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Onium Ions. 17.^{1a} Improved Preparation, Carbon-13 Nuclear Magnetic Resonance Structural Study, and Nucleophilic Nitrolysis (Nitrative Cleavage) of Diarylhalonium Ions

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An improved method of preparation of diarylchloronium and diarylbromonium ions is described from their corresponding arenediazonium ions by decomposition in haloarenes in the presence of trifluoro- (trichloro-) acetic acid or 2,2,2-trifluoroethyl alcohol. ¹³C NMR spectroscopic study of the prepared halonium ions shows that nearly equal amounts of charge are transmitted into the two aryl rings regardless of the methyl substitution in one or both rings, suggesting that canonical structures such as I–III are only limited resonance contributors. The potential utility of symmetrical and unsymmetrical diarylchloronium, -bromonium, and -iodonium ions in their nucleophilic nitrolysis with sodium nitrite, giving nitroarenes, was studied. The relative reactivity of the 4-tolyl, phenyl, 3-tolyl, and 2-tolyl salts has been established as 1.0, 3.0, 3.6, and 14.1, respectively. Substitution of tetraphenylborate for hexafluorophosphate as counterion did not affect the product distribution in the nitration reaction. The data reported are best accommodated by an S_N2-like mechanism controlling the collapse of ionic diarylchloronium nitrites, initially formed by displacement of the corresponding counterion, to give nitro- and chlorobenzene derivatives.

Whereas diaryliodonium ions have been extensively studied,² only limited data are available on diarylchloronium and -bromonium ions² in spite of the high potential utility of these ions as electrophilic arylating agents.³ This can be attributed to the extremely low yields (0.6–6.6%) obtained in their preparation by Nesmeyanov and co-workers using the decomposition of aryldiazonium tetrafluoroborates in chloro- or bromoarenes.^{4–7} Recently Nesmeyanov and co-workers reported an improved preparation of diarylbromonium ions by reacting aryllithiums with BrF₃ in 9–28% yields.⁸ This method is limited to the preparation of symmetrical diarylbromonium ions. Further difficulties involved in handling BrF₃ and its explosive nature with phenyllithium make the method of little use.

The preparative utility of diarylbromonium tetrafluoroborates was demonstrated by McEwen and Lubinkowski^{9a} in their nucleophilic displacement reaction with sodium alkoxides, giving exclusively phenyl alkyl ethers. The corresponding diaryliodonium salts gave under the same conditions, however, aromatic hydrocarbons as the major products^{9b} (via a radical path). Reutov and co-workers^{9c} carried out the reaction between diarylhalonium salts and triphenylphosphine in light to give (via a radical path) tetraphenylphosphonium ions in 82–92% yields. Nesmeyanov and his co-workers^{9d} briefly reported that diarylbromonium and -chloronium ions are quite reactive toward many common nucleophiles, including amines, sodium nitrate, sodium azide, and sodium cyanide. Diphenyliodonium tetrafluoroborate treated with sodium nitrite in aqueous dioxane gave nitrobenzene in 70% yield.^{9a} A similar reaction with phenyl-*p*-tolylidonium tetrafluoroborate yielded a mixture of nitrobenzene and *p*-nitrotoluene in a ratio of 2.5:1.^{9d}

A systematic study of the reactivity of diarylchloronium and

-bromonium ions with nucleophiles, however, has not yet been reported since these halonium salts have been obtained previously only in extremely low yields and were believed to be quite unstable compounds.¹⁰

Interested in the chemistry of organic halonium ions, we now wish to report an improved method of preparation of diarylchloronium and diarylbromonium ions from their corresponding arenediazonium ions by decomposition in haloarenes in the presence of trifluoro- (trichloro-) acetic acid or 2,2,2-trifluoroethyl alcohol. The developed, improved general method for the preparation of these halonium ions also allowed a systematic study of the nucleophilic nitration of a series of methyl-substituted diarylhalonium salts with sodium nitrite.

Results and Discussion

Preparation of Diarylchloronium and Diarylbromonium Ions. When phenyldiazonium hexafluorophosphate was heated at 60–65 °C in chlorobenzene in the presence of trifluoroacetic acid for 2 h, the reaction mixture subsequently extracted with water, and the aqueous solution neutralized with sodium hydrogen carbonate, the addition of sodium tetraphenylborate caused precipitation of the diphenylchloronium tetraphenylborate salt. The yield of the purified salt recrystallized from acetone–ether was 13%. GC and IR analysis of the organic layer indicated the presence of fluorobenzene (36%), formed in the competitive Schiemann reaction, and phenyl trifluoroacetate. In addition to trifluoroacetic acid, 2,2,2-trifluoroethyl alcohol, acetic acid, and trichloroacetic acid were also found to be effective; they give the diphenylchloronium salt in 9.0, 4.0, and 8.0% yields, along with fluorobenzene in 40, 51, and 33% yields, respectively. Phenyl 2,2,2-trifluoroethyl ether, phenyl acetate, and phenyl trichloroacetate were formed (based on IR and/or NMR spectroscopy) as the byproducts. Similar arylation failed to take

