evaporated to dryness *in vacuo* to yield 6.0 g. (71%) of crude **3-nitrodiphenyliodonium fluoride**. This was recrystallized from a mixture of alcohol and ether to give a microcrystalline product, m.p. 120–124° dec. A product of greater purity was obtained by shaking the bromide in aqueous suspension with excess silver oxide for 1–2 hr., followed by filtration and neutralization with 5% hydrofluoric acid. Evaporation to dryness *in vacuo* gave material of m.p. 143–146° dec.

3-Nitro-4'-methoxydiphenyl Ether.—A solution of 1.0 g. of *p*-methoxyphenol in 50 ml. of 0.1 *M* sodium hydroxide was shaken with 1.95 g. (3.80 mmoles) of 3-nitro-4'-methoxydiphenyliodonium tosylate. The oil which formed was extracted with methylene chloride, and shaken with 5% sodium hydroxide and with water. The solvent was evaporated and the residue flash distilled at 1 mm. The fraction collected below 100° was identified as *p*-iodoanisole, 0.74 g. (83%). Above 150°, a yellow oil distilled which solidified on cooling. Recrystallization from aqueous methanol gave 0.53 g. (57%) of 3-nitro-4'-methoxydiphenyl ether, m.p. 73–74°.

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.81; H, 4.61; N, 5.56.

3,3'-Dinitrodiphenyl Ether.—A solution of 1.0 g. of *m*-nitrophenol in 50 ml. of 0.1 *M* sodium hydroxide was shaken with 2.0 g. (3.9 mmoles) of 3-nitro-4'-methoxydiphenyliodonium tosylate. The oil which formed was extracted as described in the preparation of 3-nitro-4'-methoxydiphenyl ether. Distillation at 1 mm. gave 0.85 g. (93%) of *p*-iodoanisole, and at 150–200° there distilled an oil which crystallyzed at room temperature. Recrystallization from aqueous ethanol gave pale yellow needles of 3,3'-dinitrodiphenyl ether, 0.54 g. (50%), m.p. 124–125°.

Anal. Calcd. for $C_{12}H_8N_2O_5$: C, 55.49; H, 3.09; N, 10.77. Found: C, 55.60; H, 3.16; N, 10.71.

Isolation of Products from Hydrolysis.—The products were extracted continuously from aqueous solution with ether. Unreacted iodonium salt was precipitated from aqueous solution as the bromide. Phenols were separated from neutral products by shaking the ether extracts with 5% sodium hydroxide solution. The basic extracts were acidified and continuously extracted with ether. In initial runs, the ether was evaporated and the products in the residue were separated by fractionation through a Holzmann column and identified as the pure compounds. In subsequent runs, the products were flash distilled at 1 mm., and the composition of the distillate was determined by means of infrared analysis. The ether extracts of neutral products were worked up in the same way as the acidic extracts; the products were similarly identified by separation into the pure compounds and the composition was determined by infrared analysis. In the case of 3-methyldiphenyliodonium tosylate the composition of the neutral products was found by the method of refractive indices. In the hydrolysis of 3-nitrodiphenyliodonium fluoride and 3-nitro-4'-methoxydiphenyliodonium tosylate, the phenols were not equimolar with the iodo compounds. Additional high boiling neutral products were observed which were identified from their infrared spectra as diaryl ethers. Hydrolysis in the presence of fluoroboric or *p*-toluenesulfonic acids considerably reduced the amount of ether formation. The ethers from the hydrolysis of 3-nitro-4'-methoxydiphenyl iodonium tosylate were identified as 3-nitro-4'-methoxy- and 3,3'-dinitrodiphenyl ethers.

