The Ortho Effect in the Pyrolysis of Iodonium Halides. A Case for a Sterically Controlled Nucleophilic Aromatic (SN) Substitution Reaction[1]

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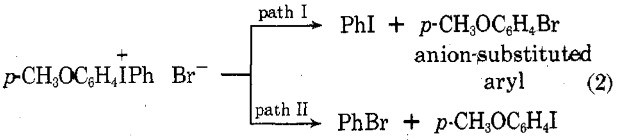
A series of arylphenyliodonium chlorides, bromides, and iodides-131 were pyrolyzed and the product compositions determined by GC. In most cases the quantities of the aryl halides obtained were those expected if a nucleophilic aromatic substitution (SN) mechanism were operative. However, in those cases in which an ortho methyl group was present on one of the aryl rings, the anion preferentially attacked that ring, giving product compositions opposite of those expected from nucleophilic aromatic substitution. The presence of a second ortho methyl group increased this effect. Also, pyrolysis of phenyl-2,5-dimethylphenyliodonium halides gave more 2-halo-*p*-xylene than phenyl-2,4-dimethylphenyliodonium halides gave 2-halo-*m*-xylene. These data are best accommodated by a nucleophilic aromatic substitution mechanism in which product formation is stericallycontrolled when ortho methyl groups are present.

Diaryliodonium halides decompose upon heating to give mixtures of aryl iodides and aryl halides derived from the halide ion of the iodonium salt (eq 1).[3-10]

$$\mathrm{Ar\overset{+}{I}Ar'}\ \mathrm{X^-} \xrightarrow{\text{heat}} \mathrm{ArI} + \mathrm{Ar'X} + \mathrm{ArX} + \mathrm{Ar'I} \qquad (1)$$

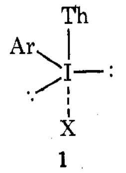
For example, phenyl-*p*-anisyliodonium bromide decomposes by two paths, one leading to *p*-bromoanisole and iodobenzene (path I) and the other to *p*-iodoanisole and bromobenzene (path II) (eq 2).[9]



$$p\text{-}\mathrm{CH_3OC_6H_4\overset{+}{I}Ph\ Br^-} \begin{cases} \xrightarrow{\text{path I}} \mathrm{PhI} + \underset{\text{anion-substituted aryl}}{p\text{-}\mathrm{CH_3OC_6H_4Br}} \\ \xrightarrow{\text{path II}} \mathrm{PhBr} + p\text{-}\mathrm{CH_3OC_6H_4I} \end{cases} \qquad (2)$$

(For the purpose of clarity, in this paper path I will always indicate the mechanism in which the halide ion attacks the *substituted* aryl ring, leading to anion-substituted aryl and iodobenzene.)

Recently, a study of the mechanism of this pyrolysis has been carried out by Yamada and co-workers.[5-7] Substituted phenyl-*p*-tolyliodonium bromides were pyrolyzed and the products were accounted for in terms of a bimolecular nucleophilic aromatic substitution mechanism.[7] Also studied were a number of aryl-2-thienyliodonium chlorides and bromides, and the product compositions suggested that the reaction proceeds by interaction of the thienyl group and the halide ion, the intermediate having a trigonal bipyramidal structure (1).[6] However, when the diaryliodonium bromides were substituted with an ortho methyl group, the bromide ion preferentially attacked the aryl group least able to bear the developing negative charge, i.e., the aryl ring containing one or more methyl groups. To account for this effect of the ortho methyl substituents, these workers proposed a mechanism involving a methyl-substituted phenyl cation.[5]



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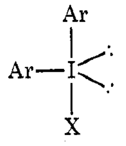
Th = thienyl

