was removed from the reaction mixture, leaving 13.3 g. of a thick brown oil. Benzoic acid (104 mg., 0.03% yield, $G$ = 0.009) was isolated by chromatography[8] and identified by direct comparison of the melting point and infrared spectrum of its *p*-bromophenacyl ester with those of authentic *p*-bromophenacyl benzoate.

Cyclohexane was similarly converted to cyclohexanecarboxylic acid (0.07% yield, $G$ = 0.02).

**Cyanation of Hydrocarbons by Hydrogen Cyanide. A. Benzene.**—A solution of 50 ml. of hydrogen cyanide (freshly distilled from phosphorus pentoxide) in 435 ml. of benzene was irradiated with a 500-watt beam of 2-Mev. electrons for 60 minutes under the conditions used in the formic acid experiments. Distillation of the reaction mixture through a six-inch Claisen still-head gave the following fractions boiling above benzene: I, 2.2 g., b.p. 24–75° (23 mm.), $n^{25}\mathrm{D}$ 1.5203; II, 0.4 g., b.p. about 88° (3 mm.), $n^{25}\mathrm{D}$ 1.5662; III, 9.7 g. of resin not volatile at 225° (3 mm.). Fraction II partly crystallized in ice. The solid portion of this fraction, weight 110 mg., was recrystallized from methanol and was identified as biphenyl by its melting point (68–69° alone or mixed with an authentic sample).

The infrared spectrum of fraction I indicated that it was benzonitrile of 90–95% purity. This corresponds to a 1.5% yield based on hydrogen cyanide ($G$ = 0.21). A weak band at 4.7 μ may have been caused by phenyl isocyanide.

In order to characterize fraction I further, 2.0 g. of it was refluxed for an hour with 75% sulfuric acid.[11] Under these conditions, benzonitrile and phenyl isocyanide should be converted to benzoic acid and aniline, respectively. Benzoic acid sublimed into the condenser during the reaction. After recrystallization from water it weighed 0.60 g. It melted at 121–123° alone or mixed with authentic benzoic acid and had the characteristic infrared spectrum of benzoic acid. The hydrolysate was diluted with water and extracted with chloroform. Titration of the extract indicated that it contained an additional 0.7 g. of benzoic acid.

The odor of fraction I suggested that it contained phenyl isocyanide. The presence of aniline in the hydrolysate was demonstrated as follows. The chloroform-extracted hydrolysate was made basic with 10% sodium hydroxide and distilled. The first 40 ml. of distillate was adjusted to *p*H 2 with hydrochloric acid, cooled in ice, and treated successively with 1.0 ml. of 0.5 $N$ sodium nitrite, 1.0 ml. of 0.5 $N$ sulfamic acid and 1.2 ml. of 0.5 $M$ ethanolic 2-naphthol, with 5-minute intervals between additions. The mixture was made basic with 10% sodium hydroxide, causing 0.052 g. of 1-phenylazo-2-naphthol to precipitate. After recrystallization from ethanol it melted at 132–133° alone or mixed with an authentic sample and had the same visible absorption spectrum as an authentic sample. Based on the amount of azo compound isolated, it appears that about 25 mg. of phenyl isocyanide was formed (0.03% yield based on hydrogen cyanide; $G$ = 0.004). No aniline could be detected in distillate subsequent to the first 40 ml.

B. **Toluene.**—The experiment was repeated with toluene in place of benzene. Distillation gave a series of fractions shown by ultraviolet and infrared spectroscopy to consist principally of bitolyls and the four tolunitrile isomers in the following amounts: *para*, 1.1 g.; *ortho*, 1.0 g.; *alpha*, 0.5 g.; *meta*, 0.3 g. The presence of the *p*- and *o*-isomers was further demonstrated by acid hydrolysis[11] of suitable fractions; *p*-toluic and *o*-toluic acid were isolated by fractional crystallization and identified by their melting points and infrared spectra. A small quantity of toluidines was detected in the hydrolysate by means of diazotization and coupling with 2-naphthol. The yield of tolunitriles, based on hydrogen cyanide, was 1.9% ($G$ = 0.27).

C. **Cyclohexane.**—Similar irradiation of a mixture of 425 ml. of cyclohexane and 50 ml. of hydrogen cyanide for 45 minutes gave 3.9 g. (1.2% yield, $G$ = 0.7) of bicyclohexyl (identified by infrared analysis) and 0.4 g. (0.3% yield, $G$ = 0.05) of cyclohexanecarbonitrile. The identity of the nitrile was established by its hydrolysis[11] to cyclohexanecarboxylic acid, isolated as the *p*-bromophenacyl ester.

**Dehydrogenative Coupling of Propionitrile.**—Propionitrile (550 g.) was placed in a stainless-steel pan 25.3 cm. long and 7.7 cm. wide covered with aluminum foil 0.03 mm. thick. A slow stream of nitrogen passed over the nitrile by means of openings at each end of the pan. The pan was placed in an ice-bath to maintain the temperature of the nitrile at 10–20° and was passed through a beam of 2-Mev. electrons 25 times, receiving 11 joules/cm.$^2$ at each pass. Unchanged propionitrile was removed at 100° (50 mm.), and the residue, 2.9 g. of thick dark oil, was stirred and refluxed with 18 ml. of 12 $N$ hydrochloric acid for five hours. The mixture was cooled to 25° and the aqueous portion was decanted from a little resin and evaporated nearly to dryness on a steam-bath. The residue was taken up in water and extracted with five 10-ml. portions of 2-butanone. The combined extracts were dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed on silicic acid[8] to give 114 mg. of a mixture of acids having the peak elution volume characteristic of α-methylglutaric acid and its isomers. Infrared analysis indicated that the mixture was principally α-methylglutaric acid and adipic acid in a 4:1 ratio, with possibly a few per cent. of α,α-dimethylsuccinic acid also present. Based on the amount of acids isolated, propionitrile was converted to a mixture of α-methylglutaronitrile and isomers in about 0.03% yield ($G$ = 0.18).

Similar irradiation of 10% aqueous propionitrile gave the same products in similar proportions; $G$ = 0.15. The mechanism in this experiment, as in the conversion of propionitrile to α-methylglutaronitrile and isomers by Fenton reagent,[12] may involve the attack of hydroxyl radicals on propionitrile.

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[11] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," fourth edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 258.

[12] D. D. Coffman, E. L. Jenner and R. D. Lipscomb, THIS JOURNAL, 80, 2864 (1958).

WILMINGTON, DEL.

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

# Diaryliodonium Salts. XIII. Salts in which the Cations Bear Carboxyl, Hydroxyl, Alkoxyl or Amino Groups[1,2]

BY F. MARSHALL BERINGER[3a] AND IRVING LILLIEN[3b]

RECEIVED APRIL 27, 1959

This paper describes the synthesis and some reactions of carboxy-, hydroxy-, alkoxy- and aminodiphenyliodonium salts and the products of attempted condensations of iodosobenzene with benzenes bearing functional groups.

As part of a program to investigate the electronic effects of the iodonium group in aromatic compounds, this paper reports the synthesis of carboxy-, hydroxy-, alkoxy- and amino-substituted diphenyliodonium salts. A later report will discuss the absorption spectra and acid–base properties of these salts.

