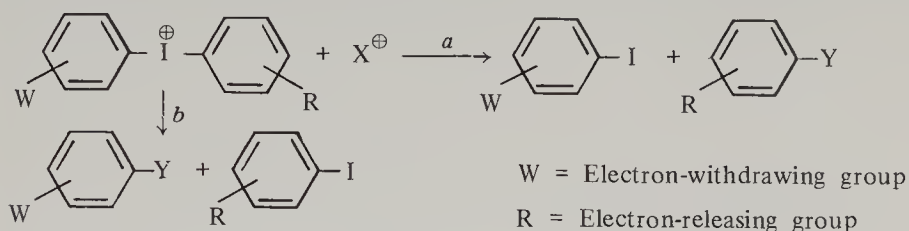
ing aromatic compounds. The decreasing order of reactivity of various nucleophiles was found to be.¹²⁵



When cupric sulfate is present, cyanide ion is more reactive than nitrite ion.

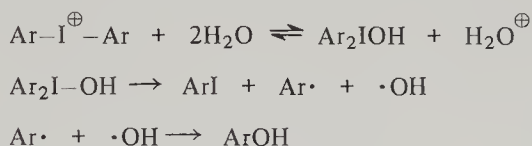


In the reaction of unsymmetric iodonium ions with inorganic nucleophiles, there are two competing reaction paths (*a* and *b*). When bearing an electron-



withdrawing group the C-1 phenyl carbon is attacked more easily by the nucleophile than when bearing an electron-releasing group.¹²⁶ Beringer et al. have reported kinetic solvent effects in the reaction of diphenyliodonium ions with various nucleophiles.

The hydrolysis of diphenyliodonium ion proceeds homolytically.¹²⁷



Copper(I) salts are extremely efficient for the decomposition of diaryliodonium ions.¹²⁸ In the decomposition of diphenyliodonium chloride, cuprous chloride acts as a good catalyst to give chlorobenzene, iodobenzene, and phenol. The effect of solvents on the reaction is shown in Table 31.

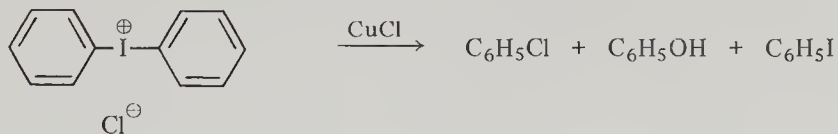
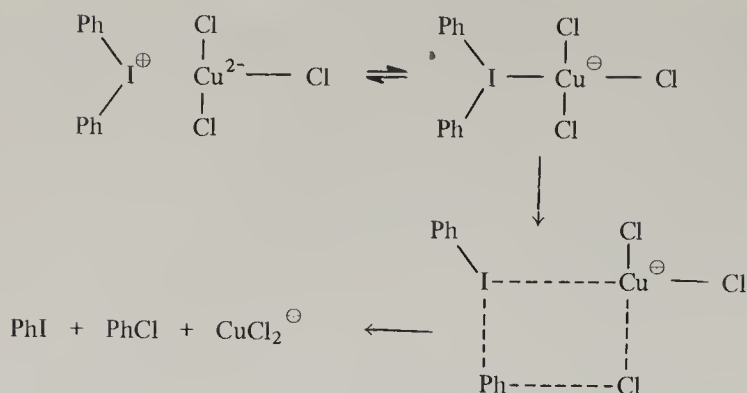


TABLE 31
Decomposition of Diphenyliodonium Ion
by Cuprous Chloride

Solvent	C ₆ H ₅ Cl (%)	C ₆ H ₅ OH(%)
H ₂ O	95	5
CH ₃ OH	100	
Acetone	100	

The reaction proceeds by the following mechanism



Chromium(V) and especially titanium(III) chlorides are also good catalysts in the decomposition of diphenyliodonium chloride in water to give quantitatively chlorobenzene and iodobenzene (Table 32).

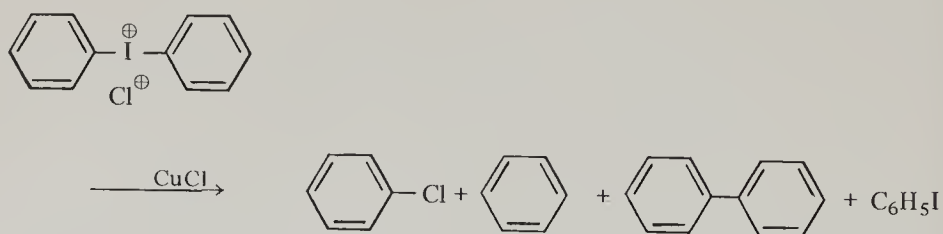
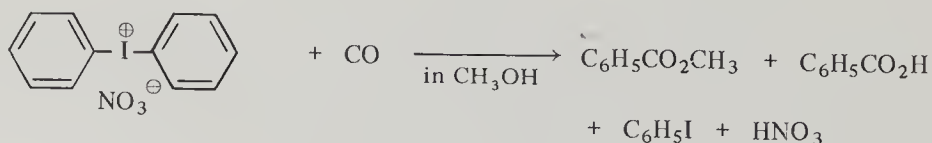


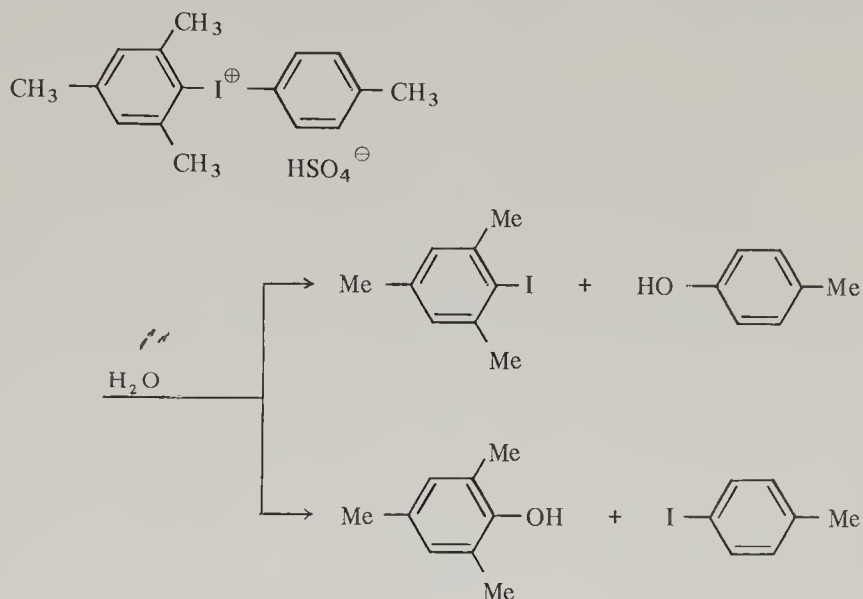
TABLE 32
Decomposition of Diphenyliodonium Ion with Chromium(V)
Chloride and Titanium(III) Chloride

Solvent	Catalyst	Reaction (%)	C ₆ H ₅ Cl	C ₆ H ₅	C ₆ H ₅ —C ₆ H ₅
H ₂ O	TiCl ₃	100	100		
CH ₃ OH	TiCl ₃	10	100		
H ₂ O	CrCl ₃	61	11	50	39

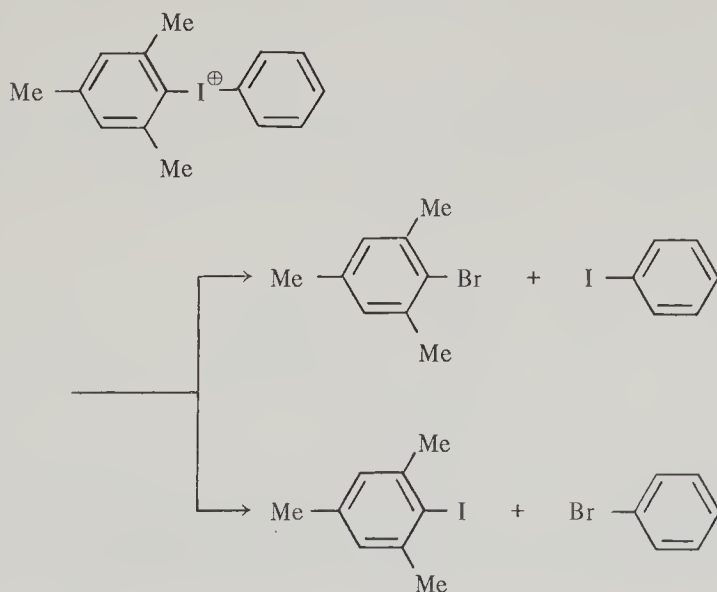
The reaction of diphenyliodonium nitrate with carbon monoxide, carried out in methanol at 110° under 120 atm, has been reported to give methyl benzoate and benzoic acid.¹²⁹



In the reaction of mesityl-*p*-tolyliodonium bisulfite in water, the nucleophile attacks the C-1 *p*-tolyl carbon more easily than the C-1 mesityl carbon.¹³¹ This can be explained by the obvious steric hindrance of the two ortho methyl groups of the mesityl group. However, Yamada and Okawara¹³¹ have



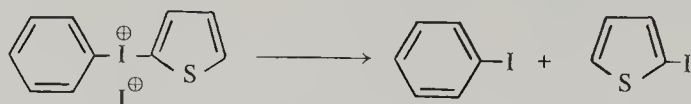
reported a reverse steric effect. In the reaction of *o*-tolymesityl- and phenyl-mesityliodonium bromide, bromide ion attacks the *o*-substituted C-1 phenyl carbon preferentially. These findings are best explained by the effects of



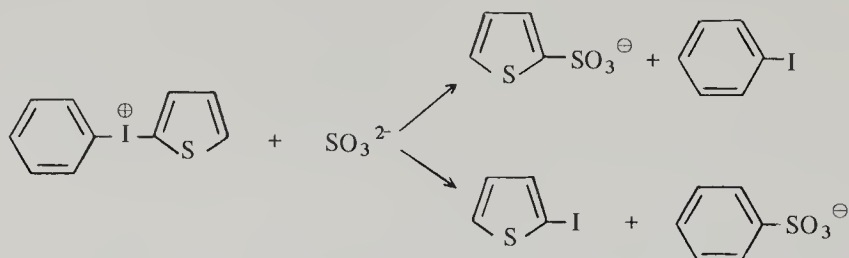
intramolecular strain, due to the presence of ortho methyl groups, causing the reaction to proceed also by an S_N1 mechanism.

Reactions of Hetroaryliodonium Ions

The thermolytic reaction of phenyl-2-thienyliodonium iodide gives iodobenzene and 2-thienyl iodide.⁵⁷ Phenyl-2-thienyliodonium ion reacts with sulfite

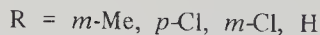
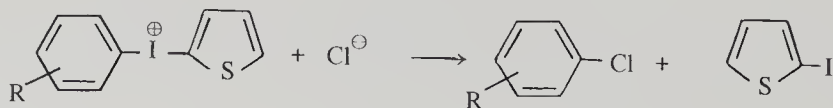


ion to give thiophene 2-sulfonate and iodobenzene, or benzenesulfonate and 2-iodothiophene. The ratio of attack on the thiophene ring to attack on



the benzene ring is 2:1. The replacement of a phenyl group in the diphenyliodonium ion by a 2-thienyl group enhances halonium ion susceptibility to nucleophilic attack.

Yamada and Okawara¹³² have, however, reported that chloride and bromide ions are more likely to attack the phenyl rather than the 2-thienyl ring in the reactions of substituted phenyl-2-thienyliodonium ions. Specifically, chloride ions attack the C-1 phenyl carbon, despite the presence of substituent groups.



Bromide ions attack not only the phenyl ring but also the thienyl ring to give the corresponding bromides. The phenyl ring is, however, much more reactive than the 2-thienyl ring (Table 33).

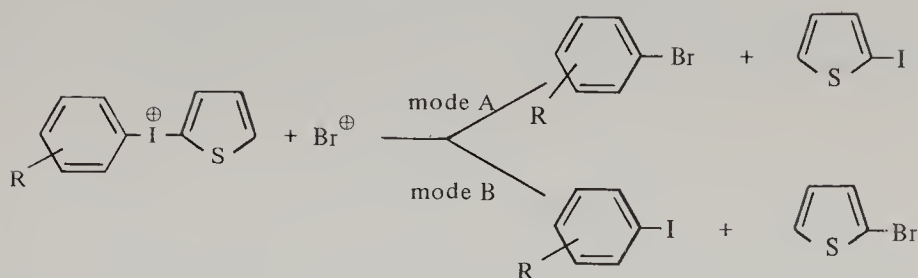
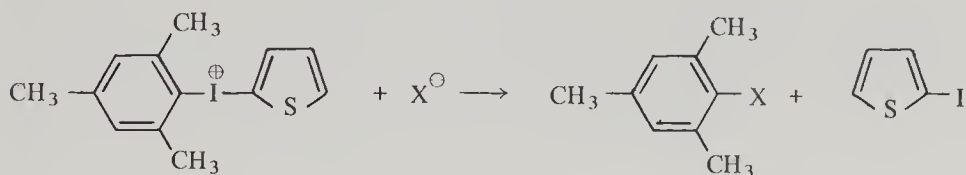


TABLE 33
Mode of Attack of Bromide Ion on
Phenyl-2-Thienyliodonium Ion in
DMP at 100°

R	Mode A	Mode B
H	100	0
<i>m</i> -Cl	100	0
<i>p</i> -Cl	76.1	23.9
<i>m</i> -Me	100	0
<i>p</i> -Me	70.7	29.3
<i>p</i> -MeO	60.0	40.0

When methyl groups are present in the ortho position of the aryl-2-thienyliodonium ion, the aryl ring becomes much more reactive, as a result of obvious intramolecular strain.¹³¹



5.1.5 Biological Activity

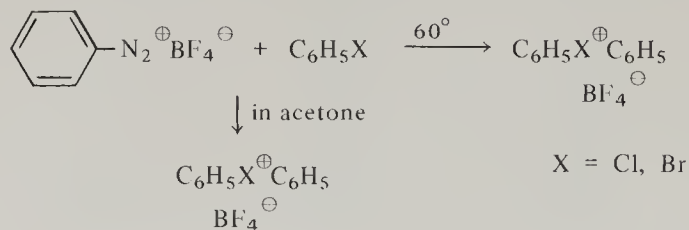
Positive iodine compounds have, in general, good oxidizing power, and as a result certain biocidal properties generally ascribed to "iodine"—tinctures, preparations, and complexes—were found for iodonium ions. Bis(3,4-dichlorophenyl)iodonium chloride and bis(2,4-dichlorophenyl)iodonium sulfate were evaluated as bactericides; the latter proved most effective against gram-negative bacteria.¹³⁶ Several substituted diaryliodonium chlorides were found to be inert to type-A influenza virus, although it was reported that ring chlorination

increased the activity in this respect.^{137,138} Diphenyliodonium salts were found to have active spermicidal properties in aqueous solutions of 0.5% or less.¹³⁹

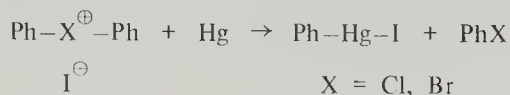
5.2 DIARYLBROMONIUM AND -CHLORONIUM IONS

Whereas diaryliodonium ions have been extensively studied, only very limited data are so far available on diarylbromonium and -chloronium ions.

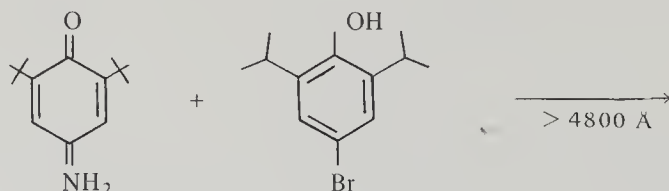
Phenyldiazonium salts, as observed by Nesmeyanov,¹³³ react with bromo- and chlorobenzene to give the corresponding diphenylbromonium and -chloronium ions. The reaction, however, gives only exceedingly low yields. The decomposition of phenyldiazonium salts in halobenzene at 60° gives diphenylhalonium ion in 0.5% yield. If acetone is used as the solvent, the yield rises to 6%.

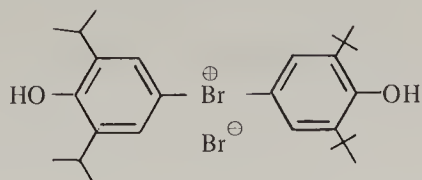


Bromonium and chloronium ions are less stable than the corresponding iodonium ions and readily decompose to give halobenzenes. Diphenylbromonium and chloronium ions react with amines and pyridine to give the corresponding *N*-phenylated compounds. Halonium iodides react with mercury to give the corresponding phenylmercuric iodides.¹³³ However, when the counterion is the tetrafluoroborate anion, phenylmercuric compounds are not obtained.

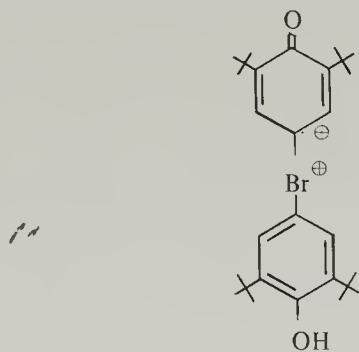


In the photolysis reaction of 3,5-di-*tert*-butylbenzene-1,4-diazooxide with 2,6-diisopropyl-4-bromophenol, diarylbromonium bromide was obtained in 15%





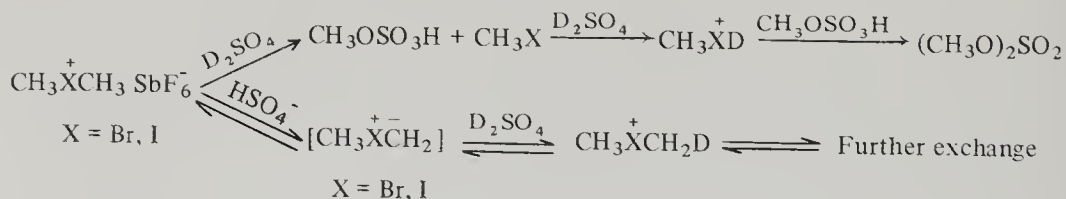
yield.¹³⁴ A bromonium ylide was suggested to be the reaction intermediate.



Halonium Ylides

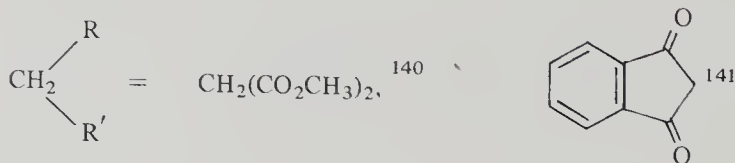
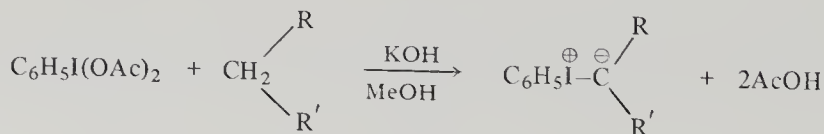
6.1 ALKYLHALONIUM YLIDES

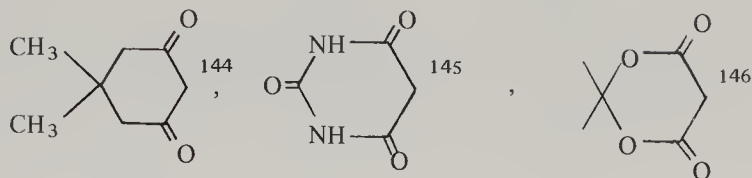
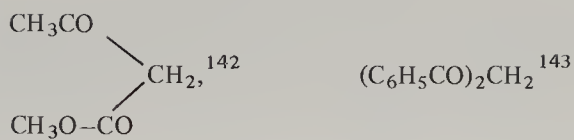
Dimethylhalonium ions, as discussed are good methylating reagents for a wide range of n and π donors.^{3,26} The reaction with H_2SO_4 is typical.²⁴ When dimethylbromonium or iodonium ion complexes are added (as stable hexafluoroantimonate salts) to H_2SO_4 , no reaction occurs below 0° , but at 30° dimethyl sulfate is formed. When D_2SO_4 is reacted at 30° , the pmr spectrum indicates that H-D exchange occurs during the course of the reaction. (When dimethylchloronium ion is reacted, it slowly dissolves in D_2SO_4 to give dimethyl sulfate, but no H-D exchange is observed.) After 2 hr, spectra of the H_2SO_4 -soluble layer indicate the presence of dimethyl sulfate and a second species resonating at δ 4.00 (pmr) and δ 1.2 (cmr), which was shown to be the methylhydriodonium ion ($\text{CH}_3\text{I}^+\text{H}$). The H-D exchange indicates that methylene-methyliodonium and -bromonium ylides, the first reported alkylhalonium ylides, are intermediates.²⁴ Attempts to trap the ylides produced under basic conditions have so far been unsuccessful.



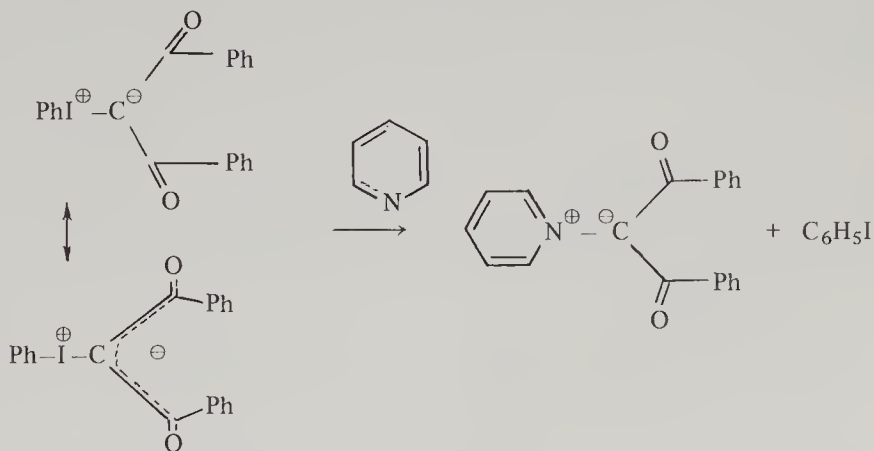
6.2 ARYLHALONIUM YLIDES

Neilands and his coworkers¹⁴⁰⁻¹⁴⁶ first investigated iodonium ylides. Phenyl-iodoso acetate reacts with active methylene groups in the presence of alkali to give the corresponding iodonium ylides.

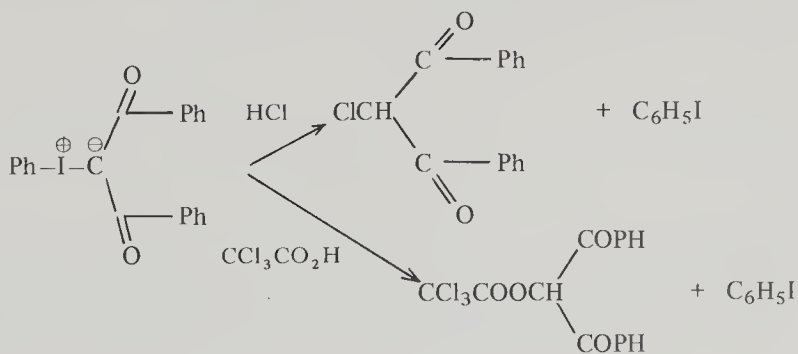




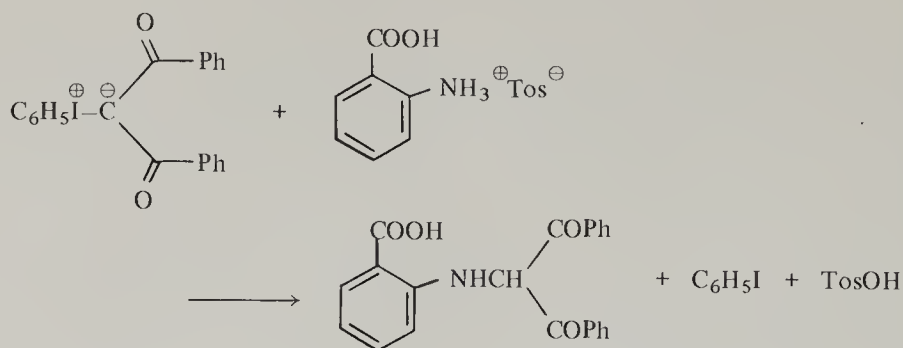
The iodonium ylides react with pyridine to give pyridinium ylides (by an ylide exchange reaction).¹⁴⁷



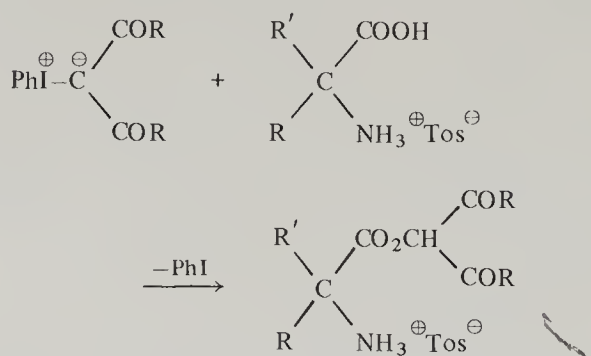
In the reaction with acids, such as HCl and trichloroacetic acid, products of the addition of the acid to the carbanion center of the iodonium ylide were obtained, with cleavage of iodobenzene.



In the presence of cupric sulfate or cupric cyanide as a catalyst, the iodonium ylide reacts with pyridine to give pyridinium ylides in good yield.¹⁴⁷ In the reaction with the *p*-toluenesulfonic acid salt of *o*-aminobenzoic acid, the *N*-alkylated compound is obtained.¹⁴⁸ However, in the reaction with the

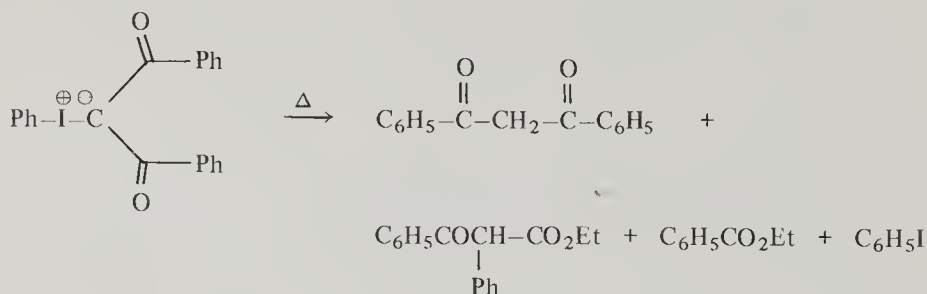


p-toluenesulfonic acid salt of α -amino acids, *O*-alkylated products are obtained.¹⁴⁹

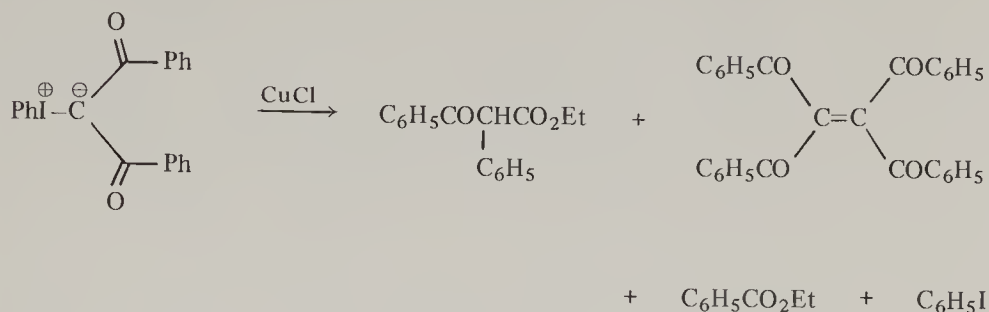


Iodonium ylides react with more acidic active methylene groups, transferring PhI to them to give new iodonium ylides and liberating weaker acids.