We have observed this ortho effect before in the pyrolysis of sulfonium halides. For example, pyrolysis of phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium bromide at 250 °C afforded bromobenzene, *p*-bromotoluene, and 2-bromo-*p*-xylene in the ratio of 1.9:1.0:11.8, respectively, along with the corresponding diaryl sulfides. As the halide ion was varied from chloride to bromide to iodide the yield of 2-halo-*p*-xylene increased markedly. These results are best accommodated by a mechanism involving nucleophilic attack of halide ion upon the sulfur atom in the sulfonium cation to form a tetracovalent sulfur intermediate, with subsequent SN-like collapse to form products. The increase in yield of the 2-halo-*p*-xylene formed as the size of the halide ion is increased is attributed to increased crowding in the tetracovalent intermediate, the major decomposition pathway of which being that providing maximum relief of steric strain.[11]

The similarities of product compositions obtained from the pyrolyses of the sulfonium and iodonium salts suggested to us that the iodonium halides might be behaving in an analogous manner; namely, nucleophilic attack upon the positive iodine atom in the iodonium cation to form a tricovalent iodine intermediate (2), with subsequent SN-like collapse to form products. Accordingly, we have pyrolyzed a series of arylphenyliodonium chlorides, bromides, and iodides-131 in order to test this hypothesis.



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Results

Synthesis of Arylphnyliodonium Halides. Substituted arylphenyliodonium halides were prepared in good yield and purity from the appropriate aryliodo diacetate or iodosobenzene and aromatic compound in a solution of acetic anhydride and concentrated sulfuric acid (Table I). When mesitylene and *p*-xylene were employed the position of substitution was unambiguous. Use of *m*-xylene, anisole, and toluene opened up possibilities of isomer formation; in practice, however, exclusive para substitution occurred with toluene and anisole, while *m*-xylene yielded exclusively the phenyl-2,4-dimethylphenyliodonium salt. The iodonium iodides prepared by metathesis were contaminated with iodonium bromide, but the desired degree of purity could be achieved by recrystallization. These observations are in accord with those of Beringer.[4]

Product Compositions. Product compositions for the pyrolysis of the series of iodonium halides are listed in Table II. In iodonium halides which contained a methyl or methoxyl

Table I. Preparation of Diaryliodonium Halides

Starting compd	Registry no.	ArH	Registry no.	Iodonium cation	Anion	Registry no.	Mp, °C	Yield, %
Iodosobenzene	536-80-1	Anisole[a]	100-66-3	Phenyl-*p*-anisyl-	Br^-		176–178[b]	80
Phenyl-*p*-anisyliodonium bromide	2665-61-4			Phenyl-*p*-anisyl-[f]	I^-		173–174[c]	65
Iodosobenzene diacetate	3240-34-4	Toluene	108-88-3	Phenyl-*p*-tolyl-	Br^-		169–170[d]	57
Iodosobenzene diacetate	3240-34-4	Toluene	108-88-3	Phenyl-*p*-tolyl-	Cl^-	56530-34-8	197–199	53
Phenyl-*p*-tolyliodonium bromide	2665-60-3			Phenyl-*p*-tolyl-	I^-	56391-18-5	160–162	34
Iodo-*o*-tolyl diacetate	31599-59-4	Benzene	71-43-2	Phenyl-*o*-tolyl-	Cl^-	59907-04-9	177–178	30
Iodo-*o*-tolyl diacetate	31599-59-4	Benzene	71-43-2	Phenyl-*o*-tolyl-	Br^-	38821-84-0	203–205	37
Phenyl-*o*-tolyliodonium bromide	38821-84-0			Phenyl-*o*-tolyl-	I^-	59907-07-2	155–156	69
Iodosobenzene diacetate		Mesitylene	108-67-8	Mesitylphenyl-	Cl^-	37567-18-3	162–164	43
Iodosobenzene diacetate		Mesitylene	108-67-8	Mesitylphenyl-[g]	Br^-		155–157[e]	48
Iodosobenzene diacetate		Mesitylene	108-67-8	Mesitylphenyl-	I^-	59907-06-1	137–140	26
Iodosobenzene diacetate		*m*-Xylene	108-38-3	Phenyl-2,4-dimethylphenyl-	Cl^-	59907-07-2	175–177	46
Iodosobenzene diacetate		*m*-Xylene	108-38-3	Phenyl-2,4-dimethylphenyl	Br^-	2014-20-2	169–171	64
Iodosobenzene diacetate		*m*-Xylene	108-38-3	Phenyl-2,4-dimethylphenyl-	I^-	59907-08-3	153–154	66
Iodosobenzene diacetate		*p*-Xylene	106-42-3	Phenyl-2,5-dimethylphenyl-	Cl^-	59907-09-4	171–172	79
Iodosobenzene diacetate		*p*-Xylene	106-42-3	Phenyl-2,5-dimethylphenyl-	Br^-	59907-10-7	174–175	73
Iodosobenzene diacetate		*p*-Xylene	106-42-3	Phenyl-2,5-dimethylphenyl	I^-	59907-11-8	155–157	76