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Table I. Preparation of Diarylhalonium Tetrakisphenylborates

Diazonium salt	Registry no.	Haloarene	Registry no.	Halonium ion	Registry no.	Mp (dec), ^a °C	Yield ^b from aryldiazonium, %	
							PF ₆ ⁻	BF ₄ ⁻ CF ₃ CO ₂ ⁻
Phenyl	369-58-4	Chlorobenzene	108-90-7	1 Diphenylchloronium	64146-75-4	160-161	13.0	6.6 (3.3) ⁷
Phenyl		Bromobenzene	108-86-1	2 Diphenylbromonium	64146-76-5	172 (166) ^c	8.1	(6.6) ⁷
Phenyl		Iodobenzene	591-50-4	3 Diphenyliodonium	64146-77-5	192 (177)	6.0	
<i>o</i> -Tolyl	19296-22-1	<i>o</i> -Chlorotoluene	95-49-8	4 Di- <i>o</i> -tolylchloronium	64175-35-5	137-138 (122)	7.6	
<i>m</i> -Tolyl	672-82-2	<i>m</i> -Chlorotoluene	108-41-8	5 Di- <i>m</i> -tolylchloronium	64146-79-8	138-139	8.9	
<i>p</i> -Tolyl	673-44-9	<i>p</i> -Chlorotoluene	106-43-4	6 Di- <i>p</i> -tolylchloronium	64146-81-2	136-137	8.6	
<i>o</i> -Tolyl		Chlorobenzene		7 Phenyl- <i>o</i> -tolylchloronium	64146-82-3	139 (136) ^d	9.3	5.2 (0.6) ^e
<i>m</i> -Tolyl		Chlorobenzene		8 Phenyl- <i>m</i> -tolylchloronium	64146-84-5	147-148 (136)	9.8	5.0
<i>p</i> -Tolyl		Chlorobenzene		9 Phenyl- <i>p</i> -tolylchloronium	64146-85-6	128 (112) ^e	10.1	5.6 (1.8) ^e
<i>m</i> -Tolyl		<i>p</i> -Chlorotoluene		10 <i>m</i> -Tolyl- <i>p</i> -tolylchloronium	64146-87-8	141-142 (137)	6.7	
<i>p</i> -Chlorophenyl	1582-27-0	Chlorobenzene		11 Phenyl- <i>p</i> -chlorophenylchloronium	64146-88-9	157 (142)	14.0	

^a Temperatures at which crystals changed are given in parentheses. ^b Yields reported in the literature are given in parentheses. ^c Lit.⁴ mp 164-165 °C dec. ^d Lit.⁵ mp 160-161 °C. ^e Lit.⁶ mp 127 °C dec.

Table II. ¹³C NMR Chemical Shifts^{a, b} for Diarylhalonium Hexafluorophosphates

Ar-X-Ar'	Registry no.	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₁ '	C ₂ '	C ₃ '	C ₄ '	C ₅ '	C ₆ '	CH ₃
1	64146-89-0	139.7 (134.3)	133.6 (124.6)	129.1 (129.8)	134.7 (126.5)	129.1 (129.8)	133.6 (124.6)							
2 ^c	64146-90-3	133.4		130.9	133.9	130.9								
3	58109-40-3	136.0	114.2	132.7	133.3	132.7	114.2							
4	64146-74-3	138.4 ^d	137.9 ^d	131.3	135.0	129.3	134.6							18.8
		(134.4)	(135.9)	(130.9)	(127.0)	(126.4)	(129.0)							
5	64146-91-4	139.4	133.1	144.8	135.3	126.0	129.1							20.9
		(134.0)	(129.1)	(139.7)	(127.1)	(129.3)	(125.5)							
6	64146-92-5	136.8	134.0	128.8	146.2	128.8	134.0							20.7
		(131.2)	(128.3)	(130.4)	(136.2)	(130.4)	(128.3)							
7	64146-93-6	139.2	133.6	128.5	135.0	128.5	133.6	138.9	138.4	131.3	135.0	130.3	134.0	18.0
8	64146-94-7	139.6	133.6	129.0	134.7	129.0	133.6	139.4	133.1	144.9	135.4	126.0	129.0	20.8
9	64146-95-8	140.0	133.6	128.9	134.6	128.9	133.6	136.3	134.0	128.9	146.3	128.9	134.0	20.8
10	64146-96-9	139.8	133.1	144.8	135.2	128.9	125.8	136.2	134.0	128.9	146.3	128.9	134.0	20.8, 20.8
11	64146-97-0	139.9	133.7	129.0	134.8	129.0	133.7	137.1	133.4	130.9	140.7	130.9	133.4	

^a Carbon chemical shifts are relative to external (capillary) Me₄Si. Spectra were recorded in acetone solution at room temperature. ^b Chemical shifts for the corresponding haloarenes¹¹ are given in parentheses for comparison. ^c Values differ from those previously obtained by Olah et al.¹² for 2 in SO₂ solution at -40 °C. ^d Assignments considered interchangeable.