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[1] This paper is taken from the dissertation of Irving Lillien, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] References to the recent literature of iodonium salts are given in article XII of this series: F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, in press.

[3] (a) Visiting Associate Professor, Yale University, 1958–1959; (b) Alfred P. Sloan Foundation Research Fellow, 1956–1959.

**Carboxydiphenyliodonium Salts and Their Derivatives.**—The three isomeric carboxydiphenyliodonium iodides have been prepared[4] by oxidation of the iodobenzoic acids with potassium persulfate in sulfuric acid followed by *in situ* condensation with benzene. Analytically pure samples of the 3- and 4-carboxydiphenyliodonium iodides could be obtained by recrystallization from alcohol, while attempts to recrystallize the 2-isomer led to a material with a high carbon analysis (loss of hydrogen iodide). However, pure material was obtained by washing the crude salt with water and organic solvents.

$$\begin{tikzcd}
IC_6H_4COOH \arrow[r, "K_2S_2O_8", "H_2SO_4"'] & (HO_3SO)_2IC_6H_4COOH \arrow[d, "C_6H_6"] \\
C_6H_5\overset{+}{I}C_6H_4CO_2^- & C_6H_5\overset{+}{I}C_6H_4COOH \arrow[l, "OH^-"']
\end{tikzcd}$$

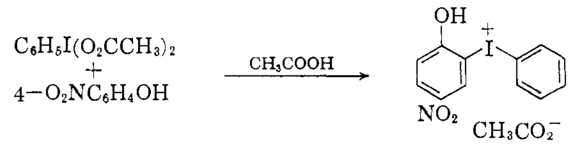
4-Carboxydiphenyliodonium iodide dissolved in aqueous base with the rapid formation of a white precipitate, formulated as the inner salt,[5] 4-$C_6H_5\overset{+}{I}C_6H_4CO_2^-$, on the basis of its mode of formation, high decomposition point, insolubility, analysis and infrared spectrum. The compound readily dissolved in concentrated sulfuric acid; dilution with water and addition of potassium iodide solution gave back the parent acid iodide.

2-Carboxydiphenyliodonium iodide gave similar reactions. The anhydro base, which held small amounts of sodium hydroxide non-stoichiometrically but tenaciously, was soluble in organic solvents, thus differing from the 4-betaine. It has been proposed[6] on the basis of evidence from polarography that the 2-carboxylate group reacts with neighboring iodine to form a 5-membered ring. 3-Carboxydiphenyliodonium iodide differs from the 2- and 4-isomers in that it does not give a precipitate with aqueous base.

While 4-carboxydiphenyliodonium iodide was readily esterified by hot methanol containing sulfuric acid and the 3-acid was esterified by methanol containing hydrogen chloride, the 2-acid was left unreacted by both procedures.

The 4-acid was converted *via* the acid chloride to the amide, which did not yield the 4-amine by the Hofmann reaction. Further, attempts to obtain amines from the acids by the Schmidt reaction[7a] gave only unchanged starting materials.[7b] This unreactivity may result from the inability of the acid to form an acyl cation or from the reluctance of the substituted phenyl group to migrate in concert with the loss of nitrogen.[7c]

**Hydroxydiphenyliodonium Salts.**—The only hydroxydiphenyliodonium salt heretofore reported[8] was prepared by the condensation of iodosobenzene diacetate with 4-nitrophenol in acetic acid.



In view of this result, and the numerous acid-catalyzed condensations of iodosobenzene and its derivatives reported from this Laboratory,[2,4,9] we attempted to prepare hydroxydiphenyliodonium salts by condensing iodosobenzene or iodosobenzene diacetate with phenol in the presence of acetic, phosphoric, trifluoroacetic and polyphosphoric acids and of boron trifluoride etherate. These attempts were uniformly unsuccessful; when an iodonium salt resulted, it had the diphenyliodonium cation.[10] The coupling of iodosobenzene in an acid (and probably reducing) medium to form diphenyliodonium cation has not been heretofore described.

The success of the condensation of iodosobenzene diacetate with 4-nitrophenol may be due in part to decreased susceptibility of the phenol to oxidation, resulting from the presence of the nitro group.

It has, however, been possible to prepare 4-hydroxydiphenyliodonium salts by two paths.[11] An unequivocal procedure applied the classic[12] synthesis to the condensation of iodoxybenzene with 4-iodosophenyl benzyl ether and gave the 4-benzyloxydiphenyliodonium cation. Cleavage of the ether linkage with hydrobromic acid gave the desired 4-hydroxydiphenyliodonium salt. The product so formed was identical[13] to that formed by hydrolysis of the condensation product of iodosobenzene and phenyl acetate[4] (see reaction above).

$$\begin{tikzcd}
\begin{array}{l}4\text{-}OIC_6H_4OCH_2C_6H_5\\ +\ C_6H_5IO_2\end{array} \arrow[r, "Ag_2O"] & 4\text{-}C_6H_5\overset{+}{I}C_6H_4OCH_2C_6H_5 \arrow[d, "HBr"] \\
C_6H_5IO + C_6H_5O\overset{O}{\overset{\|}{C}}CH_3 \arrow[r, "1,\ F_3CCOOH", "2,\ H_3O^+"'] & 4\text{-}C_6H_5\overset{+}{I}C_6H_4OH
\end{tikzcd}$$

**Aminodiphenyliodonium Salts.**—Attempts to condense aniline or N,N-dimethylaniline with

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[4] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, THIS JOURNAL, **81**, 342 (1959).

[5] Related inner salts also reported include 4-$C_6H_5\overset{+}{I}C_6H_4OCH_2CO_2^-$ and 4-$C_6H_5\overset{+}{I}C_6H_4OCH_2CH_2SO_3^-$: see F. M. Beringer and R. A. Falk, *ibid.*, **81**, 2997 (1959).

[6] H. E. Bachofner, F. M. Beringer and L. Meites, *ibid.*, **80**, 4274 (1958).

[7] (a) H. Wolff, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 307. (b) Compare the unreactivity of anthranilic acid and various pyridine- and quinolinecarboxylic acids: ref. 7a, p. 312. (c) For a discussion of mechanisms of this reaction see J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, p. 319. (d) For experimental procedures see the dissertation of Irving Lillien (ref. 1).

[8] A. R. Fox and K. H. Pausacker, *J. Chem. Soc.*, 295 (1957).

[9] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

[10] Attempts to oxidize iodobenzene with potassium persulfate in sulfuric acid and condense it *in situ* with phenol, aniline or acetanilide (*cf.* condensations in ref. 4) gave 4-iododiphenyliodonium salts. The first report of an iodonium salt described the production of the 4-iododiphenyliodonium cation upon treatment of iodosobenzene with concentrated sulfuric acid: C. Hartman and V. Meyer, *Ber.*, **27**, 426 (1894).