[a] Basis for calculation of yield; all other yields are based on amount of starting compound. [b] Lit. mp 185,[3] 180,[9] 191–192 °C.[26] [c] Lit. mp 162.5–163.5,[3] 168–169 °C.[26] [d] Lit. mp 176–177,[3] 183–184 °C.[7] [e] Lit. mp 170–172 °C.[4] [f] Registry number, 53904-18-0. [g] Registry number, 38821-85-1.

Table II. Pyrolysis of Diaryliodonium Halides at 235 ± 3 °C

Iodonium halide		Products	% pathways for anions[a]		
			Cl^-	Br^-	$^{131}I^-$
$4\text{-}CH_3C_6H_4\overset{+}{I}Ph\ X^-$	path I	$PhI + 4\text{-}CH_3C_6H_4X$	37 (1.8)[b]	34 (1.4) (38.2)[d]	39
	path II	$PhX + 4\text{-}CH_3C_6H_4I$	63[c]	66 (61.8)[d]	61
$2\text{-}CH_3C_6H_4\overset{+}{I}Ph\ X^-$	path I	$PhI + 2\text{-}CH_3C_6H_4X$	84 (1.9)	87 (1.5) (86.7)[d]	65
	path II	$PhX + 2\text{-}CH_3C_6H_4I$	16	13 (13.3)[d]	35
$2,4\text{-}(CH_3)_2C_6H_3\overset{+}{I}Ph\ X^-$	path I	$PhI + 2,4\text{-}(CH_3)_2C_6H_3X$	72 (2.4)	73 (3.3)	57
	path II	$PhX + 2,4\text{-}(CH_3)_2C_6H_3I$	28	27	43
$2,5\text{-}(CH_3)_2C_6H_3\overset{+}{I}Ph\ X^-$	path I	$PhI + 2,5\text{-}(CH_3)_2C_6H_3X$	86 (1.6)	86 (0.9)	68
	path II	$PhX + 2,5\text{-}(CH_3)_2C_6H_3I$	14	14	32
$2,4,6\text{-}(CH_3)_3C_6H_2\overset{+}{I}Ph\ X^-$	path I	$PhI + 2,4,6\text{-}(CH_3)_3C_6H_2X$	95 (1.5)	96 (0.3) (96.5)[d]	84
	path II	$PhX + 2,4,6\text{-}(CH_3)_3C_6H_2I$	5	4 (3.5)[d]	16
$4\text{-}CH_3OC_6H_4\overset{+}{I}Ph\ X^-$	path I	$PhI + 4\text{-}CH_3OC_6H_4X$		44 (1.8)[e]	19
	path II	$PhX + 4\text{-}CH_3OC_6H_4I$		56	81
$2,3,5,6\text{-}(CH_3)_4C_6H\overset{+}{I}Ph\ X^-$	path I	$PhI + 2,3,5,6\text{-}(CH_3)_4C_6HX$		97.7[d]	
	path II	$PhX + 2,3,5,6\text{-}(CH_3)_4C_6HI$		2.3	

[a] Average of six runs for chlorides and bromides, one run for iodide-131. [b] Standard deviation. [c] Path II by difference. [d] Reference 5. [e] Average of 12 runs.

group in the para position and no ortho methyl group, the amount of halobenzene produced from the halide ion and of substituted iodoaryl compound (path II) was greater than the amount of iodobenzene and anion-substituted aryl compound (path I). On the other hand, introduction of an ortho methyl group reversed the major direction of decomposition from path II to path I, with the anion-substituted aryl and iodobenzene predominating. As the number of ortho methyl groups was increased to two, so did the yields of products arising from path I.

