[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. I. Synthesis[1]

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The formation of symmetrical diaryliodonium salts by the direct coupling of aromatic compounds has been studied, and the scope of the reaction has been enlarged. Unsymmetrical as well as symmetrical diaryliodonium salts have been made available by a novel Friedel and Crafts type of condensation between an iodoso compound and another aromatic compound.

Most diphenyliodonium salts[2] have been prepared by one of the following methods: A, the base-catalyzed condensation of iodoso compounds with iodoxy compounds

$$ArIO + Ar'IO_2 \longrightarrow Ar\overset{+}{I}Ar'\ IO_3^- \qquad (A)$$

B, the reaction of aryliodosodichlorides with diarylmercury compounds; and C, the direct coupling of two aromatic hydrocarbons or their halogen derivatives.

$$Ar_2Hg + Ar'ICl_2 \longrightarrow Ar\overset{+}{I}Ar'\ Cl^- + ArHgCl \quad (B)$$

Method A has been frequently used but is time-consuming. Method B is limited by the availability of diarylmercury compounds, while method C has been used only by Masson and co-workers.[3]

$$4ArH + (IO)_2SO_4 \longrightarrow 2Ar_2\overset{+}{I}SO_4^{=} + 2H_2O \quad (C)$$

By variations of Masson's procedures benzene, toluene, anisole and acetanilide were converted to a diphenyliodonium salt and its 4,4'-dimethyl,[4] 4,4'-dimethoxy[5] and 4,4'-diacetamido[6] derivatives. Further it was found that by treatment with iodyl sulfate and prolonged stirring in sulfuric acid nitrobenzene and benzoic acid were converted to 3,3'-dinitro-[7] and 3,3'-dicarboxydiphenyliodonium salts. The structures of the iodonium salts from toluene, anisole, acetanilide and benzoic acid follow from the thermal conversion of their iodides to *p*-iodotoluene, *p*-iodoanisole, *p*-iodoacetanilide and *m*-iodobenzoic acid. Thus 3,3'- and 4,4'-disubstituted diphenyliodonium salts are available in one step from benzenes having *m*- or *o,p*-directing groups, respectively.

In the present work there has also been developed a novel Friedel and Crafts type of condensation of an iodoso compound with an aromatic compound in the presence of sulfuric acid to give an iodonium salt, either symmetrical or unsymmetrical.

$$ArIO + Ar'H + H_2SO_4 \longrightarrow Ar\overset{+}{I}Ar'\ HOSO_3^- + H_2O \quad (D)$$

By this method iodosobenzene was condensed with benzene, toluene and anisole to give a diphenyliodonium salt and its 4-methyl[4b,8] and 4-methoxyl[9] derivatives. Likewise, *o*- and *m*-nitroiodosobenzene with benzene and *n*-butylbenzene gave 2- and 3-nitrodiphenyliodonium salts.[7] It seems likely that the sulfuric acid converts the iodoso compound into its conjugate acid, which then makes an electrophilic attack on another aromatic ring.

These results lend substance to the hypothesis[3] that the formation of iodonium salts from aromatic compounds proceeds with the intermediate formation of iodoso compounds. Thus in the reaction of nitrobenzene with iodyl sulfate, *m*-nitroiodosobenzene may be isolated or it may be left in solution to react, slowly with more nitrobenzene or rapidly with benzene or a substituted benzene.

Discussing the formation of iodonium salts by the use of iodine pentoxide and sulfuric acid,[3b] Masson and Hanby[3c] proposed that by the oxidation of some of the aromatic compound the iodine pentoxide would be reduced to iodyl sulfate. Such an oxidation–reduction scheme would be in accord with our successful formation of iodonium salts from benzene and its derivatives bearing activating groups by treatment with sodium or potassium iodate and sulfuric acid in acetic acid–acetic anhydride. *A priori* another reaction path would also seem possible: formation of an iodoxy compound, which would then react with an aromatic compound to give an iodonium ion, with reduction occurring either before or after condensation. This possibility was suggested by the observed reaction of iodoxybenzene and benzene in acetic acid–acetic anhydride–sulfuric acid to give the diphenyliodonium ion.