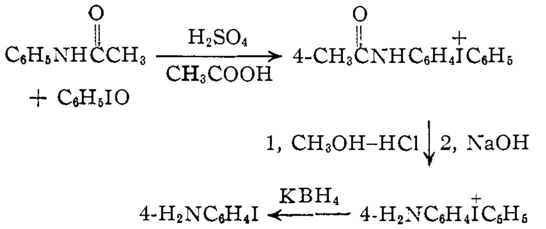
[11] Unsuccessful attempts to prepare 2- and 3-hydroxydiphenyliodonium salts are summarized in the Experimental section.

[12] C. Willgerodt, "Die Organischen Verbindungen mit mehrwertigen Jod," F. Enke, Stuttgart, Germany, 1914.

[13] The absorption spectra of substituted iodonium salts will be discussed in a forthcoming article.

iodosobenzene or iodosobenzene diacetate in the presence of acids (including phosphorus pentoxide or boron trifluoride etherate) were unsuccessful. With iodosobenzene and N,N-dimethylaniline in trifluoroacetic acid, there was oxidation–reduction, as shown by the formation of N,N,N′,N′-tetramethylbenzidine.

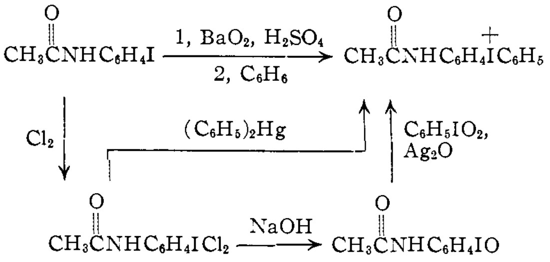
Iodosobenzene has been condensed[4] with acetanilide in mixed acetic and sulfuric acids to give the 4-acetamidodiphenyliodonium cation. The structure of this condensate has been shown by methanolysis to a 4-aminodiphenyliodonium salt, which on reduction with potassium borohydride gave, *inter alia*, 4-iodoaniline.[14]



In a series of related condensations the three isomeric iodoacetanilides were oxidized with barium peroxide in sulfuric acid and condensed with benzene to give acetamidodiphenyliodonium salts in 10–25% yields.[4,15] The aminodiphenyliodonium salts were obtained from these by solvolysis and neutralization.

Both the 2- and 3-aminodiphenyliodonium salts were obtained by the condensation of the iodosoacetanilides with iodoxybenzene in the presence of silver oxide[12,16] followed by methanolysis.

The preparation of the 4-isomer by this method[16] is made difficult by the instability of 4-iodosoacetanilide. A successful alternate synthesis used the reaction of 4-acetamidoiodosobenzene dichloride with diphenylmercury[17] to give 4-acetamidodiphenyliodonium chloride.



Ultraviolet and infrared spectra[13] of the isomeric aminodiphenyliodonium salts were different, while the spectra of samples of a given isomer prepared by various methods were identical.

4,4′-Diaminodiphenyliodonium iodide was prepared by reaction of acetanilide with sodium iodate in mixed sulfuric and acetic acids to give 4,4′-diacetamidodiphenyliodonium iodide,[4,9] followed by hydrolysis or methanolysis.

Investigation of the behavior of 3-amino-, 4-amino- and 4,4′-diaminodiphenyliodonium iodides on ascending paper chromatograms showed clear-cut separation of spots. Development gave spots of different colors for the 3- and 4-isomers. Details are included in the Experimental section.

**Acknowledgment.**—The authors wish to thank Robert A. Falk for the preparation of a sample of 4-hydroxydiphenyliodonium bromide from its acetyl derivative. We are indebted to the Alfred P. Sloan Foundation, Inc., for its generous support of this work. The hospitality of Yale University during the preparation of this manuscript is much appreciated.

## Experimental[18]

**Starting Materials.**—Iodobenzene, iodobenzoic acids, 2-iodophenol, 3-iodoanisole, 4-iodoacetanilide, iodonitrobenzenes, diphenylmercury and standard reagents were commercial products. Boron trifluoride etherate was redistilled before use. Polyphosphoric acid was obtained from the Victor Chemical Co. Iodosobenzene,[19] iodosobenzene diacetate,[20] iodoxybenzene,[21] 3-[22] and 4-iodophenol,[23] 2- and 3-iodoacetanilide[24] were prepared as described in the literature.

**Carboxydiphenyliodonium Salts and Derivatives. 2-, 3- and 4-Carboxydiphenyliodonium Iodide.**[25]—The preparation of 4-carboxydiphenyliodonium iodide has been reported.[4] Departures of the preparation of the 2-acid from this procedure follow. The reaction mixture was stirred for 24 hours after it reached room temperature. After dilution with water and clarification, the solution was treated with aqueous sodium bisulfite and potassium iodide. Trituration of the gummy precipitate with water transformed it into a tan powder. It was slurried with acetone, washed with ether and air-dried away from strong light. The yield of **2-carboxydiphenyliodonium iodide** was 44%. After being washed repeatedly with chloroform and ether and being dried overnight in a vacuum desiccator, a sample had a m.p. of 136–138° (if inserted at 100°) and 140–142° (if inserted at 130°).

Runs in which the crude salt was recrystallized from alcohol, in which it is fairly soluble (in contrast to the other isomers), gave products with high carbon analyses. This is possibly due to loss of hydrogen iodide with formation of betaine (*vide infra*).

**Betaine from 2-Acid (2-Phenyliodoniobenzoate).**—Treatment of 2-carboxydiphenyliodonium iodide with an excess of 5 *N* sodium hydroxide caused precipitation of an oil. This oil could be extracted with chloroform to yield, on concentration, a white powder which left a slight residue on combustion. Repeated recrystallizations from chloroform-ether and methanol–water gave a material with m.p. 229–230°.

*Anal.* Calcd. for $C_{13}H_9IO_2$: C, 48.15; H, 2.78. Found: C, 47.89; H, 2.84.

If the compound were examined after only one or two recrystallizations, it was found even then to leave an ignition

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[14] Compare the reaction of diphenyliodonium bromide with lithium aluminum hydride to give iodobenzene and benzene: F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2708 (1953).

[15] Similar reactions using iodonitrobenzenes and benzene or acetanilide gave nitro- or acetamidonitrodiphenyliodonium salts.[4] The latter have been hydrolyzed to 3- and 4-nitro-4′-aminodiphenyliodonium salts; see Experimental section.

[16] C. Willgerodt and W. Nägeli, *Ber.*, **40**, 4070 (1907).

[17] C. Willgerodt, *ibid.*, **30**, 56 (1897); **31**, 915 (1898).

[18] Unless otherwise indicated, melting points were taken in a capillary inserted at the temperature specified in a Hirshberg apparatus whose temperature was raised about 2–4° per minute. Since the majority of iodonium salts decompose rather than melt, physical state, sample size, rate of heating and temperature at which inserted can affect the reproducibility of these decomposition points. Melting points are uncorrected. Analyses were carried out by Dr. K. Ritter, Basel, Switzerland, and by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

[19] H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 482.

[20] C. Willgerodt, *Ber.*, **25**, 3494 (1892).

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

[22] E. Nölting and T. Stricker, *Ber.*, **20**, 3078 (1887).

[23] F. B. Dains and F. Eberly, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 355.

