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Steric Effect in the Nucleophilic Attack of Bromide Anion on Diaryl- and Aryl-2-thienyliodonium Ions

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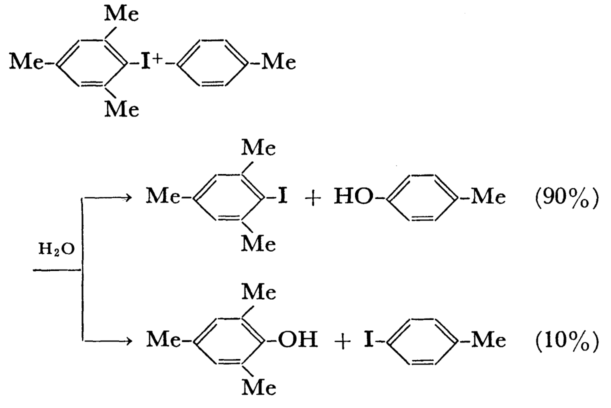
Duryl-, mesityl-, and *o*-tolyl-phenyl- and 2-thienyliodonium bromides have been synthesized. When these substances were allowed to decompose in molten (235°C) and solution (100°C) states, the nucleophile (bromide anion) preferentially attacked the substituted phenyl ring. Steric and electronic effects of phenomena have been discussed.

The nucleophilic substitution reaction on the aryl ring of diaryliodonium salts is usually influenced by the inductive and resonance effects of the substituent group.[1] Generally, the nucleophile preferentially attacks the phenyl ring containing the electron-withdrawing group. The site of the nucleophilic attack, however, is influenced by the steric hindrance of the substituent group.

Le Count and Reid reported on the steric effect by the *ortho*-methyl group in the reaction of diaryliodonium salts.[2] Hydrolysis of *p*-tolylmesityliodonium bisulfate which contains two methyl groups *ortho* to the iodine atom, gives 90% of iodomesitylene and 10% iodotoluene.



We showed that the nucleophile (bromide and chloride ions) attacks the aryl ring rather than the thienyl ring in the reaction of aryl-2-thienyliodonium halides.[3] The reaction seems to be an aromatic bimolecular substitution reaction and to proceed *via* the π-p orbital interaction of the aryl ring and halide ion in the trigonal-bipyramidal structure of iodonium salt. However, if the methyl group is introduced into the *ortho*-position on the phenyl ring of phenyl-2-thienyliodonium salt, it can be expected that the nucleophile attacks the thienyl ring predominantly. The same situation can be expected in the case of diaryliodonium salt. The present paper describes the steric effect in the reaction of substituted diphenyl- and substituted phenyl-2-thienyliodonium bromides containing the *ortho*-methyl substituent on the phenyl ring.

Results and Discussion

Substituted phenyl-2-thienyl- (I) and substituted diphenyl-iodonium bromides (II) were synthesized from substituted phenyliodoso acetate and thiophene or benzene in a mixture of acetic anhydride and concentrated sulfuric acid, respectively. The products are summarized in Table 1.

The thermal decomposition of the iodonium salts I and II was carried out in the molten state (23±55°C) for 5 min and the reaction products aryl halides and 2-thienyl halides were confirmed by gas chromatography in comparison with their authentic samples. The reaction of I and II proceeds along the following paths, the bromide ion competitively attacking the aryl ring or the thienyl ring (or phenyl ring.) The results are given in Table 2. The results in the solution state (100°C) of the iodonium bromides in N,N-dimethylformamide (DMF) and DMF-dioxane

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[1] F. M. Beringef, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2708 (1953).

[2] D. J. Le Count and J. A. W. Reid, *J. Chem. Soc.*, *C*, **1967**, 1298.

[3] Y. Yamada and M. Okawara, This Bulletin, in press.