While the amount of anion-substituted aryl compound (path I) was essentially the same for both chloride and bromide ions for all of the iodonium cations, the amount of products produced by path I decreased somewhat when the anion was iodide-131, except for the phenyl-*p*-tolyliodonium cation. A considerably more marked decrease in products from path I was observed in going from phenyl-*p*-anisyliodonium bromide to its iodide-131, 44% to 19%, respectively. Sandin[9] has reported a value of 12% for the bromide salt; however, we have rechecked our value, for a total of 12 runs, and believe it to be correct.

Discussion

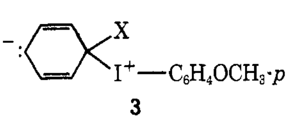
The product compositions clearly preclude a mechanism involving free radicals. First, small quantities of biaryls would be expected to be formed from such a process, and none were found in any of the pyrolysates. Further, a free-radical mechanism will not show a significant dependence upon substituents on the aryl rings,[12,13] and our results and those reported in the literature[5,7] show that there is indeed a substituent effect. For example, even phenyl-*p*-tolyliodonium bromide gave 34% iodobenzene and *p*-bromotoluene (path I), while *p*-tolyl-*p*-nitrophenyliodonium bromide[7] gave only a 4% yield of *p*-nitroiodobenzene and *p*-bromotoluene (path I).

Another mechanistic pathway might be the initial decomposition of the iodonium cation into an areneonium ion and an aryl halide (eq 3).

$$\mathrm{Ar\overset{+}{I}Ar'} \longrightarrow \mathrm{Ar^+} + \mathrm{Ar'I} \xrightarrow{X^-} \mathrm{ArX} \qquad (3)$$

In this case the major products formed would be expected to follow the order of stability of the incipient areneonium ions formed, namely, mesitylonium the most followed by xyleneonium, tolueneonium, and benzeneonium in that order. For instance, the pyrolysis of phenyl-*p*-tolyliodonium halides should yield as major products iodobenzene and *p*-halotoluenes. Instead, these products are formed in only 14–32% yields, depending upon the halide ion. Also, phenyl-*p*-anisyliodonium halides should give predominantly iodobenzene and *p*-haloanisoles, but these actually are formed in lesser amounts.

With the exception of the amounts of products obtained from the pyrolysis of ortho methyl substituted iodonium salts, the data are consistent with a nucleophilic aromatic substitution (SN) mechanism as proposed by Yamada.[7] In all cases, the halide ion preferentially attacks the aryl ring best able to accommodate a developing negative charge. For example, if halide ion were to attack the phenyl-*p*-anisyliodonium cation in this manner, formation of *p*-iodoanisole and bromobenzene (path II) would be expected to predominate over that of *p*-bromoanisole and iodobenzene (path I), since the phenyl group would be able to accommodate negative charge development better than would the *p*-anisyl group. This is clear from the resonance structures 3 and 4. The methoxyl group, being electron donating in nature, would oppose negative charge development in 4.



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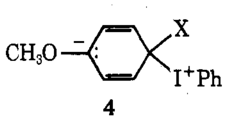

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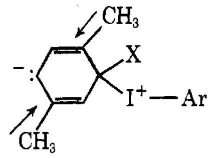
The anomalous ortho methyl effect has previously been accounted for on the basis of formation of an aryl cation.[5] However, the product compositions from pyrolysis of the phenyl-2,4-dimethyl- and phenyl-2,5-dimethylphenyliodonium halides do not support this conclusion. With all halide ions, the 2,4-dimethylphenyl group gave *less* anion-substituted aryl compound (path I) than did the 2,5-dimethylphenyl group.