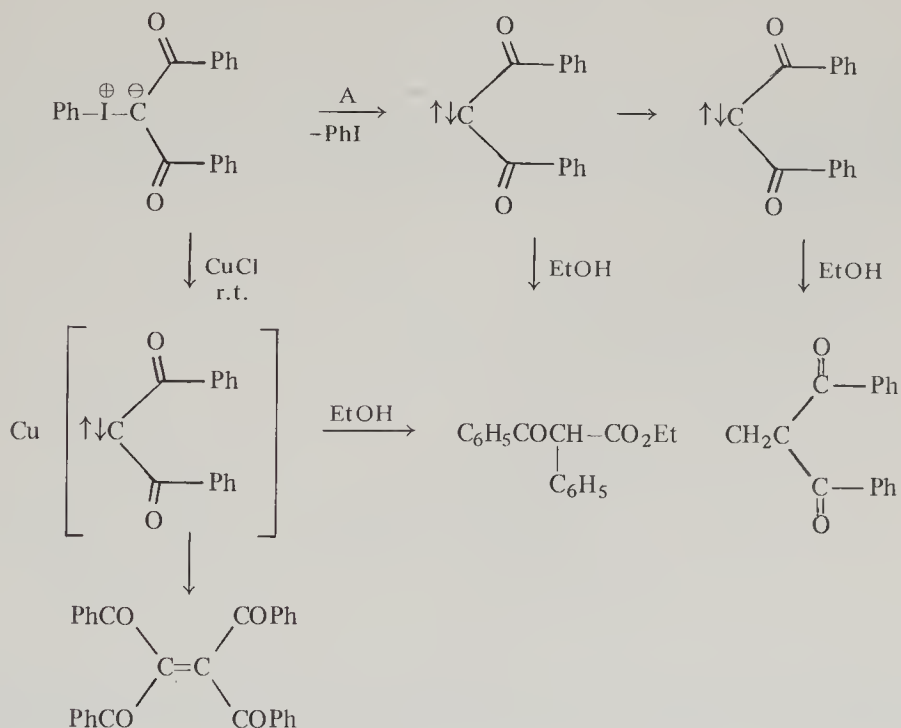
Hayashi et al.¹⁵⁰ have suggested that carbenes are intermediates in the decomposition of iodonium ylides. In the thermal reaction (in refluxing ethanol, 2 hr) dibenzoylmethane was obtained as a major product.



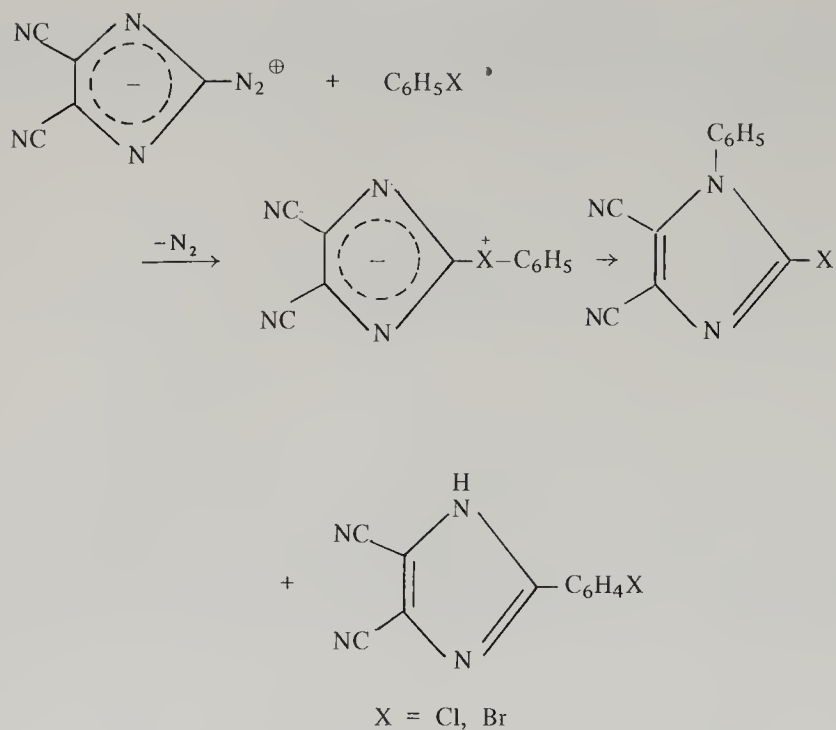
In the presence of cuprous chloride the iodonium ylide decomposes spontaneously to give ethyl α -phenyl acetate, α -benzoyl acetate, and tetrabenzoyl ethylene as major products.



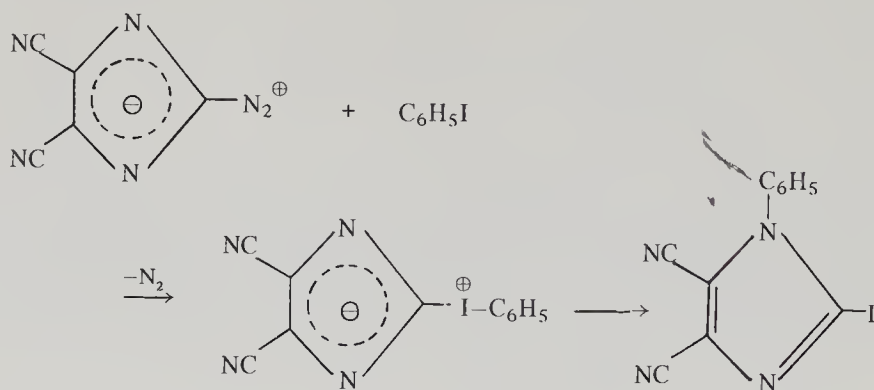
The different distribution of the reaction products between thermal and catalytic decomposition was suggested to be dependent on the nature of the carbene intermediate. The following mechanism was suggested for the reactions.



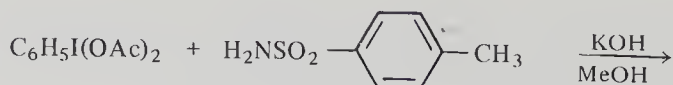
Diazodicyanoimidazole reacts with bromo- and chlorobenzene to give the corresponding bromonium and chloronium ylides which decompose to afford 1-phenyl-2-bromo-(or chloro)-4,5-dicyanoimidazole.¹⁵¹

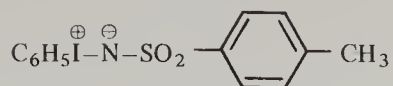


Iodobenzene reacts similarly with diazodicyanoimidazole to give the dicyanoimidazole iodonium ylide which on decomposition gives 1-phenyl-2-iodo-4,5-dicyanoimidazole.¹⁵²

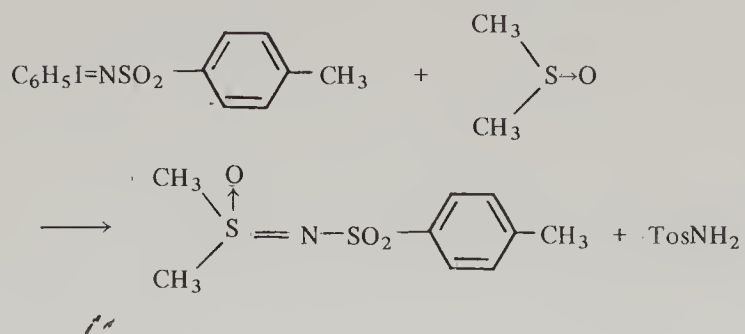


Yamada and Okawara¹⁵² synthesized an I-N ylide from phenyliodoso acetate and *p*-toluenesulfonic acid in the presence of potassium hydroxide,





which reacts with dimethyl sulfoxide to give a sulfoxylimine.





PART B

Cyclic Halonium Ions

14

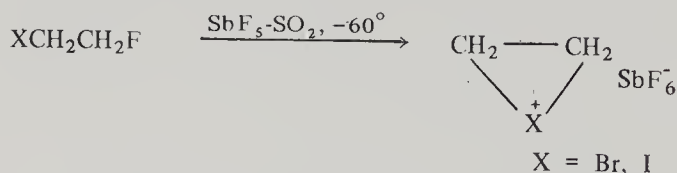
Ethylenehalonium Ions

7.1 PREPARATION BY NEIGHBORING HALOGEN PARTICIPATION AND PMR STUDY

Roberts and Kimbal⁴ first suggested that the carbenium ion formed in the electrophilic attack of bromine on ethylene is stabilized by bridging by the neighboring β -bromine atom. They expected the ethylenebromonium ion to be slightly unsymmetric. Winstein and Lucas,⁶ in subsequent studies on the stereochemical role of neighboring bromine in displacement reactions, concluded that the ethylenebromonium ion is either symmetric or that there is an extremely low barrier between the two unsymmetric forms. It is significant to point out that nothing in the original concept of neighboring-group participation, developed by Hughes and Ingold, and by Winstein,¹⁵³ requires momentary equivalence of the two carbon atoms involved in bromine bridging. It does require that an energy minimum or minima correspond to some degree of bonding of the carbocationic center to the neighboring halogen atom. Olah and Bollinger⁹ reported in 1967 the first direct observation, by pmr spectroscopy, of tetramethylethylenehalonium ions under stable ion conditions in low nucleophilicity $\text{SbF}_5\text{-SO}_2$ solution. Subsequently, tri-, di-, monomethyl-, and even the parent ethylenehalonium ions were also obtained under related experimental conditions.¹⁴ The pmr parameters of these ethylenehalonium ions are summarized in Table 34.

7.1.1 Parent Ethylenehalonium Ions

The parent ethylenehalonium ions ($\text{X} = \text{Br}$ and I) were obtained when 1-halo-2-fluoroethanes were ionized in $\text{SbF}_5\text{-SO}_2$ solution at -60° .¹⁴ The pmr spectra of the ethylenebromonium and iodonium ions show a singlet at δ 5.53 and

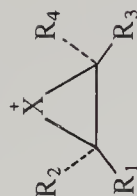


5.77, respectively. Under similar experimental conditions, when 1,2-dichloroethane and 1-chloro-2-fluoroethane were treated with $\text{SbF}_5\text{-SO}_2$ solution, donor-acceptor complexes were only formed instead of the ethylenechloronium ion.



Recently, however, the ethylenechloronium ion was also prepared.¹⁵⁴ When, instead of SO_2 , SO_2ClF was used as the solvent, the reaction of antimony

TABLE 34

Pmr Data of Ethylenehalonium Ions^a

X	R ₁	δ R ₁ ^b	R ₂	δ R ₂ ^b	R ₃	δ R ₃ ^b	R ₄	δ R ₄ ^b
Cl	H	5.90 (s)	H	5.90 (s)	H	5.90 (s)	H	5.90 (s)
Br	H	5.53 (s)	H	5.53 (s)	H	5.53 (s)	H	5.53 (s)
I	H	5.77 (s)	H	5.77 (s)	H	5.77 (s)	H	5.77 (s)
Cl ^c	CH ₃	3.00 (s)	H	6.24 (s)	H	6.24 (s)	H	6.24 (s)
Br	CH ₃	2.98, (d) <i>J</i> = 6	H	7.84 (m)	H	5.86 (d)	H	5.86 (d)
I	CH ₃	3.32, (d) <i>J</i> = 6	H	7.33 (m)	H	5.77 (d)	H	5.77 (d)
Br	CH ₃	2.61 (m)	H	6.72 (m)	CH ₃	2.61 (m)	H	6.72 (m)
Br	CH ₃	2.61 (m)	H	6.72 (m)	H	6.72 (m)	CH ₃	2.61 (m)
I	CH ₃	3.07 (m)	H	6.87 (m)	H	6.87 (m)	CH ₃	3.07 (m)
I	CH ₃	3.07 (m)	H	7.14 (m)	CH ₃	3.07 (m)	H	7.14 (m)
Br	CH ₃	3.32 (s)	CH ₃	3.52 (s)	H	5.55 (s)	H	5.55 (s)
I	CH ₃	3.45 (s)	CH ₃	3.45 (s)	H	5.72 (s)	H	5.72 (s)
Cl	CH ₃	3.41 (s)	CH ₃	3.41 (s)	CH ₃	2.49, (d) <i>J</i> = 6	H	6.35, (q) <i>J</i> = 6
Br	CH ₃	3.10 (s)	CH ₃	3.10 (s)	CH ₃	2.62, (d) <i>J</i> = 6	H	6.58, (q) <i>J</i> = 6

TABLE 34
Pmr Data of Ethylenichalonium Ions^a (continued)

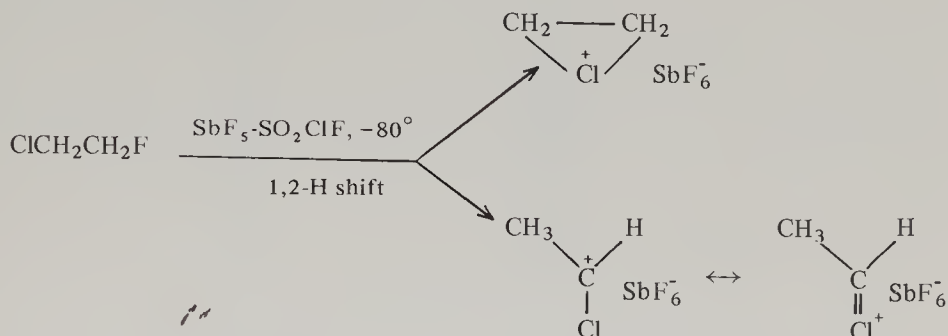
X	R ₁	δ R ₁ ^b	R ₂	δ R ₂ ^b	R ₃	δ R ₃ ^b	R ₄	δ R ₄ ^b
I	CH ₃	3.23 (s)	CH ₃	3.23 (s)	CH ₃	2.92, (d) J = 6.5	H	6.75, (q) J = 6.5
Cl	CH ₃	2.72 (s)	CH ₃	2.72 (s)	CH ₃	2.72 (s)	CH ₃	2.72 (s)
Br	CH ₃	2.86 (s)	CH ₃	2.86 (s)	CH ₃	2.86 (s)	CH ₃	2.86 (s)
I	CH ₃	3.05 (s)	CH ₃	3.05 (s)	CH ₃	3.05 (s)	CH ₃	3.05 (s)

^aProton chemical shifts are referred to external capillary TMS in SbF₅-SO₂ solution at -60°.

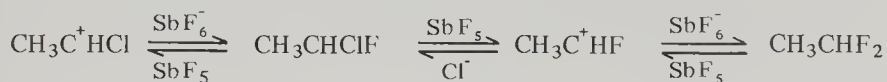
^bThe multiplicities are shown in parentheses. s, singlet; d, doublet; q, quartet; m, multiplet.

^cRapidly equilibrating with open-chain ions, see text.

pentafluoride with 1-chloro-2-fluoroethane at -80° gave a solution whose pmr spectrum consisted of these absorptions: a doublet (δ 4.6, 3H, $J = 6$ Hz), a quartet (δ 13.3 1H, $J = 6$ Hz), and a singlet (δ 5.9), consistent with the presence in the solution of the ethylenechloronium ions and methylchlorocarbenium ions, respectively.

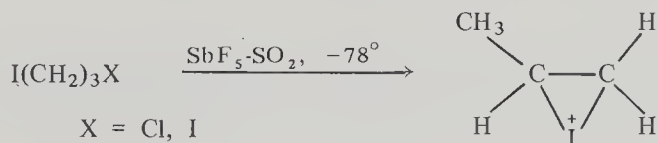


The ratio of these ions depends on the conditions under which they are prepared. If care is taken to keep the reactants below -80° , the ethylenechloronium ion predominates. Available data also show that the ions are not interconvertible. As the temperature is raised to -50° , the doublet and quartet of the ethylenechloronium ion disappear, and a new set of more shielded signals appears at δ 4.3 (doublet, 3H, $J = 1.8$ Hz) and δ 10.3 (quartet, 1H, $J = 1.8$ Hz), respectively. At the same time, the signal from the ethylenechloronium ion does not change its position and intensity. These data suggest the formation of the methylfluorocarbenium ion which is in equilibrium with 1,1-difluoroethane under the reaction conditions.¹⁵⁵



7.1.2 Propylenehalonium Ions

When 2-fluoro-1-iodopropane and 2-fluoro-1-bromopropane were ionized in $\text{SbF}_5\text{-SO}_2$ solution at -60° , propyleneiodonium and propylenebromonium ions were formed, respectively.¹⁴ The pmr spectrum of the propylenebromonium ion is shown in Figure 7. In an attempt to prepare trimethylenehalonium ions when 1,3-dihalopropanes were treated with $\text{SbF}_5\text{-SO}_2$ or $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ solution at -78° (see Section 0.0), the corresponding propylenehalonium ions were formed instead. The corresponding propylenechloronium ion could not



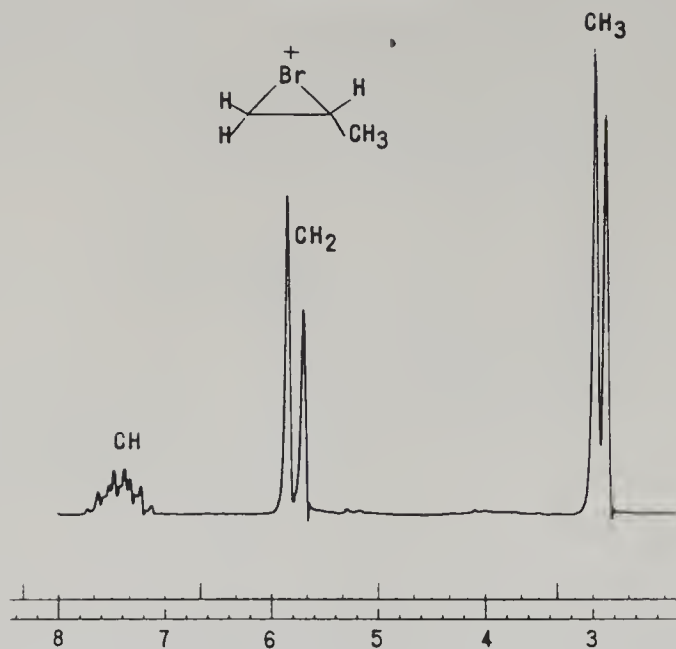
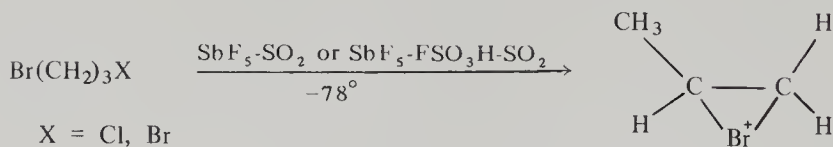
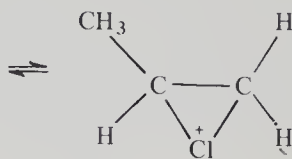
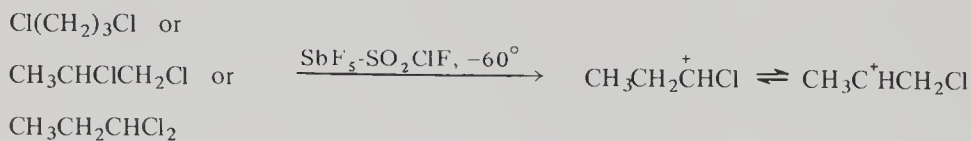


Figure 7. Pmr spectrum of the propylenebromonium ion.



be obtained from dichloropropanes in $\text{SbF}_5\text{-SO}_2$ solution under similar conditions. Instead, when 1,1-, 1,2- or 1,3-dichloropropane was ionized in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -60° ; rapidly equilibrating ethylchlorocarbenium ions were formed. The equilibration processes is expected to also involve an unsymmetric bridged ion.



It is of interest to compare ethylenechloronium and propylenechloronium ions. The former once formed are stable and are not transformed in the temper-

ature range from -80° to -50° into methylchlorocarbenium ions. Thus the ethylenechloronium ion is a "static" ion, while the propylenechloronium ion is not.

7.1.3 2,3-Dimethylethylenehalonium Ions

Bridged 2,3-dimethylethylenehalonium ions were formed from *meso*- and *dl*-dibromobutanes, and from *erythro*- and *threo*-*dl*-2-bromo-3-fluorobutanes under stable ion conditions.¹⁴ Starting from either conformational isomer in the brominated materials resulted in a mixture of two ions, that is, *cis* and *trans* halonium ions. The pmr spectra of the ions are shown in Figure 8.

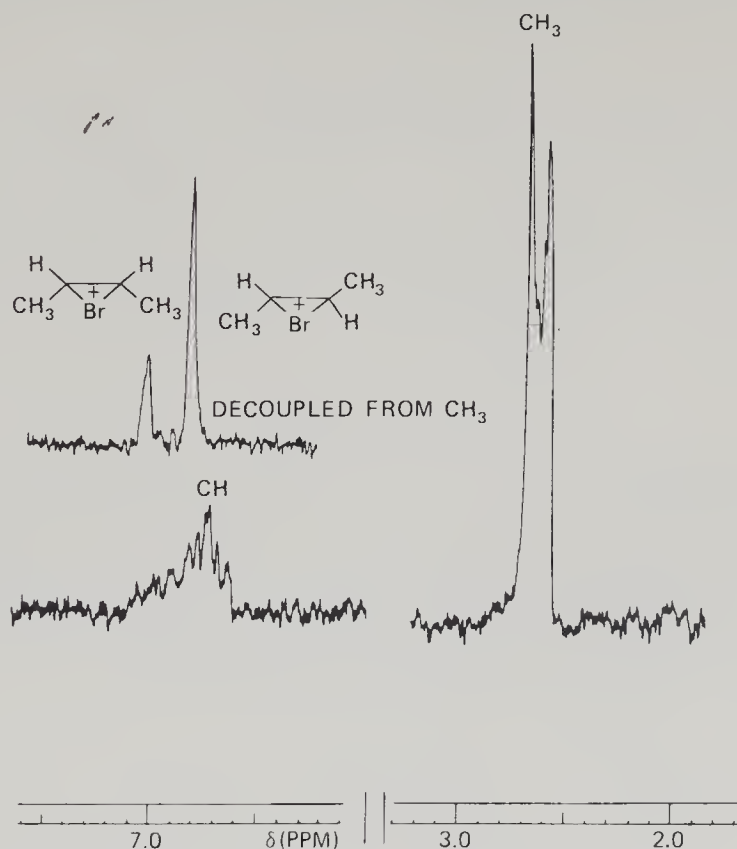
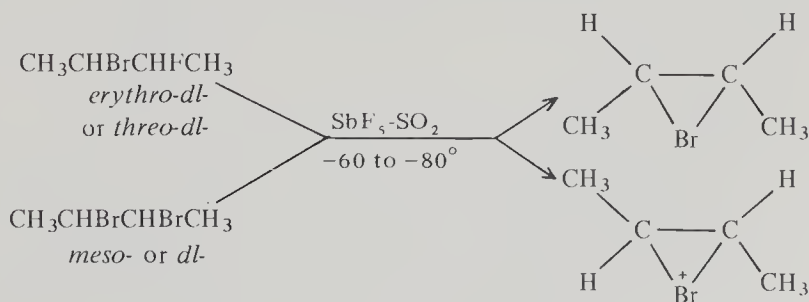
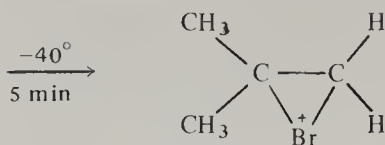
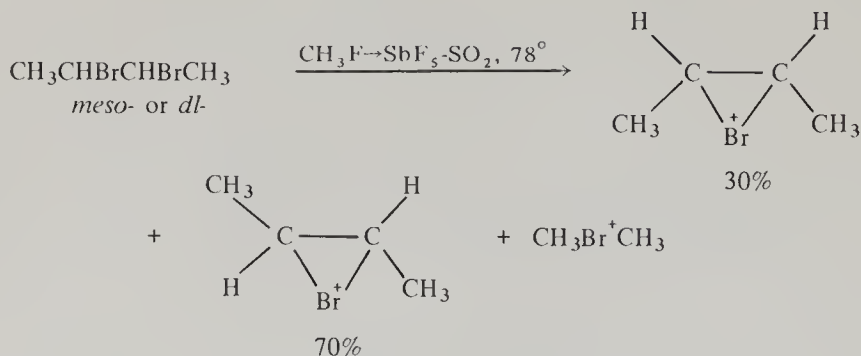


Figure 8. Pmr spectra of *cis*- and *trans*-2,3-dimethylethylenebromonium ions.

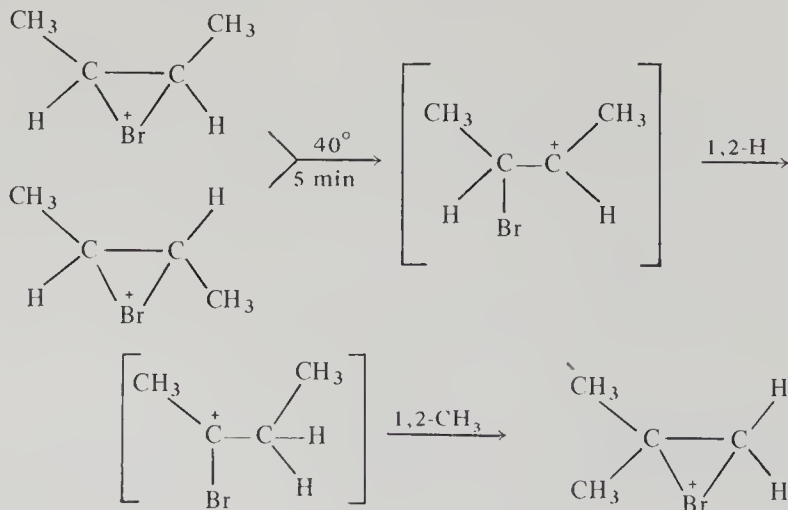




The pmr spectra are complex (that of AA'XX' system), but double irradiation decoupled them, revealing the presence of two (somewhat broadened) singlets in the methine region separated by 12 Hz. Regardless of the care used in the preparation of the ions, the same mixture was obtained. Furthermore, the same ratio of ions was also observed when *meso*- and *dl*-2,3-dibromobutane were treated with $\text{CH}_3\text{F} \rightarrow \text{SbF}_5\text{-SO}_2$ solution at -78° . Under these conditions



dimethylbromonium ion was also formed. Warming the isomeric 2,3-dimethylethylenebromonium ions to -40° for about 5 min causes isomerization to take place to give 2,2-dimethylethylenebromonium ions. The mechanism of this transformation is interesting. The breaking of a carbon-bromine bond must be followed by subsequent 1,2-hydrogen and 1,2-methyl shifts. The two involved intermediates were not observed, however, as long-lived ions.