Under some conditions treatment of an iodoso compound with an aromatic hydrocarbon in the presence of sulfuric acid effected its reduction to an iodo compound. The factors governing such reductions are not understood. Thus in the attempted condensations with benzene, *m*-nitroiodosobenzene gave iodonium salts in both sulfuric acid and acetic acid–acetic anhydride, while *o*-nitroiodosobenzene gave iodonium salts in sulfuric acid and suffered reduction in the organic solvents. All attempted condensations of *p*-nitroiodosobenzene with benzene gave *p*-nitroiodobenzene, as did attempts to condense *p*-nitroiodosobenzene dichloride with benzene in the presence of alumi-

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(1) This paper is largely based on dissertations submitted by Milton Drexler, E. Melvin Gindler and Charles C. Lumpkin in partial fulfillment of the requirements of the degree of Master of Science in Chemistry in June, 1952, and was presented in part at the 121st National Meeting of the American Chemical Society in Buffalo, N. Y., March 23–27, 1952; see Abstracts, p. 3K.

(2) For a full description of the preparation and properties of organic derivatives of polyvalent iodine reported to 1914 see C. Willgerodt, "Die organischen Verbindungen mit mehrwertigen Jod," F. Enke, Stuttgart, Germany (1914). For a summary of later work see R. B. Sandin, *Chem. Revs.*, **32**, 249 (1943), and N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, 1950, p. 1255.

(3) (a) I. Masson, *Nature*, **139**, 150 (1937); (b) I. Masson and E. Race, *J. Chem. Soc.*, 1718 (1937); (c) I. Masson and W. E. Hanby, *ibid.*, 1699 (1938); (d) I. Masson and C. Argument, *ibid.*, 1702 (1938).

(4) (a) J. McCrae, *Ber.*, **28**, 97 (1895); (b) H. Peters, *J. Chem. Soc.*, **81**, 1350 (1902).

(5) R. A. Mastropaolo, *Anales asoc. quim. argentina*, **28**, 101 (1940); *C. A.*, **35**, 734 (1941).

(6) C. Willgerodt and W. Nägeli, *Ber.*, **40**, 4072 (1907).

(7) C. Willgerodt and E. H. Wikander, *ibid.*, **40**, 4066 (1907).

(8) C. Willgerodt, *ibid.*, **31**, 915 (1898).

(9) R. B. Sandin, M. Kulka and R. McCready, THIS JOURNAL, **58**, 157 (1936).

num chloride. Nor is the pattern clear when the condensation of iodosobenzene with other aromatic hydrocarbons is attempted. Good yields of iodonium salts were obtained with benzene, toluene and anisole, but with bromobenzene, acetanilide, phenyl acetate and naphthalene iodobenzene was formed.

As for the iodonium halides, their solubilities in general decrease with increasing atomic weight of the halide ion. This makes the relatively insoluble iodides easily isolated but hard to get into solution for further reactions.[10] One preparative approach to the relatively soluble chlorides was to isolate the iodonium iodides and convert them to the chlorides by the procedure of Forster and Schaeppi.[11] This involved chlorination of the iodides to the di- or tetrachloroiodates, which when dissolved in acetone reacted to give the iodonium chlorides. Another approach, altering preparative conditions so as to favor direct isolation of the chloride, gave diphenyliodonium chloride in 52% yield.

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Experimental[12]

Analytical Procedures.—Analyses for combined iodine, combined bromine and total halogen were performed according to A.O.A.C. procedures.[13] Halide ions in iodonium salts were determined argentimetrically in warm methanol or 50% aqueous acetic acid, iodide ion by the Volhard procedure, bromide ion with ferric thiocyanate as indicator, chloride ion with dichlorofluorescein as indicator. Iodoso and iodoxy compounds were determined iodimetrically.[14] Microanalyses for carbon, hydrogen and nitrogen were performed by Drs. Weiler and Strauss, 164 Banbury Road, Oxford, England.