[24] A. Bayer, *Ber.*, **38**, 2760 (1905); W. Körner and K. Wender, *Gazz. chim. ital.*, **17**, 490 (1887).

[25] M.p.'s and analyses reported in ref. 4.

residue, and an analysis of one sample (recrystallized twice) suggested considerable retention of sodium hydroxide. The compound at this stage had a m.p. of 216–217°.

*Anal.* Calcd. for $C_{13}H_{10}INaO_3$: C, 42.85; H, 2.75; I, 34.90. Found: C, 39.84; H, 2.53; I, 35.34.

Alternatively, if 2-carboxydiphenyliodonium iodide were treated with a stoichiometric amount of aqueous sodium hydroxide, it quickly dissolved with the slow precipitation of a crystalline material which again, even after several recrystallizations from chloroform, contained non-combustible material, presumably sodium hydroxide or iodide. After recrystallization from hot water and then isopropyl alcohol the material still left a non-combustible residue. However, after treatment with hot 20% aqueous formic acid a material with a new crystalline form was produced. This material did not leave an ignition residue; it melted at 175° (inserted at 100°) with the loss of vapor, and resolidified to melt again at 226°. This material may be 2-carboxydiphenyliodonium formate, which loses formic acid at 175° to re-form the inner salt. Upon pyrolysis of the suspected formate, both iodobenzene and formic acid were identified as volatile products.

**Betaine from 4-Acid (4-Phenyliodoniobenzoate).**—Solution of 4-carboxydiphenyliodonium iodide in 5 *N* sodium hydroxide gave a colorless precipitate which was washed with water and air-dried. It was insoluble in common organic solvents, hot aqueous sodium hydroxide and hot concentrated hydrochloric acid but dissolved readily in concentrated sulfuric acid. This solution when diluted with water and treated with potassium iodide gave back 4-carboxydiphenyliodonium iodide. The inner salt was combustible, burning with a smoky yellow flame and leaving no residue. It sintered over a wide range, 210–220°, and did not melt completely up to 230°.

*Anal.* Calcd. for $C_{13}H_9IO_2$: C, 48.15; H, 2.78. Found: C, 48.07; H, 2.94.

**Methyl Ester of 4-Carboxydiphenyliodonium Iodide.**—A mixture of the acid with a large excess of methanol and a few drops of concentrated sulfuric acid was refluxed for 15 minutes. The solution was chilled, and the precipitate was collected, washed with ether and recrystallized twice from methanol. It was insoluble in dilute aqueous sodium hydroxide. **4-Carbomethoxydiphenyliodonium iodide** had a m.p. of 147–148° (inserted at 100°).

*Anal.* Calcd. for $C_{14}H_{12}I_2O_2$: C, 36.05; H, 2.58. Found: C, 35.97; H, 2.43.

**Methyl Ester of 3-Carboxydiphenyliodonium Iodide.**—A small amount of the acid in methanol was saturated with dry hydrogen chloride at 0° and kept one week at room temperature. After dilution with water, chilling and addition of potassium iodide solution, the precipitate was collected and recrystallized twice from methanol. The product was not soluble in dilute aqueous sodium hydroxide. **3-Carbomethoxydiphenyliodonium iodide** had a m.p. of 128–130° (inserted at 100°).

*Anal.* Calcd. for $C_{14}H_{12}I_2O_2$: C, 36.05; H, 2.58. Found: C, 36.02; H, 2.69.

**Amide of 4-Carboxydiphenyliodonium Iodide.**—Two grams of 4-carboxydiphenyliodonium iodide was heated under reflux for 30 minutes with 15 ml. of thionyl chloride. The chilled solution was slowly poured into 30 ml. of ice-cold ammonia, and the precipitate was collected, washed and recrystallized from methanol–water. White crystals, insoluble in aqueous base, were obtained which charred at 152–153° after sintering but did not melt completely. After recrystallization twice from methanol the light yellow product sintered from 142° up, decomposing at 195° (if inserted at 100°) and sintered at 155–158° (if inserted at 140°). 4-Iodobenzamide melts at 217°.[26]

*Anal.* Calcd. for $C_{13}H_{11}I_2NO$: C, 34.59; H, 2.44. Found: C, 34.58; H, 2.81.

**Methoxy-, Benzyloxy- and Hydroxydiphenyliodonium Salts. 3-Methoxydiphenyliodonium Iodide.**[27]—3-Iodoanisole (20 g., 85.5 mmoles) was chlorinated in a chilled chloroform–ether mixture. Chilling with Dry Ice was necessary to precipitate the dichloride, which was air-dried and weighed 15.7 g. (51.6 mmoles, 60%), m.p. 62–64°. It was hydrolyzed[19] with 13 g. of sodium carbonate and 35 ml. of 5 *N* sodium hydroxide to yield 7.3 g. (29.2 mmoles, 52%) of **3-methoxyiodosobenzene** after washing with water and acetone and drying in the vacuum oven at 50°. This material was shaken in an amber jar for 40 hours with 7 g. of iodoxybenzene,[21] a liter of water and silver oxide freshly precipitated from 15 g. of silver nitrate. After filtration and clarification of the resultant solution, addition of potassium iodide solution yielded 5 g. (11.4 mmoles, 39%) of **3-methoxydiphenyliodonium iodide**, m.p. 176–177° (Fisher–Johns apparatus, inserted at 100°).

*Anal.* Calcd. for $C_{13}H_{12}I_2O$: C, 35.61; H, 2.74. Found: C, 35.45; H, 2.56.

Prolonged treatment of refluxing methanolic solutions of the iodide and bromide salts with aqueous hydrobromic acid failed to cleave the methoxy group.

**4-Benzyloxydiphenyliodonium Iodide.**—While the dichloride of 4-iodophenol has been reported to decompose rapidly,[28] acyl and alkyl groups were shown to enhance the stability of the corresponding iododichlorides.[29]

4-Iodophenol[23] (22.8 g.) was converted to its benzyl ether[29] in 54% yield. This 4-iodophenyl benzyl ether (16.7 g., 54 mmoles) was chlorinated in about 50 ml. of dry chloroform for 40 minutes at ice-bath temperature. Addition of ether precipitated the **dichloride of 4-iodophenyl benzyl ether**, 17 g. (48 mmoles, 89%), m.p. 74–75°, after washing with ether and air-drying in the dark. It was hydrolyzed[19] by grinding in a mortar with ice, 12 g. of sodium carbonate and 34 ml. of 5 *N* sodium hydroxide. The product was filtered, washed with water, chloroform and ether, and air-dried. The yield of **4-benzyloxyiodosobenzene** was 14 g. (43 mmoles, 90%). The compound was shaken in an amber jar for 40 hours with 11 g. of iodoxybenzene,[21] a liter of water and silver oxide freshly precipitated from 20 g. of silver nitrate. After removal of solids the solution gave with potassium iodide solution a precipitate of **4-benzyloxydiphenyliodonium iodide** (6.9 g., 13.4 mmoles, 32%). A portion recrystallized from ethanol had a m.p. of 186–189° (inserted at 100°).