These data are consistent with an SN-type mechanism, since under these circumstances the 2,5-dimethylphenyl group would accommodate the developing negative charge better than the 2,4-dimethylphenyl group as shown by resonance structures 5 and 6. In 5 the electron-donating effect of the 3-methyl group is one carbon atom removed from developing negative charge at the para position; hence this methyl group will be less destabilizing in 5 than will the 4-methyl group in 6.



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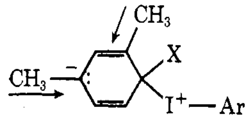

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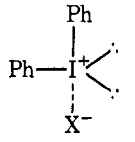
The structure of diphenyliodonium halides is thought to be trigonal bipyramidal (7), with one phenyl ring and the two lone electron pairs occupying the equatorial positions and the other phenyl ring and halide ion at the apical positions.[14] Such a structure has also been reported for iodobenzene dichloride (8)[15] and aryl-2-thienyliodonium halides (1).[6] On the basis of these structures, substituted diaryliodonium halides should have a similar structure. Since the equatorial positions are roomier than the axial positions, it is reasonable that a bulkier group would preferentially occupy one of these, rather than a more crowded axial position. Introduction of one or more ortho methyl groups would considerably increase the "bulk" of an aryl group, increasing the tendency for it to occupy an equatorial position (9). This effect would increase with the number of ortho methyl groups present. In this configuration, only the group which is equatorial is capable of reacting with the halide ion, the axial group being too distant.[6] The steric crowding of the ortho methyl group(s), then, must be of sufficient magnitude to force the ortho-substituted aryl group into a reactive equatorial position, even though electronic factors governing an SN reaction would dictate that the ring bearing the least number of electron-donating groups be attacked.



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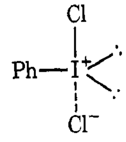

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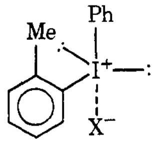

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That this ortho effect is primarily steric is shown by comparison of the product percentages obtained from pyrolysis of phenyl-*o*-tolyl- and phenyl-2,5-dimethylphenyliodonium halides, which both have one ortho methyl group and about the same electronic requirements. These decompose by path

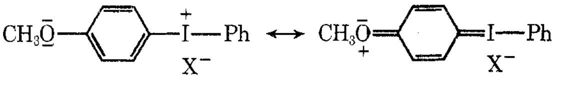
I, respectively; chlorides, 84% and 86%; bromides, 87% and 86%; and iodides, 65% and 68%. When steric requirements are the same and electronic requirements are different, as in the case of the phenyl-2,4-dimethylphenyl- and phenyl-2,5-dimethylphenyliodonium halides, mentioned previously, electronic factors become important.

Aryl-2-thienyliodonium halides decompose upon heating to give as major products an aryl halide derived from the halide ion and 2- iodothiophene.[6] Although this effect has been accounted for on the basis of interaction between the halide ion and the thienyl group, it can also be rationalized on the basis of steric effects. An aryl group, being larger than the 2-thienyl group, would be expected to occupy the roomier, and reactive, equatorial position as in I.

The effect of different halide ions upon product quantities in the pyrolysis of iodonium halides is markedly different from that for pyrolysis of sulfonium halides. In the case of the latter, the amount of 2-halo-*p*-xylene produced from phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium halides increased as the size of the halide ion increased. By contrast, in all series of iodonium halides bearing one or two ortho methyl groups, changing from chloride to bromide ion produced little difference in product quantities, while substitution of iodide ion gave a noticeable *decrease* in the amounts of anion-substituted aryl compound (path I). These observations indicate that, although halide ion is believed to attack the positive sulfur atom to form a tetracovalent intermediate in the pyrolysis of triarylsulfonium salts, formation of an analogous tricovalent iodine intermediate probably does not occur. The decrease in products formed by path I when iodide ion is used can be accounted for nicely by an SN mechanism, since attack of a large iodide ion at a site on the ring adjacent to a methyl group would be expected to be hindered.