Kinetic Experiments.—The water employed in the kinetic runs was doubly-distilled. The dioxane was purified according to Fieser[18]; 95% ethanol was fractionally distilled before use. Reagent grade chemicals, *p*-toluenesulfonic acid, cupric chloride and cuproin were used without further purification. Aqueous solvents were prepared by mixing equal volumes of water and the organic solvent (dioxane or ethanol) at 25°. Sodium *p*-toluenesulfonate solutions were prepared by neutralization of standard *p*-toluenesulfonic acid with standard sodium hydroxide, and then dilution to the required volume.

Ten-milliliter portions of a standard iodonium salt solution were sealed in Pyrex test-tubes and immersed in an oil-bath maintained at 100.1 ± 0.05°. Tubes were withdrawn at various intervals and cooled. The contents were titrated with 0.1 *N* sodium hydroxide from a 10-ml. microburet using brom cresol green–methyl red indicator.[19]

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[19] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," revised ed., The Macmillan Co., New York, N. Y., 1943, p. 451.

PASADENA, CALIF.

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

Diaryliodonium Salts. IX. The Synthesis of Substituted Diphenyliodonium Salts[1]

BY F. MARSHALL BERINGER, ROBERT A. FALK, MARILYN KARNIOL, IRVING LILLIEN, GIULIO MASULLO, MARVIN MAUSNER AND ERWIN SOMMER

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This paper reports the synthesis of numerous diphenyliodonium salts bearing nitro, halogeno, methanesulfonyl, carboxyl alkyl, cycloalkyl, acetoxyl, acetamido, succinimido and methoxyl substituents.

The first paper[2] of this series surveyed the synthesis of diphenyliodonium salts and reported improved methods. These methods have been used and extended in the present work to prepare diphenyliodonium salts bearing nitro,[3] halogeno,[4-7] methanesulfonyl, carboxyl, alkyl,[8-12] cycloalkyl acetoxy, acetamido,[13,14] succinimido and methoxy[15,16] substituents. The methods are listed below and then discussed in connection with the experimental results.

(A) Coupling of two aromatic compounds with iodyl sulfate in sulfuric acid (Table I)

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[1] This paper is taken from the Ph.D. dissertations of Robert A. Falk, Irving Lillien and Marvin Mausner and from the M.S. theses of Marilyn Karniol, Giulio Masullo and Erwin Sommer; see also Acknowledgments. Irving Lillien was an Alfred P. Sloan Foundation Fellow, 1956–1959.

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TABLE I

SYMMETRICAL DIPHENYLIODONIUM SALTS BY REACTION A[a,b]

Substituents	Anion	M.p., °C.	Solvent	%	Eq.	T, °C. (hr.)	Ref.
None	Br	208–209	......	72	F	5–10 (2)	2*[c]
		209	Methanol	65[d]	G	0–5 (1), 20 (21)	[c]
3,3'-$(NO_2)_2$	{ HSO_4	165–167[e]	Water	25	F	10 (2), 20 (144)	2*
	{ Br	178–179	......	42			2*, V
	{ HSO_4[f]	193–194[e]	Methanol	39	F	10 (2), 20 (144)	V
	{ Cl	217[e]	Water–DMF	24			
	{ HSO_4	194–195[e]	Methanol	54	F	10 (2), 20 (24),	Exptl.
	{ Br	177–178	......	17		45 (36)	V, exptl.
3,3'-$(COOH)_2$	I	154–156[g]	Methanol	53	F	5–10 (8), 20 (15)	2*
4,4'-F_2	Cl[h]	232–233	Methanol	65[d]	G	5–10 (1), 20 (45)	
	Br[i]	226–227	Methanol	84[d]			
4,4'-Cl_2	{ HSO_4	190	Methanol	60	G	5 (1), 20 (12)	18, exptl.
	{ Cl	211[j]	Acetonitrile, then DMF	7		45 (2)	4, V, exptl.
	Br	204–205	Methanol	91	F	15 (2), 20 (48)	4, V
	I	171	Methanol	68	F	15 (2), 20 (48)	4, V
4,4'-Br_2	{ HSO_4[k]	203	Ethanol–ether	62[d]	G	5 (1), 20 (24)	5, V
	{ Cl[l]	208[m]	DMF-methanol	19[d]			
4,4'-I_2	Br[n]	198–199	Formic acid–acetic acid	71[d,o]	G	5 (1), 20 (68)	
2,2'-$(CH_3O)_2$-5,5'-$(NO_2)_2$	{ HSO_4	211–214	......	46	F	5 (3), 20 (33)	
	{ Br	206	......	7			
2,2'-$(CH_3)_2$-5,5'-$(CH_3SO_2)_2$	Cl[p]	152–153	Water	32	F	Both: 5 (1)	
		153–155	Water	34	G	20 (24), 50 (3)	