Table 1. Preparation of I and II

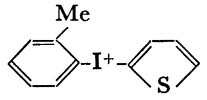
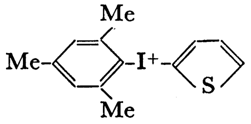
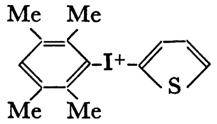
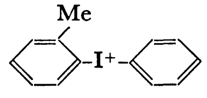
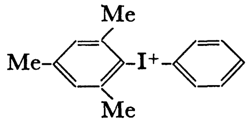
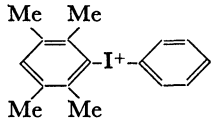
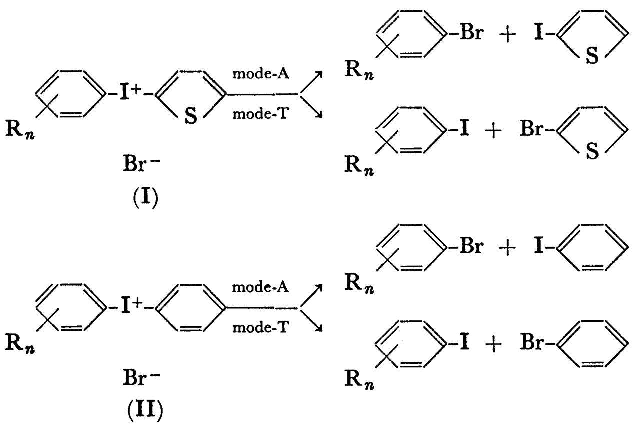
Iodonium bromide		Mp (°C)	Yield (%)	Elemental analysis (%)			
				Found		Calcd	
				C	H	C	H
	(Ia)	210—215	68.8	34.67	2.55	34.64	2.65
	(Ib)	153—156	26.3	37.90	3.39	38.17	3.45
	(Ic)	140—144	46.0	39.04	3.68	39.55	3.79
	(IIa)	205—210	47.1	41.45	3.26	41.63	3.23
	(IIb)	170—172	68.7	44.64	4.15	44.69	4.00
	(IIc)	150—152	90.1	44.83	4.54	44.74	4.53

Table 2. Cleavage tendency of I and II in molten

Aryl group	Ar-I$^+$-Th (I)		Ar-I$^+$-Ph (II)	
	mode-A	mode-T	mode-A	mode-B
o-Tolyl (a)	92.3	7.7	86.7	13.3
Mesityl (b)	100	0	96.5	3.5
Duryl (c)	100	0	97.7	2.3

Th-: Thienyl ring; Ph-: Phenyl ring



R=Methyl group, *n*=1, 3, 4

are summarized in Table 3. They are similar to those in the molten state. In every case the reaction proceeded without side reaction.

We see from Table 2 that the mode-A reaction, in which the nucleophile attacks the aryl ring, takes place completely for Ib and Ic and it is accompanied by the mode-T reaction, in which the nucleophile attacks the thienyl ring, only in the case of Ia. Similarly, for II the mode-A reaction takes place more predominantly than mode-B, in which the nucleophile attacks the phenyl ring. The reaction of II, however, does not proceed so selectively as that of I. The results are in contrast to those in the hydrolysis of *p*-tolylmesityliodonium salt reported by Le Count and Reid.

An aromatic bimolecular substitution mechanism has been proposed for *m*- or *p*-substituted phenyl-2-thienyl- and *p*-tolyliodonium salts.[5] If an aromatic bimolecular substitution mechanism is operative in the present case, the reaction of II should give unsubstituted phenyl bromide rather than methyl substituted phenyl bromide, but the result is the opposite. Thus, the *ortho*-methyl group is effective in the intramolecular strain to facilitate the dissociation of the bond between substituted phenyl 1-carbon and iodine. The substituted phenyl cation produced seems to be

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4) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2705 (1953); F. M. Beringer, H. E. Bachofner, R. A. Fakl, and M. Lett, *ibid.*, **80**, 4279 (1958).

5) Y. Yamada, K. Kashimk, and M. Okawara, Presented at the 25th Annual Meeting of the Chemical Society of Japan, Tokyo, October, 1971.

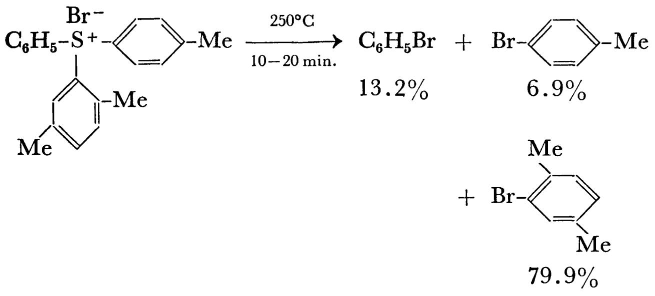
TABLE 3. CLEAVAGE TENDENCY OF I AND II IN SOLUTION STATE