This difference in mechanism between the two onium compounds is also consistent with the difference in polarity between the S–X and I–X bonds. In the series of diphenylioonium halides, the I–Cl bond is the most covalent and the I–I bond the most ionic.[16] Although this order is not known with certainty for the S–X bond in triarylsulfonium salts, the chlorides and bromides are quite ionic. The iodides, however, are much less so, as evidenced by their poor solubility in water and their ir and uv spectra.[17] In chloroform, triphenylsulfonium iodide forms a charge-transfer complex even at low concentrations. The chlorides and bromides do not.[18] It is reasonable, then, that the tendency to form a tetracovalent intermediate in the pyrolysis of sulfonium halides should be greatest with iodide ion since the S–I bond is already partly formed. Conversely, the tendency to form a tricovalent iodine intermediate should be least with iodide ion, since the covalent character of the I–I bond is initially low.

The marked decrease in the products obtained from path I in the pyrolysis of phenyl-*p*-anisyliodonium bromides and iodides-131 (44 and 19%, respectively) can also be accounted for on the basis of differences in polarity of the I–Br and I–I bonds. Resonance interaction of the nonbonded electrons on the *p*-methoxyl group with the positive iodine atom (**10**) has been shown to be important.[19] This interaction should increase as the positive character of the iodine atom is intensified, giving more double bond character to the iodine–anisyl group bond and thus making it stronger.[6] Thus, the greater polarity of the I–I bond would result in a stronger iodine–anisyl group bond and in a lesser tendency for successful attack of iodide ion there.



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Experimental Section

General. All melting points are uncorrected and were taken using a Mel-Temp apparatus. Iodonium halides decompose upon heating and their apparent melting points depend strongly upon heating rate. The method reported by Beringer[3,4] was used.

Infrared spectra were obtained using a Beckman IR-20A spectrophotometer and an end window G-M counter was used for the iodine-131 determinations. Peracetic acid (40%) was obtained from FMC Corp., Newark, Calif.

Gas chromatographic analyses were performed on an F & M Model 700 gas chromatograph (thermal conductivity detectors). A 6 ft × 0.125 in. stainless steel 10% Carbowax 20M column was used in separation of pyrolysis products except for the pyrolysates of mesitylphenyliodonium chloride and phenyl-2,4-dimethylphenyliodonium bromide and chloride. In these cases, the liquid phase was W98 silicone rubber. Preparative GC separation of the pyrolysis products of the iodonium iodides-131 was accomplished using a 6 ft × 0.25 in. stainless steel 20% Carbowax 20M column. In all cases the support was Chromosorb W.

Iodosobenzene. By treatment with chlorine in cold, dry chloroform iodobenzene was converted to iodobenzene dichloride,[20] which was hydrolyzed with aqueous sodium hydroxide to iodosobenzene.[21]

Iodobenzene Diacetate. Iodobenzene diacetate was prepared by treating iodobenzene with 40% peractic acid and acetic acid.[22]

Iodo-*o*-tolyl Diacetate. This compound was prepared by a procedure similar to that given for iodo-*m*-chlorophenyl diacetate.[23] To 22 g (0.10 mol) of *o*-iodotoluene chilled in an ice bath was added dropwise with stirring 32 ml (0.25 mol) of 40% peracetic acid. Stirring was continued for an additional 2 h, whereupon white crystals formed. The mixture was chilled for 1 h (ice bath), filtered, washed with cold water, and allowed to dry, giving 24 g (70%) of iodo-*o*-tolyl diacetate, mp 143–147 °C (lit.[5] 145–148 °C).

Phenyl-*p*-anisyliodonium Bromide. The method of Beringer[3] was used for the preparation of this compound. An 80% yield of phenyl-*p*-anisyliodonium bromide, mp 176–178 °C (lit.[3] 185 °C), was obtained.