Iodoso Compounds.—Iodosobenzene was prepared from iodosobenzene dichloride[15] by hydrolysis by base.[14] Chlorination of *o*-, *m*- and *p*-nitroiodobenzenes in cold chloroform[15] gave the nitroiodosobenzene dichlorides[16] in yields of 83, 95 and 95%, with purities of 99.3–99.7%. The nitroiodosobenzenes[16] were obtained by hydrolysis[14] in yields of 91–92%, with purities of 98.9–99.5%.

Nitrobenzene was converted to *m*-nitroiodosobenzene dibisulfate with iodyl sulfate in cold concentrated sulfuric acid essentially by the method of Masson and Hanby.[3c] Iodyl sulfate was found to be conveniently prepared by vigorously stirring stoichiometric amounts of iodine and sodium or potassium iodate in concentrated sulfuric acid.

Diphenyliodonium Bromide from Iodosobenzene.—To a cold stirred solution of 5.0 g. (22.7 mmoles) of iodosobenzene, 12.5 ml. of benzene, 65 ml. of acetic acid and 12.5 ml. of acetic anhydride there was added dropwise 5.0 ml. of sulfuric acid. After 24 hours (negative starch–iodide test) the reaction mixture was diluted with 100 ml. of water, extracted twice with ether, shaken with 5 g. of activated carbon, and filtered. The precipitate on adding 5.0 g. of sodium bromide in water was collected, washed with water and with acetone, and dried to give 6.05 g. (16.8 mmoles, 74%) of colorless **diphenyliodonium bromide**, m.p. 208° (dec.), lit.[11] 210°.

Diphenyliodonium Bromide from Iodoxybenzene.—To a mixture of 5.0 g. (21 mmoles) of iodoxybenzene,[17] 15 ml. of benzene, 65 ml. of glacial acetic acid and 65 ml. of acetic anhydride well-stirred in an ice-bath there was added after 15 minutes a cold solution of 2 ml. of sulfuric acid in 3 ml. of glacial acetic acid. The reaction mixture was kept in the ice-bath for three hours (negative starch–iodide test). The reaction mixture was diluted with 100 ml. of water and 15 ml. of ether and was treated with 5.0 g. of sodium bromide in water. The precipitate was collected, crystallized from 50% aqueous acetic acid, washed with water and with ether and dried to give 4.1 g. (11.4 mmoles, 54%) of **diphenyliodonium bromide**, m.p. 207° (dec.), lit.[11] 210° (dec.).

Other Diphenyliodonium Salts.—Diphenyliodonium iodide (9.9 g., 21.8 mmoles) in 200 ml. of chloroform at 0° was treated with chlorine. After the suspension turned brown, there was formed a clear solution, from which separated a voluminous yellow precipitate of **diphenyliodonium dichloroiodate**, m.p. 135–136°. Crystallization from chloroform raised the m.p. to 137.5–138°, lit.[11] 138°. Solution of this material in excess acetone was followed by rapid crystallization of 6.2 g. (19.6 mmoles, 90%) of **diphenyliodonium chloride**, m.p. 227–228° (dec.), lit.[11] 225° (dec.).

To a hot solution of 2.00 g. (5.54 mmoles) of diphenyliodonium bromide in 100 ml. of water there was added with stirring a hot solution of 5.54 mmoles of sodium picrate in water. From the cooled solution there was obtained 2.75 g. (5.41 mmoles, 98%) of **diphenyliodonium picrate** as orange platelets, m.p. 147.5–148.5°, lit.[18] 145°.

By treatment of aqueous diphenyliodonium bromide with aqueous silver nitrate, removal of the silver bromide and concentration of the solution there was obtained diphenyliodonium nitrate, m.p. 149–150.5° (dec.), lit.[19] 153–154° (dec.).