Ionization of *erythro*- or *threo*-*dl*-2-iodo-2-fluorobutane is at least 70% stereospecific. The ionization of *erythro*-*dl*-2-iodo-2-fluorobutane produces an ion to which *trans* configuration can only be assigned, but ionization of *threo*-*dl*-2-iodo-2-fluorobutane produces 70% *cis*-configuration ion and 30% *trans*-1,2-dimethylethylenehalonium ion. The structural assignments of the ions was based on the analysis of their pmr shifts and coupling constants (Figure 9),

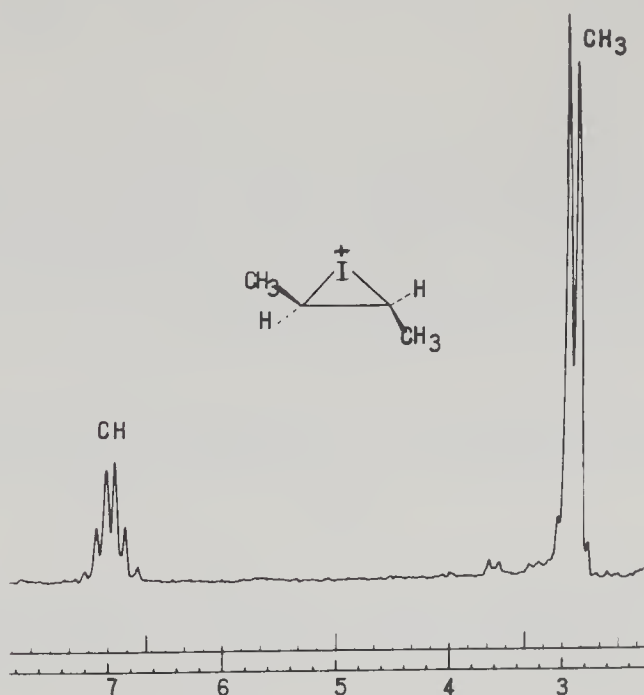
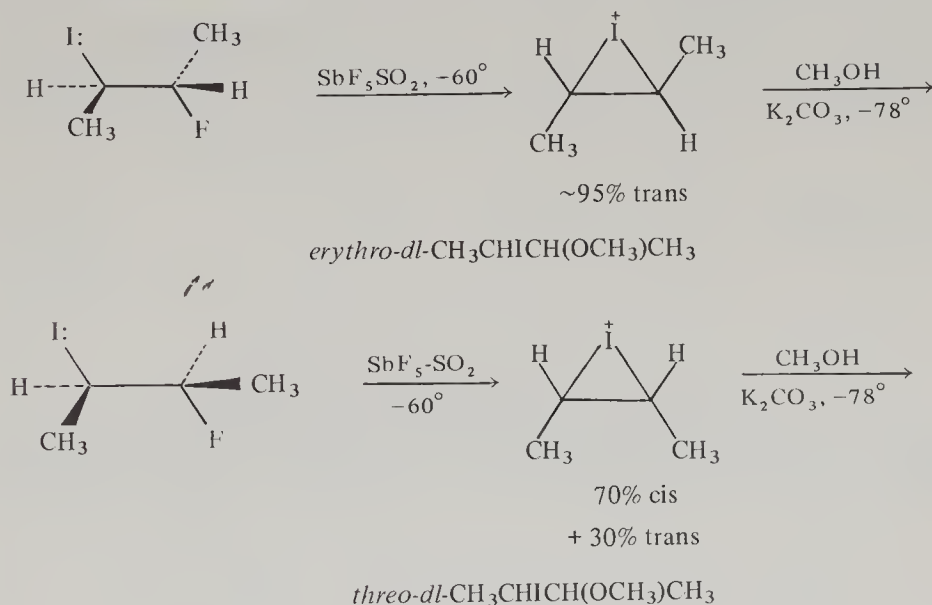
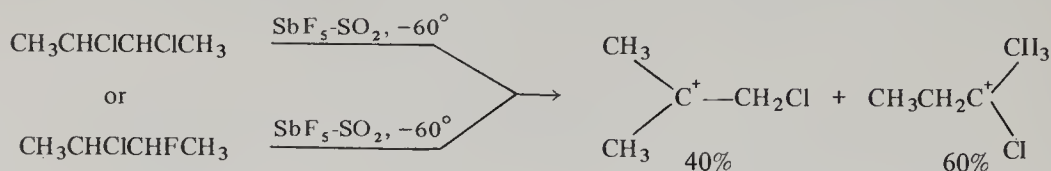


Figure 9. Pmr spectrum of the *trans*-2,3-dimethylethyleneiodonium ion.

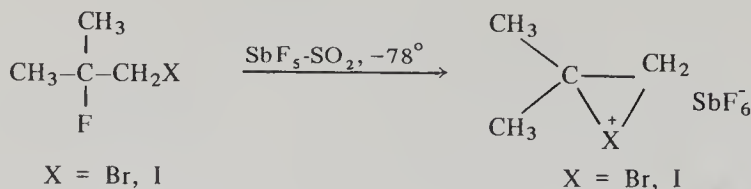
as well as on methanolysis of the ions in the presence of solid potassium carbonate, which produced *erythro-dl*-2-iodo-3-methoxybutane and *threo-dl*-2-iodo-3-methoxybutane, respectively. Surprisingly, no corresponding rearrangement of the 2,3-dimethylethyleneiodonium ion to the 2,2-dimethylethyleneiodonium ion, or interconversion of the stereoisomers, could be detected after 10 min at -15° , although prolonged storage at about this temperature results in some conversion of each isomer to other.

Ionization of *erythro*- or *threo*-2-fluoro-3-chlorobutane or *meso* or *dl*-2,3-dichlorobutane results in immediate rearrangement to a mixture of dimethyl-, chloromethyl-, and methy, ethylchlorocarbenium ions in a 40:60 ratio.

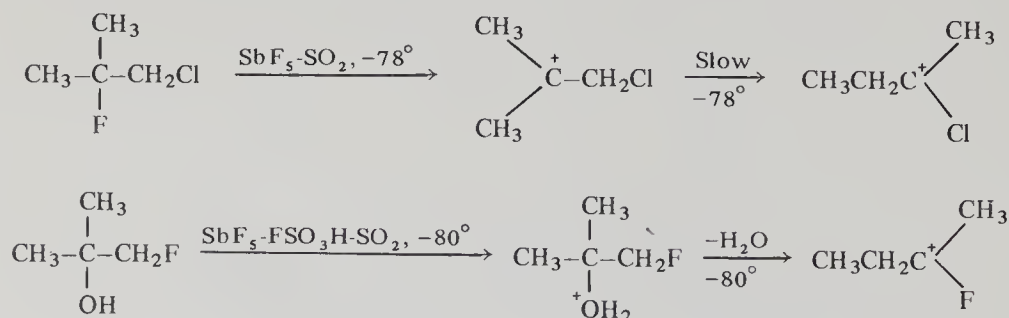


7.1.4 2,2-Dimethylethylenehalonium Ions

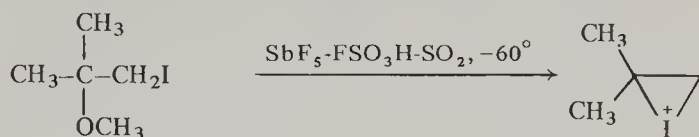
When 1-halo-2-fluoromethylpropanes are ionized in SbF_5SO_2 solution at -78° , dimethylethylenehalonium ions are formed with bromine and iodine



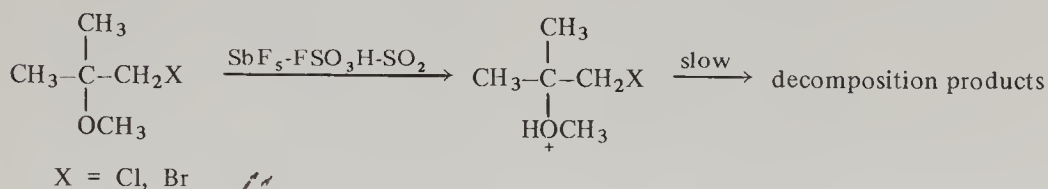
acting as *n*-donor participating atoms.^{14c} The pmr spectra for the bromo- and iodonium ions are similar, and each displays two singlet absorptions at δ 3.32 (3H) and 5.55 (1H) or δ 3.45 (3H) and 5.72 (1H), respectively. Chlorine and fluorine, however, show no ability to form bridged ions, and the corresponding ions exist solely as open-chain halocarbenium ions.



Furthermore, protonation of 1-iodo-2-methoxy-2-methylpropane in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ solution immediately gives the 2,2-dimethylethyleneiodonium ion and protonated methanol, while the corresponding chloride and bromide are

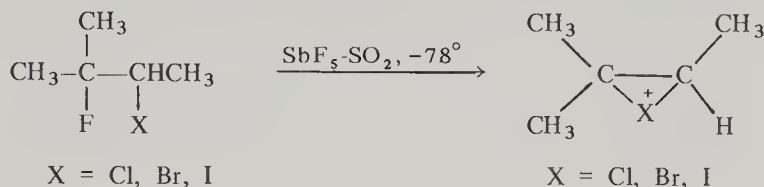


O-protonated and then slowly decompose to unidentified products (polymers).



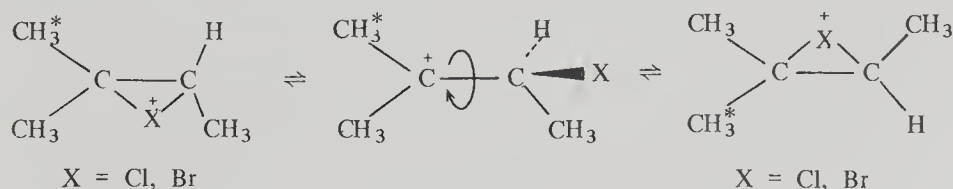
7.1.5 Trimethylethylenehalonium Ions

When 2-fluoro-3-chloro(or bromo or iodo)-2-methylbutane is ionized in $\text{SbF}_5\text{-SO}_2$ solution at -78° , stable trimethylethylenehalonium ions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are formed.^{14a} The pmr data of the ions are summarized in Table 34. The



pmr spectra of the trimethylethylenebromonium and iodonium are shown in Figure 10a and b. The deshielding effects of both the methyl and methine protons decrease going from chlorine to iodine, indicating the significant charge at the halogen atoms. The unsymmetric nature of the carbon-halogen bonding and the increased charge located at the tertiary center is shown by the large difference in deshielding of the single methyl group compared to the geminal methyl groups.

In the spectra of trimethylethylenebromonium and -chloronium ions, equivalence of the geminal methyl groups is observed. This suggests either a rapid equilibration involving the open chain halocarbenium ions



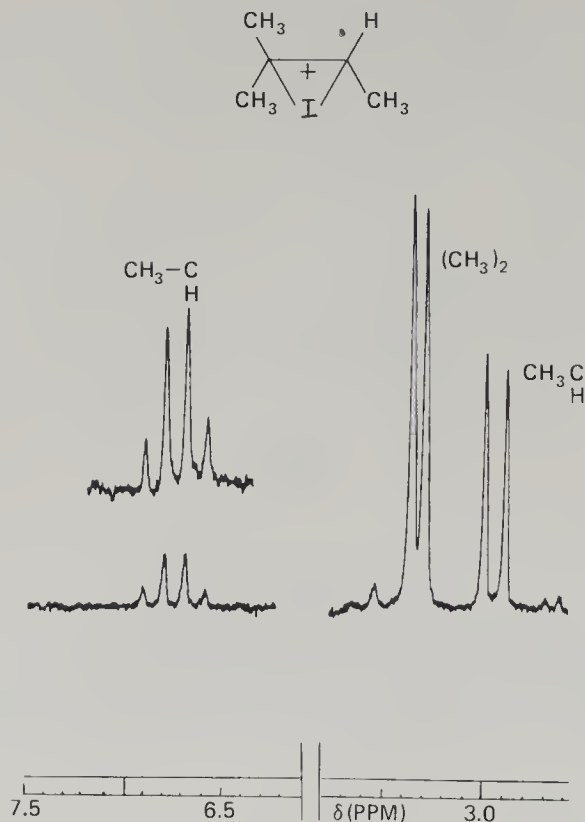
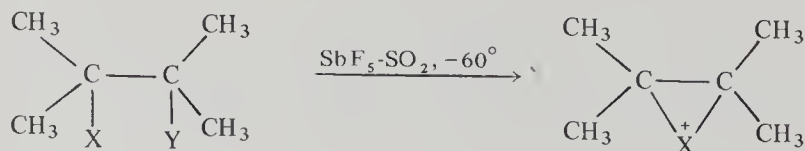


Figure 10a. Pmr spectrum of the trimethylethyleneiodonium ion.

or that the chemical shifts of the geminal methyl groups are accidentally equivalent. The former suggestion could be substantiated by the variation of the spectra of the ions with temperature, but in the temperature range so far studied this was not observed. The more suitable cmr spectra were not studied, however yet in sufficient detail.

7.1.6 Tetramethylethylenehalonium Ions

The first direct observation of ethylenehalonium ions in solution was made by Olah and Bollinger⁹ in 1967, when 2,3-dihalo-2,3-dimethylbutanes were ionized in $\text{SbF}_5\text{-SO}_2$ solution at -60° . Stable tetramethylethylenehalonium ions were formed with chlorine, bromine, and iodine acting as donor atoms.



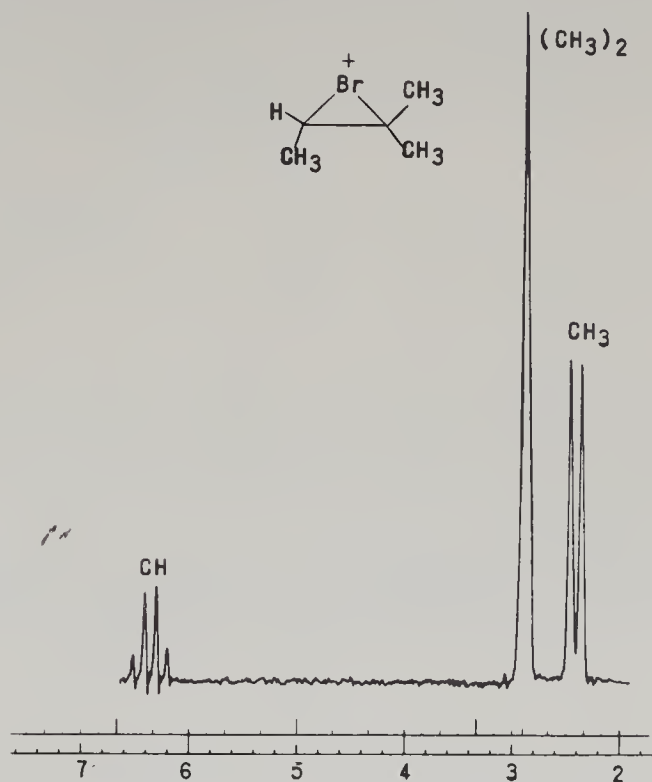


Figure 10b. Pmr spectrum of the trimethylethylenebromonium ion.

X = Cl; Y = F, Cl

X = Br; Y = F, Br

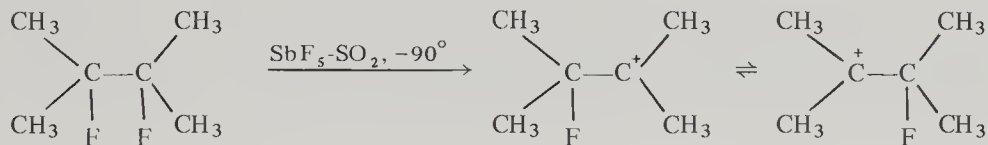
X = I; Y = F

X = Cl

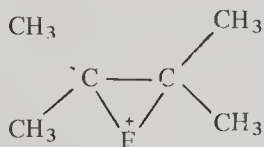
X = Br

X = I

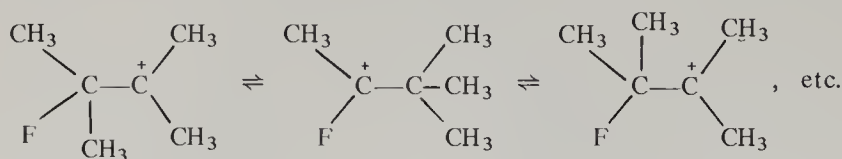
Fluorine as a neighboring group, however, gave only the rapidly equilibrating open-chain β -fluorocarbenium ion, even at -90° .



Whether this equilibration process involves a higher-lying, fluorine-bridged transition state (or intermediate) not yet observed, as suggested by Clark,¹⁵⁶



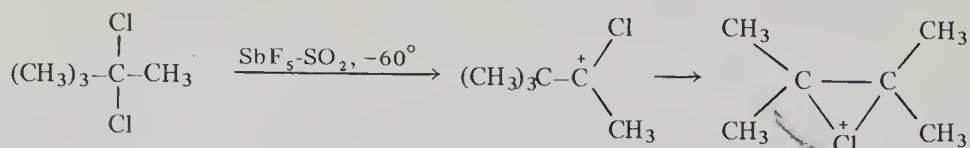
or, more probably, as suggested by Olah and Bollinger,⁹ an equilibration process including 1,2-methyl shifts (in their ability to stabilize tertiary carbonium centers methyl and fluorine are not too different), cannot be determined by



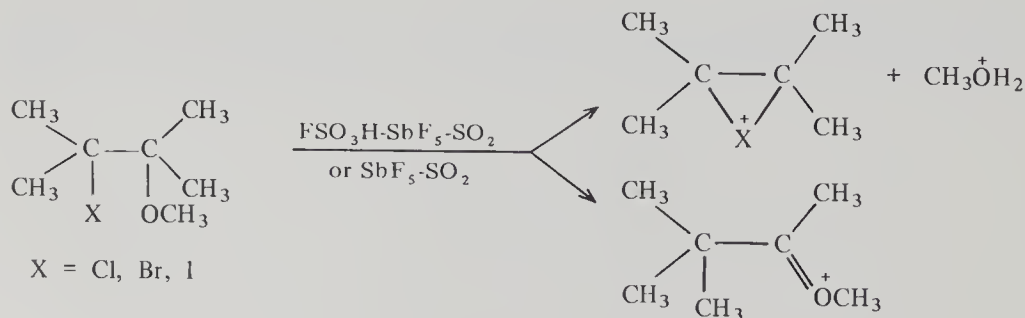
direct experimental evidence. However, in solution chemistry there seems to be no indication of the formation of any positively charged fluorine species. Bridged fluoronium ions therefore also seem to be unlikely, and the latter equilibrium seems to well explain the experimental data without the necessity of involving a bridged fluoronium ion.

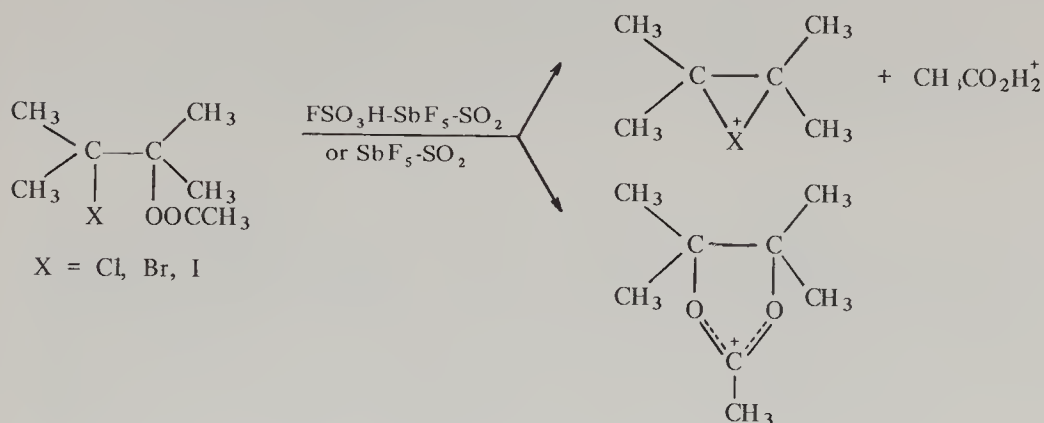
The pmr spectra of tetramethylethylenehalonium ions show singlet absorptions at δ 2.72 (X = Cl), 2.86 (X = Br), and 3.05 (X = I). The rapidly equilibrating fluorinated ion, in contrast, shows a doublet at δ 3.10 ($J_{\text{HF}} = 11$ Hz) in its pmr spectrum.

2,2-Dichloro-3,3-dimethylbutane (pinacolone dichloride) is also ionized in $\text{SbF}_5\text{-SO}_2$ solution at -60° to give the tetramethylethylenechloronium ion formed through the unstable chlorocarbenium ion intermediate. Ionization



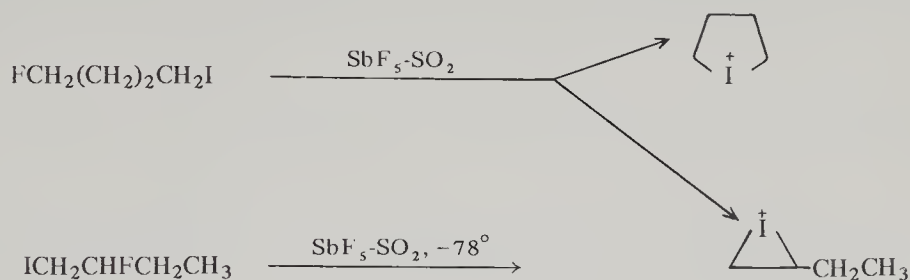
of 2-halo-2-methoxy- and 2-halo-3-acetoxy-2,3-dimethylbutanes in either $\text{SbF}_5\text{-SO}_2$ or $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ solution yields a mixture of tetramethylethylenehalonium ions, acetoxonium ions, and methylated ketones.



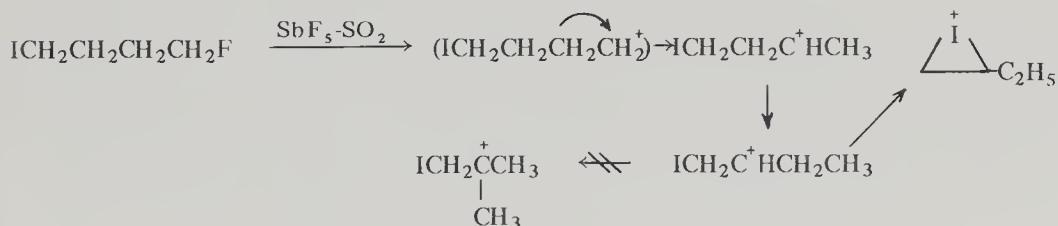


7.1.7 1-Butyleneiodonium Ion (2-Ethylethyleneiodonium Ion)

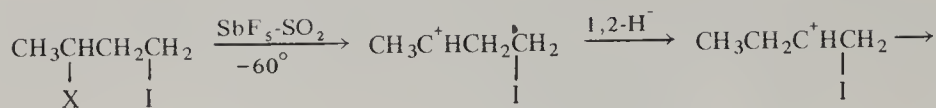
Olah and Peterson reported the preparation of the 1-butyleneiodonium ion from the ionization of either 1-fluoro-4-iodobutane or 1-iodo-2-fluorobutane



with $\text{SbF}_5 \cdot \text{SO}_2$ solution at -78° .¹⁵ Tetramethyleneiodonium ion was also formed in the reaction of 1-fluoro-4-iodobutane. The mechanism of its formation may be the following.

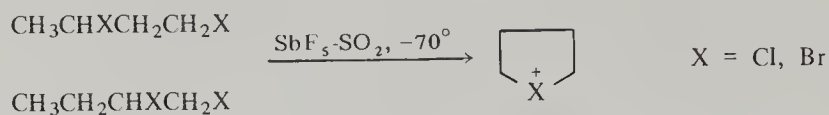


Furthermore, ionization of 1-iodo-3-halobutanes in $\text{SbF}_5 \cdot \text{SO}_2$ solution at -60° gives only the 1-butyleneiodonium ion. Obviously, ionization takes place at the secondary carbon atom to give an intermediate ion which then undergoes a 1,2-hydrogen shift. Subsequent iodine participation would form the stable 1-butyleneiodonium ion. However, when 1,2- and 1,3-dibromo(or chloro)butanes

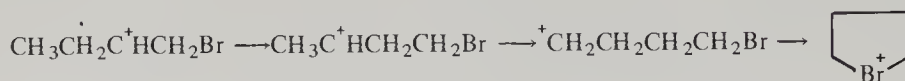


X = Cl, Br, I

are treated with $\text{SbF}_5 \cdot \text{SO}_2$ solution under similar conditions, only the corresponding tetramethylenehalonium ions are obtained. Their formation is an unusual reaction for a cationic species in strong acid media in which one



usually finds nonbranched cations rearranging to branched ones, but rarely the reverse. The driving force for this rearrangement is assumed to be the formation of a very stable five-membered-ring ion. The mechanism for this rearrangement



may involve successive 1,2-hydrogen shifts. Thus far, 1-butylenebromonium or -chloronium ions are not yet known.

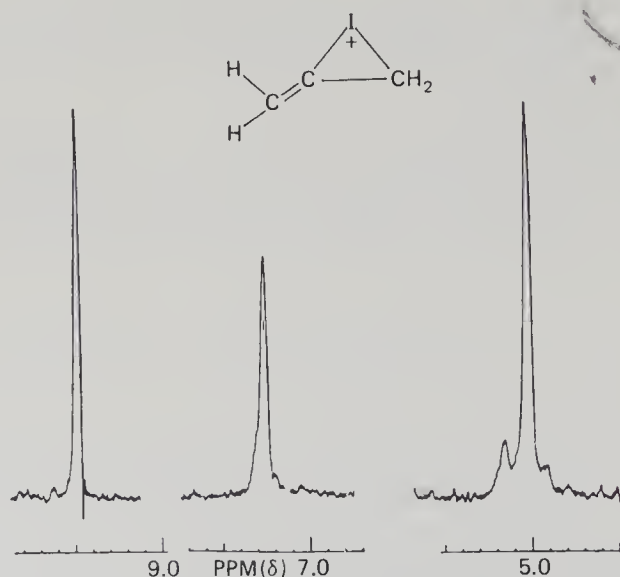
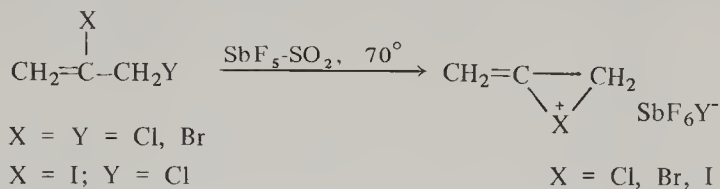


Figure 11. Pmr spectrum of the propadienyliodonium ion in $\text{SbF}_5 \cdot \text{SO}_2$ solution at -80° .

7.1.8 Propadienylhalonium Ions

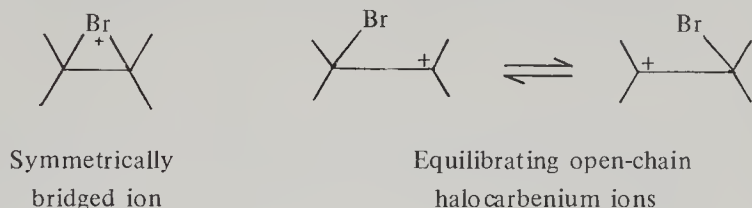
Propadienylhalonium ions were prepared from 2,3-dihalopropenes and $\text{SbF}_5\text{-SO}_2$ solution at -70° .¹⁵⁷ The pmr spectrum of the propadienyliodonium ion is



shown in Figure 11. Pmr data of the ions in each case show three singlets with a ratio of 2:1:1 (from high field to low field). Geminal and long-range couplings are not observed in the ions.

7.2 CARBON-13 NMR STUDIES OF ETHYLENEHALONIUM IONS

Olah and White¹⁵⁸ first reported carbon-13 nmr studies of ethylenehalonium ions including that of the tetramethylethylenebromonium ion. A recent more detailed reinvestigation of the cmr of ethylenehalonium ions included



a comprehensive series of ethylenebromonium, as well as ethylenechloronium and -iodonium ions.^{26d} The cmr data of the ethylenehalonium ions are summarized in Table 35.

The structures of most of the ions in Table 35 have been discussed previously in connection with their pmr spectral parameters. Cmr studies, however, give valuable further information.

There are several structural possibilities for ethylenehalonium ions: the static symmetrically bridged ion in which the $\text{C}_2\text{-X}$ bond length is equal to the $\text{C}_3\text{-X}$ bond length (1), the static unsymmetrically bridged ion in which the $\text{C}_2\text{-X}$ bond length is not equal to the $\text{C}_3\text{-X}$ bond length (2), and the halonium ion in equilibrium with a pair of open-chain β -haloalkenium ions (3). If one

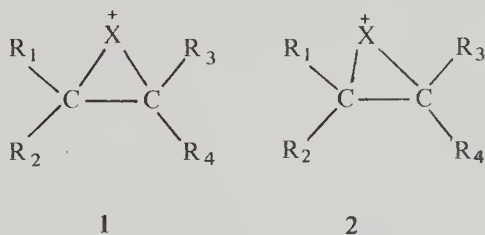
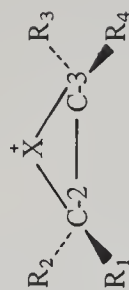
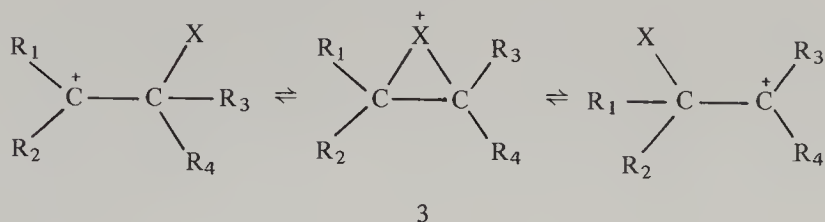


TABLE 35

Carbon-13 Chemical Shifts of Ethylenehalonium Ions^a

R ₁	R ₂	R ₃	R ₄	X	C-2	C-3	CH ₃ (C-2)	CH ₃ (C-3)
H	H	H	H	Br	73	73		
CH ₃	H	H	H	Br	122.2	72.7	25.4	
CH ₃	H	CH ₃	H	Br ^b	110.9	111.8	22.4	22.4
H	CH ₃	CH ₃	H	Br	108.8	108.8	17.4	17.4
CH ₃	CH ₃	H	H	Br	211.4	50.5	35.4	
CH ₃	CH ₃	CH ₃	H	Br	172.8	92.7	30.5	18.2
CH ₃	CH ₃	CH ₃	CH ₃	Br	139.7	139.7	29.7	26.7
H	H	H	H	Cl ^c	74.1	74.1		
CH ₃	CH ₃	CH ₃	CH ₃	Cl	151.7	151.7	28.0	28.0
H	H	H	H	I	87.9	67.9		
CH ₃	H	CH ₃	H	I	105.2	105.2	24.3	24.3
H	CH ₃	CH ₃	H	I	104.0	104.0	19.2	19.2
CH ₃	CH ₃	H	H	I	186.0	52.8	33.2	
CH ₃	CH ₃	CH ₃	CH ₃	I	124.8	124.8	28.0	28.0

^a parts per million from CS₂. In SO₂ at -40° unless otherwise indicated.^b In SO₂ at -60°.^c In SO₂ClF at -80°.



of the open ions is a primary carbenium ion its formation will be energetically particularly unfavorable.