Aryl group		Solvent	Ar–I^+–Th (I)		Ar–I^+–Ph	
			mode-A :	mode-T	mode-A :	mode-B
o-Tolyl	(a)	DMF	100	0	86.8	13.2
Mesityl	(b)	DMF	100	0	96.0	4.0
Duryl	(c)	DMF	100	0	100	0
o-Tolyl	(a)	Dioxane-DMF (1 : 1)	100	0	92.3	7.7
Mesityl	(b)	Dioxane-DMF (1 : 1)	100	0	*ca.* 100	trace
Duryl	(c)	Dioxane-DMF (1 : 1)	100	0	100	0

Th–: Thienyl ring; Ph–: Phenyl ring

stabilized by some methyl groups, and an analogous mechanism to an aromatic S_N1 is plausible. Similar results have been observed in the case of *m*- or *p*-substituted phenyl-2-thienyliodonium salts. However, there is a slight difference in the reaction tendency between I and II, *viz.*, the mode-T reaction takes place unfavorably compared to mode-B. Thus, it is very difficult for the thienyl ring to be attacked by the halide ion regardless of the position of the substituent group in the phenyl nucleus. A remarkable distinction between the reactions of the iodonium bromides containing one *ortho*-methyl group (Ia and IIa) and two *ortho*-methyl groups (Ib, c and IIb,c) was not observed either in the molten or solution states. This suggests that even the one *ortho*-methyl group affords a considerable steric strain enough to break the substituted phenyl 1-carbon-iodine bond.

Wiegand and McEwen reported on the steric effect in the pyrolysis reaction of triarylsulfonium bromides.[6] The reaction of phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium bromide gives aryl bromides in the order of preference of 2,5-dimethylbromobenzene > bromobenzene > *p*-bromotoluene. This is explained by the



fact that the sulfonium bromide decomposes preferentially in such a manner as to give maximum relief of steric strain.

Thus, it is reasonable to assume that the reaction of the iodonium bromides containing *ortho*-methyl groups proceeds by an analogous mechanism to an aromatic S_N1.

When the substituted phenyl-2-thienyliodonium bromide (I) was allowed to react in the solvent, only the mode-A reaction took place. DMF and dioxane act to stabilize the substituted phenyl cation and help the dissociation of the substituted phenyl 1-carbon-iodine bond. In the case of substituted diphenyliodonium bromide (II), the mode-A reaction increases to some extent in DMF and dioxane, but the remarkable solvent effect was not observed compared to the reactions of Ia and II is attributed to the greater reactivity of phenyl ring than that of thienyl ring.

Experimental

Substituted Phenyl Iodide. Subsittuted phenyl iodides were prepared from substituted benzene by the usual method.[7]

Subsitituted Phenyliodoso Acetate. Iodosobenzene diacetate was prepared by the oxidation of iodobenzene in a mixture of hydroge nperoxide and acetic anhydride.[8] Other subsitituted phenyliodoso acetates were prepared by a procedure like that given for mesityliodoso acetate.[9] To 24.6 g (0.1 mol) of iodomesitylene in 50 m*l* of ethyl acetate was added dropwise with stirring 95 g (0.25 mol) of 20% peracteic acid in acetic acid and ethyl acetate. The flask was chilled with an ice-water bath during the course of addition (30 min). The solution was then stirred for two hours below 10°C and allowed to stand overnight at room temperature. The solvent was removed under reduced pressure. The white crystals were washed with ether and dried overnight, giving 27.8 g of mesityliodoso acetate (yield, 78.5%), mp 110—125°C. (See Table 4 for melting points and yield data).

TABLE 4. ARYLIODOSO ACETATE

Aryl group	Mp (°C)	Yield (%)
o-Tolyl	145—148	69.2
Mesityl	110—120	78.5
Duryl	130—137	77.9

o-*Tolylphenyliodonium Bromide.* To a suspension of 3.4 g (10 mmol) of *o*-tolyliodoso acetate and 5 m*l* of benzene in 100 ml of acetic anhydride was added 5 m*l* of concd. sulfuric acid with stirring below 10°C. After stirring for one hour, the reaction mixture was allowed to stand for 5 hr at room temperature. The mixture was poured into 200 m*l* of ice water and extracted with two 50 m*l* portions of ether. The aqueous layer was treated with activated carbon and 30 g of sodium bromide in 100 m*l* of water. The precipitate was washed with water and with methanol and then dried to give 1.8 g of *o*-tolylphenyliodonium bromide. Recrystal-

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6) G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968).