2-Nitrodiphenyliodonium Bromide.—To a mixture of 300 ml. of sulfuric acid and 45 ml. (0.5 mole) of benzene cooled to 5° there was added portionwise and with stirring 66.25 g. (0.25 mole) of *o*-nitroiodosobenzene over 45 minutes. The ice-bath was removed, and the mixture was stirred until negative to starch–iodide paper (about three hours). After being poured onto 1500 g. of ice, the reaction mixture was treated with 10 g. of Celite to remove the unreacted benzene and then with a solution of 41.5 g. of sodium bromide in 200 ml. of water. The bulky yellow precipitate was collected, washed with cold water, with methanol and with ether and was dried at 50° for 24 hours to give 74–78 g. (0.182–0.192 mole, 73–77%) of **2-nitrodiphenyliodonium bromide**; m.p. 143° (dec.), unchanged by crystallization from hot water.

Anal. Calcd. for $C_{12}H_9BrINO_2$: C, 35.47; H, 2.23; Br, 19.68; I, 31.27; Br and I, 50.95; N, 3.45. Found: C, 35.5; H, 2.04; Br, 19.60 and 19.61; I, 31.12 and 31.15; Br and I, 50.9 and 51.0; N, 3.2.

3-Nitrodiphenyliodonium Salts.—A mixture of 19 ml. (0.21 mole) of benzene, 46.2 g. (0.112 mole) of *m*-nitroiodosobenzene dibisulfate, 70 ml. of acetic acid and 18.5 ml. of acetic anhydride was shaken for ten minutes to effect solution. To this solution there was then added portionwise and with shaking over ten minutes 5.8 ml. (0.11 mole) of sulfuric acid in 18.5 ml. of acetic acid. After two hours (negative starch–iodide test) the reaction mixture was diluted with three volumes of water and was extracted with ether to remove unreacted benzene. Addition of 6.9 g. of sodium bromide in water gave a colorless micro-crystalline precipitate of 44.1 g. (0.108 mole, 96%) of **3-nitrodiphenyliodonium bromide**, m.p. 172–175° (dec.). Recrystallization from water gave needles of unchanged m.p.

Anal. Calcd. for $C_{12}H_9BrINO_2$: C, 35.47; H, 2.23; Br, 19.68; I, 31.27; Br and I, 50.95. Found: C, 35.26; H, 2.30; Br, 19.57 and 19.59; I, 30.97 and 31.03; Br and I, 50.85 and 50.85.

A solution of *m*-nitroiodosobenzene dibisulfate in 200 ml. of sulfuric acid was prepared from 0.3 mole of nitrobenzene and 0.15 mole of iodyl sulfate as previously described. Ben-

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[10] For a study of the reactions of diaryliodonium salts with bases, see F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, This Journal, **75**, 2708 (1953).

[11] M. O. Forster and J. H. Schaeppi, *J. Chem. Soc.*, **101**, 382 (1912).

[12] Melting points are corrected. As most iodonium salts decompose near their melting points, these depend strongly on the duration of heating. In general, after an approximate melting point had been taken, a new sample was introduced about 10° below this point.

[13] "Methods of Analysis of the Association of Official Agricultural Chemists," 7th Ed., 1950, p. 689.

[14] I. Masson, E. Race and F. E. Pounder, *J. Chem. Soc.*, 1669 (1935); H. J. Lucas, E. R. Kennedy and M. W. Formo, *Org. Syntheses*, **22**, 70 (1942).

[15] H. J. Lucas and E. R. Kennedy, *ibid.*, **22**, 69 (1942).

[16] C. Willgerodt, *Ber.*, **26**, 362, 1311, 1809 (1893).

[17] M. W. Formo and J. R. Johnson, *Org. Syntheses*, **22**, 73 (1942).

[18] E. R. Kline and C. A. Kraus, This Journal, **69**, 814 (1947).

[19] C. Hartmann and V. Meyer, *Ber.*, **27**, 1592 (1894).

zene (54 ml., 0.6 mole) was added with stirring to the reaction mixture at 20°, the cooling bath was removed, and stirring was continued for two hours. After the reaction mixture had been poured onto ice, unreacted benzene was removed with ether. The filtered solution was treated with 51.5 g. (0.5 mole) of sodium bromide to give a precipitate, which was collected, washed with water, crystallized from water and dried *in vacuo* to give 76.2 g. (0.187 mole, 62%) of **3-nitrodiphenyliodonium bromide**, m.p. 172–175° (dec.).[20]

Addition of excess aqueous potassium iodide to hot aqueous 3-nitrodiphenyliodonium bromide precipitated **3-nitrodiphenyliodonium iodide**, m.p. 144.5–146°, lit.[7] 153°. Chlorination[11] of the iodide in chloroform gave 3-nitrodiphenyliodonium dichloroiodate, m.p. 92–96°. Solution of this material in excess acetone gave, in 89% yield from the iodide, **3-nitrodiphenyliodonium chloride**, m.p. 180–181°. Recrystallization from water raised the m.p. to 185–185.5°, lit.[7] 170–172°.