[a] Headings of Tables I–V: Salts paired with braces were obtained from the same reaction mixture; the yields are additive. The heading Ref. signifies another source of information on this material—Tables (Roman numerals), footnotes in text (arabic numerals), footnote in same table (small letter), Experimental section (Exptl.). The asterisk signifies that the data are those of the reference and are included for comparison. Each melting point is the highest observed for the salt prepared in this way and may be crude or, if solvent is given, for recrystallized material; solvent abbreviations: DMF (dimethylformamide), DMS (dimethyl sulfoxide). Yields are calculated on unrecrystallized material unless otherwise specified. The heading Eq. refers to a relevant preparative equation in text. Ratio refers to the mole ratio of reactants and is specifically defined in other tables. Reaction conditions are those for the condensation reaction; temperatures are followed by the number of hours, in parentheses. [b] See equation in text and details in Experimental section. [c] M.p. of 210° reported by M. O. Forster and J. H. Schaeppi, *J. Chem. Soc.*, **101**, 382 (1912). [d] Yield after one crystallization. [e] M.p.'s reported (ref. 3): HSO_4^-, 168.5°; Cl^-, 214°; I^-, 130.5°. [f] *Anal.* Calcd. for $C_{12}H_9IN_2O_8S$: C, 30.78; H, 1.93; N, 5.98; S, 6.85; H^+, 0.213. Found: C, 30.57; H, 2.08; N, 5.58; S, 6.72; H^+, 0.210. [g] This m.p. was obtained by recrystallization of material of m.p. 120° previously reported (ref. 2). [h] *Anal.* Calcd. for $C_{12}H_8ClF_2I$: Cl^-, 10.0. Found: Cl^-, 9.81. [i] *Anal.* Calcd. for $C_{12}H_8BrF_2I$: Br^-, 20.2. Found: Br^-, 20.0. [j] M.p.'s reported (ref. 4): Cl^-, 202°; Br^-, 190°; I^-, 163°. [k] *Anal.* Calcd. for $C_{12}H_9Br_2IO_4S$: neut. equiv., 536. Found: neut. equiv., 535 and 536. [l] *Anal.* Calcd. for $C_{12}H_8Br_2ClI$: Cl^-, 7.50. Found: Cl^-, 7.46. [m] M.p.'s reported (ref. 5): Cl^-, 209°; Br^-, 194°; I^-, 160°. [n] *Anal.* Calcd. for $C_{12}H_8BrI_3$: Br^-, 13.0. Found: Br^-, 12.8 and 13.1. [o] *p*-Diiodobenzene, m.p. and mixed m.p. 130°, also formed (16%). [p] *Anal.* Calcd. for $C_{16}H_{18}ClIO_4S_2$: Cl^-, 7.08. Found: Cl^-, 6.96 and 7.04.

$$4ArH + (IO)_2SO_4 + 3H_2SO_4 \longrightarrow 2Ar_2I^+ + 2H_3O^+ + 4HSO_4^- \quad (A)$$

(B) Coupling of two aromatic compounds with an iodate in acetic acid-acetic anhydride-sulfuric acid (Table II)

$$2ArH + IO_3^- + 2H_2SO_4 + 2Ac_2O \longrightarrow Ar_2I^+ + 2HSO_4^- + 4AcOH + [O] \quad (B)$$