Table III. Differences between Total ^{13}C Chemical Shifts in Chloroarenes^a and Diarylchloronium Ions

Diarylhalonium hexafluorophosphates	Ar group		Ar' group		Total $\Delta\Sigma\delta\text{-C}^c$
	$\Sigma\delta\text{-C}$	$\Delta\Sigma\delta\text{-C}^b$	$\Sigma\delta\text{-C}$	$\Delta\Sigma\delta\text{-C}^b$	
1	799.8 (777.6)	22.2			44.4
4	806.5 (783.6)	22.9			45.8
5	807.7 (784.7)	23.0			46.0
6	808.6 (784.8)	23.8			47.6
7	808.4 (783.6)	24.8	798.4 (777.6)	20.8	45.6
8	807.8 (784.7)	23.1	799.5 (777.6)	21.9	45.0
9	808.4 (784.8)	23.6	799.6 (777.6)	22.0	45.6
10	807.6 (784.7)	22.9	808.3 (784.8)	23.5	46.4

^a Total chemical shift values for haloarenes¹¹ are given in parentheses. ^b $\Delta\Sigma\delta\text{-C} = C_{\text{Ar(or Ar')}} \text{ in halonium ion} - C_{\text{Ar(or Ar')}} \text{ in haloarene}$. ^c $\Delta\Sigma\delta\text{-C} = \Delta\Sigma\delta\text{-C}_{\text{Ar}} + \Delta\Sigma\delta\text{-C}_{\text{Ar'}}$.

place in the presence of such acids as sulfuric acid, oleum, phosphoric acid, or trifluoromethanesulfonic acid. To change the heterogeneous nature of the reactions to a homogeneous one, acetone or acetonitrile was added as a cosolvent, but the yield of the diphenylchloronium salt decreased. This is attributed to the higher nucleophilic reactivity of these solvents than that of chlorobenzene. In fact, in the presence of acetonitrile, acetanilide¹¹ was isolated in 55% yield. The yield of diphenylchloronium tetraphenylborate decreased to 6.6% when phenyldiazonium tetrafluoroborate was used instead of the hexafluorophosphate salt. As shown in Table I, aryl-diazonium hexafluorophosphates gave consistently better yields than the tetrafluoroborates. In order to prevent the competing formation of fluoroarenes (by the Schiemenn reaction), the counterion was also changed to trifluoroacetate.¹² The yield of phenyl-, *p*-tolyl-, and phenyl-2,4-xylylchloronium tetraphenylborates prepared by this modification increased to 17%.

The reaction of phenyldiazonium hexafluorophosphate with bromobenzene and iodobenzene gave diphenylbromonium and iodonium tetraphenylborate in 7.9 and 8.6% yields, respectively.

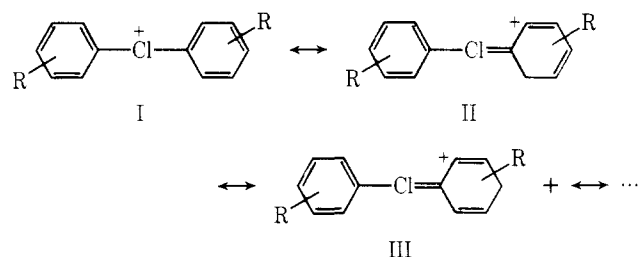
When aniline itself was reacted with sodium nitrite in trifluoroacetic acid and chlorobenzene in the presence of various dehydrating agents to remove the water generated during diazotization, diphenylchloronium tetraphenylborate was isolated in 6.9, 6.5, 6.0, and 7.0% yields in the case of molecular sieves, anhydrous sodium sulfate, phosphorus pentoxide, and trifluoroacetic anhydride, respectively.