7.2.1 Symmetrically Substituted Ethylenehalonium Ions

For symmetrically substituted ions only structures 1 and 3 are possible, and in the latter case there would be equal amounts of the two open-ion forms.

Both chemical shift and carbon-hydrogen coupling constant data show that the structure of the ethylenebromonium ion is that of the bridged ion 1. Similar considerations (i.e., chemical shift data) applied to the other parent ethylenehalonium ions indicate that they also are symmetrically bridged ions. The carbon-13 chemical shifts of the three parent ethylenehalonium ions are in the range δ_{13C} 74-68, whereas the α -carbon shifts of three related open-chain dialkylhalonium ions occur over a much wider range. This most likely arises from a larger β -substituent effect in ethylene halonium ions, because of the greater proximity of the positively charged halogen atom to the β carbon in these cyclic ions ($C_\beta-C_\alpha-X$). The carbon shift is dominated by charge effects, rather than by the individual differences in the nature of the halogen atoms. The large β -substituent effect in the cyclic ions explains why attempts to estimate their chemical shifts by regarding each carbon atom as subject to both an α - and β -substituent effect are unsuccessful (except in the case of the ethylenechloronium ion, in which the agreement may be fortuitous).

The cmr and pmr spectra of the 2,3-dimethylethylenebromonium ion, prepared from either *meso* or *dl*-dibromobutanes, reveal the presence of *cis* and *trans* isomers. The ion is therefore most likely the symmetrically bridged ion, since it would be extraordinary if noticeable amounts of open ion did not lead to the interconversion of *cis* and *trans* isomers at a rate considered rapid on the nmr time scale.

The 5-ppm upfield shift in the methyl carbon shielding of the *cis* isomer compared with the *trans* isomer reflects the larger steric interactions between the methyl groups in the former case.¹⁵⁹ A similar effect of the same magnitude is observed in the two isomers of the 1,2-dimethylethyleneiodonium ion.

The *cis/trans* ratio in the 2,3-dimethylethyleneiodonium ion depends on which precursor is used to prepare the ion. The iodonium ion, then, clearly is a symmetrically bridged ion.

The structure of the tetramethylethylenebromonium ion has been discussed in some detail.^{3,14,26,158} The cmr data first were considered inconsistent

with either a bridged species or a rapidly equilibrating pair of open ions, so the structure of the ion was proposed to be a mixture of both forms.

However, the available nmr data are still subject to two interpretations. The larger than usual substituent effect^{153,160,161} that occurs in the C-2 and C-3 shielding of the ethylenebromonium ion on methyl substitution may indicate an increased carbenium ion character for the C-2 and C-3 carbons if the ion is a static bridged ion, or some contribution of open-chain β -halocarbenium ions if the ion is a symmetrically bridged ion in equilibrium with open-ions forms. In support of the former structure, it has been argued from carbon-13 chemical shift data for the tetramethylethylenephonium ion that the ion has the symmetrically bridged structure.

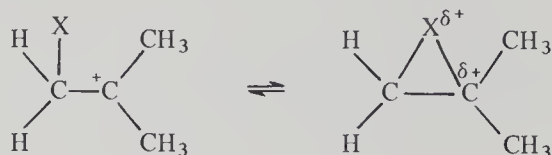
It is of interest that the differences in the ring carbon shifts of the three tetramethylethylenehalonium ions are larger than in the three parent ions. Iodine can accommodate positive charge better than chlorine or bromine, so more carbenium ion character at C-2 and C-3 exists in the tetramethylethylenebromonium or -chloronium ion than in -iodonium ion; or there is less contribution of the β -halocarbenium ion for iodine than for chlorine or bromine.

7.2.2 Unsymmetrically Substituted Ethylenehalonium Ions

2-Methyl- and 2,2-dimethylethylenebromonium ions may exist as unsymmetrically bridged ions (2) or as equilibrium mixtures of unsymmetrically bridged ions and open-chain secondary or tertiary haloalkyl cations. On the basis of cmr data for one particular temperature alone it is not possible to decide between these two possibilities.¹⁶²

The α -substituent effect of the methyl group in the 1-methyl-1,1-dimethylethylenehalonium ion is 49 ppm, while that of two geminal methyl groups in the 1,1-dimethyl- ion is 138.4 ppm. Accompanying these downfield shifts at C-1 are upfield shifts of 0.3 and 12.5 ppm for the C-2 shielding in the two ions, respectively.

The data for these ions, and those for β -bromocumyl ions, show β -bromine substituent effects, in ions of the type $RR'C^+CH_2Br$, of from 21 to 117 ppm. Apparently, the extent to which bromine may participate in the stabilization of a positively charged β carbon may vary, depending on the electron needs of the carbon. The cmr spectrum of the 2,2-dimethylethylenebromonium ion was studied at different temperatures to try to distinguish between a static unsymmetrically bridged ion whose cmr spectrum should be temperature-independent and an equilibrating system of a bridged ion with a β -halocarbenium ion whose cmr spectrum should vary with temperature. The 2,2-dimethyl-



ethylenechloronium ion has been shown to exist as a β -haloalkylcarbenium ion. Since bromine has a greater ability than chlorine to accommodate a positive charge, it is expected that the corresponding bromonium ion will be intermediate in character between a purely bridged ion and a β -haloalkylcarbenium ion, and therefore its cmr spectrum should be quite dependent on temperature.

The carbon-13 chemical shifts for the methylene and methyl carbons in the ion at several temperatures (-20 to -80°) are shown in Table 36. It

TABLE 36
Temperature Dependence of the Carbon-13 Chemical Shifts
in the 2,2-Dimethylethylenebromonium Ion

Temperature ($^\circ\text{C}$) ^b	$\delta_{13\text{C}}$ ^a			
	C-2	CH ₂	CH ₃	Δ
-20		59.10	34.21	24.89
-30		59.27	34.19	25.08
-40	211.3	59.37	33.98	25.38
-50		59.62	34.05	25.56
-60		59.58	33.71	25.87
-70		60.09	33.76	26.34
-80	206.17	59.87	33.45	26.41

^a In SO_2 ; parts per million from external capillary of TMS.

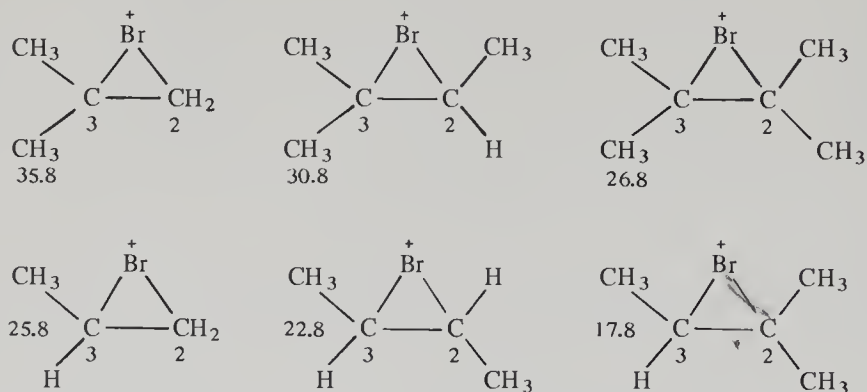
^b $\pm 1^\circ$.

was impractical to obtain the C-2 shieldings for all seven temperatures in Table 36, because of the very large number of FT accumulations necessary to observe this signal at the low ion concentrations obtainable for this low-temperature study. Signals were measured from external TMS, and it is not known how significant the small absolute changes for δ_{CH_3} and δ_{CH_2} shown in Table 36 are. However, the internal chemical shift difference ($\delta_{\text{CCH}_3} - \delta_{\text{CCH}_2}$) should be temperature-independent, so that changes in its value reflect changes in the position of the equilibrium. An increase in the open-ion form will result in a deshielding of the CH_3 and C^+ resonances, but it is not obvious what should happen to the CH_2 absorption. In the open-ion form the methylene carbon shielding is subject to α -bromine and $\alpha\text{-C}^+$ substituent effects, while in the bridged ion it experiences a partial $\alpha\text{-C}^+$ effect and an increased bromine substituent effect, since the bromine now carries more charge. (For the analogous ion in the five-membered-ring series this problem does not exist, because in the open ion the shielding of the methylene carbon bonded to bromine is not subject to an $\alpha\text{-C}^+$ effect, hence should be shielded from the corresponding resonance in a bridged structure.) The observed variation in $\delta_{\text{CH}_3} - \delta_{\text{CH}_2}$ with

temperature therefore cannot be given a detailed explanation in terms of molecular processes, but it does signify some sort of equilibrium.

The deshielding of 5 ppm in the C-2 shielding with a 40° decrease in temperature indicates that at lower temperatures more of the bridged ion is present than at higher temperatures. The relatively small change in the C-2 resonance suggests that the 2,2-dimethylethylenebromonium ion is mainly the static bridged ion in equilibrium with only a small amount of the β -haloalkyl-carbenium ion.

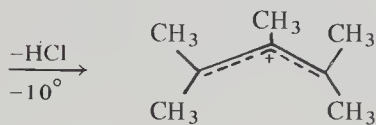
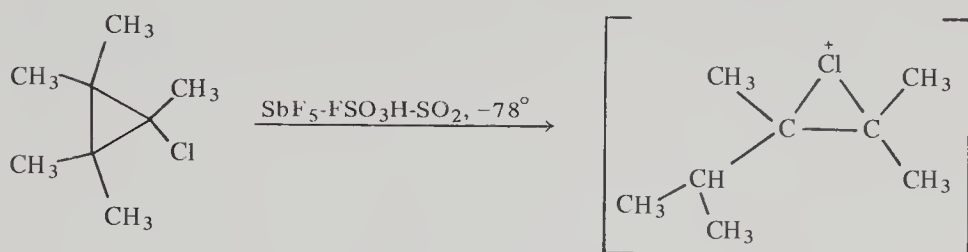
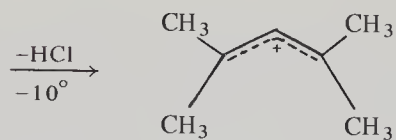
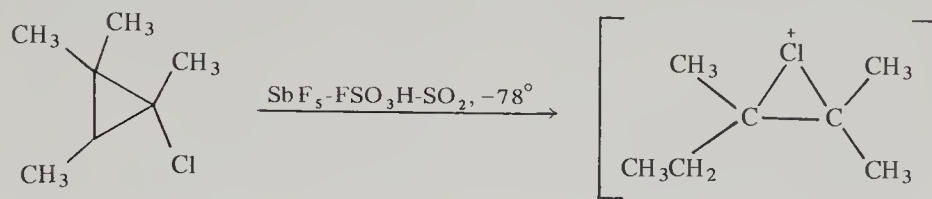
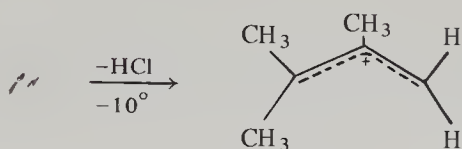
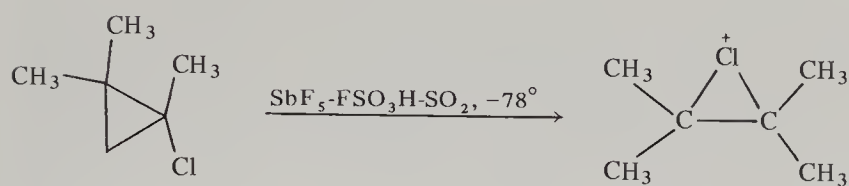
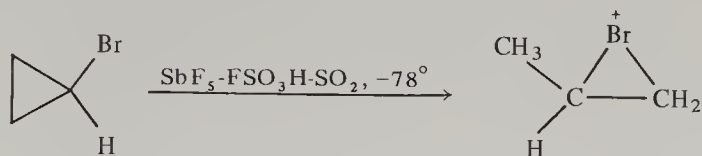
Substitution of a third methyl group into the ethylenebromonium ion results in an ion whose charge distribution is more symmetrically disposed. This is reflected by an upfield shift of 39 ppm in the C-2 shielding compared with dimethylethylenebromonium ions. The equivalency of the geminal methyl groups in both the pmr and the cmr spectra of the 2,2,3-trimethylethylenehalonium ion suggests that the ion exists as an equilibrating mixture of the unsymmetrically bridged ion and an open-ion form. It is, however, possible, although less likely, because of the large cis methyl shielding effect, that both the geminal methyl carbon and proton shielding are accidentally equivalent in the bridged ion, and that consequently equilibration does not occur.



The order of the methyl shieldings is the same as we would predict from a consideration of the relative degrees of electron deficiency at C-2 and C-3 in these ions; similarly for the methyl shifts in related ions grows. For corresponding ions in both series the methyl shift is deshielded in the former case, as expected.

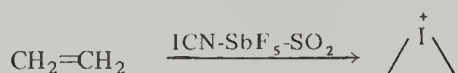
7.3 PREPARATION VIA PROTONATION OF CYCLOPROPYL HALIDES

The protonation of cyclopropyl halides in superacids gives the corresponding three-membered-ring halonium ions.¹⁶³ The highly substituted ethylenehalonium ions, on warming to -10°, dehydrohalogenate to give the corresponding substituted allyl cations.



7.4 PREPARATION VIA DIRECT HALOGENATION OF OLEFINS

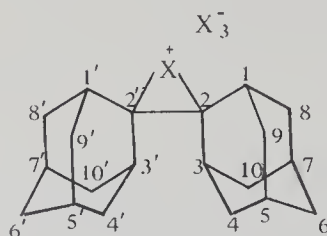
We have already discussed the preparation of ethylenehalonium ions from 1,2-dihaloalkanes and $\text{SbF}_5\text{-SO}_2$ under stable ion conditions. Electrophilic additions of halogens to olefins show high trans stereoselectivity, and consequently are assumed to take place via ethylenehalonium ion intermediates.^{4-7,164} When elementary halogens are reacted with olefins in the presence of Lewis acids (e.g., SbF_5), ethylenehalonium ions are formed. Even though the corresponding ethylenehalonium ions are formed under these stable ion conditions, the reactions could have also included an addition neighboring-halogen-elimination mechanism. Recently, Olah et al.¹⁶⁵ used cyanogen iodide or bromide in the presence of a slight excess of SbF_5 in SO_2 or SO_2ClF solution to prepare ethylenehalonium ions at a low temperature directly. For example, ethylene reacted with ICN-SbF_5 solution at -60° to give the ethyleneiodonium ion. The reaction of ethylene with BrCN-SbF_5 in SO_2



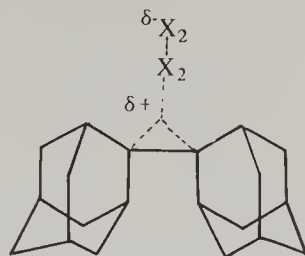
also resulted in the formation of polymeric products. However, ClCN-SbF_5 did not react with ethylene (or with 2,3-dimethyl-2-butene and adamantylideneadamantane) to give the corresponding chloronium ions, probably indicating the inverted polarity of cyanogen chloride compared with the other cyanogen halides. Tetramethylenebromo- and tetramethyleneiodonium ions have also been prepared by direct halogenation with the appropriate cyanogen halides and antimony pentafluoride.

7.5 Differentiation of π - and σ -Bonded Halogen Complexes of Alkenes

Strating, Wiering and Wynberg^{166,167} reported that adamantylideneadamantane, a sterically highly hindered olefin, reacted with chlorine in hexane and bromine in CCl_4 solution to give the corresponding chloronium and bromonium salts. They proposed the structure of these rather insoluble salts (on which no spectroscopic study was conducted) to be that of three-membered-ring ethylenehalonium ions (σ complexes). Olah and coworkers¹⁶⁵ subsequently investigated these

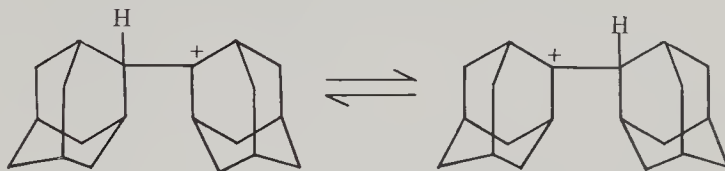


stable salts by nmr (hydrogen-1 and carbon-13) spectroscopy, and concluded that they are not three-membered-ring halonium ions but molecularly bound π complexes.



X = Cl, Br, I

Adamantylideneadamantane reacted with neat bromine or bromine in CCl_4 , SO_2 , HF-SO_2 , or $\text{FSO}_3\text{H-SO}_2$ solution, or with bromine and $\text{AgSbF}_6\text{-SO}_2$, to give the same stable bromine π complex. Similar π complexes were also prepared by treating adamantylideneadamantane with *N*-bromosuccinimide or cyanogen bromide in $\text{FSO}_3\text{H-SO}_2$ solution. At -30° adamantylideneadamantane reacted with $\text{FSO}_3\text{H-SO}_2$ to give the rapidly equilibrating carbenium ion which on treatment with bromine or chlorine forms the halogen π complexes. The



iodine complex was also obtained by adding adamantylideneadamantane to a solution of cyanogen iodide in $\text{FSO}_3\text{H-SO}_2$ at -20° . The pmr spectra of the halogen π complexes of adamantylideneadamantane are shown in Figure 12. The carbon-13 shifts are summarized in Table 37. The carbon shifts of C-2 and C-2' are decisive in determining if the complexes are indeed three-membered-ring halonium ions (σ complexes), molecularly bonded π complexes, or rapidly equilibrating 2-halocarbenium ions.

Rapidly equilibrating 2-halocarbenium ions can be eliminated, because the chemical shift of the olefinic carbons C-2 and C-2' at $\delta_{13\text{C}}$ 36.0 (X = Cl), 158.7 (X = Br), and 153.7 (X = I) do not agree with the calculated average shift (e.g., approximately $\delta_{13\text{C}}$ 204) for rapidly equilibrating systems. In addition, the steric restriction placed on the movement of the halogen atoms by the C-8 and C-10 and C-8' and C-10' protons also seems to prevent this halogen complex from being either a rapidly equilibrating ion pair, a mixture of bridged and equilibrating ions, or a rapidly equilibrating pair of partially bridged ions.

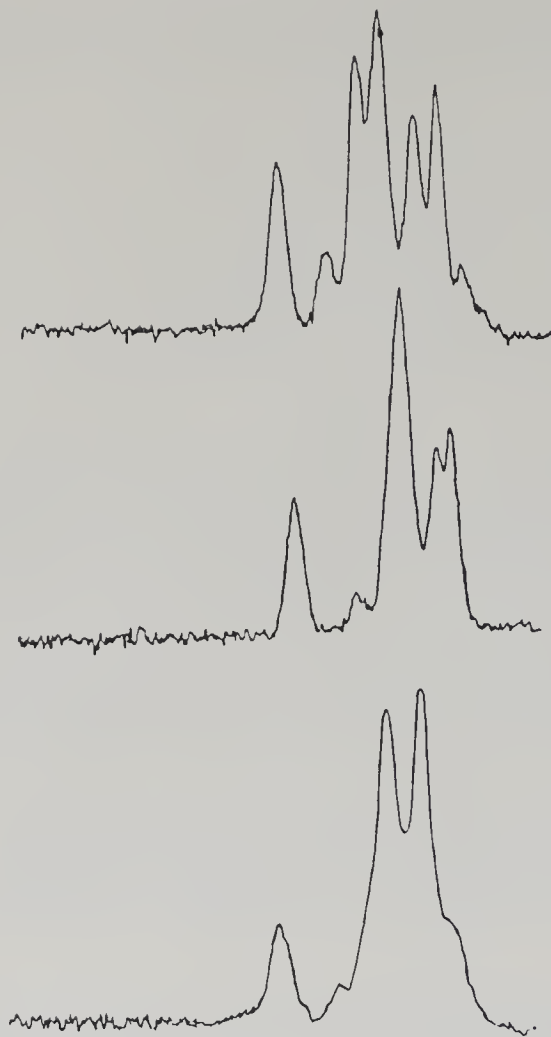


Figure 12. PMR spectra of the adamantylidenadamantane-iodine complex in $\text{FSO}_3\text{H-SO}_2$ at -20° (top), of the halogen complex in HF-SO_2 at -30° (center), and of adamantylidenadamantane in $\text{FSO}_3\text{H-SO}_2$ at -30° .

The halogen adducts therefore are most likely π -bonded halogen complexes. There is also additional evidence that these structures are different from three-membered-ring ethylenehalonium ions (σ complexes). The adamantylidenadamantane-bromine complex in CCl_4 transfers bromine irreversibly to cyclohexene or tetramethylethylene, forming the corresponding dibromides and adamantylidenadamantane. In addition, all other halogen adducts on quenching with nucleophiles also yield the precursor olefin, rather than any 1,2-addition products. Unlike ethylene, adamantylidenadamantane forms only π complexes with HF in SO_2ClF or with SbF_5 in SO_2ClF , which can be readily converted back, by the addition of nucleophiles, to the starting olefin. The

TABLE 37
Carbon-13 Chemical Shifts of Adamantylideneadamantane Complexes^a

Compound	Solvent ^b	C-2	C-1 and C-3	C-4 and C-9 (C-8 and C-10)	C-8 and C-10 (C-4 and C-9)	C-5 and C-7	C-6
Adamantylidene- adamantane	C ₆ H ₆	131.7	32.3	39.7	39.7	29.0	37.6
Protonation	SO ₂ (-80°)	208.6	50.3	46.7	46.7	31.5	37.8
Bromine complex	Br ₂	158.7	39.9	45.1	43.0	29.4	38.9
	SO ₂ ClF (-40°)	157.7	39.8	44.9	42.4	29.1	39.2
Chlorine complex	SO ₂ (-70°)	157.8	37.7	43.4	39.7	27.4	36.7
Iodine complex	SO ₂ (-70°)	153.7	38.5	44.0	43.4	28.0	37.8
SbF ₅ complex	SO ₂ (-82°)	156.7	36.8	42.4	38.8	26.6	35.8
	SO ₂ ClF (-80°)	157.3	39.6	43.6	37.6	27.4	36.6
HF complex	SO ₂ ClF (-80°)	155.1	36.0	41.6	38.1	26.0	35.2

^a Carbon-13 shifts are referred to TMS in part per million.

^b Probe temperature 30-35° unless otherwise indicated.

cmr shifts in these π complexes are very similar to those observed for the halogen complexes (Table 37). The observation of these π complexes is significant, since they seem to represent a clear differentiation of σ and π complexes in electrophilic additions to olefins.

Tetramethylenehalonium Ions

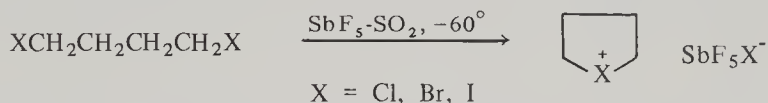
8.1 PREPARATION VIA HALOGEN PARTICIPATION AND PMR STUDY

1,4-Halogen participation was first postulated to occur in the acetolysis of 4-iodo- and 4-bromo-1-butyl tosylates.¹⁶⁸ In subsequent studies Peterson and coworkers found anomalous rates in the addition of trifluoroacetic acid to 5-halo-1-hexenes^{169,170} and 5-halo-1-pentynes.¹⁷¹ Such observations were recognized as due to 1,4-halogen participation.¹⁰ Recently, a study of the solvolysis of δ -chloro- and δ -fluoroalkyl tosylates indicated rate-accelerating 1,4-chlorine participation effects up to 99-fold.¹⁷²

Direct experimental evidence for 1,4-halogen participation comes from the direct observation (by nmr spectroscopy) of five-membered-ring tetramethylenehalonium ions by Olah and Peterson,¹⁵ and by Olah et al.¹⁷³ The pmr parameters of all the tetramethylehehalonium ions studied and directly observed are listed in Table 38.

8.1.1 Parent Tetramethylenehalonium Ions

The ionization of 1,4-dihalobutanes in $\text{SbF}_5\text{-SO}_2$ solution gave the parent tetramethylenehalonium ions.¹⁵ The pmr spectra of these ions are similar



to each other, and one of them, the tetramethylenebromonium ion, is shown in Figure 13. Subsequently it was found that even 1,2- and 1,3-dihalobutanes

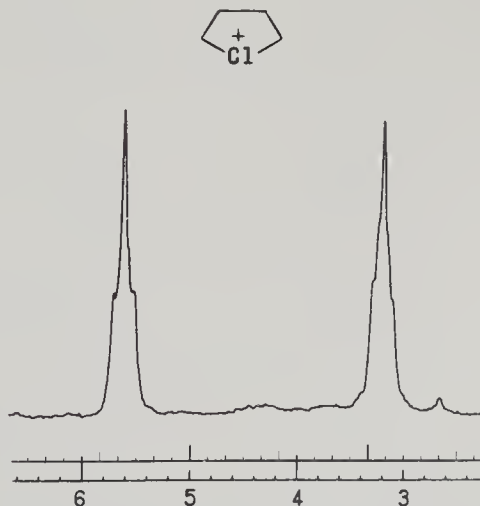
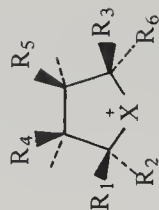


Figure 13. Pmr spectrum of the tetramethylenechloronium ion.