(C) Coupling of two aromatic compounds with an iodine(III) acylate in the presence of an acid (Table III)[17]

$$2ArH + I(O\overset{O}{\overset{\|}{C}}R)_3 + HX \longrightarrow Ar_2I^+X^- + 3R\overset{O}{\overset{\|}{C}}OH \quad (C)$$

(D) Condensation of an iodoso compound, an iodoso diacetate or an iodoxy compound with another aromatic compound in the presence of an acid (Table IV)[17]

$$ArIO + Ar'H + H_2SO_4 \longrightarrow ArI^+Ar'\ HOSO_3^- + H_2O \quad (D\text{-}1)$$

$$ArI(OAc)_2 + Ar'H + H_2SO_4 \longrightarrow ArI^+Ar'\ HOSO_3^- + 2AcOH \quad (D\text{-}2)$$

$$ArI(OAc)_2 + Ar'H + F_3CCOOH \longrightarrow ArI^+Ar'\ F_3CCO_3^- + 2AcOH \quad (D\text{-}3)$$

$$ArIO_2 + Ar'H + H_2SO_4 \longrightarrow ArI^+Ar'\ HOSO_3^- + H_2O + [O] \quad (D\text{-}4)$$

In some cases it has been possible to oxidize an iodo compound *in situ* and then to condense it with another aromatic compound (Table IV).

$$ArI \xrightarrow[H_2SO_4]{\text{oxidation}} \xrightarrow{Ar'H} ArI^+Ar'\ HOSO_3^- \quad (D\text{-}5)$$

Reaction A.—Masson and co-workers,[18] who first used reaction A, reported that iodyl sulfate could be prepared either by the thermal decomposition of iodine pentoxide in sulfuric acid or by interaction of iodine pentoxide in sulfuric acid

$$2I_2 + 3I_2O_5 + 5H_2SO_4 \longrightarrow 5(IO)_2SO_4 + 5H_2O \quad (E)$$

while later Beringer and co-workers[2] used iodine with an iodate. While this last reaction has been

$$2I_2 + 6NaIO_3 + 11H_2SO_4 \longrightarrow 5(IO)_2SO_4 + 6NaHSO_4 + 8H_2O \quad (F)$$

frequently used in the present work, it also has been found that iodine in sulfuric acid may be

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(17) These methods recently have been used to prepare 2,2'-dithienyliodonium and phenyl-2-thienyliodonium salts: F. M. Beringer, H. E. Bachofner, R. A. Falk and M. Leff, THIS JOURNAL, **80**, 4279 (1958).

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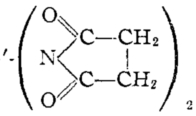
TABLE II

SYMMETRICAL DIPHENYLIODONIUM SALTS BY REACTION B[a,b]

Substituents	Anion	M.p., °C.	Solvent	%	References
None	Cl	228–229	Methanol	63	20*
	HSO_4	167–169[c]	Methanol	54	22, exptl.
	NO_3	149–151	Water	63	21,* V
4,4'-$(CH_3)_2$	Cl	190–191[d]	Methanol	39	2, 8, 9, I, exptl.
	Br	171–172[d,e]	Methanol	56	2, 8, III, exptl.
		171–173[d,e]	Methanol–water	60	2, 8, III, exptl.
	I	163[d,e]	Methanol	53	2, 8, 9, I, exptl.
		162–163[d,e]	Methanol	64	2, 8, 9, I, exptl.
2,2',4,4',6,6'-$(CH_3)_6$	Cl[f]	146[g]	......	37	10, V
4,4'-(*t*-Butyl)$_2$	Cl[h]	195[i]	Acetone	38	11, exptl., I
	Br[j]	184–185[i]	Acetone	35	11
	I	161[i]	Acetone	32	11
4,4'-(*n*-$C_{12}H_{23})_2$	Br[k]	93–96	Acetone	37	
	I[l]	99–103	Acetone	42	
4,4'-Dicyclohexyl	Br[m]	175	Acetone	35	
	I	159–160	Acetone	38	
4,4'-$(CH_3O)_2$	Br	202	Methanol	9	V
	I	190[n]	Methanol	9	2, 15, V
4,4'-$(CH_3CONH)_2$	Br	215[p]	Methanol	20	13
	I[o]	173[p]	......	48	2*, 13, 14
4,4'- 	Cl[q]	207	Formic acid	44	Exptl.
	I	184–185	Formic acid–acetic acid	88	Exptl.