3-Nitro-4′-*n*-butyldiphenyliodonium Chloride.—To a solution of 60 mmoles of *m*-nitroiodosobenzene dibisulfate in 60 ml. of glacial acetic acid and 25 ml. of acetic anhydride kept at 0°, 16.0 g. (119 mmoles) of *n*-butylbenzene was added. After 20 hours at this temperature (negative starch–iodide test) the mixture was treated with 200 ml. of water and was extracted with several portions of ether.

To half of this solution 3.6 g. of ammonium chloride in water was added. The precipitate was collected, and the filtrate was treated with an additional 3.6 g. of ammonium chloride. The combined products were washed with water, acetone and ether and dried *in vacuo* to give 11.9 g. (28.4 moles, 91%, based on 50% aliquot taken) of **3-nitro-4′-*n*-butyldiphenyliodonium chloride**, m.p. 169–170° (dec.).

Anal. Calcd. for $C_{16}H_{17}ClINO_2$: Cl, 8.49. Found: Cl, 8.48.

Treatment of this salt with sodium sulfite in boiling water gave *p*-iodo-*n*-butylbenzene, which was collected and oxidized to *p*-iodobenzoic acid, m.p. 265–266°, no depression on admixture with an authentic sample.

4-Methoxydiphenyliodonium Salts.—To a well-stirred cold solution of 25 g. (112 mmoles) of iodosobenzene, 12 ml. (110 mmoles) of anisole, 62.5 ml. of acetic anhydride and 725 ml. of glacial acetic acid there was added dropwise 7 ml. of sulfuric acid. After 30 minutes (negative starch–iodide test) the reaction mixture was added with stirring to 25 g. of sodium bromide in 100 ml. of water. The precipitate was collected, washed with water and with ether and crystallized from 950 ml. of water to give 29 g. (77 mmoles, 70%) of **4-methoxydiphenyliodonium bromide**, m.p. 185° (dec.), lit.[9] 180° (dec.). Addition of excess aqueous potassium iodide to hot aqueous 4-methoxydiphenyliodonium bromide precipitated **4-methoxydiphenyliodonium iodide**, m.p. 162.5–163.5°, lit.[9] 175°. The iodide was converted by the procedure of Forster and Schaeppi[11] to **4-methoxydiphenyliodonium chloride**, m.p. 191° (dec.), lit.[9] 181° (dec.).

Reaction of 4-methoxydiphenyliodonium bromide with hot aqueous sodium sulfite gave iodobenzene (in small amount) and *p*-iodoanisole, m.p. 51–52°, no depression on admixture with an authentic sample.

4-Methyldiphenyliodonium Bromide.—To a well-stirred cold solution of 25 g. (112 mmoles) of iodosobenzene, 15 ml. of toluene, 47.5 ml. of acetic anhydride and 475 ml. of acetic acid there was added 25 ml. of sulfuric acid. After 40 minutes (negative starch–iodide test) the reaction mixture was added to 25 g. of sodium bromide in 100 ml. of water. After removal of the precipitate the filtrate was adjusted to *p*H 4.5 with sodium hydroxide to give a second crop. The combined yield was crystallized from water to give 24.6 g. (66.6 mmoles, 58%) of **4-methyldiphenyliodonium bromide**, m.p. 176–177° (dec.).

4-Methyldiphenyliodonium bromide reacted with sodium sulfite in boiling water. The iodobenzene and *p*-iodotoluene formed were treated with hot aqueous potassium permanganate to give *p*-iodobenzoic acid, m.p. 265–266°, no depression on admixture with an authentic sample.