7) H. O. Wirth, O. Konigstein, and W. Kern, *Ann. Chem.*, **634**, 84 (1960).

8) M. Okawara and K. Mizuta, *Kogyo Kagaku Zasshi*, **64**, 232 (1961).

9) J. E. Leffier and L. J. Story, *J. Amer. Chem. Soc.*, **89**, 2333 (1967).

lization from methanol gave a pure product.

Mesitylphenyliododnium Bromide. To a well-stirred mixture of 11 g (34 mmol) of phenyliodoso acetate, 3.6 g (30 mmol) of mesitylene and 150 m*l* of acetic anhydride kept below 10°C was added 10 m*l* of concd. sulfuric acid over 30 min. After the mixture had been stirred for 6 hr at room temperature, 200 m*l* of ice-water was added, and the mixture was extracted with two 50 m*l* portions of ether. The aqueous layer was treated with activated carbon and then with 30 g of sodium bromide in 100 m*l* of water. The precipitate was recrystallized from methanol to give 8.3 g of mesitylphenyliodonium bromide.

Durylphenyliodonium Bromide. In a similar way the reaction of phenyliodoso acetate (9 g, 28 mmol) with durene (3 g, 22 mmol) gave 8.3 g of durylphenyliodonium bromide.

o-*Tolyl-2-thienyliodonium Bromide.* To a well-stirred mixture of 100 m*l* of acetic anhydride, 6.7 g (20 mmol) of *o*-tolyliodoso acetate and 5.0 g (60 mmol) of thiophene, 5 m*l* of concd. sulfuric acid was added dropwise below 10°C. After 4 hr, 200 m*l* of ice-water was added. Extraction twice with 50 m*l* portions of ether followed by treatment with activated carbon produced an almost colorless solution, which was treated with 20 g of sodium bromide in 100 m*l* of water. The precipitates were collected and crystallized from methanol to give 2.6 g of *o*-tolyl-2-thienyliodonium bromide.

Mesityl-2-thienyliodonium Bromide. To a vigorously stirred solution of 8.2 g (22 mmol) of mesityliodoso acetate, 2.8 g (33 mmol) of thiophene and 200 m*l* of acetic anhydride, was added 5 m*l* of concd. sulfuric acid below 10°C. Subsequent treatments were carried out in the same way to give 8.8 g of mesityl-2-thienyliodonium bromide.

Duryl-2-thienyliodonium Bromide. In a similar way 2.3 g of duryl-2-thienyliodonium bromide was obtained from 4.5 g (12 mmol) of duryliodoso acetate and 2.5 g (30 mmol) of thiophene.

Pyrolysis Reaction of Iodonium Bromides (I and II). 0.25 g of substituted phenyl-2-thienyliodonium bromide (I) was enclosed in a pyrex ampoule. The ampoule was then placed in an oil bath kept at 235°C for 5 min. After the end of the pyrolysis the pyrolysate was dissolved in a small quantity of ether, and the amounts of 2-iodothiophene and 2-bromothiophene were determined by a Hitachi Gas Chromatograph 025—5051 on a 1 m column packed with Silicone SE-30 at 100°C. Chlorobenzene was used as an internal standard.

The pyrolysis reaction of substituted diphenyliodonium bromide (II) was also carried out in a similar way. Amounts of iodobenzene and bromobenzene were determined in the same way.

Reaction of Iodonium Bromides (I and II) in DMF and DMF-Dioxane. The reaction of iodonium bromides was carried out by a procedure similar to that given for *o*-tolylphenyliodonium bromide. *o*-Tolylphenyliodonium bromide (0.469 g, 1.25 mmol) dissolved in 100 m*l* of DMF was held at 100°C for 5 hr. At the end of the reaction the mixture was poured into cold water, extracted twice with ether and the extract was dried over anhydrous magnesium sulfate. After removing the solvent by distillation, the residue was redissolved in a small quantity of ether and the amounts of iodobenzene and bromobenzene were determined by means of gas chromatography. Subseuqent treatment was carried out in a similar way to that for the pyrolysis reaction. In every case the concentration was kept at 0.125 mmol/*l*.