Carbon-13 NMR Spectroscopic Study of Diarylhalonium Ions. The structure of the diarylhalonium salts prepared was subsequently studied by ^{13}C NMR spectroscopy. Diarylchloronium tetraphenylborates displayed complicated ^{13}C NMR spectra since the absorptions of the ring carbons of the anions overlapped with those of the cations. Therefore, the counterion was exchanged for hexafluorophosphate, as described in the Experimental Section. The ^{13}C NMR parameters of the corresponding diarylchloronium hexafluorophosphate salts are summarized in Table II. The assignments were made on the basis of off-resonance spectra, relative intensity of the absorptions, and consideration of molecular symmetry,¹³ as well as comparison with the chemical-shift values of the parent haloarenes.¹⁴

The value of the sum of the ^{13}C NMR chemical shifts of the aryl carbons in each aryl ring is increased by 22 to 24 ppm (Table III) upon transformation of the chloroarenes into di-

arylchloronium ions, reflecting partial delocalization of the positive charge into the aryl groups.¹⁵ Phenyl and tolyl groups in these ions were shown to possess the similar ability to delocalize the positive charge from the chlorine atom since the aryl carbons undergo an overall deshielding in the ^{13}C NMR spectra of similar magnitude regardless of methyl substitution in one or both aryl rings, the position occupied by the methyl substituent in the tolyl group, or the symmetrical or unsymmetrical nature of the diarylchloronium salt. Thus, a nearly equal amount of charge is transmitted into the two aryl rings.

On the basis of carbon-13 chemical shift data of the diarylchloronium ions studied, it can be concluded that canonical structures such as I–III are only limited resonance contribu-



tors¹⁶ as the para carbon resonances when corrected for substituent effects show only extremely small or no differences.

Nucleophilic Nitrolysis (Nitratative Cleavage) of Diarylhalonium Salts. In order to study the nucleophilic nitrolysis of diarylhalonium ions as well as symmetrically substituted ions, we also prepared a series of methyl- and halogen-substituted unsymmetrical diarylhalonium tetraphenylborates.

All diarylhalonium tetraphenylborates were prepared by decomposition of the corresponding arenediazonium hexafluorophosphates in haloarenes in the presence of trifluoroacetic acid at 65–70 °C for 2 h, followed by the addition of sodium tetraphenylborate. The data are summarized in Table IV. Phenyl-2-fluorophenylchloronium tetraphenylborate was not obtained by the decomposition of 2-fluorophenyldiazonium hexafluorophosphate in chlorobenzene, but only by the related reaction of phenyldiazonium hexafluorophosphate and 2-chlorofluorobenzene. The structure of the new diarylhalonium salts was ascertained by elemental analysis and NMR spectroscopy.

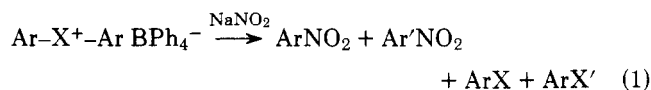
The reaction of unsymmetrically substituted diarylhalo-

Table IV. Preparation of Methyl- and Halogen-Substituted Unsymmetrical Diarylhalonium Tetraphenylborates from Aryldiazonium Hexafluorophosphates

Diazonium salt	Registry no.	Haloarene	Halonium ion	Registry no.	Mp (dec), ^a °C	Yield, %
<i>m</i> -Tolyl		<i>o</i> -Chlorotoluene	<i>o</i> -Tolyl- <i>m</i> -tolylchloronium	64146-99-2	178 (125)	6.5
<i>o</i> -Tolyl		<i>p</i> -Chlorotoluene	<i>p</i> -Tolyl- <i>p</i> -tolylchloronium	64147-01-9	140-141	9.0
2,4-Xylyl	64147-33-7	Chlorobenzene	Phenyl-2,4-xylylchloronium	64147-03-1	129-130	13.5 (17.0) ^b
		<i>p</i> -Chlorotoluene	<i>p</i> -Tolyl-2,4-xylylchloronium	64147-14-4	134-135	5.4
		<i>o</i> -Chlorotoluene	<i>o</i> -Tolyl-2,4-xylylchloronium	64147-16-6	150-152 (142)	4.0
2,3-Xylyl	64147-34-8	Chlorobenzene	Phenyl-2,3-xylylchloronium	64147-18-8	115-117 (106)	9.3
		<i>o</i> -Chlorotoluene	<i>o</i> -Tolyl-2,3-xylylchloronium	64147-20-2	126-127 (114)	5.4
Phenyl		<i>o</i> -Chlorofluorobenzene	Phenyl- <i>p</i> -fluorophenylchloronium	64147-22-4	144-146 (136)	2.5
		<i>m</i> -Chlorofluorobenzene	Phenyl- <i>m</i> -fluorophenylchloronium	64147-24-6	151-152 (132)	2.4
		<i>o</i> -Dichlorobenzene	Phenyl- <i>o</i> -chlorophenylchloronium	64147-26-8	152-153 (145)	7.3
<i>o</i> -Tolyl		Bromobenzene	Phenyl- <i>o</i> -tolylbromonium	64147-28-0	164-165 (144)	11.6
<i>p</i> -Tolyl		Bromobenzene	Phenyl- <i>p</i> -tolylbromonium	64147-29-1	141.2 (139) ^c	9.7
<i>o</i> -Tolyl		Iodobenzene	Phenyl- <i>o</i> -tolyliodonium	64147-31-5	153-154 (132)	5.7
<i>p</i> -Tolyl		Iodobenzene	Phenyl- <i>p</i> -tolyliodonium	64147-32-6	112-113 (105)	5.7

^a Temperatures at which crystals started to change are given in parentheses. ^b Yield was obtained for 2,4-xylyldiazonium trifluoroacetate. ^c Lit.⁸ mp 135 °C dec.

nium tetraphenylborates with nitrite ion gives, in a nucleophilic nitrolysis reaction, a mixture of the corresponding nitroarenes (eq 1). The nitroarene product composition reflects the effect of the substituents on the course of the nucleophilic nitrolysis.