[a] For explanation of column headings see Table I, footnote *a*. [b] See equation in text and details in Experimental section. [c] M.p. of 153–154° reported (ref. 22). [d] M.p.'s reported: Cl^-: 178° (ref. 8), 193° (ref. 9); Br^-: 178° (ref. 8), 205–207° (ref. 2); I^-: 143–156°, depending on the rate of heating (ref. 9), 146° (ref. 8), 172–174° (ref. 2). [e] Runs by independent workers; previously reported m.p.'s (ref. 2), now believed incorrect. [f] *Anal.* Calcd. for $C_{18}H_{22}ClI$: Cl^-, 8.85. Found: Cl^-, 8.89. [g] M.p. of 146° reported (ref. 10). [h] *Anal.* Calcd. for $C_{20}H_{26}ClI$: Cl^-, 8.3. Found: Cl^-, 8.3. [i] M.p.'s reported (ref. 11): Cl^-, 157°; Br^-, 144°; I^-, 142°. [j] *Anal.* Calcd. for $C_{20}H_{26}BrI$: C, 50.76; H, 5.54. Found: C, 50.49; H, 5.75. [k] *Anal.* Calcd. for $C_{36}H_{58}BrI$: Br^-, 11.46. Found: Br^-, 11.70. [l] *Anal.* Calcd. for $C_{36}H_{58}I_2$: I^-, 17.04. Found: I^-, 17.16. [m] *Anal.* Calcd. for $C_{24}H_{30}BrI$: C, 54.87; H, 5.76; Br^-, 15.2. Found: C, 54.83; H, 5.77; Br^-, 15.1. [n] M.p.'s reported: 179–182° (ref. 2), 180° (ref. 15). [o] Satisfactory analysis reported (ref. 2). [p] M.p.'s reported: Br^-, 165° (ref. 13); I^-, 176.5° (ref. 13) and 173° (ref. 14). [q] *Anal.* Calcd. for $C_{20}H_{16}ClIN_2O_4$: C, 47.03; H, 3.16; N, 5.48; Cl^-, 6.94. Found: C, 46.88; H, 3.37; N, 5.57; Cl^-, 6.85.

TABLE III

SYMMETRICAL DIPHENYLIODONIUM SALTS BY REACTION C[a]

Substituents	Anion	M.p., °C.	Solvent	%	HX	HX/I^{+3}	T, °C. (hr.)	Ref.
4,4'-$(CH_3O)_2$	CF_3CO_2	134–136	Benzene	49	[b]	3.3[d]	−10 to 0 (12), 20 (3)	V, exptl.
	$C_2F_5CO_2$	144–145	Benzene	36	[b]	3.3[d]	−15 to 0 (12), 20 (3)	
	$C_3F_7CO_2$	148–151	Benzene	31	[b]	3.3[d]	−15 to 0 (12), 20 (3)	
	CH_3CO_2	190–191	Dioxane	11	[b]	3.5[d]	0 (16), 25 (4)	
4,4'-$(CH_3)_2$	Br	206–211[e]	Water, methanol	58	[c]	1.25[d]	−10 to 25 (12)	2, II
4,4'-$(CH_3CO_2)_2$	Cl[f]	239–241	Methanol	15	[c]	1.25[d]	−15 to 0 (12), 20 (48)	V