Reduction of Iodoso Compounds to Iodo Compounds During Attempted Condensations.—Iodosobenzene was reduced to iodobenzene in attempted condensations with bromobenzene, acetanilide, phenyl acetate and naphthalene in acetic acid–acetic anhydride–sulfuric acid. Under similar conditions with benzene *o*- and *p*-nitroiodosobenzene were converted to the corresponding iodo compounds. *p*-Nitroiodobenzene was also recovered from attempted condensations of *p*-nitroiodosobenzene with benzene in concd. sulfuric acid and *p*-nitroiodosobenzene dichloride with benzene in the presence of aluminum chloride.

Iodonium Salts Direct from Aromatic Compounds. Diphenyliodonium Bromide (Iodyl Sulfate).[21]—To a stirred suspension of 38 mmoles of iodyl sulfate in 25 ml. of sulfuric acid kept below 10° there was added 15 ml. of acetic anhydride and then 20 ml. of benzene. After two hours (negative starch–iodide test) the reaction mixture, now cooled in an ice-bath, was treated with 200 ml. of water and filtered through fritted glass. The filtrate was extracted three times with ethyl acetate and three times with ether. Addition of 10 g. of sodium bromide in water precipitated 20 g. (55.4 mmoles, 72%) of **diphenyliodonium bromide** as small needles, m.p. 208–209° (dec.), lit.[11] 210° (dec.). This salt may be recrystallized from water, methanol, formic acid or 50% aqueous acetic acid.

Anal. Calcd. for $C_{12}H_{10}BrI$: Br, 22.14. Found: Br, 22.13.

Diphenyliodonium Chloride (Potassium Iodate).—To a stirred mixture of 107 g. (0.5 mole) of potassium iodate, 90 ml. (1.0 mole) of benzene and 200 ml. of acetic anhydride kept below 10° there was added a cold solution of 100 ml. of acetic anhydride and 225 ml. of concd. sulfuric acid. After being stirred overnight, the reaction mixture was poured into 400 g. of ice, extracted with two 100-ml. portions of ether and treated twice with 20 g. of charcoal. The mixture was now mixed with 100 g. of ammonium chloride in 350 ml. of water and cooled in an ice-bath. After removal of the precipitate, a second crop was obtained by a second treatment with aqueous ammonium chloride, while saturation of the mother liquid with ammonia gave a third crop. Recrystallization of the combined yield from methanol gave 81.1 g. (0.259 mole, 52%) of **diphenyliodonium chloride**, m.p. 228–229° (dec.), lit.[11] 225° (dec.).

Anal. Calcd. for $C_{12}H_{10}ClI$: Cl, 11.20. Found: Cl, 11.26.

In a similar procedure addition of aqueous sodium bromide to the hydrolyzed reaction mixture gave a 64% yield of **diphenyliodonium bromide**, m.p. 208–209° (dec.), lit.[11] 210° (dec.).

4,4′-Dimethyldiphenyliodonium Iodide and Bromide (Potassium Iodate).—To a well-stirred mixture of 20.0 g. (93.5 mmoles) of potassium iodate, 30 ml. of toluene, 90 ml. of acetic acid and 40 ml. of acetic anhydride kept below 3° there was added a solution of 20 ml. of sulfuric acid and 30 ml. of acetic acid. Stirring was continued for three hours with the ice-bath and then overnight (negative starch–iodide test). The precipitated inorganic salts were removed by filtration, and the acetic acid washings were added to the main filtrate to give a total volume of 210 ml.

To an aliquot of 100 ml. of the filtrate there was added 100-ml. portions of ether and of water. The two layers were separated, and the aqueous layer was extracted three times with ether and diluted to 500 ml. This solution was treated with a few milligrams of sodium sulfite and then with 9 g. of potassium iodide in water. The precipitate was collected, washed and dried to give 17.62 g. of **4,4-dimethyldiphenyliodonium iodide**, m.p. 172–174° (dec.), lit.[4] 146° (dec.). The yield of the iodonium salt was 91% of the theoretical on the basis of the aliquot taken.