*Anal.* Calcd. for $C_{19}H_{16}I_2O$: C, 44.35; H, 3.11. Found: C, 44.45; H, 3.14.

**4-Hydroxydiphenyliodonium Bromide.**—4-Benzyloxydiphenyliodonium iodide (5.9 g.) was metathesized to the nitrate with ethanolic silver nitrate. After clarification and saturation of the refluxing solution with hydrogen chloride, it was evaporated to dryness. The crystalline residue had a m.p. of 208–211° and was identified as 4-benzyloxydiphenyliodonium chloride, indicating that no cleavage had occurred. This salt was refluxed for 16 hours in 100 ml. of methanol containing 30 ml. of 40% hydrobromic acid. Removal of solvent at atmospheric pressure allowed isolation of the crystalline residue, which upon analysis was found to be uncleaved 4-benzyloxydiphenyliodonium bromide, m.p. 170–174° (inserted at 100°). It was therefore refluxed again with 25 ml. of hydrobromic acid in 100 ml. of ethanol for 15 more hours. After removal of solvent under reduced pressure (benzyl bromide and benzyl ethyl ether were found in the distillate) the solid residue was dissolved in ethanol and precipitated with ether to yield 0.5 g. (1.3 mmoles, 11%) of **4-hydroxydiphenyliodonium bromide**, m.p. 170–174° (inserted at 130°).

*Anal.* Calcd. for $C_{12}H_{10}BrIO$: C, 38.19; H, 2.65. Found: C, 38.38; H, 2.77.

**Attempted Hydrogenolysis of 4-Benzyloxydiphenyliodonium Iodide.**—A solution of the salt (1 g.) in 100 ml. of ethanol containing 0.6 g. of 5% palladium-on-charcoal was shaken under 26 lb. pressure of hydrogen for one hour at room temperature; no uptake occurred. The temperature was increased to 50°, and hydrogenation was continued overnight. Workup of the resulting filtered solution showed complete destruction of the iodonium salt.

**Unsuccessful Attempt to Prepare a 4-Hydroxydiphenyliodonium Salt *via* Condensation with Phenol.**[30] **Reaction of Iodosobenzene and Phenol in Boron Trifluoride Etherate.**—In a flask equipped with a drying tube, thermometer and stirrer and previously swept with nitrogen were placed 15

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[26] I. Remsen and E. E. Reid, THIS JOURNAL, **21**, 289 (1899).

[27] For the preparation of 4-methoxydiphenyliodonium salts by a similar method see R. B. Sandin, M. Kulka and R. McReady, *ibid.*, **59**, 2014 (1937).

[28] S. Brazier and H. McCombie, *J. Chem. Soc.*, 101, 968 (1912).

[29] D. Matheson and H. McCombie, *ibid.*, 1103 (1931).

[30] For other experiments see the dissertation of Irving Lillien (ref. 1).

ml. of redistilled boron trifluoride etherate and 50 ml. of dry ligroin. This mixture was chilled to −30° and 11 g. (50 mmoles) of iodosobenzene and 10 g. of phenol were added rapidly. The mixture was stirred at −30 to −20° for 40 min., then at −10° for 30 min. and at temperatures increasing to ambient over two hours. After standing overnight, the mixture was poured onto ice, filtered after removal of the organic layer and clarified with charcoal. Addition of a solution of 10 g. of potassium iodide gave 7.15 g. of white powder which turned red at 155° but did not melt up to 210°. On thermal decomposition of a portion of this salt in diethylene glycol, iodobenzene distilled, and a crystalline residue remained in the solvent. This material, probably boric oxide, imparted a green color to the flame, did not burn, smoke or char, and melted at a very high temperature. The remainder of the iodonium salt was recrystallized from methanol (leaving a residue of boron oxide) and had a m.p. of 156–157°. It was not soluble in cold dilute sodium hydroxide; boiling decomposed it. Except for some band fusion in the 9–10 μ region its infrared spectrum was identical with that of diphenyliodonium iodide. This salt is therefore probably a diphenyliodonium salt with a complex anion, perhaps $IF_2^-$.

*Anal.* Calcd. for $C_{12}H_{10}F_2I_2$: C, 32.31; H, 2.24. Found: C, 32.29; H, 2.44.

**Unsuccessful Attempts to Prepare 2- and 3-Hydroxydiphenyliodonium Salts.**—2-Iodophenyl benzoate yielded a stable dichloride[31] which resisted hydrolysis and gave back the starting iodo compound on treatment with pyridine and water. The dichloride on treatment with diphenylmercury[17] produced only a trace of iodonium salt. The benzyl ether of 2 iodophenol gave an unstable dichloride as reported[31]; even rapid treatment with aqueous base produced only starting material. 2-Iodophenyl *p*-toluenesulfonate was chlorinated[31] and hydrolyzed[19] to the iodoso compound. On reaction with iodoxybenzene and silver oxide in water in the usual fashion, a salt was obtained after addition of potassium iodide which had the analysis of diphenyliodonium iodide and whose analysis remained unchanged after prolonged treatment with hydrochloric acid. Its identity was confirmed by decomposition and examination of its infrared spectrum. This salt may possibly have been formed through disproportionation of iodoxybenzene in lieu of its ability to react with the tosylate.

3-Iodophenol[22] was converted to its benzyl ether[32] which was chlorinated in the usual fashion. However, attempted hydrolysis with aqueous base produced an immediate tar from which the iodo compound was re-obtained. 3-Iodophenyl *p*-toluenesulfonate was prepared and chlorinated[32]; here also attempted hydrolysis with base produced only starting iodo compound. The dichloride was also treated with diphenylmercury without success.

**Aminodiphenyliodonium Salts and Derivatives. 2-Aminodiphenyliodonium Iodide *via* Condensation of 2-Iodoso-Acetanilide with Iodoxybenzene.**—2-Iodoacetanilide[24] (21.3 g., 81.6 mmoles) was chlorinated in chloroform–ether at ice-bath temperature to yield 19.95 g. (60.5 mmoles, 74%) of **2-acetamidoiodosobenzene dichloride**, m.p. 77°. This was ground in a mortar with ice and 12 g. of sodium carbonate for an hour and allowed to stand overnight. After drying in the air, the coral-colored product (11.8 g.) was rinsed with acetone to give 8 g. (29 mmoles, 48%) of light yellow **2-iodosoacetanilide**. The compound was shaken for 20 hours in an amber jar with 6.85 g. of iodoxybenzene, a liter of water, and silver oxide freshly precipitated from 20 g. of silver nitrate. After filtration of the silver oxide, which was washed with water, the solution and washings were combined, clarified and treated with potassium iodide solution. The precipitate was immediately refluxed with 100 ml. of methanol containing 20 ml. of trifluoroacetic acid and several drops of sulfuric acid for three hours. The solution was cooled, filtered and poured into water, and potassium iodide and sodium hydroxide solutions were added. The precipitate was recrystallized from methanol to give 2 g. (4.7 mmoles, 16%) of fluffy yellow crystals of **2-aminodiphenyliodonium iodide**, m.p. 164–166° (inserted at 100°).