Phenyl-*p*-anisyliodonium Iodide. Addition of excess KI to 6.0 g (15 mmol) of phenyl-*p*-anisyliodonium bromide dissolved in 1.5 l. of ethanol precipitated 4.8 g (11 mmol, 65%) of phenyl-*p*-anisyliodonium iodide, mp 173–174 °C (lit. 162.5–163.5,[3] 175,[4] 204–208,[24] 168–169 °C[24]).

Phenyl-*p*-anisyliodonium Chloride. Attempts to prepare this salt by treatment of phenyl-*p*-anisyliodonium iodide in chloroform with chlorine[25] or by use of iodobenzene diacetate resulted in oils or solids of insufficient purity to be used.

Phenyl-*p*-tolyliodonium Bromide. To a well-stirred suspension of 30.7 g (95.4 mmol) of iodobenzene diacetate and 15.3 g (165 mmol) of toluene in 1000 ml of acetic anhydride kept below 10 °C was added dropwise 50 ml of concentrated H_2SO_4. Stirring was continued for 1 h and the mixture allowed to stand overnight at room temperature. The reaction mixture was then added dropwise to 400 ml of ice water contained in an ice bath and the resulting aqueous solution was extracted twice with 200-ml portions of ether. Treatment of the aqueous phase with 190 g of NaBr produced white crystals when the mixture was allowed to stand overnight. These crystals were collected by filtration and recrystallized from ethanol to yield 20.4 g (57%) of pure phenyl-*p*-tolyliodonium bromide, mp 169–172 °C (lit. 176–177,[3] 183–184 °C[7]).

Phenyl-*o*-tolyliodonium Bromide. To a well-stirred cold mixture of 41.4 g (123 mmol) of iodo-*o*-tolyl diacetate and 50 ml (360 mmol) of benzene in 500 ml of acetic anhydride was added dropwise 50 ml of concentrated sulfuric acid. Stirring was continued for 1 h and the mixture allowed to stand overnight at room temperature, whereupon it was added dropwise to 500 ml of ice water on an ice bath. The resulting aqueous solution was extracted twice with 250-ml portions of ether and treated with 130 g of NaBr in 400 ml of water. Upon standing, white crystals formed which were collected by filtration, washed with water, and dried to give 17.7 g (37%) of phenyl-*o*-tolyliodonium bromide, mp 203–205 °C (lit. 205–210,[4] 167 °C[5]).

Other Arylphenyliodonium Bromides. The other arylphenyliodonium bromides listed in Table I were prepared in the same manner as described for phenyl-*p*-tolyliodonium bromide.

Phenyl-*p*-tolyliodonium Chloride. To a well-stirred, cold solution of 9.47 g (29.4 mmol) of iodobenzene diacetate and 10.0 g (109 mmol) of toluene in 100 ml of acetic anhydride was added dropwise 10 ml of concentrated H_2SO_4. Stirring was continued for 1 h below 10 °C, and the mixture was allowed to stand overnight at room temperature, after which it was added dropwise to 200 ml of ice water contained in an ice bath. A pale yellow solution resulted which was extracted twice with 100-ml portions of ether. The aqueous layer was treated with 10 g of NaCl dissolved in 100 ml of water and the resulting white crystals were collected by filtration and washed with water and acetone to give 5.12 g (53%) of pure phenyl-*p*-tolyliodonium chloride, mp 197–199 °C.

Phenyl-*o*-tolyliodonium Chloride. To a well-stirred, cold suspension of 9.63 g (28.6 mmol) of iodo-*o*-tolyl diacetate and 10.0 ml (113 mmol) of benzene in 100 ml of acetic anhydride was added dropwise 10 ml of concentrated H_2SO_4. Stirring was continued for 1 h and the mixture was allowed to stand overnight at room temperature. The reaction mixture was then added dropwise to 200 ml of ice water contained in an ice bath and the resulting solution was extracted twice with 100-ml portions of ether. The aqueous phase was treated with 10 g of NaCl dissolved in 50 ml of water, and the white precipitate which formed was filtered, washed, and dried to give 2.89 g (30%) of phenyl-*o*-tolyliodonium chloride, mp 177–178 °C.