To carry out the nucleophilic nitration, equimolecular amounts of the diarylhalonium salts and sodium nitrite were refluxed in a mixture of acetone-water (5:1 v/v) in the presence of benzonitrile as an internal standard for subsequent GC analysis of the reaction products. In the case of the phenyl-4-tolylidonium salt, 2-nitrotoluene was substituted for benzonitrile since the latter and 4-iodotoluene gave overlapping GC peaks under the experimental conditions.

On the basis of a ¹³C NMR spectroscopic study of diarylhalonium ions, the effect of the halonium center is mostly reflected in its inductive effect on the aryl rings. As expected from the greater electronegativity of chlorine and bromine relative to iodine, diarylchloronium and -bromonium ions were found to be more reactive than the corresponding diaryliodonium ions. In fact, when diphenylchloronium or diphenylbromonium salts were reacted with sodium nitrite under similar conditions, the reactions were completed within 2 h to give nitrobenzene in 75% yield, whereas 65% of the starting diphenyliodonium salt was recovered unreacted under the same conditions.

Nitration of 2,2', 3,3', and 4,4'-ditolylchloronium tetraphenylborate gave 2-, 3-, and 4-nitrotoluene, respectively. Not even trace amounts of other isomers were detected, showing that only ipso attack occurred. This rules out the possible formation of a benzene intermediate or attack at other ring positions, which would be the case if the diarylhalonium ions would show ambident character.

In the nucleophilic substitution reactions of 4-substituted diaryliodonium salts, nucleophiles generally attack the phenyl ring carrying electron-withdrawing groups.¹⁷ This trend is also observed in the nucleophilic nitration of phenyl-4-tolylchloronium hexafluorophosphate, where the obtained nitrobenzene to 4-nitrotoluene ratio is 3.0:1.0. Nitration of phenyl-3-tolylchloronium hexafluorophosphate gave a mixture of nitrobenzene and nitrotoluene in a ratio of 1.0:1.2, indicating the weak effect of 3-methyl relative to 4-methyl substitution in the course of the reaction. On the other hand, 2-methyl substitution of one of the aryl rings was shown to exert the opposite effect on the relative reactivity of the rings. 2-Nitrotoluene was formed 4.7 times faster than nitrobenzene in the nitration of phenyl-2-tolylchloronium hexafluorophosphate. Similar effects were reported in the related pyrolysis^{18a,b} and hydrolysis.

The charge density in the phenyl ring in the series of diphenylchloronium and phenyltolylchloronium hexafluorophosphates has been shown, based on the discussed ¹³C NMR studies, to be similar, i.e., independent of the nature of the second aryl group (phenyl, *o*-, *m*-, or *p*-tolyl). A relative scale of reactivities can be established for these groups toward nucleophilic nitration assuming that the reactivity of the unsubstituted phenyl ring is predominantly controlled by its charge density (affected mainly by the inductive effect of the halonium center) and hence remains relatively constant along the series of related halonium ions. In this manner, the relative reactivity of the 4-tolyl, phenyl, 3-tolyl, and 2-tolyl rings toward nitrite ion can be established as 1.0, 3.0, 3.6, and 14.1, respectively, on the basis of the nitrobenzene to nitrotoluene product ratio formed in the nitration of phenyltolylchloronium salts. Excellent agreement was obtained in the nucleophilic nitration of unsymmetrical ditolylchloronium salts

Table V. Ratio of Nitroarenes in the Reaction $\text{Ar-X}^+-\text{Ar}'\cdot\text{BPh}_4^- \xrightarrow{\text{NaNO}_2} \text{ArNO}_2 + \text{Ar}'\text{NO}_2 + \text{ArX} + \text{Ar}'\text{X}$