[a] The column headings have the same meanings as in Table I (*q.v.*). See also footnotes to individual headings. [b] The iodine(III) acylate and the catalyzing acid contain the same acylate group as the salt isolated. [c] Iodine(III) trifluoroacetate was used with sulfuric acid. [d] The mole ratio of catalyzing acid to iodine(III) acylate. [e] A sample crystallized from water had a m.p. of about 170°, close to values in Table II. However, more thorough drying and/or recrystallization from methanol raised the m.p. to 206–211°, in agreement with the value of 205–207° reported in ref. 2. This may be a case of polymorphism. See, however, the discussion under Melting Points in the Experimental section. [f] *Anal.* Calcd. for $C_{16}H_{14}O_4ICl$: C, 44.41; H, 3.26. Found: C, 44.47; H, 3.39.

conveniently oxidized to iodyl sulfate with nitric acid.

$$I_2 + 3HNO_3 + 8H_2SO_4 \longrightarrow (IO)_2SO_4 + 3NO^+ + 4H_3O^+ + 7HSO_4^- \quad (G)$$

In the present work symmetrical iodonium salts were prepared by reaction A from benzene, the halogenobenzenes, nitrobenzene, *p*-nitroanisole and methyl *p*-tolyl sulfone (Table I). The yields were over 50% except with the last compound. The structures and purities of the products and the formation of isomers will be discussed after the presentation of the various synthetic methods.

As reaction A was initially rapid and exothermic, addition of the aromatic compound to the iodyl sulfate suspension was best done with cooling at about 5°. The first phase of the reaction may correspond to the conversion of the aromatic compound to the conjugate acid of an iodoso

$$2ArH + (IO)_2SO_4 + H_2SO_4 \longrightarrow 2ArI^+OH + 2HSO_4^- \quad (H)$$

compound. The slower second phase of the reaction corresponds to the formation of the diaryliodonium cation.

$$ArH + ArI^+OH \longrightarrow Ar_2I^+ + H_2O \quad (I)$$

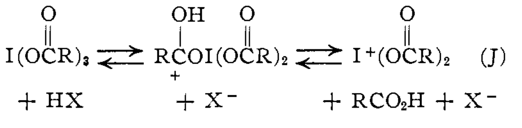
It has been reported that various mono-, di- and trialkylbenzenes have been coupled to give iodonium salts by this procedure when various amounts of water were added to the suspension of iodyl sulfate in sulfuric acid.[19]

Reaction B.—Benzene, alkylbenzenes,[19a] acetanilide and succinanil were coupled to symmetrical iodonium salts with an iodate in acetic acid–acetic anhydride–sulfuric acid (Table II). The reaction with anisole went in poor yield and was not regularly reproducible; see reaction C below.[19b] Though both reactions A and B could be used with benzene, B was the more satisfactory for the isolation of the useful soluble salts, such as the chloride,[2,20] nitrate[21] and bisulfate.[22]

If the temperature of a reaction mixture was not kept below 15° during the addition of the sulfuric acid and for some hours thereafter, a vigorous, exothermic reaction might occur. It may be that in such instances the iodate was effecting a deep-seated oxidation of the aromatic compound.

Reaction C.—This reaction is closely related to reaction B and involves the symmetrical coupling of two reactive aromatic compounds with an iodine(III) acylate and an added acid.[17] While anisole yielded a product with iodine(III) acetate and acetic acid, most work has been done with iodine(III) trifluoroacetate. This reaction makes readily available 4,4′-dimethoxydiphenyliodonium salts, recently used in the synthesis of thyroxine.[19b,23] While in this case added trifluoroacetic acid was added to allow the reaction to proceed at a useful rate, with less reactive compounds, such as toluene, a stronger acid such as sulfuric acid was needed; see Table III.

