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Substituent Effect in the Nucleophilic Attack by the Bromide Ion on the *p*-Tolyl-Substituted Phenyliodonium Ions

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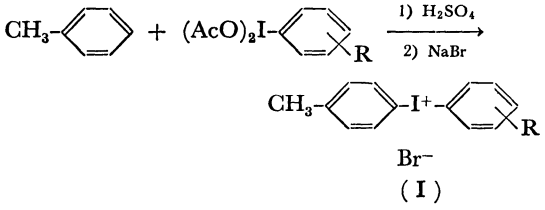
Synopsis. *p*-Tolyl-substituted phenyliodonium bromides were prepared and their nucleophilic substitution reactions were carried out in the DMF solution and molten state. Their substituent effects were discussed from the reaction products and the spectra of the iodonium salts.

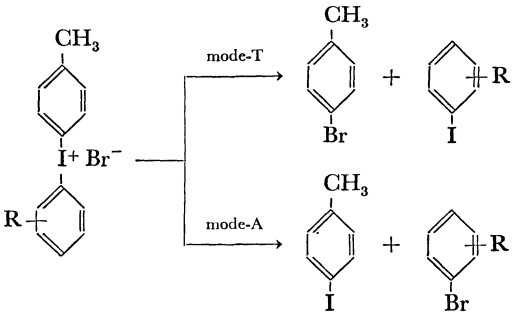
Beringer *et al.* have reported the syntheses of various diaryliodonium salts and their reactions in the solution.[1] In general, the nucleophile tends to attack the more electron-deficient phenyl-1-carbon. We have already reported the influences of the ligand and steric effect on the reaction of various iodonium salts.[2] However, a systematic investigation has not been undertaken to determine the effect of various substituents on the nucleophiles in the reaction of diaryliodonium salts.

In the present paper, we wish to report the syntheses of various *p*-tolyl-substituted phenyliodonium bromides and their reactions in both solution and molten states.

p-Tolyl-substituted phenyliodonium bromides (I) were synthesized from toluene and substituted phenyliodoso acetate. *p*-Tolyl-*p'*-carboxyphenyliodonium bromide was synthesized from *p*-iodobenzoic acid and toluene in the presence of potassium persulfate in concd. sulfuric acid according to the Beringer's method.[3] These results are summarized in Table 1. The thermal decomposition of the iodonium bromides (I) was carried out in both DMF solution (100 °C, 10 hr) and molten state (235 °C, 5 min). The results are shown in Table 2. As can be seen from this Table, the mode-T reaction, in which the bromide ion attacks the tolyl group to give *p*-tolyl bromide and substituted phenyl iodide, and the mode-A reaction, in which the bromide ion attacks the substituted phenyl group to give the substituted phenyl bromide and *p*-tolyl iodide, were found to occur competitively in both DMF solution and molten state.

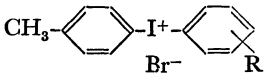


(I)



These results show that the mode-A reaction is inclined to occur in the reaction of I with electron-withdrawing substituents such as the nitro group. On the other hand, the mode-T reaction tends to occur in the reaction of I with electron-releasing substituents such as the methoxy group. The product ratios suggest that the reaction proceeds by an aromatic bimolecular nucleophilic substitution mechanism. Furthermore, there is no significant difference between the solution and molten reaction. It is of interest that the mode-A reaction is difficult to occur in the reaction of I with the *p'*-chloro group compared to that of I with the *m'*-chloro group. It can be deduced from the contribution of the resonance structure, in which the bond between iodonium ion and *p'*-chlorophenyl-1-carbon acquires some double bond character owing to the lone pair of *p'*-chloro group, to the reaction tendency. Such a resonance effect has been observed also in the case of *p*-chlorophenyl-2-thienyliodonium bromide.[2c]

TABLE 1. SYNTHESES OF *p*-TOLYL-SUBSTITUTED PHENYLIODONIUM BROMIDE



Substituent R-	Yield (%)	Mp (°C)	Elemental analyses (%) Found C	Found H	Found Halogen	Calcd C	Calcd H	Calcd Halogen
p-MeO	68.2	182—184	41.54	3.44	50.31	41.47	3.46	51.05
m-Me	92.6	180—181	42.66	3.66	52.61	43.21	3.63	53.16
H	42.6	183—184	41.66	3.05	55.09	41.63	3.23	55.14
p-Cl	90.4	192—194	38.35	2.68	58.64	38.13	2.71	59.17
m-Cl	78.9	183—184	37.91	2.77	58.97	38.13	2.71	59.17
p-COOH	50.0	193—194	39.77	3.12	50.00	40.13	2.89	49.35
p-NO_2	28.8	154—155	37.30	2.49	48.62	37.17	2.64	49.23