Halonium ion ($\text{Ar-X}^+-\text{Ar}'$)	Products		$\text{ArNO}_2/\text{Ar}'\text{NO}_2$ Ratio	
	ArNO_2	$\text{Ar}'\text{NO}_2$	Obsd	Calcd
2- $\text{CH}_3\text{C}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	2-Nitrotoluene	Nitrobenzene	4.7:1.0	
3- $\text{CH}_3\text{C}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	3-Nitrotoluene	Nitrobenzene	1.2:1.0	
4- $\text{CH}_3\text{C}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	4-Nitrotoluene	Nitrobenzene	1.0:3.0	
2- $\text{CH}_3\text{C}_6\text{H}_4-\text{Cl}^+-3'-\text{CH}_3\text{C}_6\text{H}_4$	2-Nitrotoluene	3-Nitrotoluene	3.9:1.0	3.9:1.0
2- $\text{CH}_3\text{C}_6\text{H}_4-\text{Cl}^+-4'-\text{CH}_3\text{C}_6\text{H}_4$	2-Nitrotoluene	4-Nitrotoluene	13.5:1.0	14.1:1.0
3- $\text{CH}_3\text{C}_6\text{H}_4-\text{Cl}^+-4'-\text{CH}_3\text{C}_6\text{H}_4$	3-Nitrotoluene	4-Nitrotoluene	3.4:1.0	3.6:1.0
2,4-(CH_3) ₂ $\text{C}_6\text{H}_3-\text{Cl}^+-\text{Ph}$	4-Nitro- <i>m</i> -xylene	Nitrobenzene	1.8:1.0	1.6:1.0
2,4-(CH_3) ₂ $\text{C}_6\text{H}_3-\text{Cl}^+-4'-\text{CH}_3\text{C}_6\text{H}_4$	4-Nitro- <i>m</i> -xylene	4-Nitrotoluene	3.7:1.0	4.7:1.0
2,4-(CH_3) ₂ $\text{C}_6\text{H}_3-\text{Cl}^+-2'-\text{CH}_3\text{C}_6\text{H}_4$	4-Nitro- <i>m</i> -xylene	2-Nitrotoluene	1.0:1.7	1.0:3.0
2,3-(CH_3) ₂ $\text{C}_6\text{H}_3-\text{Cl}^+-\text{Ph}$	3-Nitro- <i>o</i> -xylene	Nitrobenzene	11.0:1.0	5.6:1.0
2,3-(CH_3) ₂ $\text{C}_6\text{H}_3-\text{Cl}^+-2'-\text{CH}_3\text{C}_6\text{H}_4$	3-Nitro- <i>o</i> -xylene	2-Nitrotoluene	1.9:1.0	1.2:1.0
2- $\text{FC}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	2-Nitrofluorobenzene	Nitrobenzene	1.0:4.5	
3- $\text{FC}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	3-Nitrofluorobenzene	Nitrobenzene	1.3:1.0	
2- $\text{ClC}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	2-Nitrochlorobenzene	Nitrobenzene	1.8:1.0	
4- $\text{ClC}_6\text{H}_4-\text{Cl}^+-\text{Ph}$	4-Nitrochlorobenzene	Nitrobenzene	1.0:2.0	
2- $\text{CH}_3\text{C}_6\text{H}_4-\text{Br}^+-\text{Ph}$	2-Nitrotoluene	Nitrobenzene	7.6:1.0	
4- $\text{CH}_3\text{C}_6\text{H}_4-\text{Br}^+-\text{Ph}$	4-Nitrotoluene	Nitrobenzene	1.0:3.1	
2- $\text{CH}_3\text{C}_6\text{H}_4-\text{I}^+-\text{Ph}$	2-Nitrotoluene	Nitrobenzene	9.6:1.0	
4- $\text{CH}_3\text{C}_6\text{H}_4-\text{I}^+-\text{Ph}$	4-Nitrotoluene	Nitrobenzene	1.0:2.7	

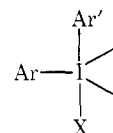
between the observed product distributions and those calculated from the relative reactivity values for the phenyl and tolyl rings, respectively (Table V). Less satisfactory correlation was, however, observed in the case of phenyl- and tolylxylylchloronium salts.

Nearly identical product distributions were obtained in the nitration of phenyl-4-tolylchloronium, -bromonium, and -iodonium salts. However, the *o*-methyl substituent effect increased in the sequence phenyl-2-tolylchloronium < -bromonium < -iodonium ions. The amount of 2-nitrotoluene obtained from the iodonium ion was approximately twice as much as that obtained from the chloronium ion. Nitration of phenyl-2,6-xylylchloronium, -bromonium, and -iodonium ions gave 2-nitro-*m*-xylene and the corresponding haloarene almost exclusively, indicating the reinforced ortho effect. The effect of the chloronium center upon the relative reactivity of the phenyl and the chlorophenyl rings in the nitration of phenyl-4-chlorophenyl- and phenyl-2-chlorophenylchloronium ions was shown to be smaller than that observed in the case of methyl substitution, although attack by the nitrite ion took place in the same direction. However, in the case of the phenyl-2-fluorophenylchloronium ion, a reversed ortho effect was observed; the 2-nitrofluorobenzene to nitrobenzene ratio was 1.0:4.5.

Substitution of tetraphenylborate for hexafluorophosphate as counterion did not affect the product distribution in the nitration of phenyl-2-tolyl- and phenyl-4-tolylchloronium salts. These results suggest that the counterion has no particular effect on the reactions.