*Anal.* Calcd. for $C_{12}H_{11}I_2N$: C, 34.04; H, 2.60. Found: C, 34.26; H, 2.70.

**3-Aminodiphenyliodonium Iodide[33] *via* Condensation of 3-Iodoacetanilide[24] with Benzene.**—This synthesis is similar to that for the 4-isomer (see below); the reaction was run at −10° during the barium peroxide addition, 0° for one hour after the benzene addition and 60 hours at room temperature. The yield of **3-acetamidodiphenyliodonium iodide** was 40%; it had a m.p. of 138–140° (inserted at 100°). A solution of 3 g. of this salt in 40 ml. of methanol and 3 ml. of concentrated hydrochloric acid was boiled for one hour, cooled and diluted with ether. The gummy precipitate was removed and dissolved in 50% sulfuric acid. The solution was clarified and potassium iodide solution added, giving a precipitate. The solution was diluted with more water, and the gummy precipitate was dissolved by gentle warming. The solution was clarified again and neutralized with dilute sodium hydroxide. The tan precipitate was recrystallized from methanol, giving 1.5 g. (3.5 mmoles, 55%) of **3-aminodiphenyliodonium iodide** as fluffy yellowish crystals, m.p. 163–164° (inserted at 100°).

*Anal.* Calcd. for $C_{12}H_{11}I_2N$: C, 34.04; H, 2.60. Found: C, 34.27; H, 2.67.

**3-Aminodiphenyliodonium Nitrate *via* Condensation of 3-Iodosoacetanilide with Iodoxybenzene.**—3-Iodoacetanilide (13.1 g., 50 mmoles) was chlorinated in a chloroform–ether mixture at ice-bath temperature to yield 14 g. (42 mmoles, 84%) of yellow **3-acetamidoiodosobenzene dichloride**, m.p. 85–90°.[34] This was hydrolyzed[19] by grinding in a mortar with ice, 11 g. of sodium carbonate and 6.15 g. of dissolved sodium hydroxide. After several hours of treatment the product was collected, washed, air-dried and washed with chloroform to give 9.2 g. (33 mmoles, 78%) of **3-iodosoacetanilide**, m.p. 75°. It was shaken for 20 hours in an amber jar with 7.9 g. of iodoxybenzene, a liter of water and silver oxide freshly precipitated from 20 g. of silver nitrate. After filtration of the silver oxide, which was washed with water, the solution and washings were combined, clarified and treated with sulfur dioxide until the color of the precipitated tar became light. It was collected, dissolved in hot methanol and heated on the steam-bath while hydrogen chloride gas was passed in until the solution was saturated. The solution was concentrated to about 10 ml. under reduced pressure. Some methanol was added, and the solution was treated with charcoal several times and concentrated to a few ml. of sirup. Ether was added, and the solution was chilled. The product was washed with ether, dried and recrystallized from methanol to give 5 g. (10.9 mmoles, 33%) of **3-aminodiphenyliodonium chloride hydrochloride** as white crystals, m.p. 153–155° (inserted at 100°). The salt was dissolved in a solution of sodium hydroxide and treated with charcoal and then potassium iodide solution. The precipitate was washed, dried and dissolved in methanol. Alcoholic silver nitrate was carefully added dropwise until the metathesis was complete. The filtered solution was decolorized and evaporated under reduced pressure. The yellow salt was recrystallized from a mixture of methanol–chloroform–ether to give 3 g. (8.4 mmoles, 77%) of **3-aminodiphenyliodonium nitrate**, m.p. 142–145° (inserted at 100°).

*Anal.* Calcd. for $C_{12}H_{11}IN_2O_3$: C, 40.22; H, 3.07. Found: C, 40.41; H, 2.95.

**4-Aminodiphenyliodonium Salts *via* Condensation of Iodosobenzene with Acetanilide.**[35]—Acetanilide (33.8 g., 0.25 mole) in 125 ml. of concentrated sulfuric acid, 100 ml. of glacial acetic acid and 25 ml. of acetic anhydride at −20° was treated with 27.5 g. (0.125 mole) of iodosobenzene added portionwise. The mixture was stirred at −20 to −10° (3 hr.), at 5° (2 hr.) and at room temperature (22 hr.). Hydrolysis, clarification and addition of potassium iodide solution formed a viscous gum which on trituration in the mother liquor gave 27.3 g. (58.8 mmoles, 47%) of yellow crude **4-acetamidodiphenyliodonium iodide**. Metathesis of the salt with silver nitrate in hot methanol gave 13.3 g. (33.3 mmoles, 57%) of brownish crude **4-acetamidodiphenyliodonium nitrate**. An ethanolic solution of this material

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[31] S. Buchan and H. McCombie, *J. Chem. Soc.*, 137 (1931).

[32] S. Buchan and H. McCombie, *ibid.*, 2857 (1932).

[33] The synthesis of the acetamide has been previously reported without details; see ref. 4.

[34] Reported m.p. 66°; C. Willgerodt and E. Wikander, *Ber.*, **40**, 4066 (1907).

[35] (a) This procedure varies from that reported in ref. 4. (b) When the condensation of iodosobenzene with acetanilide was attempted in sulfuric acid, only 4-iododiphenyliodonium salt could be isolated.

TABLE I

PAPER CHROMATOGRAPHY OF AMINODIPHENYLIODONIUM IODIDES

| Solvent$^a$ | | Time$^b$ | Temp., °C. | $R_f$'s and $R_f$ ratios | | |
|---|---|---|---|---|---|---|
| | | | | 4,4'-Diamine | 3-Amine | 4-Amine |
| 1, Benzene | 3.5 | 235 | 23 | 0.602(1) | 0.670(1.11) | 0.685(1.14) |
| Methanol | 3.0 | | | | | |
| 1-Butanol | 2.5 | | | | | |
| Water | 1.0 | | | | | |
| 2, Benzene | 8.0 | 365 | 19 | .126(1) | .245(1.94) | .258(2.05) |
| Methanol | 3.0 | 280 | 21 | .139(1) | .250(1.80) | .285(2.05) |
| 1-Butanol | 6.0 | | | | | |
| Water | 1.0 | | | | | |
| 3, Benzene | 3.5 | 290 | 21 | .503(1) | .552(1.10) | .576(1.15) |
| Methanol | 2.0 | | | | | |
| 1-Butanol | 2.0 | | | | | |
| Pyridine | 2.0 | | | | | |
| Water | 1.3 | | | | | |
| 4, Methanol | 1.0 | 150 | 20 | $^d$ | .697(1) | .706(1.02) |
| Water | 1.0 | | | | | |

$^a$ Parts by volume. $^b$ Minutes. $^c$ Ratios with diamine value as denominator are given in parentheses. $^d$ *p*-Nitroaniline reference; value 0.926 (1.33).

saturated with hydrogen chloride was boiled for 1.5 hr. The precipitate of crude **4-aminodiphenyliodonium chloride hydrochloride** (8 g., 21.8 mmoles, 65%) was dissolved in water and neutralized. The precipitate from the chilled solution was washed and dried to give 2.6 g. (7.8 mmoles, 36%) of **4-aminodiphenyliodonium chloride**, m.p. 181–183° (inserted at 100°) after recrystallization from methanol.