TABLE 38
Pmr Data of Tetramethylenehalonium Ions^a

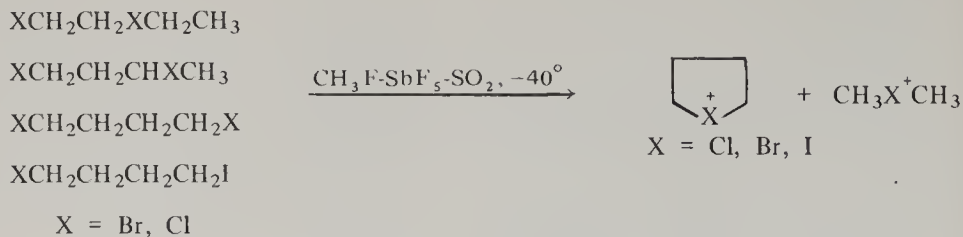


R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	X	δ CH ₂ ⁺ X	δ CH ₂ CX ⁺	δ CCHX ⁺	δ CH ₃	δ CH
H	H	H	H	H	H	Cl	5.20	2.73			
H	H	H	H	H	H	Br	5.20	2.85			
H	H	H	H	H	H	I	5.00	2.80			
CH ₃	H	H	H	H	H	Cl	5.20	2.85	6.60	2.10	
CH ₃	H	H	H	H	H	Br	5.19	2.85	6.60	2.10	
CH ₃	H	H	H	H	H	I	4.98	2.88	6.25	2.12	
H	H	H	CH ₃	H	H	Cl	4.9-5.4	2.1-2.7		1.17	2.9-3.2
CH ₃	H	CH ₃	H	H	H	Cl		2.8	6.32	2.08	
H	CH ₃	CH ₃	H	H	H	Cl		2.8	6.32	2.08	
CH ₃	H	CH ₃	H	H	H	Br		2.9	6.43	2.15	
H	CH ₃	CH ₃	H	H	H	Br		2.9	6.43	2.16	
CH ₃	H	CH ₃	H	H	H	I		2.83	6.30	2.12	
H	CH ₃	CH ₃	H	H	H	I		2.83	6.30	2.22	
C ₂ H ₅	H	H	H	H	H	Cl	5.1	2.1;2.8;3.1	6.4	1.20	
C ₂ H ₅	H	H	H	H	H	Br	5.1	2.1;2.4;2.9	6.4	1.20	

CH ₃	CH ₃	CH ₃	H	H	H	Cl	2.88-2.61	5.82	1.77 (d)
CH ₃	CH ₃	CH ₃	H	H	CH ₃	Cl	2.87 (s)		2.23 (s)
H	H	H	Cl	H	H	Cl	2.6-3.2		2.13 (s)
H	H	H	Br	H	H	Br	2.7-3.3		
H	H	H	Cl	Cl	H	Cl	5.0-5.7	5.0-5.7	5.0-5.7
H	H	H	(CH ₂) ₂	(CH ₂) ₂	(CH ₂) ₂	Cl	4.9-5.6	4.9-5.6	4.9-5.6
							5.52-5.75	5.27	5.27
							4.8-5.7	2.9-3.1	2.9-3.1

^aFrom external capillary TMS in parts per million. Spectra were recorded at -60°. s, singlet; d, doublet.

when reacted with $\text{SbF}_5\text{-SO}_2$ or $\text{CH}_3\text{F-SbF}_5\text{-SO}_2$ solution¹⁷⁴ give the same tetramethylenehalonium ions.¹⁷⁵

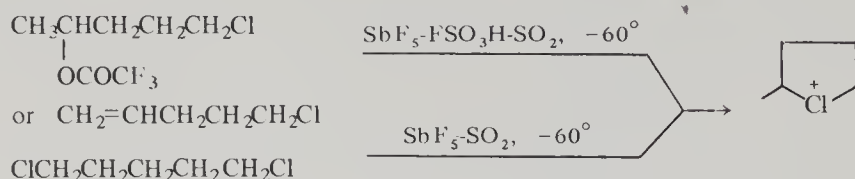


Reaction of 1-fluoro-4-iodobutane with $\text{SbF}_5\text{-SO}_2$ solution, however, gives, besides the tetramethyleneiodonium ion also the 1-butyleneiodonium ion. The mechanism of the formation of the latter seems to involve ring opening and hydrogen shift, leading to the formation of the butyleneiodonium ion.

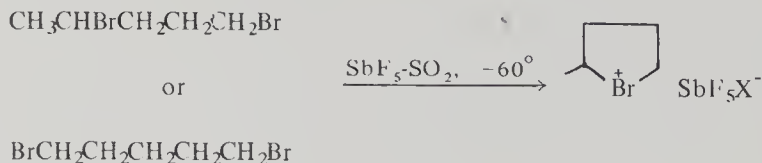
1,4-Difluorobutane, however, reacts with $\text{SbF}_5\text{-SO}_2$ or $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ solution to give rearranged, open-chain fluorocarbenium ions, indicating the lack of bridging ability of fluorine. To our knowledge no fluoronium ions have thus far been identified in solution.

8.1.2 2-Methyltetramethylenehalonium Ions

Several alternate methods have been found for preparing 2-methyltetramethylenehalonium ions. For example the 2-methyltetramethylenechloronium ion can be obtained (1) by protonation of 5-chloro-1-pentene in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ solution at -60° (π route),¹⁵ (2) by ionization of 5-chloro-2-pentyl trifluoroacetate with the same superacid system (σ route),¹⁵ and (3) by ionization of 1,5-dichloropentane with $\text{SbF}_5\text{-SO}_2$.¹⁷⁶

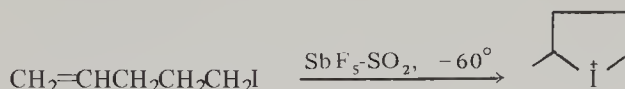


The corresponding bromonium ion¹⁵ can be prepared by (1) reaction of 1-bromo-4-chloropentane and (2) 1,5-dibromopentane with $\text{SbF}_5\text{-SO}_2$ solution at -60° . In the latter case, the six-membered-ring pentamethylenebromonium



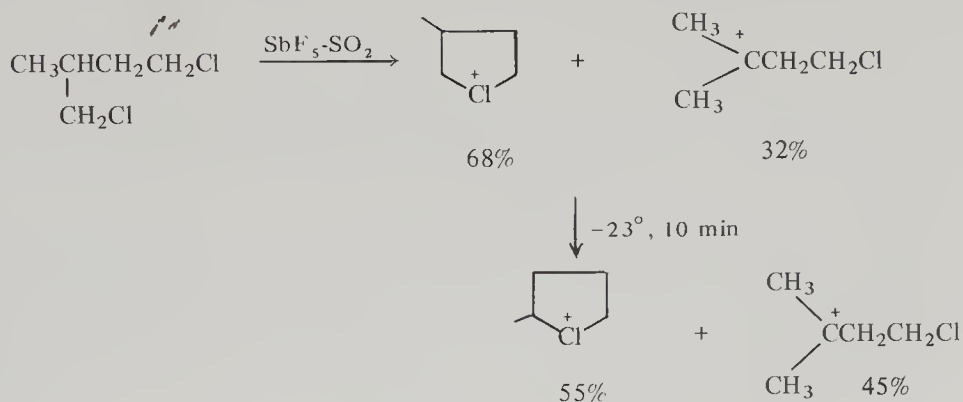
ion was not observed, or else was formed as an intermediate which rearranged to give the more stable 2-methyltetramethylenebromonium ion.

5-Iodo-1-pentene reacted with $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ in a similar fashion to give the 2-methyltetramethyleneiodonium ion. The pmr spectral data of ions



(X = Cl, Br, I) are listed in Table 38.

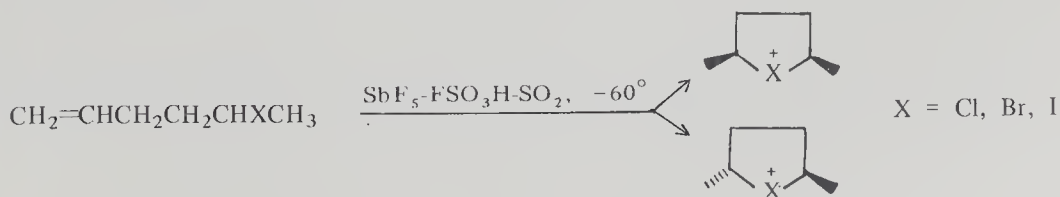
Recently, Peterson and Bonazza¹⁷⁷ reported the preparation of the 3-methyltetramethylenechloronium ion from 1,4-dichloro-2-methylbutane in $\text{SbF}_5\text{-SO}_2$ solution at -78° . The dimethyl- β -chloroethylcarbenium ions (32%) was also formed in the reaction (68%). The structure of the ions was based on their pmr



parameters. When the solution containing the mixture is warmed at -23° for 10 min, the 3-methyltetramethylenechloronium ion undergoes an apparent 1,2-dimethyl shift to give the 2-methyl-substituted ion. The increase in the relative amount of the dimethyl- β -chloroethylcarbenium ion indicates that the 3-methyltetramethylenechloronium ion on warming gives the hydrogen-shifted product (dimethyl- β -chloroethylcarbenium ion) along with the methyl-shifted product (2-methyltetramethylenechloronium ion).

8.1.3 2,5-Dimethyltetramethylenehalonium Ions

The π route of preparation through protonation of 5-halo-1-hexenes was used for the preparation of 2,5-dimethyltetramethylenehalonium ions.¹⁵ 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-dimethyltetramethyleneiodonium ion (Figure 14).

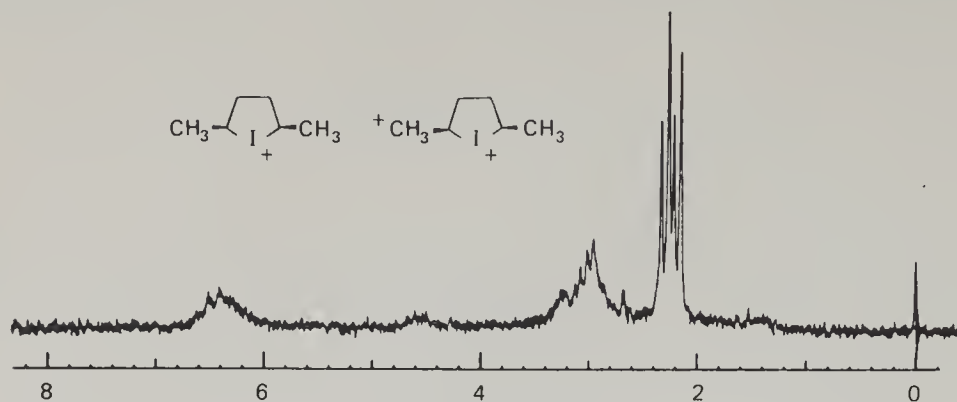
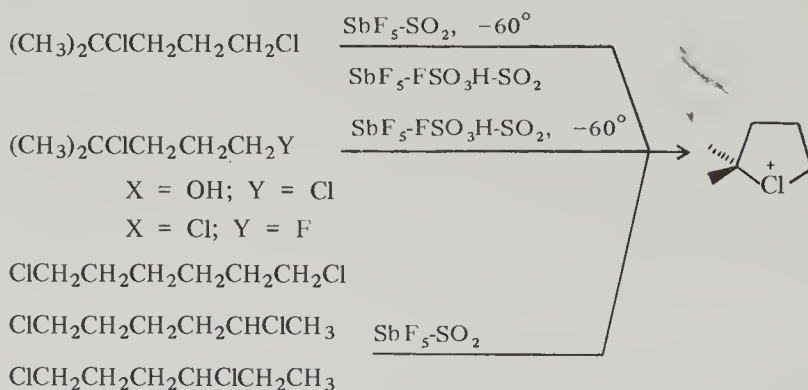


Figure 14. Nmr spectrum of *cis*- and *trans*-2,5-dimethyltetramethyleneiodonium ions.

The isomeric (*cis* and *trans*) 2,5-dimethyltetramethylenebromonium ions were also obtained (as an equimolar mixture) when 2,5-dibromohexanes were treated with $\text{SbF}_5\text{-SO}_2$ solution at -70° .¹⁶⁹

2,2-Dimethyltetramethylenehalonium ions can also be prepared in several ways. Thus the 2,2-dimethyltetramethylenechloronium ion was obtained by ionization of (1) 2,5-dichloro-2-methylpentane in $\text{SbF}_5\text{-SO}_2$ or $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$, (2) 2-methyl-5-chloro-2-pentanol in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$, (3) 4-chloro-1-fluoro-4-methylpentane¹⁷³ in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$, and (4) dichlorohexanes¹⁷⁶ in $\text{SbF}_5\text{-SO}_2$.



The mechanism of the formation of the 2,2-dimethyltetramethylenechloronium ion from 4-chloro-1-fluoro-4-methylpentane was postulated to involve a fluoronium ion as an unstable intermediate (although without involvement of a fluoronium ion an equally reasonable mechanism could also be suggested).

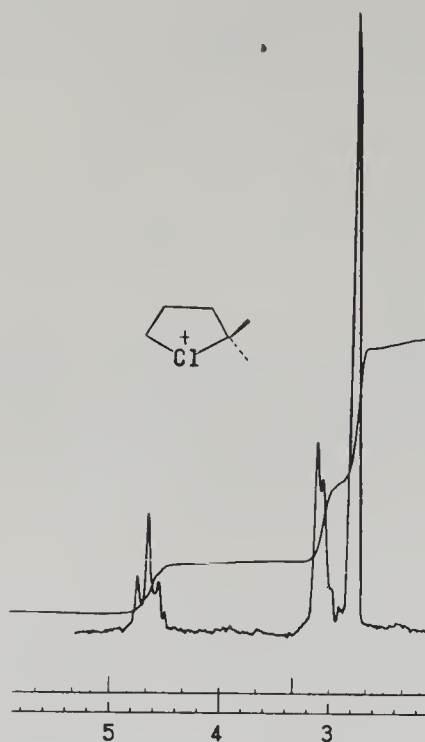
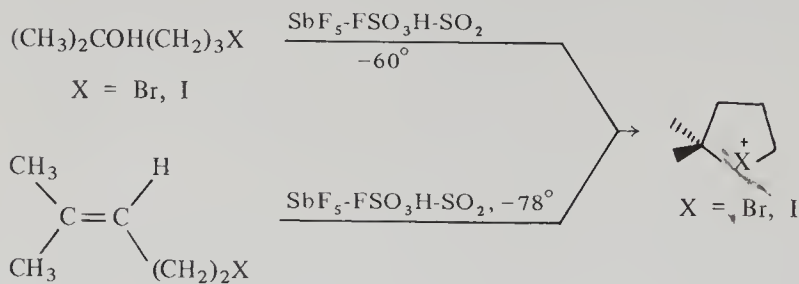
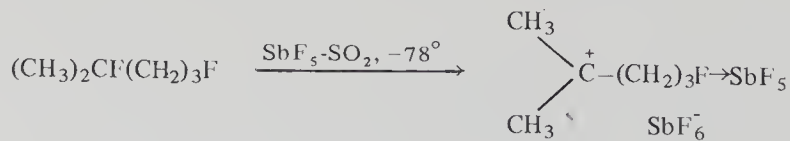


Figure 15. Pmr spectrum of the 2,2-dimethyltetramethylenechloronium ion.



Attempts were made to prepare the 2,2-dimethyltetramethylenefluoronium ion by ionizing the potential difluoride precursors in $\text{SbF}_5\text{-SO}_2$, but only open-chain tertiary ions were formed.¹⁷³ The lack of aliphatic fluorine resonance absorption of J_{HF} coupling indicates that the fluorine atom is complexed

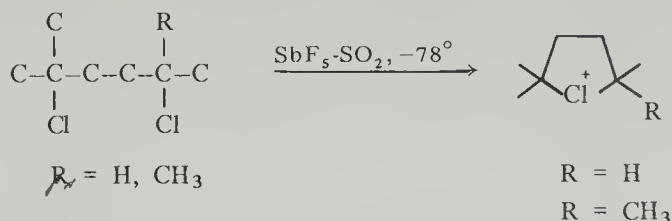


and rapidly exchanges with SbF_5 (a similar rapidly exchanging donor-acceptor complex of methyl fluoride with SbF_5 has been reported¹⁷⁹).

The pmr data of the 2,2-dimethyltetramethylenehalonium ions are summarized in Table 38.

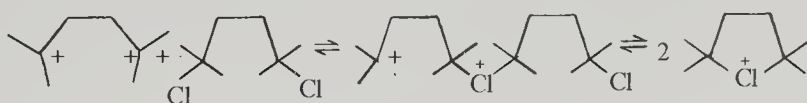
8.1.4 Tri- and Tetramethyltetramethylenehalonium Ions

Peterson and Henrichs¹⁷⁸ reported the preparation of 2,2,5-trimethyl- and 2,2,5,5-tetramethyltetramethylenechloronium ions from 2,5-dichloro-2-methylhexane and 2,5-dichloro-2,5-dimethylhexane, respectively. The structure of these ions was studied by both proton and carbon-13 nmr spectroscopy (Tables 38 and 39).

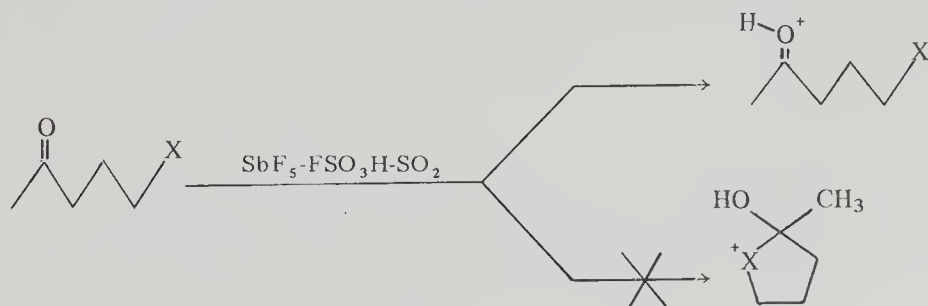


It is of interest to note the observation of only one proton and carbon-13 absorption line for the nonequivalent geminal methyl groups in the dimethyltetramethylenechloronium ion. These data, as well as the modest temperature dependence of the carbon shifts, suggests that an equilibrium exists with the open-chain carbenium ion causing the seeming equivalence of the methyl groups.

It would be expected that the tetramethyltetramethylenechloronium ion could be prepared from 2,5-dichloro-2,5-dimethylhexane, but an earlier study indicated that an open-chain dicarbenium ion is instead obtained. It was found, however, that the halonium ion could be obtained when additional dichloride was added to the solution of the dication. A possible reaction pathway is

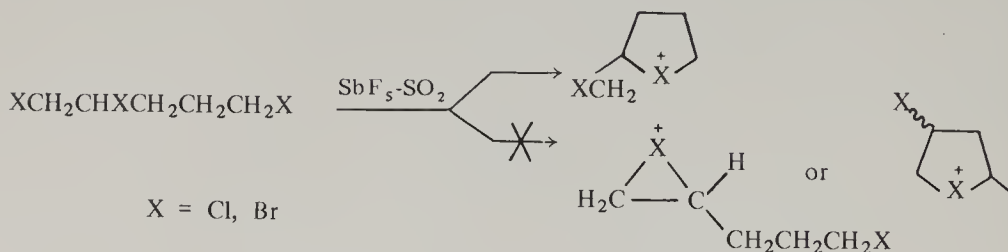


Attempts to prepare 2-hydroxy-2-methyltetramethylenehalonium ions by protonation of methyl γ -halopropyl ketones in superacids were unsuccessful.¹⁷⁸ Instead, the open-chain ions were formed with no halogen participation.



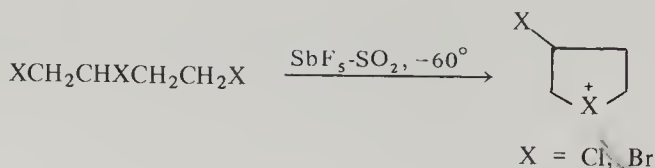
8.1.5 Halogenated Tetramethylenehalonium Ions

Peterson and coworkers¹⁷⁶ reported the preparation of 2-halomethyltetramethylenehalonium ions ($X = \text{Cl}, \text{Br}$) by the ionization of 1,2,5-trihalopentanes

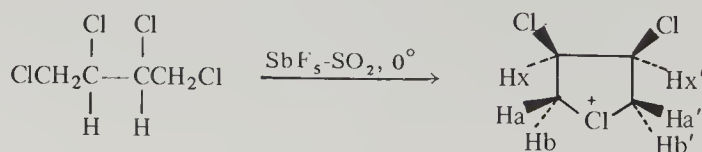


in $\text{SbF}_5\text{-SO}_2$ solution. As expected, ionization took place at the secondary rather than the primary halide centers. Isomeric halonium ions were not formed under the experimental conditions.

When 1,2,4-trichloro- and 1,2,4-tribromobutane were allowed to react with $\text{SbF}_5\text{-SO}_2$ at -60° , the 3-chlorotetramethylenechloronium ion and the 3-bromotetramethylenebromonium ion, respectively, were obtained.¹⁷⁷ The pmr data are tabulated in Table 39.

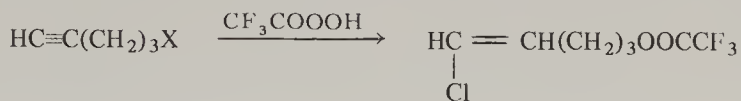


Similarly, when *meso*-1,2,3,4-tetrachlorobutane was ionized in $\text{SbF}_5\text{-SO}_2$ solution at -23° for approximately 1.5 hr, or at 0° for 1 min, the *cis*-4,5-dichlorotetramethylenechloronium ion was formed.¹⁷⁷

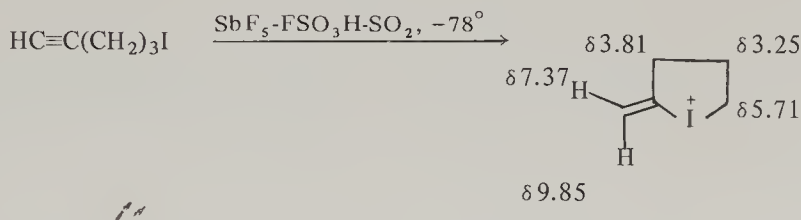


8.1.6 2-Methylenetetramethylenehalonium Ions

Peterson and coworkers¹⁷¹ obtained evidence for halogen participation in the addition of trifluoroacetic acid to 5-halo-1-pentynes. Olah and coworkers



subsequently examined the protonation of 5-halo-1-pentyne in superacids in order to see whether the corresponding 2-methylenetetramethylenehalonium ions could be observed as stable species in superacid solutions. The results



showed that 5-iodo-1-pentyne was smoothly protonated to give the corresponding 2-vinyltetramethyleneiodonium ion. However, protonation of 5-chloro- or 5-fluoro-1-pentyne in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ gave only unidentifiable products.

8.2 CARBON-13 NMR STUDY OF TETRAMETHYLENEHALONIUM IONS

The carbon-13 nmr of tetramethylenehalonium ions has been studied by Olah^{26d} and Peterson¹⁸⁰ and their coworkers. Carbon-13 chemical shift data for tetramethylenehalonium ions are shown in Table 39. The C-3 and C-4 resonances in unsymmetrically substituted tetramethylenehalonium ions were differentiated by assuming that C-2 had greater electron deficiency than C-5 and thus exerted a slightly larger deshielding α -substituent effect. The α -substituent effect of a positively charged carbon has been observed to be that of deshielding in a large number of carbenium ions.

The ions in Table 39 can be divided into symmetrically and unsymmetrically substituted ions.

8.2.1 Symmetrically Substituted Ions

Whereas the approach of observing α - and β - ^+XR substituent effects to estimate ring carbon shifts in ethylenehalonium ions was unsuccessful, good results were obtained for five-membered-ring halonium ions. For example, the methyl shift in *n*-butylalkylchloronium ions should be very similar to the methyl shift in *n*-butane ($\delta_{13\text{C}}$ 13.3), since the δ -substituent effect for ^+XR should be negligible. Cyclization of the $\text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{Cl}^+$ group to the tetramethylenechloronium ion should result in a downfield shift of 67.5 ppm in the methyl carbon shielding. The estimated shift of $\delta_{13\text{C}}$ 80.8 for C-2 and C-5 in the tetramethylenechloronium ion is in good agreement with the experi-

TABLE 39

Carbon-13 Nmr Shifts of Tetramethylethalonium Ions^{a,26d,180}

Halonium ion	Substituent	Temp. (°C)	C-2	C-3	C-4	C-5	CH ₂	CH ₃
Cl ^b		-40°	77.9	33.9				
Br ^b		-40°	70.8	36.4				
I ^b		-40°	51.1	38.8				
Cl ^c	2-CH ₃	-67.8°	113.6	41.5	35.5	75.4		22.6
		-54.3°	113.8	41.5	35.5	75.4		22.6
		-36.0°	113.8	41.5	35.3	75.3		22.6
		-10.0°	115.6	42.9	36.7	76.7		22.9
Br	2-CH ₃	-40°	107.0 (106.7)	44.8 (44.3)	37.5 (36.9)	69.8 (69.7)		24.2 (23.7)
I ^d	2-CH ₃	-55°	83.6	41.8	38.4	49.4		24.9
Cl	3-CH ₃	-55°	80.0	43.0	40.6	78.4		25.1
Br (cis)	2,5-(CH ₃) ₂	-40°	97.5	39.1				19.3
Br (trans)	2,5-(CH ₃) ₂	-40°	98.9	40.9				19.8
Cl ^e	2,2-(CH ₃) ₂	-69.3°	192.4	49.0	37.1	66.4		35.3
		-56.1°	198.4	49.5	37.0	65.5		35.7
		-41.3°	204.8	50.0	37.0	64.5		36.2
		-40°	198.2	52.5	37.8	63.9		38.7
Br	2,2-(CH ₃) ₂	-69.3°	151.1	50.2	37.8	66.2		33.9
		-56.1°	152.0	50.2	37.8	66.0		33.9
		-41.3°	153.1	50.3	37.8	65.8		34.0
		-40°	195.8	50.3	37.7	65.5		33.9
Cl	2-C ₂ H ₅	-65°	121.5	39.3	35.4 ^e	74.4	23.9 ^e	13.8
Br	2-C ₂ H ₅	-55°	117.2	42.7	37.6	69.1	32.7	16.0
		-65° ^f	115.9	41.8	36.9 ^e	68.5	31.7 ^e	15.4
I	2-C ₂ H ₅	-65°	95.5	45.3 ^e	38.6	40.7	32.8 ^e	18.0

Cl	2,2,5-(CH ₃) ₃	-67.8°	154.8	47.6	43.6	99.5	33.1	22.6
		-54.3°	154.8	47.6	43.5	99.0	33.1	22.5
		-36.0°	160.7	47.8	43.6	98.4	33.4	22.6
Cl	2,2,5,5-(CH ₃) ₄	-67°	137.3	47.6	47.6	137.3	32.2	
		-56°	137.6	47.7	47.7	137.6	32.2	
Cl	3-Cl	-55°	81.3	62.0	42.5	77.0		
Br	3-Br	-55°	74.4	52.4	44.9	69.5		
Cl (cis)	4,5-Cl ₂	-55°	86.0	64.9				

^aCarbon shifts are referred to TMS in SO₂ solution in parts per million.

^bFor symmetric ions C-2 and C-3 are equivalent to C-5 and C-4, respectively.

^dAssignment of C-3 and C-4 may be reversed.

^eAssignments are tentative.

mentally determined value of δ_{13C} 77.9. This procedure is also successful in estimating the C-3 and C-4 shift in the ion, as well as the C-2 and C-5 and C-3 and C-4 shifts in related bromonium and iodonium ions.

α - and β -substituent effects for the RX^+ group in the parent tetramethylenehalonium ions are therefore the same as in dialkylhalonium ions. Since the equilibrium positions with open-chain halocarbenium ions are far to the side of bridged ions for primary systems, it follows that the parent tetramethylenehalonium ions all exist as static bridged species, with no rapid equilibration with open-chain ω -haloalkylcarbenium ions being involved.

The cmr and pmr spectra of the 1,4-dimethyltetramethylenebromonium ion reveal the presence of *cis* and *trans* isomers in equal amounts, also indicating that the ion is a symmetrically bridged ion. If it is in equilibrium with an open-chain form, it is a slow equilibrium with an undetectable (by nmr) amount of the open-chain ω -haloalkylcarbenium ion. The larger than usual methyl substituent effect (28 ppm) probably indicates an increased carbenium ion character for the C-2 and C-5 carbons.

The methyl carbon absorbance of the *cis* isomer is shielded by 2.5 ppm from that of the *trans* isomer, reflecting the larger steric interaction between the methyl groups in the former case. The effect is smaller than in *cis*- and *trans*-1,2-dimethylethylenebromonium ions, indicating that the methyl groups are closer in the *cis* isomer of this ion than in the *cis*-1,4-dimethyltetramethylenebromonium ion.

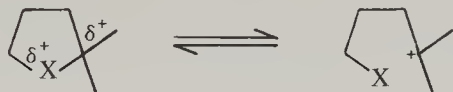
8.2.2 Unsymmetrically Substituted Ions

Replacement of a proton on C-2 by a methyl group in tetramethylenehalonium ions results in a deshielding of 32-38 ppm in the C-2 absorbance. This may indicate an unsymmetric bridged ion, or be a result of these ions being in equilibrium with open-chain ω -haloalkylcarbenium ions. However, the latter possibility is unlikely, as the methyl substituent effect is approximately the same for chlorine, bromine, and iodine, so that the equilibrium constants would have to be the same in all three cases.

Furthermore, a consideration of the cmr spectrum of 2-methyltetramethylenechloronium ions at different temperatures showed that the difference between the C-2 and C-5 chemical shifts changes only 0.7 ppm on lowering the temperature from -20 to -90° , while the corresponding change in $\delta_{C-2} - \delta_{C-3}$ is only 0.10 ppm.