In the studied reactions, nitroarenes were obtained in 70–75% yield, and only relatively small amounts of phenols (<8%) and biphenyls (<10%) were detected. The presence of water in the reaction media as well as the ambident nature of the nitrite ion can account for the formation of phenols. Since biphenyl was detected even from ditolylchloronium tetraphenylborate, but in substantially decreased yield (~2%) in the case of diphenylchloronium hexafluorophosphate, it must be mostly formed from the tetraphenylborate anion and not as a reaction byproduct from the diarylhalonium ion. In the nitration of phenyl-4-tolylchloronium and 3,3'-ditolylchloronium tetraphenylborate, a small amount of toluene and trace amounts of 4-tolylbenzene and 3,3'-dimethylbiphenyl, respectively, were detected by GC. These results indicate that radical side reactions take place only to a minor degree.

Yamada and Okawara^{18a} reported in the pyrolysis of diaryliodonium bromides that the predominant attack of the bromide ion was on the *o*-methyl-substituted aryl ring, proposing a methyl-substituted phenyl cation intermediate. Wiegand and co-workers^{18b} observed a similar ortho effect in the pyrolysis of a series of phenylaryliodonium chlorides, bromides, and iodides-131, suggesting the formation of a tricovalent iodine intermediate with subsequent S_N-like displacement leading to products. Since only the equatorial aryl ring is capable of reacting with the halide ion (X⁻) and the bulkier ortho-substituted aryl ring (Ar) should be expected



to preferentially occupy the equatorial position, the observed ortho effect^{18b} was satisfactorily explained for diaryliodonium halides.

Although this mechanism involving a tricovalent iodide intermediate could be applied in the case of nitration of the phenyl-2-tolylidonium salt, it should not be applicable to the nitration of diarylchloronium salts since the formation of the corresponding tricovalent chlorine intermediate represents a much more unlikely path because of the inherently lesser ability of chlorine relative to the iodine to form such tricovalent compounds.⁶ The bond between chloronium ions and their counterion in diarylchloronium salts must be considered to be mostly ionic. Furthermore, a mechanism involving a phenyl cation intermediate is less probable, at least for the nitration reaction under our experimental conditions, since in this case phenols would be expected to be also inevitably formed in aqueous acetone media, which was not the case.

The data reported herein for the nucleophilic nitration of diarylchloronium salts are best accommodated by a S_N2-like mechanism controlling the collapse of ionic diarylchloronium nitrites initially formed by displacement of the corresponding counterion (tetraphenylborate or hexafluorophosphate) to give nitro- and chlorobenzene derivatives. The nitrite ion attacks the most activated (by the negative inductive effect) ipso carbon position. *p*-Methyl substitution relative to the ipso carbon (C₁) decreases the latter's charge density, and hence it deactivates C₁ to undergo nucleophilic attack, in comparison to the ipso carbon (C₁') in the unsubstituted phenyl ring.

m-Methyl substitution hardly affects the reactivity of the ipso carbon (C_1'), which is in good agreement with expectations on the basis of the proposed S_N2 mechanism.²⁰ In the case of the *o*-methyl-substituted diarylchloronium ions, steric strain due to the ortho substituent (s) will be operative and weakens the carbon-chlorine bond, thus activating the ipso carbon (C_1) in the ortho-substituted aryl ring. Results show that the steric ortho effect is much more important than the deactivating effect due to the electron-donor character of the methyl group. Similarly to the case of unsymmetrical ditolylchloronium salts, good agreement between the observed and the calculated product distributions was obtained in the nitration of phenyl-, 4-xylyl-, 4'-tolyl-2,4-xylyl-, and especially phenyl-2,3-xylyl-chloronium salts, where additional steric factors are introduced in the latter case. Larger than expected amounts of 3-nitro-*o*-xylene were found; i.e., the 2,3-xylyl group was found to be more reactive than the 2-tolyl group in nucleophilic nitration of the corresponding chloronium salts.

The remarkable decrease of the ortho effect in phenyl-2-chlorophenyl- and phenyl-2-fluorophenylchloronium salts can be accounted for by the mesomeric effect of the halogen atom and the electrostatic repulsion between the nitrite ion and the halogen substituent.

Experimental Section

General. All melting points reported in Table I are uncorrected and were measured on a Fischer-Johns melting point apparatus.

Carbon-13 NMR spectra were obtained using a Varian Model XL 100 spectrometer equipped with a broad-band decoupler and a Fourier transform accessory. It was operated in the pulse Fourier transform mode, employing typically 3000–5000 (5) μ s pulses in order to obtain a satisfactory signal to noise ratio.