*Anal*. Calcd. for $C_{12}H_{11}ClIN$: C, 43.44; H, 3.32. Found: C, 43.57; H, 3.63.

The residual water solution was treated with potassium iodide. The precipitate was recrystallized from methanol to give 3.8 g. (9 mmoles, 41%) of **4-aminodiphenyliodonium iodide**, m.p. 176–178°[36] (inserted at 100°).

*Anal*. Calcd. for $C_{12}H_{11}I_2N$: C, 34.04; H, 2.60. Found: C, 34.08; H, 2.67.

Both salts were easily soluble in dilute acid, from which they could be reprecipitated by neutralization.

A solution of 1 g. of 4-aminodiphenyliodonium iodide in methanol–water containing an excess of potassium borohydride was heated on the steam-bath until methanol was removed. Further heating revealed the presence of iodobenzene (identified by refractive index and odor) which distilled with steam. The residual suspension was cooled and extracted with ether. The extract was dried and concentrated. The brown tar remaining was extracted hot with light petroleum ether, which deposited 4-iodoaniline as long white needles, m.p. and mixed m.p. 67–68°.

**4-Aminodiphenyliodonium Iodide**[33] ***via* Condensation of 4-Iodoacetanilide with Benzene.**—To 4-iodoacetanilide (13.1 g., 50 mmoles) dissolved in 100 ml. of sulfuric acid there was added 50 ml. of dry benzene. With efficient stirring, and while maintaining the temperature below 20° by external cooling when necessary, 8.5 g. (50 mmoles) of barium peroxide was added portionwise. Stirring was continued for 16 hours. After hydrolysis and clarification of the water solution the addition of potassium iodide solution produced a sticky, tarry precipitate, which solidified on trituration with the mother liquor. Washing and air-drying gave 5.1 g. (11 mmoles, 22%) of **4-acetamidodiphenyliodonium iodide**, m.p. 160–163° (inserted at 100°) after crystallization from methanol–ether.[37]

*Anal*. Calcd. for $C_{14}H_{13}I_2NO$: C, 36.13; H, 2.79. Found: C, 36.12; H, 2.87.

A solution of 4 g. (8.6 mmoles) of the amide in 40 ml. of methanol and 4 ml. of concentrated hydrochloric acid was refluxed for one hour, chilled and diluted with ether. The precipitate was added to 50 ml. of 50% sulfuric acid. After removal of insoluble material the solution was decolorized and diluted with 100 ml. of warm water. Aqueous potassium iodide was added, followed by base. The precipitate was recrystallized from methanol to give 2.8 g. (6.6 mmoles, 77%) of 4-aminodiphenyliodonium iodide, m.p. 188–190°[36] (Fisher–Johns apparatus, inserted at 145°).

*Anal*. Calcd. for $C_{12}H_{11}I_2N$: C, 34.04; H, 2.60. Found: C, 34.32; H, 2.47.

**4-Aminodiphenyliodonium Nitrate *via* Condensation of 4-Acetamidoiodosobenzene Dichloride with Diphenylmercury.**—4-Iodoacetanilide (40 g., 153 mmoles) was chlorinated in an acetic acid–chloroform mixture at ice-bath temperature. After washing the precipitate with ether and air-drying, 49.2 g. (149 mmoles, 97%) of **4-acetamidoiodosobenzene dichloride** was obtained. Twenty grams of this product together with 21.4 g. of diphenylmercury (both 60 mmoles) were mixed in 500 ml. of water and stirred vigorously at 40–50° for 12 hours. The pink precipitate was collected and boiled with water; this extract was combined with the main solution. After decolorization of the solution, it was treated with potassium iodide solution. The crude precipitate was recrystallized from methanol after being washed with sodium bisulfite solution, giving 2.72 g. (5.8 mmoles, 10%) of crude yellow **4-acetamidodiphenyliodonium iodide**, m.p. 168–170° (inserted at 100°).[37] This salt was dissolved in a minimum of boiling ethanol and treated dropwise with 1.02 g. of silver nitrate in ethanol. The resulting solution, after being filtered and clarified, was evaporated almost to dryness, diluted with ether and chilled, giving crude brown crystals. These were recrystallized from chloroform–alcohol with the addition of ether to give 1.63 g. (4.1 mmoles, 70%) of tan crystals of **4-acetamidodiphenyliodonium nitrate**, m.p. 185–190° (inserted at 100°, sintered at 140°).

*Anal*. Calcd. for $C_{14}H_{13}IN_2O_4$: C, 42.00; H, 3.25. Found: C, 42.26; H, 3.69.

A solution of the salt in 25 ml. of ethanolic hydrogen chloride was refluxed for 1.5 hours. After the alcohol was removed under reduced pressure, the crystals were washed repeatedly with ether and dried. The beautifully crystalline **4-aminodiphenyliodonium chloride hydrochloride** melted at 170–174° (inserted at 100°, sintered over wide range). This salt was neutralized and converted to the iodide, thence to the nitrate which was recrystallized several times from chloroform–methanol and 2-propanol–ethanol–ether to give 0.8 g. (2.2 mmoles, 55%) of **4-aminodiphenyliodonium nitrate**, m.p. 128–130° (inserted at 100°).

*Anal*. Calcd. for $C_{12}H_{11}IN_2O_3$: C, 40.22; H, 3.07. Found: C, 40.41; H, 3.09.

**4,4'-Diaminodiphenyliodonium Iodide.**—A solution of 4,4'-diacetamidodiphenyliodonium iodide[4,9] (10 g., 19.1 mmoles) in 100 ml. of methanol and 10 ml. of concentrated hydrochloric acid was refluxed for one hour, cooled and diluted with ether. The precipitated salt was removed and dissolved in 50% sulfuric acid. After treatment with charcoal, potassium iodide and then base were added. The precipitate was recrystallized from methanol to give 3.0 g. (6.8 mmoles, 36%) of **4,4'-diaminodiphenyliodonium iodide**, m.p. 170–177° (inserted at 100°), 187–198° (inserted at 180°).

*Anal*. Calcd. for $C_{12}H_{12}I_2N_2$: C, 32.88; H, 2.74. Found: C, 33.00; H, 2.89.

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(36) Reported m.p. 164°; see ref. 16.

(37) Reported m.p. 174°; see ref. 16.

**Paper Chromatography of Aminodiphenyliodonium Salts.**—Ascending paper chromatograms of the 3- and 4-amino- and 4,4′-diaminodiphenyliodonium salts (applied from freshly prepared methanol solutions) were developed by diazotization and coupling with β-naphthol. The same isomers from different synthetic sources gave the same values; see Table I.