Other Arylphenyliodonium Chlorides. The other arylphenyliodonium chlorides listed in Table I were prepared in the same manner as described for phenyl-*p*-tolyliodonium chloride.

Phenyl-*p*-tolyliodonium Iodide. A saturated solution of 10.2 g (27.2 mmol) of phenyl-*p*-tolyliodonium bromide in ethanol was treated with excess KI to give a precipitate of 3.90 g (34%) of phenyl-*p*-tolyliodonium iodide.

Other Arylphenyliodonium Iodides. The other arylphenyliodonium iodides listed in Table I were prepared by metathesis of the appropriate bromide salt in the same manner as for phenyl-*p*-tolyliodonium iodide.

Preparation of Labeled Iodonium Iodides. A ~20% aqueous KI solution was spiked with iodide-131. This solution was used to prepare the labeled iodonium iodides by metathesis of the appropriate iodonium bromides in ethanol.

Proof of Structure. Infrared spectra were in accord with the structure of the aromatic systems of the respective iodonium halides. In a series of halides for a given salt, the spectra were similar.

Pyrolysis products were identified using GC retention times. All of the iodonium salts, when pyrolyzed, gave the products expected from their thermal decomposition, and in no case was any significant amount of unexpected product found.

Product Compositions, Chlorides and Bromides. All of the iodonium chlorides and bromides listed in Table I were pyrolyzed for 5 min at 235 ± 3 °C in 6-mm Pyrex tubes about 30 cm long sealed at one end. Only about 2 cm of the sealed end of the tube was immersed in the oil bath, the remainder of the tube acting as an air condenser. Six runs were made for each individual salt, except in the case of phenyl-*p*-anisyliodonium bromide, where 12 runs were made.

All of the gas chromatograms obtained had sufficient resolution and peak shape to permit calculation of the amounts of aryl halides contained in the pyrolysates. Areas of the peaks were obtained by multiplying the peak height by the peak width at half height, and were corrected for differences in detector sensitivity. The results of these analyses are given in Table II.

Pyrolysis of Iodonium Iodides Labeled with Iodide-131. The pyrolysis products were collected by preparative GC, weighed (approximately 0.1 g), and counted in an end window G-M counter. Because of limited amounts of materials only one sample of each labeled salt was used. The data, presented in Table II, are probably good to ±2%.

Registry No.—Iodobenzene, 591-50-4; *o*-iodotoluene, 615-37-2; peracetic acid, 79-21-0; acetic acid, 64-19-7; acetic anhydride, 108-24-7.

References and Notes

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Kinetics and Mechanism of Benzylation of Anilines

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Second-order rate constants for the reactions of benzyl halides (Cl, Br, I) and some para-substituted benzyl chlorides (OCH_3, CH_3, Cl, NO_2) with substituted anilines (*p*-OCH_3, *p*-CH_3, H, *p*-Cl, *m*-Cl) were measured in ethanol solution. The reactivity order found for benzyl halides (I > Br > Cl) is in accord with the leaving group polarizability. The reaction rate is increased by electron-donating substituents and decreased by electron-withdrawing ones, both in the nucleophile and in the substrate. Hammett plots are linear on varying the substituents in the aniline, but show remarkable curvature on varying those in the benzyl chloride. The reaction can be adequately described as an SN2 bimolecular process. The reaction rate depends on the electronic availability on the nitrogen atom (bond making) and on the mesomeric interaction between the substrate substituent and the reaction center, which favors the halogen displacement (bond breaking). Electron-donating (electron-withdrawing) groups make the transition state looser (tighter). The C–halogen bond breaking is more advanced with respect to the C–N bond formation.

Solvolytic and nucleophilic reactions of benzyl halides can proceed through an unimolecular, bimolecular, or mixed substitution mechanism, depending on the solvent polarity and on the substrate and nucleophile structures.[1] Benzylation of tertiary amines (Menschutkin reaction) was widely studied and it has long been regarded as one of the best examples of