Materials. Aryldiazonium hexafluorophosphates were synthesized according to a procedure of Rutherford et al.²¹

Diphenylchloronium Tetraphenylborate. Preparation from Phenylidiazonium Hexafluorophosphate. A well-stirred heterogeneous mixture of phenylidiazonium hexafluorophosphate (2.5 g, 10 mmol), trifluoroacetic acid (3 mL), and chlorobenzene (10 mL) was heated at 65–70 °C for 2 h. during which time the evolution of nitrogen gas was completed. After addition of ethyl ether and petroleum ether (1:1, 20 mL), the reaction mixture was extracted with water (15 mL \times 3). The aqueous phase was neutralized by sodium hydrogen carbonate. Addition of sodium tetraphenylborate (~2 mmol) produced a white precipitate, which was collected and washed with water. The precipitate was dissolved in hot acetone, and the small amount of insoluble material was filtered off. The acetone was evaporated under reduced pressure, and the residual solid was redissolved in hot acetone. Addition of ethyl ether precipitated crystals of the salt (0.66 g, 13%); mp 160–160.5 °C (lit.⁷ 160–161 °C).

The other diarylhalonium tetraphenylborates listed in Table I were prepared from the corresponding aryldiazonium hexafluorophosphates (or tetrafluoroborates) and haloarenes in the same manner as described above.

Preparation from Aniline. To a mixture of aniline (930 mg, 10 mmol), sodium sulfate (1.42 g, 10 mmol), and chlorobenzene (10 mL) trifluoroacetic acid (4 mL) was added. The mixture was cooled in an ice bath, and sodium nitrite (690 mg, 11 mmol) was slowly added with stirring. The mixture was stirred for 1 h at 10 °C and then heated at 60 °C for 2 h. The same workup described above gave 0.339 g (6.5%) of the product.

Diarylhalonium Hexafluorophosphates. To a suspension of the corresponding diarylhalonium tetraphenylborate (0.4 mmol) in ethyl ether (4 mL) 40% hexafluorophosphoric acid (0.5 mL) was added with stirring at room temperature. The reaction was exothermic, and before complete dissolution of the starting material the corresponding diarylhalonium hexafluorophosphate precipitated. After 1.5 h, ethyl ether/*n*-pentane (1:7 v/v) was added, and the salt was filtered and washed with the ethyl ether/pentane mixture; yield 70–80%. ¹³C NMR spectra of these salts were recorded without further purification.

All diarylhalonium salts gave correct elemental analyses (Galbraith Laboratories Inc.).

Nitration of Diarylchloronium Salts. Diarylchloronium tetraphenylborate or hexafluorophosphate (0.1 mmol), sodium nitrite (10 mg), and benzonitrile (10 mg, as an internal standard for GC) in acetone (2.5 mL)–water (0.5 mL) were refluxed for 2 h. After the addition of ethyl ether–*n*-pentane (1:1 v/v), an aqueous layer was separated. The organic layer was washed with diluted aqueous sodium

chloride. The combined aqueous layer was extracted with ethyl ether–*n*-pentane, and the combined organic layer was dried over sodium sulfate. The solvents were distilled out at atmospheric pressure below 60 °C, and after the addition of a small amount of acetone the residue was analyzed by GC. When the phenol generated interfered with the integration of the peak of the nitro compound, the organic layer was washed with 5% aqueous sodium hydroxide.

Nitration of Diarylbromonium Salts. Diarylbromonium tetraphenylborate (0.1 mmol), sodium nitrite (10 mg), and benzonitrile (10 mg) in dioxane (2.5 mL)–water (0.5 mL) were refluxed for 1 day. The reaction mixture was treated similarly as described above and analyzed by GC.

Nitration of Diaryliodonium Salts. Diaryliodonium tetraphenylborate (0.1 mmol), sodium nitrite (10 mg), and benzonitrile (10 mg) in dioxane (4 mL)–water (1 mL) were refluxed for 2 days. The reaction mixture was worked up as described above and analyzed by GC.

Gas chromatographic analyses of the reaction products were performed on a Perkin-Elmer Model 226 gas chromatograph equipped with a hydrogen flame ionization detector and open tubular capillary columns. Peak areas were obtained with a Columbia Scientific Industries Model CS1-208E printing integrator. A 150 ft \times 0.01 in capillary column coated with butanediol succinate was used for the analyses of nitrobiphenyl and -phenol derivatives at a standard temperature of 160 °C and a helium flow rate of 20 psi. Biphenyl and phenol derivatives were analyzed similarly except for using a 100-ft long column at 140 °C and a helium flow rate of 20 psi. Toluene was detected by using a 150 ft \times 0.01 in capillary column coated with *m*-bis(*m*-phenoxyphenoxy)benzene and Apiezon L.

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Registry No.—Sodium tetraphenylborate, 143-66-8; aniline, 62-53-3; hexafluorophosphoric acid, 16940-81-1; sodium nitrite, 7632-00-0.

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