**4-Amino-3′-nitrodiphenyliodonium Nitrate[33] *via* Condensation of 3-Iodonitrobenzene with Acetanilide.**—3-Iodonitrobenzene (20 g., 80 mmoles) dissolved in 200 ml. of concentrated sulfuric acid was treated at room temperature, with external cooling when necessary, with 21.6 g. (80 mmoles) of potassium persulfate in small portions. After 20 minutes a solution of 13.5 g. of acetanilide in 100 ml. of sulfuric acid, 50 ml. of acetic acid and 25 ml. of acetic anhydride was added at once with cooling. The mixture was stirred at 0° for 48 hours. After hydrolysis, clarification and addition of potassium iodide solution, the resulting gelatinous precipitate was difficult to filter and dry. Boiling with methanol, in which the precipitate was quite insoluble, gave 28.1 g. (55 mmoles, 69%) of **4-acetamido-3′-nitrodiphenyliodonium iodide** in a purer state; it had a m.p. of 167° (inserted at 110°), 172–173° (inserted at 160°).

*Anal.* Calcd. for $C_{14}H_{12}I_2N_2O_3$: C, 32.94; H, 2.35. Found: C, 33.34; H, 2.49.

The iodide was metathesized to the nitrate[38] by addition of a solution of 9.35 g. (55 mmoles) of silver nitrate in methanol to a suspension of the salt in boiling methanol. After filtration, the resulting solution was clarified and evaporated under reduced pressure to give 11.3 g. (25.4 mmoles, 46%) of crude iodonium nitrate which was recrystallized from ethanol–chloroform to yield 8 g. (18 mmoles, 33%) of light tan **4-acetamido-3′-nitrodiphenyliodonium nitrate**. Anhydrous hydrogen chloride was passed into boiling ethanol containing these crystals for 30 min., giving a white precipitate. Reflux was continued for three hours. The precipitate was dissolved in water and neutralized with sodium hydroxide. The tar which formed was dissolved in hot methanol. Water was added to the point of cloudiness, followed by potassium iodide solution. The precipitate was washed and metathesized in methanol by dropwise addition of alcoholic silver nitrate. The resulting solution was clarified, concentrated under reduced pressure and diluted with ether. The crude salt was recrystallized from chloroform–methanol to give 1.5 g. (3.7 mmoles, 21%) of yellow **4-amino-3′-nitrodiphenyliodonium nitrate**, m.p. 134–138° (inserted at 105°).

*Anal.* Calcd. for $C_{12}H_{10}IN_3O_5$: C, 35.88; H, 2.48. Found: C, 36.0; H, 2.36.

**4-Amino-4′-nitrodiphenyliodonium Iodide[32] *via* Condensation of 4-iodonitrobenzene with Acetanilide.**—The procedure and workup were similar to those for the 3-isomer (see above). However, due to the difficulty of dissolving 4-iodonitrobenzene in sulfuric acid, the solvent used was 100 ml. each of sulfuric and fuming sulfuric acids, in which it easily dissolved. The crude **4-acetamido-4′-nitrodiphenyliodonium iodide** weighed 25.75 g. (50.4 mmoles, 63%). A sample recrystallized from methanol–Cellosolve and washed with ether had a m.p. of 125–130° (inserted at 105°; sintered over wide range). A portion was metathesized to the nitrate with alcoholic silver nitrate and recrystallized from methanol–water to give **4-acetamido-4′-nitrodiphenyliodonium nitrate** as light yellow crystals, m.p. 150–153° (inserted at 100°).

*Anal.* Calcd. for $C_{14}H_{12}IN_3O_6$: C, 37.75; H, 2.69. Found: C, 37.62; H, 2.66.

The 4-acetamido-4′-nitrodiphenyliodonium salts were considerably less stable than those of the 3-nitro isomer, and both the iodide and nitrate decomposed when solvolysis by reflux with alcoholic hydrogen chloride was attempted. However, the following method was successful in low yield. Fifteen grams (28.6 mmoles) of 4-acetamido-4′-nitrodiphenyliodonium iodide in 100 ml. of methanol and 15 ml. of concentrated hydrochloric acid was refluxed for 15 minutes. The solution was chilled and diluted with ether, and the precipitate was removed and dissolved in 50% sulfuric acid. The solution was clarified and treated with potassium iodide solution. A precipitate, presumably unhydrolyzed amide, was removed. The solution was neutralized with sodium hydroxide, and the precipitate was removed, washed and air-dried. The acid-insoluble precipitate above was retreated in the same manner as the original amide, a further crop of amine salt being obtained. (The production of 4-iodonitrobenzene indicated decomposition of the iodonium salt.) The crude amine was recrystallized from methanol to give only 0.4 g. (0.85 mmole, 3%) of **4-amino-4′-nitrodiphenyliodonium iodide** as bright gold-yellow crystals, m.p. 147–149° (inserted at 100°), 153–154° (inserted at 145°).

*Anal.* Calcd. for $C_{12}H_{10}I_2N_2O_2$: C, 30.51; H, 2.12. Found: C, 30.52; H, 2.07.

**Unsuccessful Attempts to Condense Iodosobenzene with Amines and Amides.[30] Reaction of Iodosobenzene with N,N-Dimethylaniline in Boron Trifluoride Etherate.**—The reaction was conducted in the same manner as the analogous reaction with phenol, with 7.6 g. (50 mmoles) of N,N-dimethylaniline in place of the phenol, and gave 5 g. of an apparently identical salt. It was insoluble in dilute hydrochloric acid or sodium hydroxide. A sodium fusion test for nitrogen was negative. Further experiments verified that the salt had a diphenyliodonium cation and a complex anion containing boron.

**Reaction of Iodosobenzene with N,N-Dimethylaniline with Phosphorus Pentoxide.**—To 50 ml. of dry Skellysolve A in a flask equipped with an efficient stirrer and a drying tube there were added 11 g. (50 mmoles) of iodosobenzene and 5 g. of phosphorus pentoxide at 0°. Vigorous stirring was maintained overnight at 0–10°. Hydrolysis and the usual workup produced only **diphenyliodonium iodide**. Its infrared spectrum was superimposable on that of authentic material.

*Anal.* Calcd. for $C_{12}H_{10}I_2$: C, 35.29; H, 2.45. Found: C, 35.46; H, 2.59.

**Reaction of Iodosobenzene with N,N-Dimethylaniline in Trifluoroacetic Acid.**—To 30 ml. of trifluoroacetic acid and 10 g. of N,N-dimethylaniline (82.5 mmoles) kept at −20° was added slowly and with stirring 11 g. (50 mmoles) of finely-powdered iodosobenzene over a period of 45 minutes. Small amounts of solvent were used to wash down the walls of the flask. The mixture was stirred at −10 to −20° for one hour and then for 24 hours at room temperature, after which it was poured onto ice, extracted with ether and clarified. Neutralization of the aqueous solution gave 1.3 g. (5.4 mmoles, 11%) of crude N,N,N′,N′-tetramethylbenzidine, m.p. 193–194°. Crystallization from methanol raised the m.p. to 196–197°, reported[39] m.p. 197°. The monomethiodide after two recrystallizations from ethanol had a m.p. of 263–264°, reported[40] m.p. 263°.

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[38] Several attempts to hydrolyze the iodide salt directly before conversion to the nitrate met with no success, probably because of its extreme insolubility.

[39] F. Ullman and P. Dieterle, *Ber.*, **37**, 29 (1904).

[40] W. Michler and S. Pattinson, *ibid.*, **14**, 2163 (1881).