Thermal decomposition of 2 g. of this iodonium salt gave *p*-iodotoluene, identified by oxidation with potassium permanganate to *p*-iodobenzoic acid, m.p. 266–267°, no depression on admixture with an authentic sample.

A 20-ml. aliquot from the 210 ml. of filtrates was diluted with water to 40 ml., extracted with ether and treated with 2.0 g. of sodium bromide in water to give 2.3 g. (67%) of **4,4′-dimethyldiphenyliodonium bromide** as short, heavy needles, m.p. 205–207° (dec.), lit.[4] 178° (dec.).

Anal. Calcd. for $C_{14}H_{14}BrI$: Br, 20.54. Found: Br, 20.56.

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[20] A reaction similar to this was run with *m*-dinitrobenzene replacing nitrobenzene. There was obtained a small yield of a salt, m.p. 195° (dec.), presumably 3,5-dinitrodiphenyliodonium bromide. Reaction of this salt with hot aqueous sodium nitrite gave in good yield 1,3,5-trinitrobenzene, m.p. 121–122°, no depression on admixture with an authentic sample.

[21] This procedure is a modification of that of Masson (reference 3d). The iodyl sulfate was prepared as described earlier, in the preparation of *m*-nitroiodosobenzene dibisulfate.

4,4′-Dimethoxydiphenyliodonium Iodide (Potassium Iodate).—To a well-stirred mixture of 20.0 g. (101 mmoles) of sodium iodate and 200 ml. of acetic acid kept below 10° there was added during one hour a solution of 50 ml. (457 mmoles) of anisole, 50 ml. of acetic anhydride and 25 ml. of sulfuric acid. After the reaction mixture had been stirred overnight at room temperature, it was poured onto 500 ml. of ice-water and extracted with five 100-ml. portions of ether. Two treatments with charcoal were followed by addition of 40 g. of potassium iodide in water to give 5.2 g. (11.1 mmoles, 11%) of **4,4′-dimethoxydiphenyliodonium iodide**, m.p. 179–182° (dec.), lit.[5] 180°.

Thermal decomposition of this salt gave *p*-iodoanisole, m.p. 50–52° after crystallization from methanol; no depression on admixture with an authentic sample.

4,4′-Diacetamidodiphenyliodonium Iodide (Potassium Iodate).—To a vigorously stirred solution of 83.4 g. (0.618 mole) of acetanilide and 50 ml. of sulfuric acid in 300 ml. of acetic acid and 100 ml. of acetic anhydride cooled with a water-bath to 20°, 66.0 g. (0.309 mole) of potassium iodate was added over 2.5 hours. After an additional 24 hours of stirring (negative starch–iodide test) the reaction mixture was diluted with 500 ml. of ice water and insoluble material was removed by filtration. Addition of a small amount of sodium sulfite was followed by 150 g. of potassium iodide in water. The precipitate was collected, washed with alcohol and with ether until the washings were colorless, and dried *in vacuo* to give 77.0 g. (0.148 mole, 47.7%) of **4,4′-diacetamidodiphenyliodonium iodide**, m.p. 173° (dec.), lit.[6] 176.5°.

Anal. Calcd. for $C_{16}H_{16}I_2N_2O_2$: I^-, 24.30. Found: I^-, 24.22.

Thermal decomposition of this salt gave *p*-iodoacetanilide, m.p. 184° after crystallization from alcohol, no depression on admixture with an authentic sample.

3,3′-Dinitrodiphenyliodonium Salts (Iodyl Sulfate).—To a stirred cold suspension of iodyl sulfate (0.30 mole) in 400 ml. of sulfuric acid there was added during two hours 147.6 g. (1.20 moles) of nitrobenzene. After the reaction mixture had been stirred at room temperature for six days, it was poured onto 2500 g. of ice. The precipitate was collected, washed with water and crystallized from water (charcoal) to give 70.7 g. (0.151 mole, 25.2%) of **3,3′-dinitrodiphenyliodonium bisulfate**, m.p. 165–167° (dec.), lit.[7] 168.5°. From the combined mother liquors by the addition of 60 g. of sodium bromide in water there was obtained 46.6 g. (0.103 mole, 17.2%) of **3,3′-dinitrodiphenyliodonium bromide**, m.p. 178–179° (dec.). The combined yield of iodonium salts was thus 42.4%.