Large downfield shifts at C-2 are observed on the C-2 substitution of a second methyl group into 2-methyltetramethylenechloronium and -bromonium ions. In the former case the α -substituent effect is 82 ppm, and in the latter 46 ppm. These large changes most likely indicate increasing carbenium ion character at C-2 with increasing methyl substitution. This is also suggested by the comparatively large downfield methyl shifts in 2,2-dimethyltetramethylene-

chloronium and -bromonium ions (38.7 and 33.9 ppm, respectively). The cmr spectra of the ions have also been recorded at different temperatures by Henrichs and Peterson⁷⁸, who found that the 1,1-dimethyltetramethylenechloronium ion is in rapid equilibrium with substantial amounts of the open-chain ω -chloroalkylcarbenium ion. They also found that the 1,1,4-trimethyltetramethylenecarbenium ion and 1,1-dimethyltetramethylenebromonium ion are in equilibrium with smaller amounts of the open-chain ion.



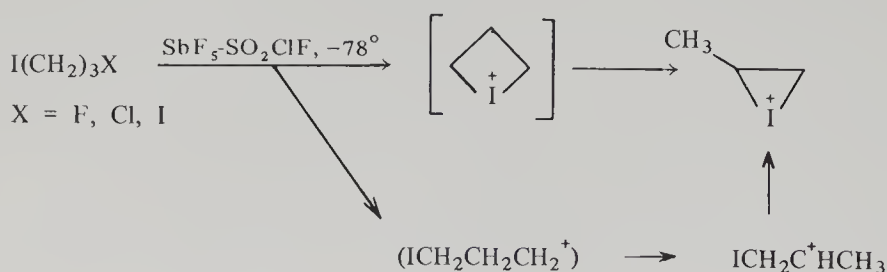
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In contrast to the deshielding of the C-2 shift in less substituted ions, the C-5 shift becomes shielded, relative to the unsubstituted ion, with increasing methyl substitution. These effects are relatively small for monomethyl-, but more substantial in 2,2-dimethyl-substituted ions. For the methyldimethyltetramethylenechloronium ion the shift is further shielded (14 ppm) than in the corresponding -bromonium ion (5.3 ppm), because of the greater contribution of the equilibrating open-chain form in the former case. This is quite reasonable, considering the greater stability of a positively charged bromine atom as compared with a positively charged chlorine atom.

Tri- and Pentamethylenehalonium Ions

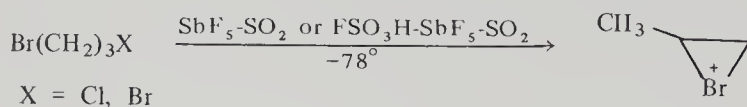
9.1 TRIMETHYLENEHALONIUM IONS

Attempts to prepare trimethylenehalonium ions by ionizing the appropriate 1,3-dihalopropanes with $\text{SbF}_5\text{-SO}_2$ or with 1:1 $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution at low temperature were unsuccessful.¹⁷⁴ The ions obtained were either three- or five-membered-ring halonium ions, formed through ring contraction or expansion, respectively. For example, when 1-halo-3-iodopropanes were reacted with $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -78° , the propyleneiodonium ion was formed. This ion could be formed through the trimethyleiodonium ion which was, however, not observed as an intermediate. Alternatively, the nonassisted primary ion



could undergo rapid 1,2-hydrogen shift to the secondary ion, which then would form the propyleneiodonium ion via iodine participation.

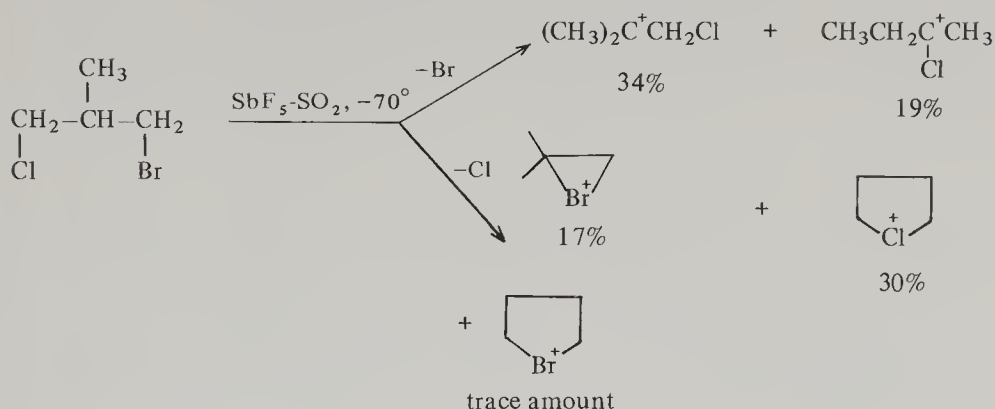
Similarly, when 1-halo-3-bromopropanes were treated in the same way at -78° , the propylenebromonium ion was obtained. However, when dichloro-



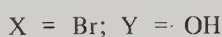
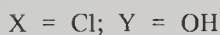
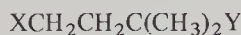
propanes were treated with $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -60° , a rapidly equilibrating system was formed (see Section 7.1.2).

When 1-iodo-3-halobutanes were treated with $\text{SbF}_5\text{-SO}_2$ solution at -60° , three-membered-ring halonium ions were formed. In contrast, 1,2- and 1,3-dibromo(or chloro)butanes gave tetramethylenehalonium ions.

The ionization of 1,3-dihalo-2-methylpropanes with $\text{SbF}_5\text{-SO}_2$ solution gave both three- and five-membered-ring halonium ions and open-chain halocarbenium ions.



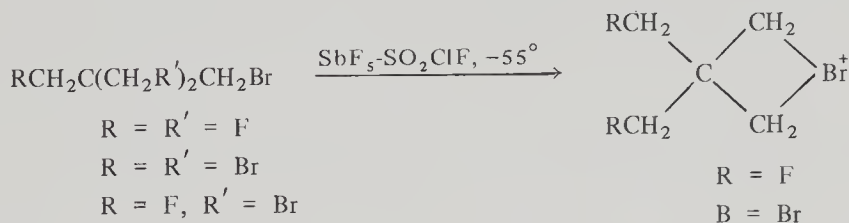
Another possible route to four-membered-ring halonium ions could be through dimethyl- β -haloethylcarbenium ions. These ions can be prepared from dihalopentanes with $\text{SbF}_5\text{-FSO}_3\text{-SO}_2$ solution at -78° . The proton and carbon-13 nmr data of the systems, however, indicated the absence of halogen participation.^{26d}



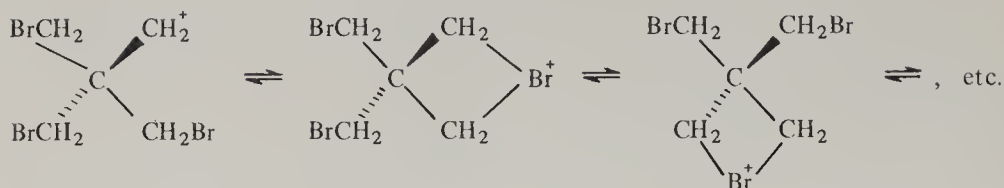
or



The only reported preparation of long-lived four-membered-ring halonium ions is that of Exner et al.¹⁸ 3,3-Bis(halomethyl)trimethylenebromonium ions were prepared by treating tetrahaloneopentanes with $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at low temperature. Seemingly, halogen substitution stabilizes the four-membered-ring compared to ring contraction or expansion. The pmr spectrum of fluorinated ions shows a singlet at δ 5.28 and a doublet at δ 4.68 ($J_{\text{HF}} = 47$

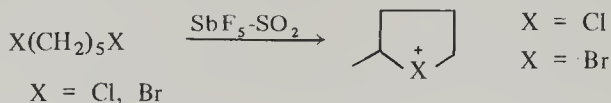


Hz). In contrast, the brominated ion displays a temperature-dependent proton absorption at δ 5.17 (from internal $\text{Me}_4\text{N}^+\text{BF}_4^-$), indicating that the following exchange process occurs.

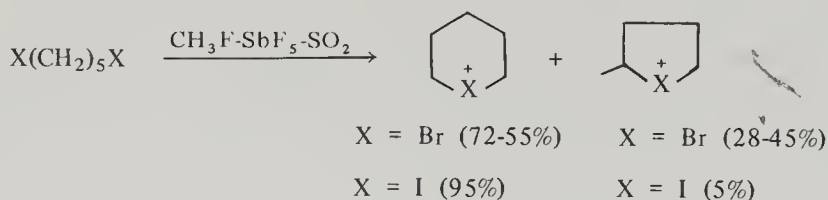


9.2 PENTAMETHYLENEHALONIUM IONS

As discussed, attempts to prepare six-membered-ring halonium ions by treating 1,5-dihalopentanes with $\text{SbF}_5\text{-SO}_2$ gave exclusive rearrangement to five-membered-ring halonium ions. Recently, however, Peterson et al.¹⁶ prepared

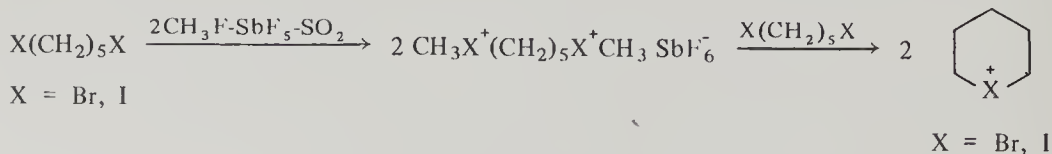


six-membered-ring halonium ions by the methylation of 1,5-dihalopentanes with methyl fluoroantimonate ($\text{CH}_3\text{F-SbF}_5$) in SO_2 solution. Some rearrangement to five-membered-ring halonium ions was also observed.

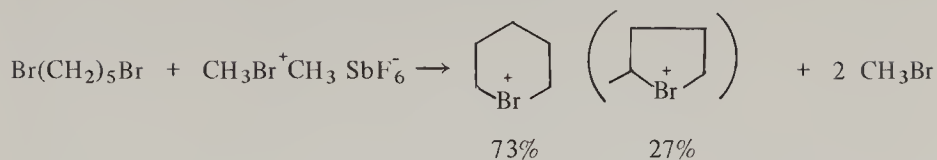


Alternatively, six-membered-ring halonium ions were also formed when equimolar methyl fluoroantimonate was added to dihalonium ions.

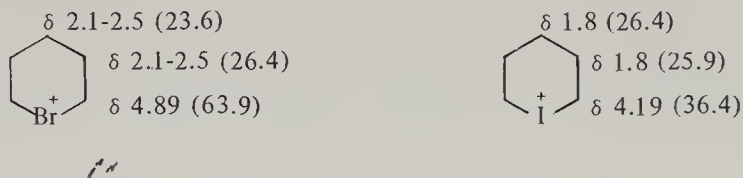
The dihalonium ions were prepared from 1,5-dihalopentane and 2 moles of



methyl fluoroantimonate. Furthermore, the dimethylbromonium ion is also a sufficiently active methylating agent to form cyclic pentamethylenebromonium ions from 1,5-dibromopentane.



The proton and carbon-13 shifts (the latter shown in parentheses) of pentamethylenehalonium ions are consistent with their structures. The penta-

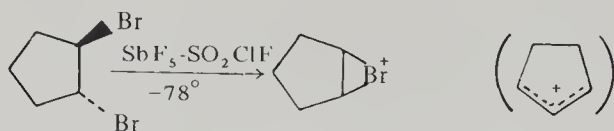


methyleniodonium ion rearranged in part to 2-methyltetramethyleniodonium ions after 2 hr at room temperature in SO_2 solution. The pentamethylenebromonium ion, however, rearranged smoothly to the 2-methyltetramethylenebromonium ion (50%) over a period of 20 min at -20° (complete rearrangement requires a longer period of time). Quenching of a mixture of the iodonium ions with methanol gave a 60% isolated yield of the corresponding ω -iodoalkyl ethers, $\text{I}(\text{CH}_2)_5\text{OCH}_3$ and $\text{I}(\text{CH}_2)_3\text{CH}(\text{OCH}_3)\text{CH}_3$.

Bicyclic Halonium Ions

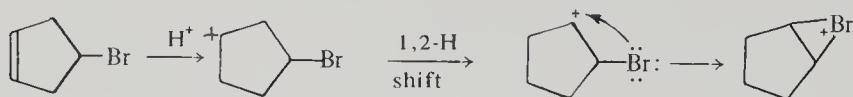
10.1 CYCLOPENTENEBROMONIUM ION (2-BROMONIA[3.1.0]BICYCLOHEXANE)

Although halogen additions to cycloalkenes are also assumed to proceed through the corresponding bicyclic halonium ions, these ions are quite elusive. Olah, Liang and Staral²³ recently prepared the cyclopentenebromonium ion by the ionization of *trans*-1,2-dibromocyclopentane in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -120° . The pmr (60 MHz) spectrum of the ion solution showed a broadened peak at δ 7.32



(two protons) and two broad peaks centered at δ 3.14 (four protons) and δ 2.50 (two protons). The nmr spectra of the solution also showed the presence of the related cyclopentenyl cation. When the solution was slowly warmed to -80° , the cyclopentenebromonium ion gradually and cleanly transformed into the allylic ion. The cyclopentenyl ion present initially in solution might be formed as a result of local overheating during preparation.

The cyclopentenebromonium ion was also obtained via protonation of 4-bromocyclopentene in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution at -120° , through the following reaction sequence.



The proton noise-decoupled carbon-13 spectrum of the cyclopentenebromonium ion (Figure 16) shows three carbon resonances at $\delta_{13\text{C}}$ 114.6 (doublet, J_{CH} 190.6 Hz), 31.8 (triplet, J_{CH} 137.6 Hz), and 18.7 (triplet, J_{CH} 134.0 Hz). In addition, the cmr spectrum shows three additional minor peaks which exactly correspond to those reported for the cyclopentenyl cation [The cmr assignments were made with the aid of proton-coupled cmr spectra (Figure 16).] The bicyclic structure of the cyclopentenebromonium ion is therefore firmly established.

It is instructive to compare both proton and carbon shifts of the cyclopentene-

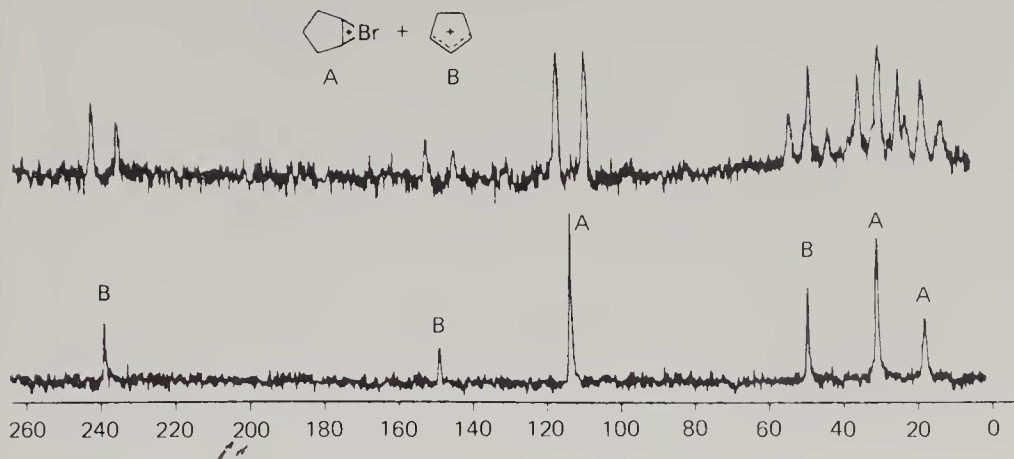
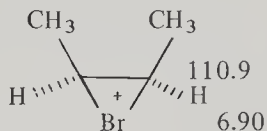
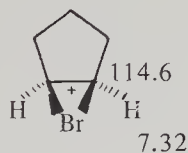


Figure 16. (a) Proton noise-decoupled carbon-13 nmr spectrum of 1 (peaks marked A) and 3 (peaks marked B). (b) Proton-coupled carbon-13 nmr spectrum.

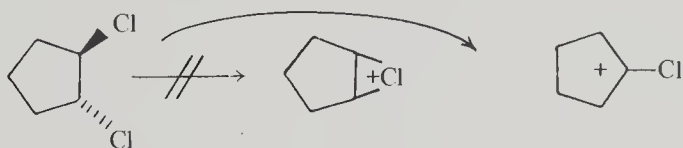
bromonium ion with those of suitable model ions. The most closely related known cyclic bromonium ion containing a three-membered ring is the *cis*-1,2-dimethylethylenebromonium ion.

The chemical shift for the two carbon atoms where bridging takes place is found at δ_{13C} 110.9, which is in good agreement with that in cyclopentene-



bromonium ion (114.6). The proton shifts for the two equivalent olefin-type protons in both ions are also similar.

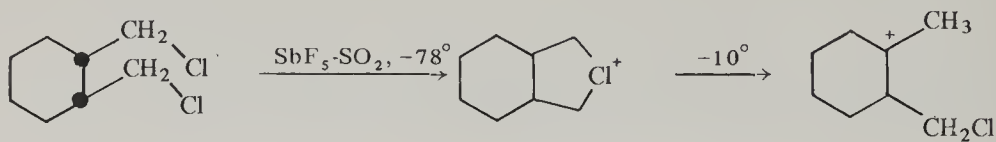
Attempts were also made to prepare the cyclopentenechloronium ion via ionization of *trans*-1,2-dichlorocyclopentane in SbF_5-SO_2ClF at -120° . However, instead of the cyclopentenechloronium ion, only the 1-chloro-1-cyclopentyl cation was obtained. Apparently, the participation of the smaller chlorine atom could not effectively compete with the fast 1,2-hydride shift forming the



tertiary ion. The larger bromine atom, however, preferentially participates with the neighboring electron-deficient center, forming the bicyclic bridged ion.

10.2 3-CHLORONIA[4.3.0]BICYCLONONANE

Peterson and Bonazza²² reported that ionization of *cis*-1,2-bis(chloromethyl)-cyclohexane in $\text{SbF}_5\text{-SO}_2$ solution at -78° gives the bicyclic five-membered-ring chloronium ion along with smaller amounts of other species. Warming the solution containing the ion to -10° leads to the formation of the open chain tertiary carbenium ion.



Stability and Chemical Reactivity of Alicyclic Halonium Ions

11.1 STABILITY OF CYCLIC HALONIUM IONS

The stability of halonium ions as long-lived species depends on two types of stability:

1. Thermodynamic stability, as expressed, for example, by ΔH (heat of formation) from their precursors.
2. Kinetic stability, which in the absence of side reactions generally can be determined by the rate of reaction with suitable nucleophiles.

The heats of formation of a series of methyl-substituted ethylene and tetramethylenebromonium ions from the appropriate dihaloalkane precursors were measured calorimetrically by Larsen and Metzner¹⁸¹ in 11.5 mole % $\text{SbF}_5\text{-FSO}_3\text{H}$ solution at -60° . Data are summarized in Table 40. The

TABLE 40
Relative Heats of Formation of Bromonium Ions (ΔH_{obs}) in 11.5 Mole %
 SbF_5 According to Larsen and Metzner¹⁸¹



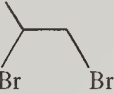

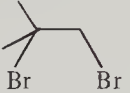

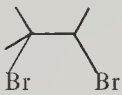
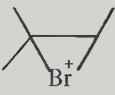
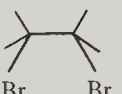
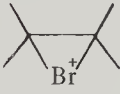
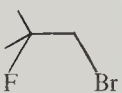
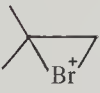
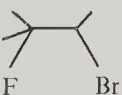
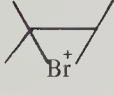
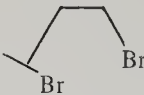
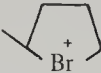
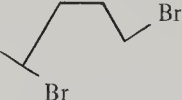
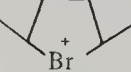
Precursor	Ion	ΔH_{obs}
		$\sim \Delta.0$
		-3.29 ± 0.51
		-8.39 ± 0.87
		-13.4 ± 0.90
		-22.9 ± 4.00
		-11.3 ± 1.83
		-15.5 ± 2.15

TABLE 40

Relative Heats of Formation of Bromonium Ions (ΔH_{obs}) in 11.5 Mole % SbF_5 According to Larsen and Metzner¹⁸¹ (continued)

Precursor	Ion	ΔH_{obs}
		-13.8 ± 1.87
		-13.3 ± 1.93

tetramethylenebromonium ion is about as stable as the *tert*-butyl cation, and is ca. 10 kcal/mole more stable than a correspondingly substituted ethylenebromonium ion. The tetramethylenechloronium ion is ca. 7.5 kcal/mole less stable than its bromo analog.

The stability of the three-membered-ring bromonium ions seems more sensitive to methyl substitution than that of five-membered-ring ions. With both bromine and fluorine as the leaving group, substitution of a methyl for a hydrogen atom results in about a 5-kcal/mole increase in the stability of the ion for all ions except the tetramethylethylenehalonium ions. Calculations indicate that increasing strain in the starting dihalide with increasing methyl substitution is not the source of this effect. The strain energy of 2,3-dimethyl-2,3-dibromobutene may be enough to explain the large exothermic heat of formation of the tetramethylethylenebromonium ion. This would require, however, a larger value for gauche Br-CH_3 interactions than that given by Benson et al.,¹⁸² There seems to be no reason to expect exceptional stabilization of the cation by the fourth methyl group. A better knowledge of the heats of formation of haloalkanes would be helpful in interpreting this value. It is worth noting that the heat of formation of the ethylenebromonium ion was estimated by Larsen to be about 2 kcal/mole. This is quite consistent with the observed substituent effect. While errors in the heats of formation of five-membered-ring ions can be significant, it is apparent that the effect of a methyl substituent is considerably reduced.

11.2 THE ROLE OF σ - AND π COMPLEXES IN THE ADDITION OF HALOGEN TO ALKENES AND ALKYNES

Three-membered-ring alkenehalonium ion intermediates (σ complexes) have been assumed in the electrophilic addition of halogen to alkenes for many years, based on the high stereospecificity of the reactions.^{4-7,164} Their exist-

ence has been confirmed more recently by their preparation and spectroscopic observation (by both σ and π routes) under stable ion conditions.

Other mechanistic paths have also been suggested, including charge transfer complexes (molecular complexes)¹⁸³ and π complexes.^{184,185} In electrophilic aromatic substitution, kinetic and product distribution data (i.e., consideration of substrate and positional selectivity) have shown that the position of the transition state of highest energy is not fixed but can resemble, depending on reaction conditions and the nature of the electrophile, either the most stable intermediates (σ complexes) or the starting material (π complexes).¹⁸⁵ The generalized concept of electrophilic reactions was discussed by Olah¹⁸¹ on the basis of extensive studies of the nature of intermediate carbocations.

The formation of alkene-bromine π complexes has been suggested to explain both the kinetic^{188,189} and spectroscopic^{190,191} behavior of these systems. In addition, a low-temperature thermographic study of the propene-bromine system has also been reported,¹⁹² in which repeated freeze-thaw cycles were employed to increase the concentration of the complex so that "upon warming a virtually explosive reaction" occurred. Also related is the report¹⁸⁸ that considerable rate enhancement occurs when bromination is carried out first by cooling an alkene-bromine system (presumably to accumulate the π complex) and then allowing it to warm up, rather than carrying out the whole reaction exclusively at the later temperature. While these observations appear to indicate the formation of intermediate bromine complexes, there was until recently no direct evidence available either on the nature of these complexes or on the role they may play in the bromination of alkenes.

11.2.1 Alkenes

The relative rates of bromination of alkenes in polar solvents, such as methanol, were extensively studied, most notably by Dubois.¹⁹³ The data show a close relationship of rate ratios to the electronic effect of alkyl groups, reflecting their effect on the intermediate alkenebromonium ions (σ complexes). Olah and Hockswender¹⁹⁴ determined the relative reactivities of the bromination of a series of representative alkenes in a low-polarity medium, 1,1,2-trichlorotrifluoroethane (Freon 113) solution under strictly controlled conditions in an all Teflon apparatus (the reactions are sensitive to external effects including that of glass). The reactivities compared to ethene were determined by the competitive technique at -35° and are summarized in Table 41, along with those of Dubois¹⁹³ for the bromination of the same alkenes in methanol.

The rate of reaction of alkenes with bromine in 1,1,2-trichlorotrifluoroethane solution is too fast to measure by noncompetitive methods. However, the competitive method of rate determination overcomes this difficulty, and the data obtained preclude either diffusion- or encounter rate-controlled reactions.

TABLE 41
Relative Rates of the Addition of Bromine to Alkenes
Compared to Ethene

Alkene	Br ₂ in CF ₂ ClCFCl ₂ , k_{rel}^a	Br ₂ in CH ₃ OH, k_{rel}^b
Ethene	1.0	1.0
Propene	14	
1-Butene	20	95.7
1-Pentene	12	69.0
1-Hexene	10	65.7
3,3-Dimethylbutene	9	
2-Methylpropene	204	
<i>trans</i> -2-Butene	200	
<i>cis</i> -2-Butene	320	
<i>cis</i> -2-Hexene	460	2890
<i>cis</i> -2-Pentene	881	4160
<i>cis</i> -3-Hexene	846	6435
<i>trans</i> -3-Hexene	676	
<i>cis</i> -3-Methyl-2-pentene	1030	118,800
2-Methyl-2-butene	2300	
2,3-Dimethyl-2-butene	5680	924,000

^aOlah and Hockswender.¹⁹⁴

^bIn CH₃OH plus 0.2 *N* NaBr at 25°. Data of Dubois.¹⁹³

While in 1,1,2-trichlorotrifluoroethane solution much lower substrate selectivities were observed than in more polar media, the rate differences are still incompatible with limiting encounter rate-controlled or diffusion-controlled conditions.

Data summarized in Table 41 indicate that bromination reaction in the low-polarity solvent system reflect a lesser degree of charge development in the transition state, which consequently is considered of the alkene-bromine π -complex type. This complex can be envisioned as arising from the initial interaction of the π system of the alkene with the electrophilic bromine, that is, the polarized bromine molecule via interaction with the back lobe of the antibonding orbital of bromine (Figure 17). This interaction would then lead to a three-center-bonded π complex such as proposed in general for the reaction of electrophiles with alkenes¹⁸⁴ and postulated for the reaction of borane with alkenes.¹⁸⁵ It is of particular interest to note that related complexes were indeed observed under stable ion conditions in the reaction of adamantylidenadamantane with bromine, as well as with other electrophiles.¹⁶³

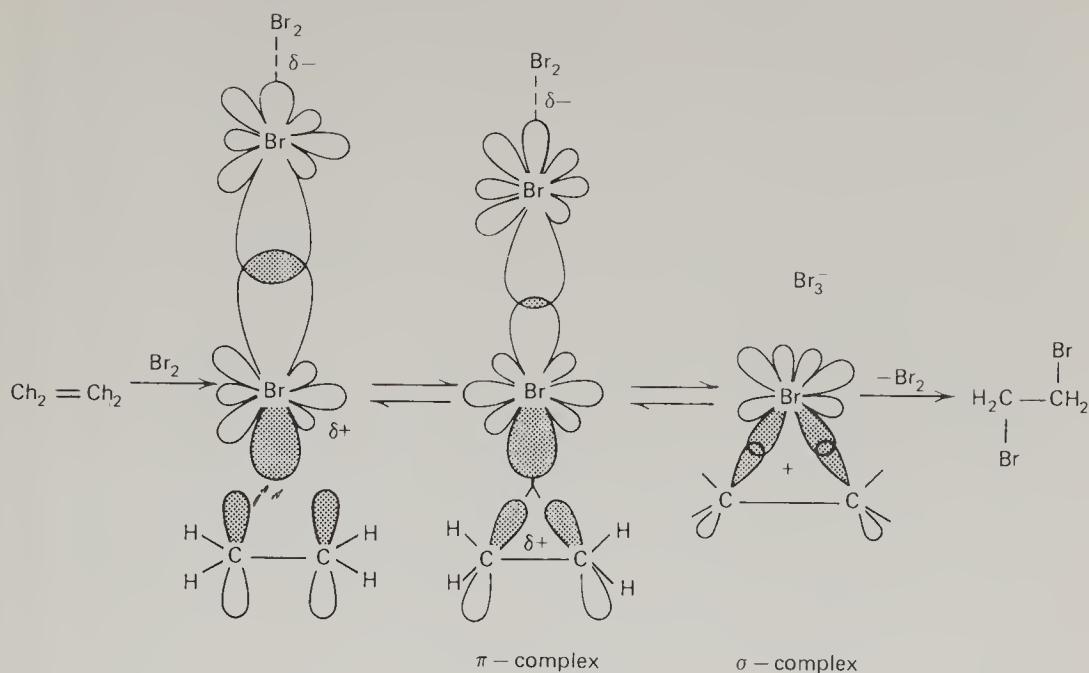


Figure 17. The path of addition of bromine to ethene.