Table 2. Cleavage tendency of *p*-tolyl-substituted phenyliodonium bromides

Substituent R-	Molten state		Solution state	
	mode-T	mode-A	mode-T	mode-A
p-MeO	80.9	19.1	72.9	27.1
H	38.2	61.8	26.8	73.2
p-Cl	40.0	60.0	30.9	69.1
m-Cl	34.6	65.4	19.4	80.6
p-COOH	13.3	86.7	7.5	92.5
p-NO_2	3.7	96.3	—	—

Table 3. UV spectra of *p*-tolyl-substituted phenyliodonium bromide in methanol

Substituent R-	λ_{max} (nm)	log ε_{max}
p-MeO	247	4.21
m-Me	232	4.47
H	232	4.38
p-Cl	238	4.38
m-Cl	233	4.20
p-COOH	239	4.44
p-NO_2	253	4.32

From the UV spectra of I (Table 3), the increase in λ_{max} in going from unsubstituted or *m'*-chloro substituted to *p'*-chloro substituted iodonium bromide suggests the presence of such a conjugated system. The increase in λ_{max} of the iodonium bromides with the electron-withdrawing substitutents such as the nitro and carboxyl groups at the *p'*-position and their cleavage tendencies suggest the presence of the resonance structure owing to the hyperconjugation effect of *p*-methyl group enhanced by the *p'*-electron-withdrawing substituent. In these cases, the mode-A reaction becomes to be increasingly liable to occur owing to both the inductive and resonance effects.

Experimental

All the melting points are uncorrected. The ultraviolet spectra were measured with a Hitachi EPS-3T-type spectrometer. A Hitachi 023-5051-type gas chromatograph analyzer was used with a column (stainless 1 m) packed with Silicone SE 30 on Celite 545 at 100 °C.

p-Tolyl-Substituted Phenyliodonium Bromide (I). *p*-Tolyl-substituted phenyliodonium bromides were prepared by a procedure like that given for *p*-tolyl-*p'*-methoxyphenyliodonium bromide. To a well-stirred mixture of 5.28 g (15 mmol) of *p*-methoxyphenyliodoso acetate, 2.76 g (30 mmol) of toluene, and 50 ml of acetic anhydride kept below 10 °C there was added 12 ml of concd. sulfuric acid. After having been stirred at room temperature for 3 hr, the reaction mixture was diluted with 200 ml of ice-water, extracted with ether until color was no longer removed and treated with active carbon. The aqueous layer was added to 10.3 g (100 mmol) of sodium bromide dissolved in 50 ml of water, giving 4.0 g *p*-tolyl-*p'*-methoxyphenyliodonium bromide.

p-Tolyl-p'-carboxyphenyliodonium Bromide. To a solution of 2.98 g (12 mmol) of *p*-iodobenzoic acid in 100 ml of concd. sulfuric acid there was added with stirring 6.5 g (42 mmol) of potassium persulfate at −10 °C and then, after 15 min, 16 g (174 mmol) of toluene at −20 °C. The mixture was stirred at −10 °C for 1 hr and at 0 °C for 3 hr and then was processed as in the preceding manner to give 2.5 g of *p*-tolyl-*p'*-carboxyphenyliodonium bromide.

Pyrolysis Reaction of p-Tolyl-Substituted Phenyliodonium Bromide in the Molten State. About 0.2 g of *p*-tolyl-substituted phenyliodonium bromide was enclosed in a Pyrex tube. The ampoule was then placed in an oil bath kept at 235 °C for 5 min. After the end of the pyrolysis reaction the pyrolysate was disolved in a small quantity of ether and the amounts of *p*-iodotoluene and *p*-bromotoluene were determined by a gas chromatograph. Chlorobenzene was used as an internal standard.

Reaction of p-Tolyl-Substituted Phenyliodonium Bromide in DMF Solution. The reaction of iodonium bromide was conducted by a procedure like that given for *p*-tolyl-*p'*-methoxyphenyliodonium bromide. *p*-Tolyl-*p'*-methoxyphenyliodonium bromide (0.214 g, 0.2 mol) dissolved in 50 ml of DMF was held at 100 °C for 10 hr. At the end of the reaction the mixture was poured into cold water, extracted with ether two times 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 then treated in the same manner as shown above. In every case the concentration was held at 0.25 mol/l.

References

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