From other reaction mixtures there were also isolated the **3,3′-dinitrodiphenyliodonium chloride**, m.p. 203–205° (dec.), lit.[7] 214°, and **3,3′-dinitrodiphenyliodonium iodide**, m.p. 127–128°, lit.[7] 130.5°.

3,3′-Dicarboxydiphenyliodonium Iodide (Iodyl Sulfate).—To a suspension of iodyl sulfate prepared from 3.85 g. (15.2 mmoles) of iodine, 10.0 g. (46.4 mmoles) of potassium iodate and 40 ml. of sulfuric acid and kept below 10° there was added 1 ml. of acetic anhydride and 19.0 g. (156 moles) of benzoic acid. After being stirred for 8 hours in an ice-bath and for 15 hours at room temperature (negative starch–iodide test), the mixture was treated with 200 ml. of water below 25°. An ether-soluble precipitate was removed by filtration and the filtrate was extracted with ether. To the clear solution there was added 12.9 g. of potassium iodide and a few mg. of sodium bisulfite in 25 ml. of water. The precipitate was collected, washed with water and with ether and dried *in vacuo* to give 20.2 g. (40.6 mmoles, 53%) of **3,3′-dicarboxydiphenyliodonium iodide**, m.p. about 120° (dec.).

The structure of this salt is shown by its conversion at its m.p. to *m*-iodobenzoic acid, m.p. 184–185° after crystallization from aqueous acetic acid, no depression on admixture with an authentic sample.

BROOKLYN 2, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. II. The Phenylation of Organic and Inorganic Bases[1,2]

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Our results, taken with those in the literature, show that under relatively mild conditions organic and inorganic bases effect nucleophilic displacements on the 1-carbons of diphenyliodonium ions to form new bonds with carbon, hydrogen, oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic, antimony and the halogens. Thus iodonium salts show promise as general phenylating agents.

While alkyl halides may be used for the alkylation of bases, the more inert aryl halides react with bases only at elevated temperatures of 200–300°.[3] Such high temperatures not only necessitate the use of pressure equipment but also limit the reactions to compounds that can withstand such drastic conditions. In a search for a group more susceptible to nucleophilic displacement, attention was drawn to the 'onium salts, the positive charges in which should facilitate polar fission of the bonds to the aromatic systems. Consideration was given to the common aromatic 'onium salts: diazonium, ammonium, phosphonium, sulfonium and iodonium salts.

Thus it is well known that the diazonium group may be displaced by water, alcohol, iodide ion, thiourea, thiosulfate ion and sulfide ion without catalysts and by chloride ion, bromide ion,[4] nitrite ion and cyanide ion with the aid of copper catalysts. Limitations on the generality of the displacement of the diazonium group by bases are offered by the following common reactions: with hydroxide ion to give a diazotate, with sulfite or bisulfite ions to give a hydrazine group, with phenoxide ion to give an azophenol and with acetoacetic ester to give a benzeneazo derivative, which rearranges to a phenylhydrazone.

Simple alkyl aryl ammonium ions with bases give displacement or elimination reactions with formation of alcohols or olefins and tertiary amines. With nitro or carbonyl groups in *o*- or *p*-positions, displacement of the ammonio group[3] may occur to give substituted phenyl derivatives of the bases.

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[1] This paper is largely based on dissertations submitted by Milton Drexler, E. Melvin Gindler and Charles C. Lumpkin in partial fulfillment of the requirements of the degree of Master of Science in Chemistry in June, 1952, and was presented in part at the 121st National Meeting of the American Chemical Society in Buffalo, N. Y., March 23–27, 1952; see Abstracts, p. 3K.

[2] For the first paper of this series see F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

[3] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[4] The second-order reaction of the *p*-nitrobenzenediazonium ion with bromide ion has been recently reported: E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).