Bromination data in the low-polarity system indicate that the transition states of the highest energy of the reactions lie early along the reaction coordinate and resemble more the starting alkenes than the intermediate alkenebromonium ions. The transition states therefore have the character of molecularly π -bonded complexes. This complex, subsequently, via cleavage of the bromine-bromine bond, and simultaneous participation by the non-bonded electron pairs of the rehybridized bromine atom with the developing carbenium center, forms the three-membered-ring bromonium ion intermediate (σ complex) (Figure 17). The latter alkylenebromonium ion is then displaced by a bromide ion from the accessible backside, accounting for the observed exclusive trans stereospecificity of the bromine addition reactions. This is a reaction path similar to that found in electrophilic substitution reactions of benzene and alkylbenzenes with strong electrophiles,^{186,187} and is well-differentiated from reactions showing "late" transition-state character, with the transition state of highest energy resembling alkenebromonium ion intermediates (or σ complexes). If the transition state occurred early along the reaction coordinate, similar to that in electrophilic aromatic substitutions with strong electrophiles, it would be expected that there would be less demand for its stabilization by alkyl substituents, and rate differences would more closely parallel the π -donor ability of the corresponding alkenes instead of the stability of the related alkylenebromonium ions (σ complexes).

Although it is difficult to compare^b directly the stabilities of π and σ complexes of alkenes with bromination rates of the same alkenes, comparisons can be made with available data on silver alkene π complexes on the one hand and the stabilities of cyclic alkylenebromonium ions on the other. Although the stability constants of Ag^+ complexes (summarized in Table 42) show some dependence on a composite of steric, electronic, and solvent effects, the importance of these values lies in the fact that they cover only a very limited range and show only a slight increase in complex stability with increasing alkyl substitution.

In contrast, as shown in Table 42, based on the data of Larsen, the heats of formation of σ -bonded, three-membered-ring ethylenebromonium ions, generated from the corresponding vicinal dibromides, show a striking effect of alkyl substitution. Although it is generally accepted that a more stable intermediate ion (a carbocation or a halonium ion) would be formed faster under kinetic conditions, thermochemical data do not allow a direct conversion of relative stability into relative rates of formation (from an alkene and bromine). How-

TABLE 42
Heats of Formation of Alkenebromonium Ions^a and the Relative
Stability of Alkene-Silver π Complexes^b

Ion	ΔH (kcal/mole) ^c	π complex	Relative stability constant
	+1.0		1.0
	-3.3		0.41
	-11.3		0.18
	-15.5		0.36
	-22.9		0.005

^aMeasured at -60° in 11.5 mole % SbI_5 in FSO_3H by Larsen.¹⁸¹

^bRef. 195.

^cHeats of formation of halonium ions (and anions) are from the corresponding vicinal dihalide precursors (in 11.5 mole % SbI_5 in FSO_3 at -60°). Since the heat of formation of the anion produced is not known, ΔH is a relative quantity. Differences in ΔH represent differences in the heat of formation of the ions from the dihalide precursors in solution with the same leaving groups (anions).

ever, data of Table 41 clearly indicate that a very wide range in order of magnitude of relative rates would be expected for a reaction in which the transition state occurs late along the reaction coordinate and thereby resembles in nature the cyclic bromonium ion. This is more the case in the work by Dubois¹⁹³.

While neither the measured bromonium ion nor silver ion complex stabilities are directly comparable with rates of bromination of alkenes,¹⁹⁶ they indicate that the relative rates observed in low polarity systems are much more in accord with a π -complex-type transition state for the reaction than the σ -complex mechanism proposed in polar solvent systems. It has been shown for electrophilic aromatic substitutions that a similar change in relative rates is observed in reactions involving either early (π -complex-type) or late (σ -complex-type) transition states, illustrating how relative-rate data reflect the nature of the transition states in the reaction.

While previously it was assumed that a π -complex-type mechanism for alkene additions would result only in negligible spread of relative-rate values (corresponding to silver ion-alkene π -complex stability constants¹⁸³ or iodine-alkene stability data,¹⁹⁷ since both are qualitatively similar), the differences observed in brominations in low-polarity solvents^{189,194} do not support this assumption. Theoretical calculations¹⁹⁸ are also in accord with this suggestion and indicate that significant differences are to be expected. These calculations on systems involving an alkene and an interacting electrophile show that only a weak interaction exists between ethene and silver ion or molecular chlorine, but that significant stabilization in the latter case can be obtained by increased chlorine-chlorine bond length and partial charge development. Therefore it seems likely that since iodine, like silver ion, forms only a weak complex with alkenes, a strict correspondence between measured stability constants and relative rates is not expected. However, because the halogen-halogen bond is not greatly deformed and the alkene and halogen are in close proximity, some approximate correlation seems reasonable.

In addition, the development of a partial charge would allow a general parallelism between increased alkyl substitution and increased reactivity, as observed in the bromination and in other electrophilic reactions of alkenes.

The relative reactivities of the bromination of cyclohexene, cyclopentene, and norbornene were also determined. The results are listed in Table 43 along with, for comparison, some other reported data on additions to the same cycloalkenes. In the case of the more strained alkenes, higher rates are expected with increasing ring size, which should result in greater relief of strain in the transition state, relative to a smaller size ring.¹⁹⁹ The data in Table 43 do seem to support this hypothesis, and relative-rate data of the studied brominations indicate that the transition states of highest energy of the reactions are early and resemble the starting alkenes.²⁰⁰

TABLE 43
Relative Rates of Addition to Cycloalkenes^a

Reagent	Cyclopentene	Norbornene
Bromine	4.2	36
Chromyl chloride	4.9	312
Ag ⁺	2.0	17
Diethyl aluminum hydride	9.4	
Ozone	3.9	4.3
Osmium tetroxide	22	72
Diimide	15.5	450

^aCyclohexene = 1.0.

11.2.2 Alkynes

The relative rates of bromine addition to some alkyl-substituted alkynes in 1,1,2-trichlorotrifluoroethane solution at 0° were determined.¹⁹⁴ These results are listed in Table 44, along with related data obtained by Pincock and Yates²⁰¹ for bromination in acetic acid. Temperature effects on the bromination in acetic acid lead to a large negative entropy effect, which was interpreted as being due to the involvement of an intermediate alkynebromonium ion. Although the range of rates reported by Pincock and Yates is not very broad, bromination in 1,1,2-trichlorotrifluoroethane does lead to reduced selectivity, as also noted for alkenes. In addition, while alkynes react at rates similar to, or even greater than, those of the corresponding alkenes in some electrophilic reactions, for reactions that involve strained bridged (cyclic) transition states, they react up to 10⁵ times more slowly than alkenes.²⁰² Similar behavior was also noted in a bromination study in which alkynes were found to react more slowly by at least a factor of 10⁴ than the corresponding alkenes. Although no corresponding π - and σ -complex stability data are available for alkynes, the data summarized in Table 44 are also considered to indicate in the bromination of alkynes a mechanism with an early transition state of a π -complex nature, similar to that of the related bromination of alkenes.

The difference in behavior of alkenes and alkynes is quite reasonable when one considers that the decreased reactivity of alkynes results from an increase in the energy required for initial π -complex formation. Since the unsaturated bond in alkynes has cylindrical symmetry along the carbon-carbon bond axis and involves a measure of electron delocalization,²⁰³ total electron availability for complex formation is reduced. This then requires increased energy for π -complex formation and results in slower rates of reaction.

TABLE 44
Relative Rates of Addition of Bromine to Alkynes

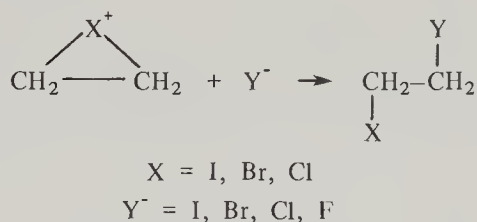
Alkyne	Br ₂ in CF ₂ ClCCl ₂ F ^a	Br ₂ in CH ₂ COOH ^b
3,3-Dimethylbutyne	1.0	1.0
2-Butyne	1.6	
1-Hexyne	2.4	0.61
2-Hexyne	3.0	
3-Hexyne	3.2	33.6

^aFor the reaction at 0° ref 194.

^bFor the reaction at 24.8°, relative second-order rate constants.

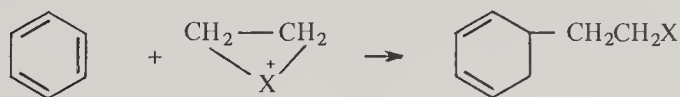
11.3 REACTIONS OF ETHYLENEHALONIUM IONS

The chemical reactivity of ethylenehalonium ions has not yet been studied in any detail.²⁰⁴ With halide ions they give vicinal dihalides with exclusive trans stereospecificity, in accordance with the long-suggested addition mechanism of halogens to olefins.

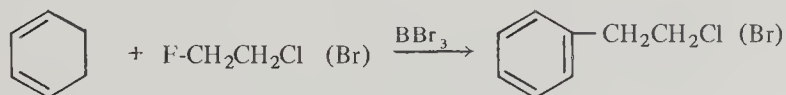


Alcohols and other nucleophiles give β-haloethyl ethers and related products, in addition to elimination products.

When reacted with aromatic hydrocarbons, ethylenehalonium ions give β-haloethylarenes.



The β-haloethylation reaction seems to be of general utility. Ethylenehalonium ions may also be responsible for β-haloethylations observed with 1-fluoro-2-chloro(or bromo)ethane²⁰⁵.

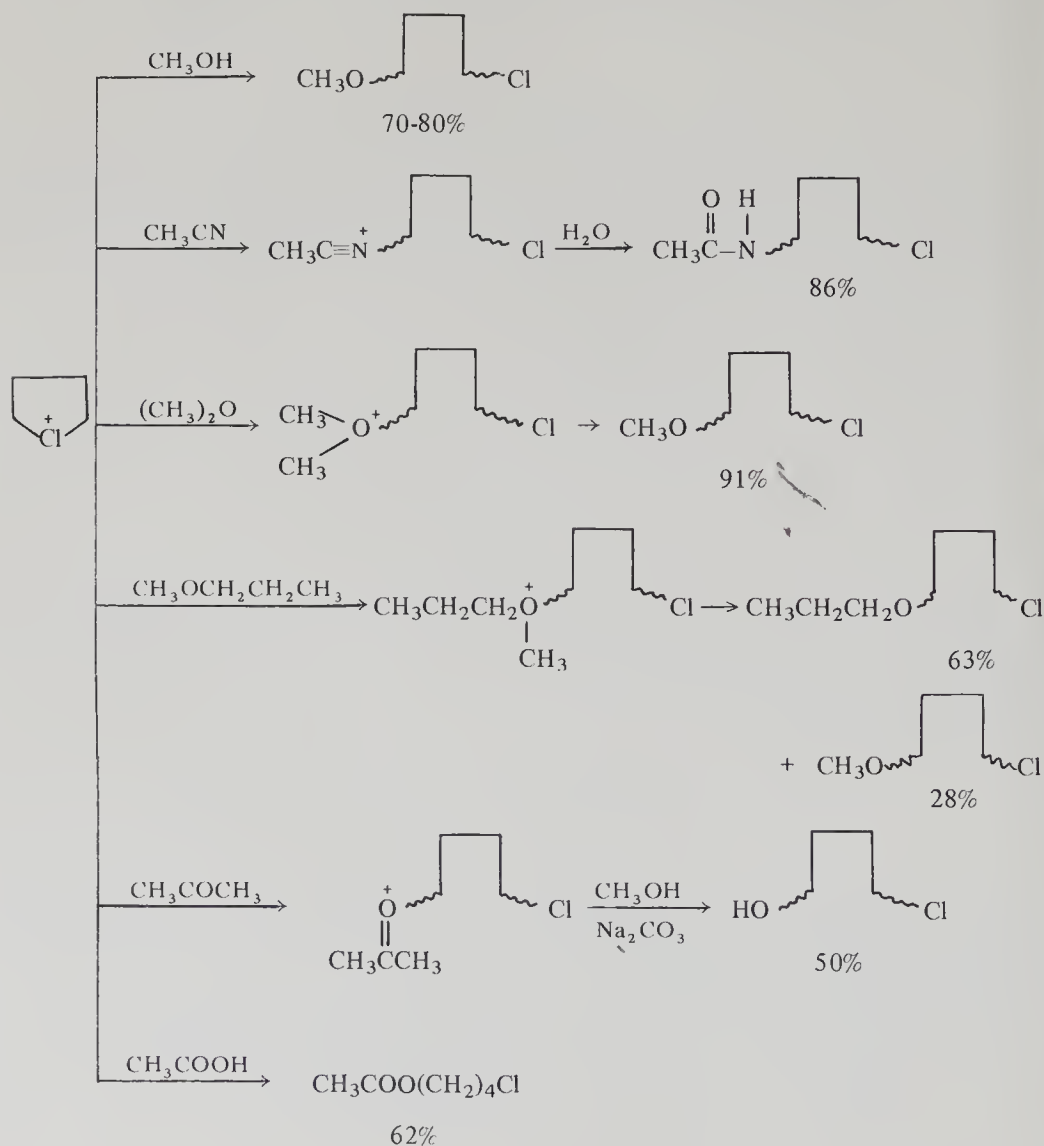


Ethylene dihalides are also potential carcinogens, and their biological alkylating ability could also indicate β -halogen participation forming ethylene-chloronium ion-like reactive intermediates.²⁰⁴

A more detailed study of the chemical reactivity of ethylenehalonium ions clearly is indicated and is expected to provide much interesting data.

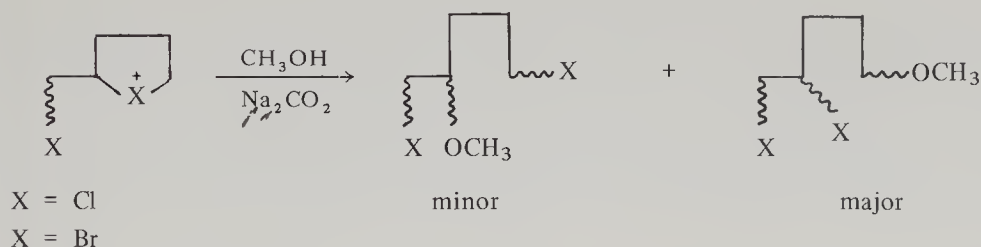
11.4 REACTIONS OF TETRAMETHYLENEHALONIUM IONS

The synthetic utility of tetramethylenehalonium ions has been demonstrated by Peterson and coworkers.¹⁷⁶ The tetramethylenechloronium ion was used to alkylate methanol, acetonitrile, dimethyl ether, methyl propyl ether, acetone, and acetic acid. The initially formed intermediate open-chain ions of these

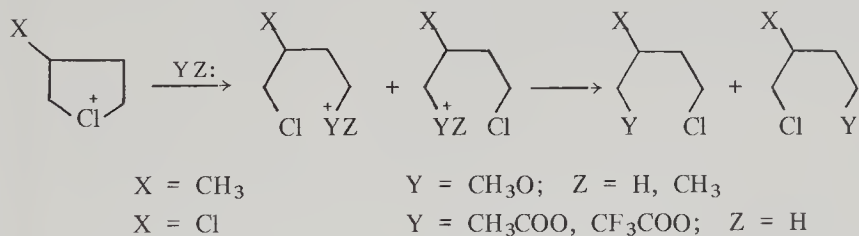


reactions were directly observed by nmr at -60° . The final reaction products were obtained by further reactions (quenching), generally in fair to good yield.

However, the cleavage of unsymmetric tetramethylenehalonium ions in reactions carried out with various nucleophiles (such as methanol, dimethyl ether, acetic acid, and trifluoroacetic acid) generally gave two products. In the methanolysis of 2-halomethyltetramethylenehalonium ions major and minor products were obtained.



Peterson and Bonazza¹⁷⁷ also reported the reaction of three-substituted tetramethylenechloronium ions with a variety of nucleophiles under similar conditions, according to the following equation.

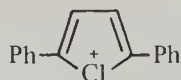


Heteroaromatic Halophenium Ions

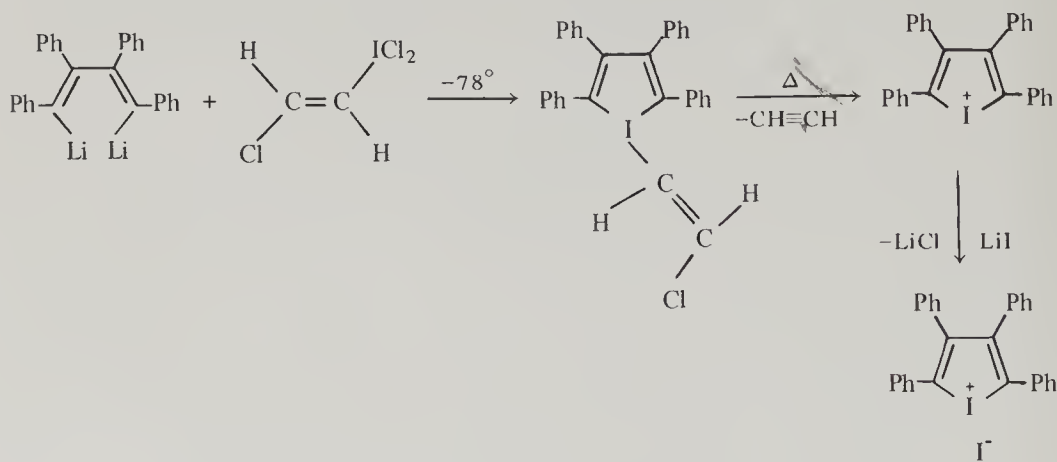
In certain cases the heteroatom in heteroarenes can also be ionic halogen. The systems studied so far centered on halophenium ions (five-membered-ring halonium analogs of thiophene¹⁹).

12.1 HALOPHENIUM IONS

Silver-assisted solvolysis of $\text{PhCCl}=\text{CHCH}''=\text{CBrPh}$ in HOAc and in Ac_2O gave $\text{PhCCl}=\text{CHCH}=\text{CPh}-\text{OAc}$ and $\text{PhCCl}''\text{CHC}''\text{CPh}$. Analyses of the deuterium distribution in the products from deuterated starting material showed that 24% (in HOAc) and 30% (in Ac_2O) of the reaction proceeds through a chlorophenium ion intermediate.²⁰⁶ Similar results were obtained from a study of the solvolysis products.



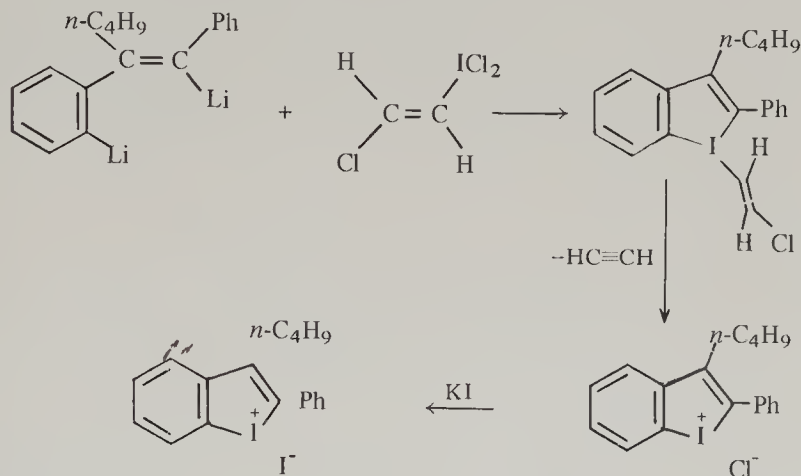
Beringer et al.²⁰⁷ found that 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene reacts with *trans*-chlorovinylidiodo dichloride at -78° to give, in low yield, 2,3,4,5-tetraphenyliodophenium chloride which is converted to tetraphenyliodophenium iodide by treatment with LiI.



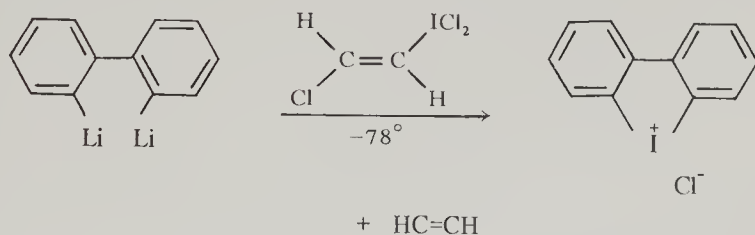
12.2 BENZIODOPHENIUM IONS

Beringer and coworkers²⁰⁷ reported that the low-temperature reaction of *trans*-1-lithio-2-*o*-lithiophenyl-1-phenyl-1-hexene with *trans*-chlorovinylidiodo dichloride in ether gave a 26% yield of 3-butyl-2-phenylbenziodophenium

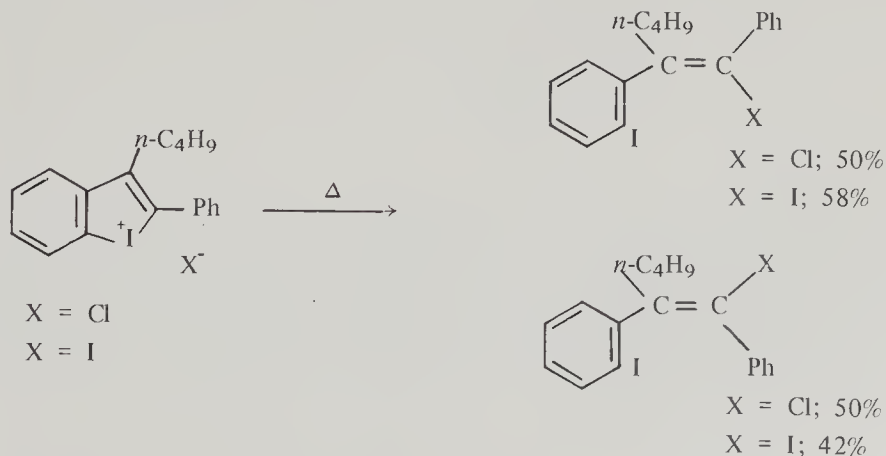
chloride which was converted by metathesis with ICl to 3-butyl-2-phenylbenziodophenium iodide. It was suggested that the reaction probably proceeds via the trivalent organoiodine intermediate.



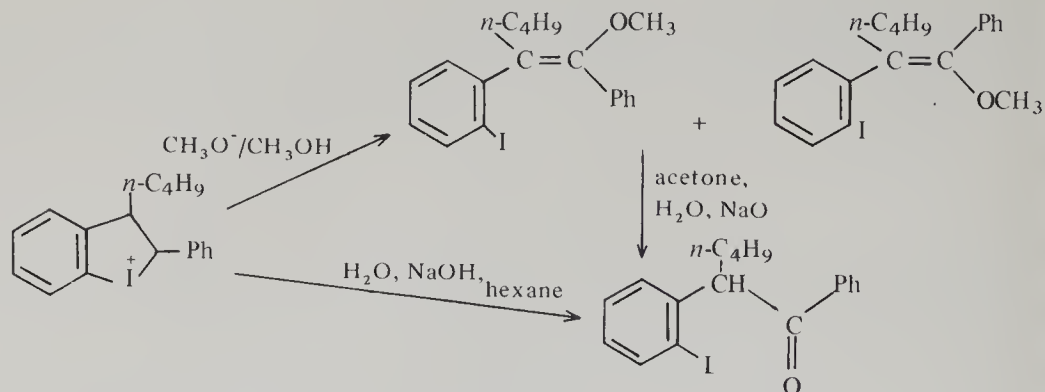
Another five-membered halonium ion, the dibenziodophenium ion, was also prepared by Beringer and Nathan.²⁰⁸ The X-ray crystal structures of the ions were also determined.



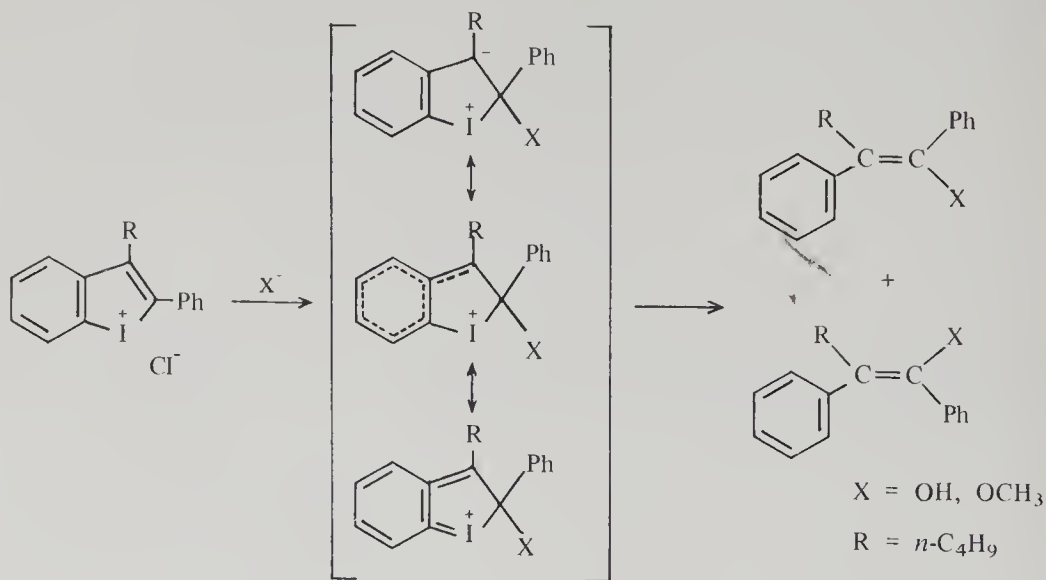
Beringer and coworkers²⁰⁸ reported reactions of benziodophenium salts. Thermal decomposition of the salts at their melting points gave a mixture of *cis*- and *trans*-stilbenes.



Reaction with sodium methoxide in anhydrous methanol gave an equimolar mixture of *cis*- and *trans*-2-iodophenyl-1-methoxy-1-phenyl-1-hexene. The mixture then underwent acid-catalyzed hydrolysis.

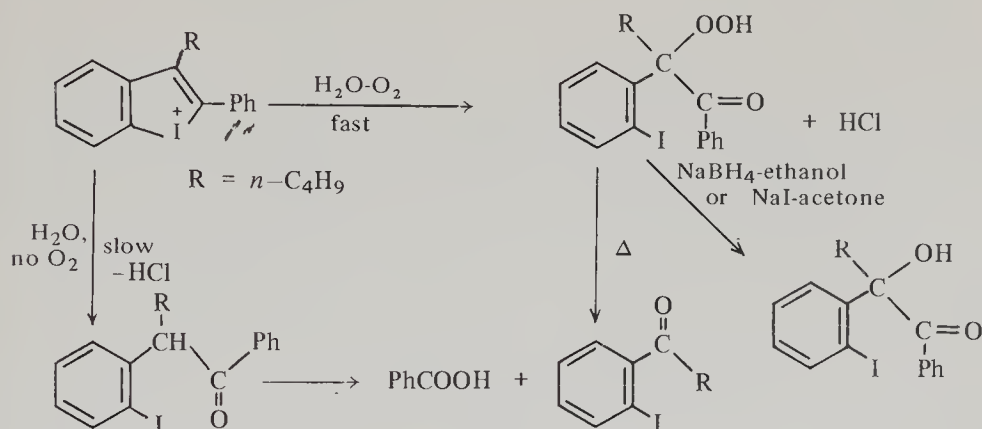


The mechanism of the reaction, which shows attack by nucleophiles exclusively at the 2-position to give almost equal amounts of *cis*- and *trans*-stilbenes, was suggested to be



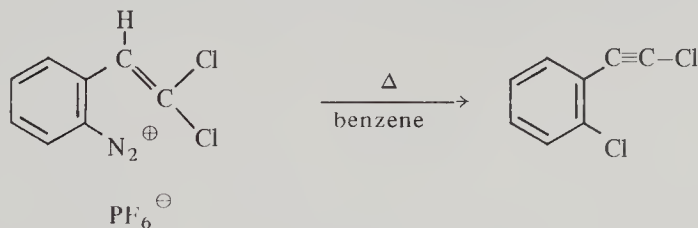
Attack of the nucleophile at the 2-position from above or below the plane of the ring can occur with equal probability, giving a dipolar intermediate. Delocalization of the negative charge into the aromatic ring and into the d or f orbitals of iodine might help to stabilize the intermediate. E_1 elimination of the I^+ group would give equal amounts of the *cis* and *trans* isomers.

When benziiodophenium ions are treated with water in the presence of oxygen, oxidative hydrolysis occurs rapidly (ca. 1-2 hr). Under the same conditions but in the absence of oxygen, a very slow (ca. 1-month) hydrolysis occurs in almost quantitative yield. Reduction with either sodium borohydride in ethanol or sodium iodide in acetone gives the hydroxy ketone. The hydroxy ketone is oxidatively cleaved with lead tetraacetate to benzoic acid and ketone, which are also formed by thermal cleavage of the intermediate oxidation product.

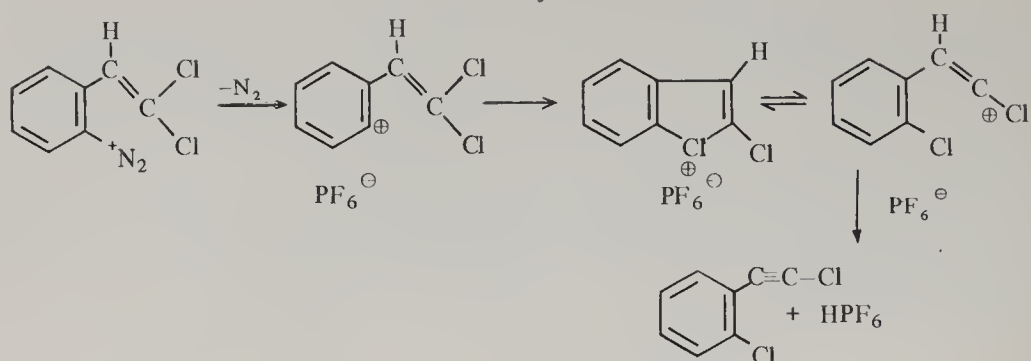


12.3 BENZCHLOROPHENIUM IONS

In an attempt to prepare and study benzchlorophenium ions, *o*-(β,β -dichloroethenyl)phenyl- and *o*-(α -methyl- β,β -dichloroethenyl)phenyldiazonium fluorophosphates were used as precursors by Olah and Yamada.¹⁹ In their thermal decomposition the desired benzchlorophenium ion could not be isolated, but *o*-(β -chloroethynyl)chlorobenzene was obtained in good yield. Its formation

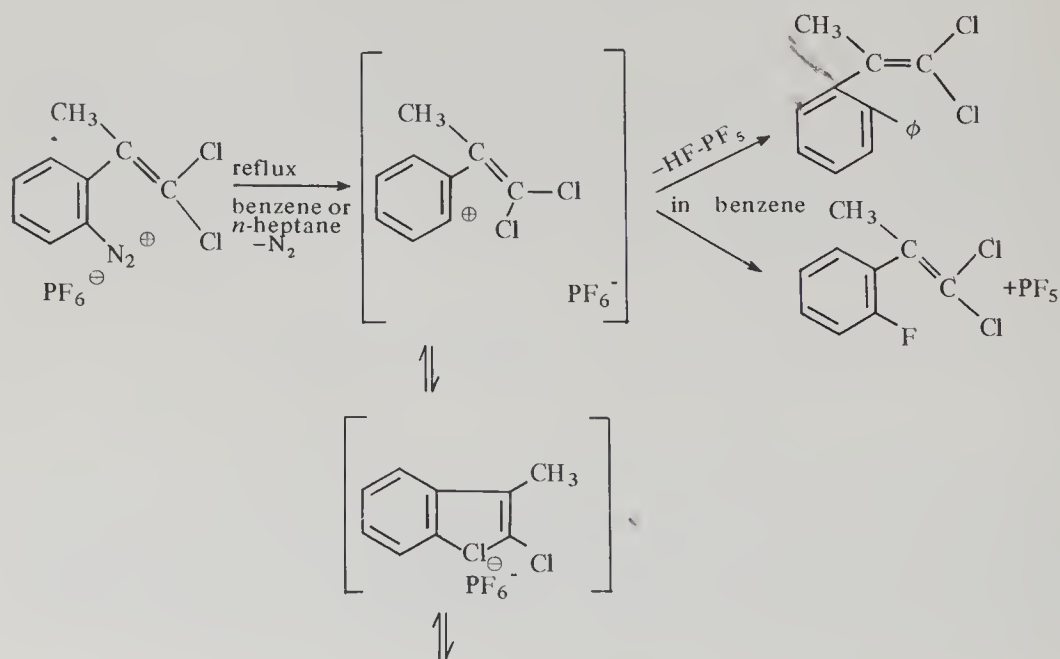


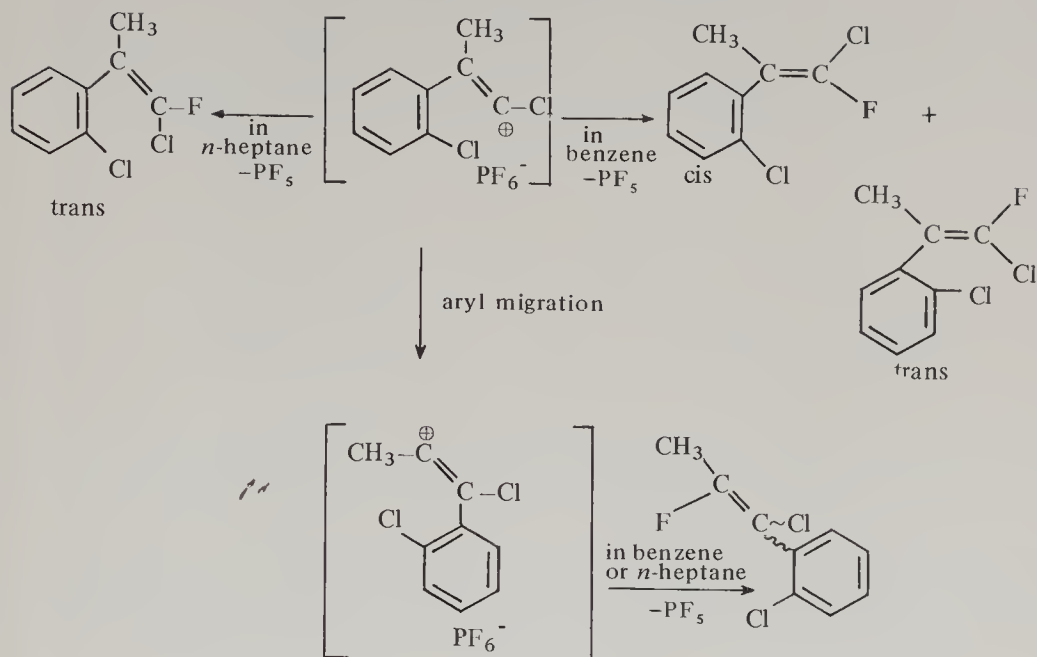
clearly shows that the benzchlorophenium ion is an intermediate which via ring opening and deprotonation gives the observed product. The presence of the highly acidic proton at C-3 facilitates ring opening of the benzchlorophenium ion (and subsequent deprotonation).



If the acidic proton is absent in the benzochlorophenium ion, a different behavior is observed. The thermal decomposition of *o*-(α -methyl- β,β -dichloroethenyl)phenyldiazonium fluorophosphate in refluxing benzene (for 0.5 hr) gave a mixture of 1-chloro-1-fluoro-2-(*o*-chlorophenyl)propene-1 and 1,1-dichloro-2-(*o*-fluorophenyl)propene-1 (25.6%), 1-chloro-1-(*o*-chlorophenyl)-2-fluoropropene-1 (24.5%), and 1,1-dichloro-2-(2-biphenyl)propane-1 (46.5%).

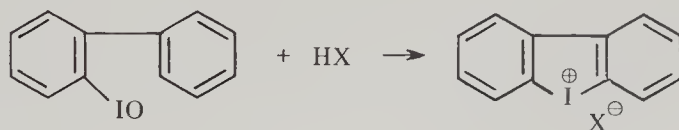
The formation of 1-chloro-1-fluoro-2-(*o*-chlorophenyl)propene-1 and 1-chloro-1-(*o*-chlorophenyl)-2-fluoropropene-1 shows the presence of the 2-chloro-3-methylbenzochlorophenium ion as the intermediate, since only its ring opening can introduce chlorine into the ortho position of the phenyl ring. Additional products observed arise from the incipient phenyl cation.



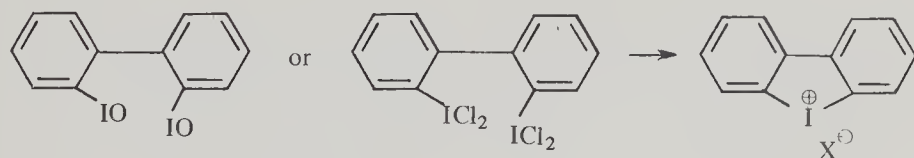


12.4 DIBENZHALOPHENIUM IONS

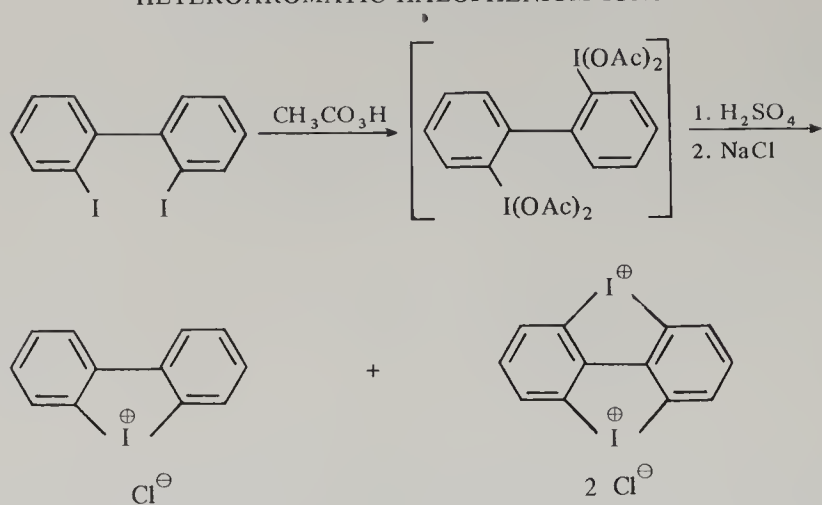
The dibenziodophenium ion containing an aromatic five-membered iodonium ring was first prepared from 2-iodosobiphenyl²⁰⁹



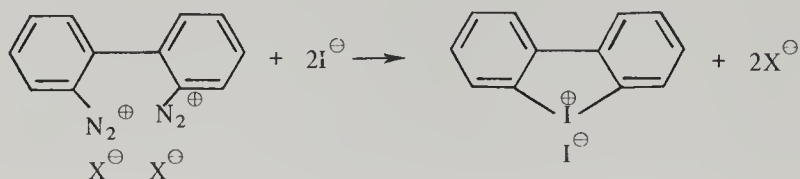
2,2'-Diiodoso-, and 2,2'-diiodosodichlorobiphenyl were also treated with water and SO₂ to give dibenziodophenium ions.²¹⁰ However, 2,2'-diiodobiphenyl,



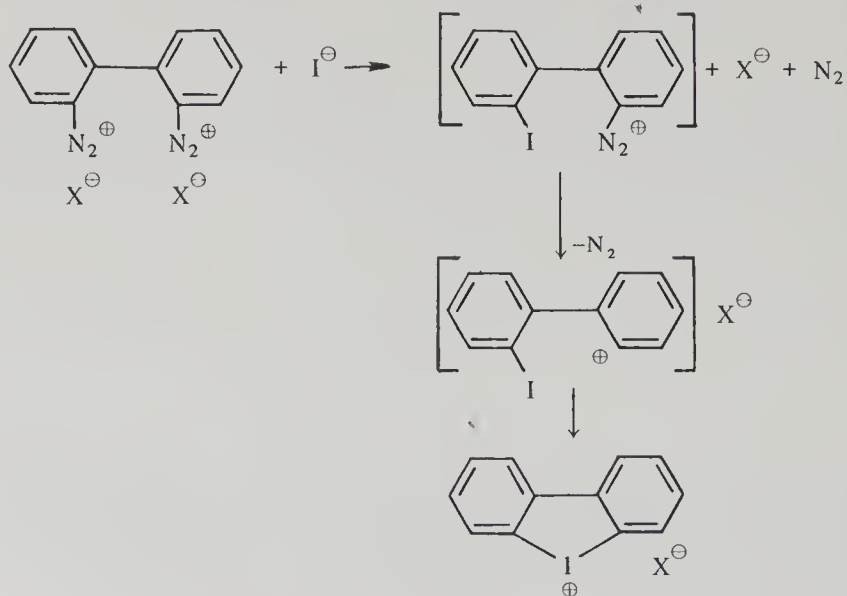
when treated with peracetic acid (to give the corresponding diiodosoacetate derivative) and subsequently with H₂SO₄ and NaCl, gave not only the dibenziodophenium ion but also a bisiodonium ion.²¹¹ The reactions are indicated to



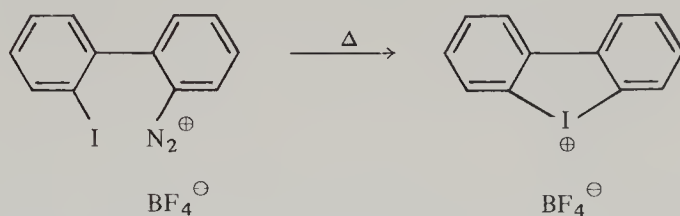
proceed via three-valent iodine compounds that is, R-ICl_2 , R-IO , $\text{RI}(\text{OAc})_2$. However, the dibenziodolphenium ion was also prepared from diazotized 2,2'.



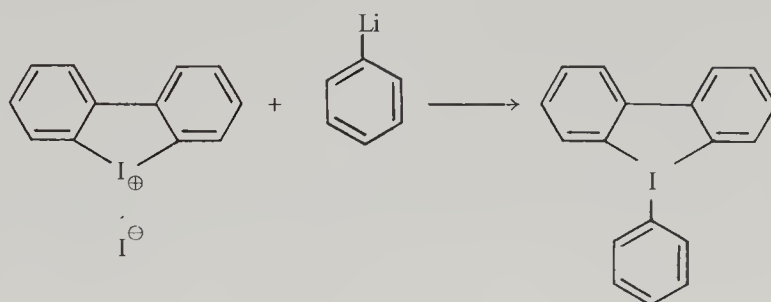
diaminobiphenyl and iodide ion.²¹² This reaction could proceed in the following manner.



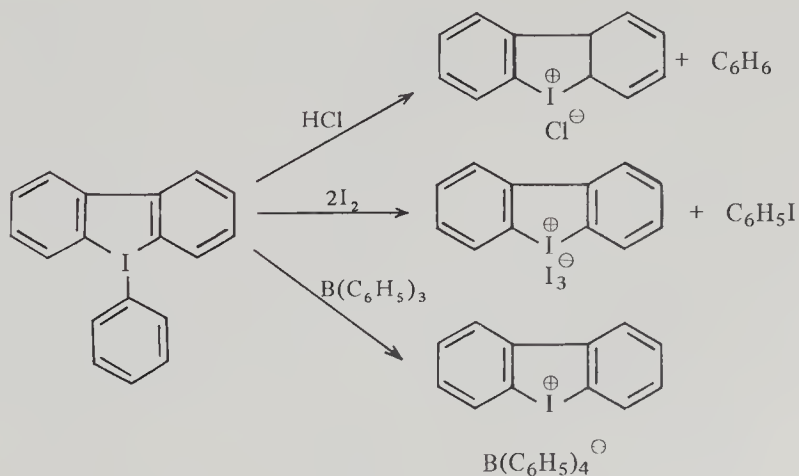
Heaney²¹³ and Sandin²¹⁴ prepared the dibenziodophenium ion by thermolysis of 2-(2'-iodobiphenyl)diazonium fluoroborate. The dibenziodophenium ion react



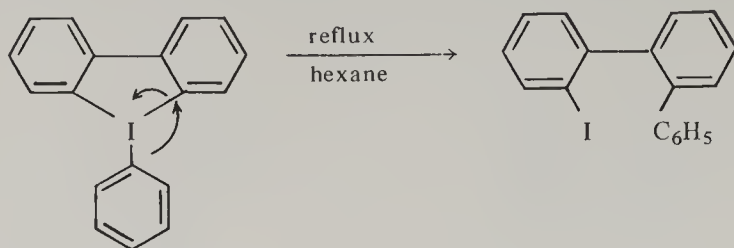
with phenyllithium to give 5-phenyl-5*H*-dibenziodole, which is stable at room temperature for several days.²¹⁵ The phenyl-iodine bond is easily cleaved by



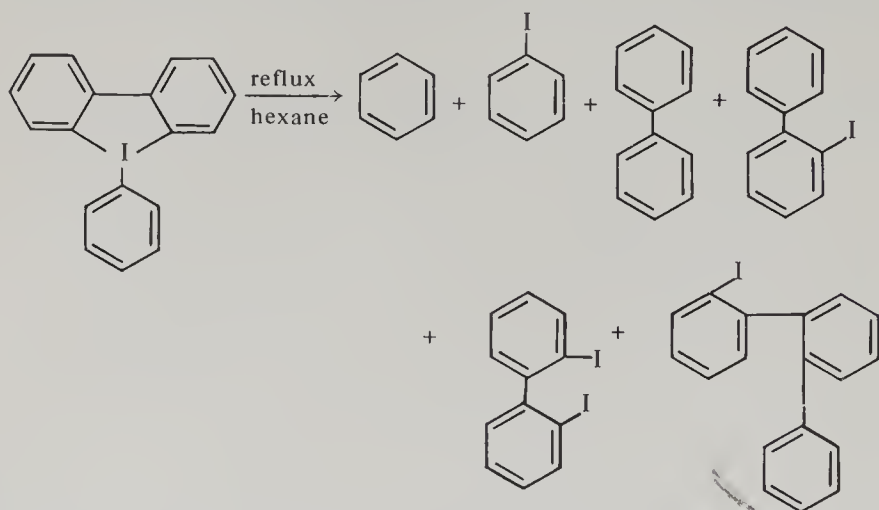
hydrogen chloride, iodine, and triphenylboron to give the dibenziodophenium ion.



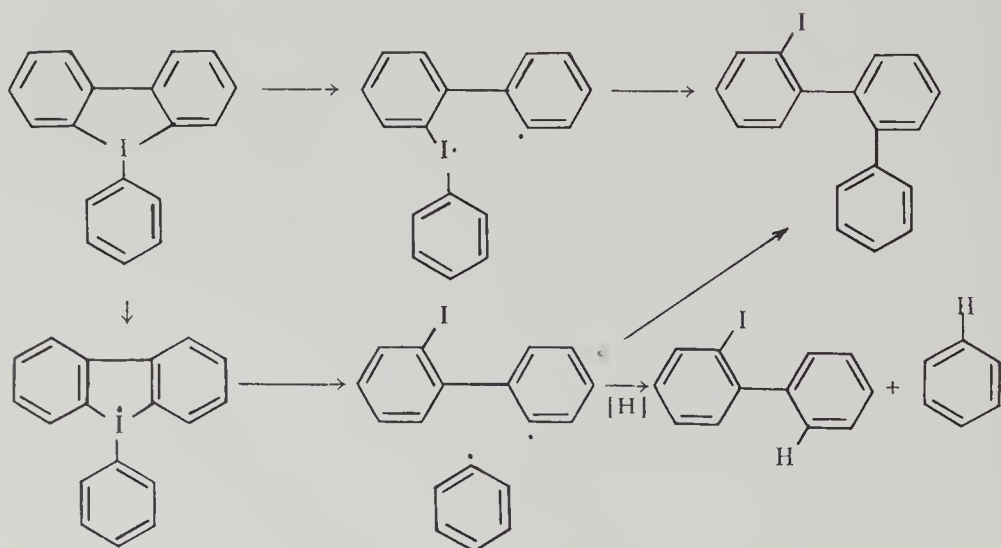
The thermal reaction of 5-phenyl-5*H*-dibenziodole in refluxing hexane gives 2-diodo-2'-phenylbiphenyl (formed via an ionic mechanism).



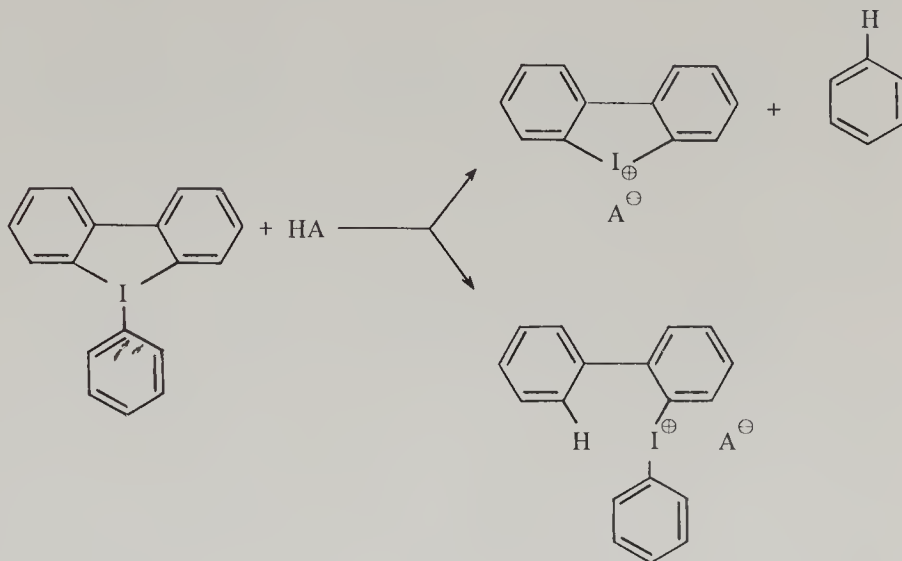
In the reaction in hexane at room temperature, however, not only the ionic but also a radical reaction occurs,^{216,217} giving the following products.



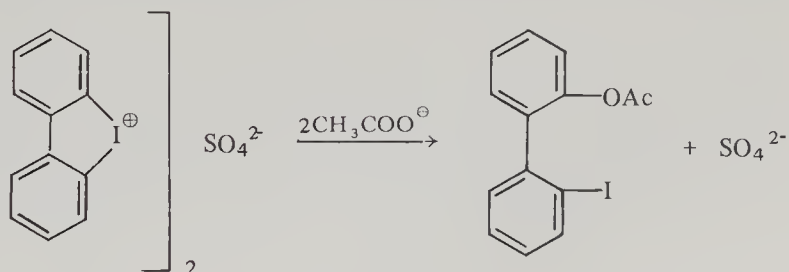
The reaction proceeds in the following way.



In the presence of protic or Lewis acids the reaction proceeds by the heterolytic mechanism to give cyclic and acyclic iodonium ions in good yield.²¹⁷

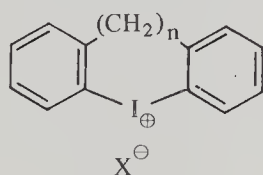


Dibenziodophenium sulfate reacts with acetate ion to give 2-iodo-2'-biphenyl acetate. In the reaction with methoxide ion, the products are not 2-iodo-2'-

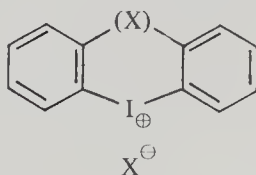


methoxybiphenyl but biphenyl, 2-iodobiphenyl, and 2,2'-diiodobiphenyl. This suggests that the reaction did not proceed heterolytically but homolytically.²¹⁸ Usually, the reactivity of the dibenziodophenium ion is lower than that of diphenyliodonium ions, which can be explained by the aromatic five-membered iodonium ring (the "iodophene" system).

Six-, seven- and eight-membered-ring iodonium ions have also been synthesized, as were six-membered-ring iodonium ions containing hetero atoms.¹¹

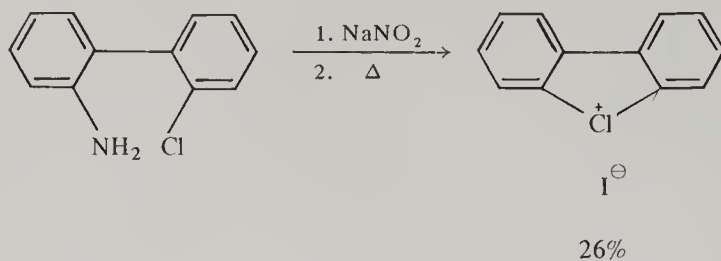
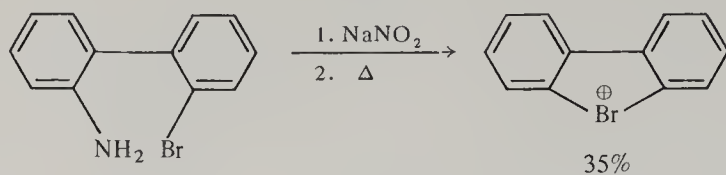


$$n = 1, 2, 3$$

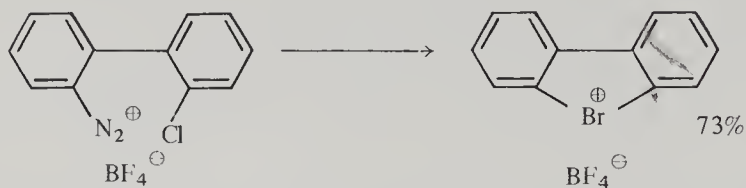


$$X = O, S, NH$$

Sandin and Hay²¹⁴ synthesized five-membered-ring cyclic bromonium and chloronium ions from the corresponding 2-amino-2'-halobiphenyls in aqueous solution.



Heany et al.²¹³ prepared the same halonium ions from the corresponding diazonium salts in benzene solution and isolated them in good yield.



Conclusions and Future Outlook

Halonium ions are not only the reaction intermediates in electrophilic halogenations, but also represent in their own right a significant class of organic onium compounds of substantial preparative and chemical structural interest. Nearly all types of halonium ions with structures related to other analogous onium ions (acyclic as well as cyclic or even bicyclic) can now be prepared. Halonium ions can be prepared *in situ* or isolated as stable salts for further reactions. Recent developments mostly emphasized the preparation and spectroscopic study of halonium ions. Their utility as reagents in organic synthesis is in its formative stage and can be expected to undergo fast development.

Alkyl halides are some of the most useful laboratory alkylating agents. Aryl halides, however, are considerably less reactive. However, diphenylhalonium ions (especially iodonium ions) are reactive phenylating agents. That is, the bond between the phenyl ring and the halonium center is easily cleaved on reaction with a nucleophile to give phenylated products. Iodonium ions bearing a thiophene, furan or pyridine ring as a ligand are expected to be able to trans-arylate nucleophiles via transferring the heterocyclic group. Iodonium ions bearing olefinic or acetylenic groups as ligands are also expected to have significant reactivity. Iodonium ylides ($-I^{\oplus}-\overset{\oplus}{C}<$ or $-I^{\oplus}-\overset{\oplus}{N}-$) are interesting reactive intermediates for carbenes or nitrenes.

Organic halonium ions and their related ylides, although still in their infancy as compared with such well-developed classes of onium ions as ammonium, oxonium, sulfonium, and phosphonium ions, nevertheless, promise substantial utility and significance. It is hoped that this review will further interest in and future development of the fascinating field of organic halonium ions.

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