Results to date do not distinguish between the protonated iodine(III) acylate and the related iodonium ion as the effective electrophilic species.



$$\mathrm{I(O\overset{\overset{O}{\|}}{C}R)_3} + \mathrm{HX} \rightleftarrows \mathrm{R\overset{\overset{OH}{|}}{\underset{+}{C}}OI(O\overset{\overset{O}{\|}}{C}R)_2} + \mathrm{X^-} \rightleftarrows \mathrm{I^+(O\overset{\overset{O}{\|}}{C}R)_2} + \mathrm{RCO_2H} + \mathrm{X^-} \qquad (J)$$

Reaction D.—This reaction comprises various condensations of an iodoso compound or an iodoxy compound with another aromatic compound in the presence of an added acid; see Table IV. In general, when the iodoso compound had electron-withdrawing groups, the reaction proceeded satisfactorily in sulfuric acid, while if electron-releasing groups were present in either reactant, the reaction proceeded better in acetic acid–acetic anhydride–sulfuric acid. Condensations with anisole and with thiophene[17] were catalyzed with trifluoroacetic acid.

A difficult condensation to effect was that of 4-nitroiodoso-benzene with benzene. As previously reported,[2] all early attempts gave the reduction product, 4-nitroiodobenzene. However, by running the reaction between −30 and −20°, a 43% yield of 4-nitrodiphenyliodonium salts was obtained. It was found that this same reaction could be run with 4-nitroiodoxybenzene instead of the iodoso compound. Here it may be that the iodoxy compound was reduced to the iodoso compound, which then coupled.

In most of the above cases the iodoso (or iodoxy) compounds were first prepared from iodo compounds *via* the dichlorides. In some cases a

$$\begin{tikzcd}
\mathrm{ArI} \arrow[r, "\mathrm{Cl_2}"] & \mathrm{ArICl_2} \arrow[r, "\mathrm{NaOH}"] \arrow[dr, "\mathrm{NaOCl}"'] & \mathrm{ArIO} \quad (K) \\
& & \mathrm{ArIO_2} \quad (L)
\end{tikzcd}$$

convenient short-cut was to oxidize the iodo compound *in situ* to an iodoso or iodoxy compound, which could then undergo the coupling reaction. Barium peroxide and potassium persulfate were successful oxidants. While no intermediates were isolated, the oxidations to iodoso compounds may be

$$\mathrm{ArI} + \mathrm{BaO_2} + 3\mathrm{H_2SO_4} \longrightarrow \mathrm{ArI(OSO_3H)_2} + 2\mathrm{H_2O} + \mathrm{BaSO_4} \qquad (M)$$

$$\mathrm{ArI} + \mathrm{K_2S_2O_8} + 2\mathrm{H_2SO_4} \longrightarrow \mathrm{ArI(OSO_3H)_2} + 2\mathrm{KHSO_4} \qquad (N)$$

While this work was in progress, Sandin and coworkers[24] reported a similar oxidation (with peracetic acid) and condensation of iodaryl compounds (of the type $2\text{-}\mathrm{IC_6H_4(CH_2)}_n\mathrm{C_6H_5}$, where n ranged from 0 to 3) to give cyclic iodonium salts.

Salts Prepared by Metathesis.—From the salts prepared by condensation reactions others were prepared by metathesis and are reported in Table V. As the solubility of the iodonium halides in water decreases with increasing atomic number of the halide ion, the bromide and iodide salts easily could be prepared from the chloride.[2,20] Other salts prepared in the same way from the chloride are the picrate,[2] perchlorate,[25] tetraphenylborate[26] and 2,4,6-tribromobenzenesulfonate.[27]

Diphenyliodonium benzenesulfonate[28] and tosylate[28,29] and 4-nitrodiphenyliodonium tosylate, convenient for studies of solvolysis,[28,29] were prepared by metathesis of iodonium halides with the soluble lead salts of the sulfonic acids. A similar metathesis with silver fluoroborate give the previously reported diphenyliodonium fluoroborate[30] and with silver nitrate gave the nitrates.

Structures of the Iodonium Salts.—The structures of many iodinium salts have been proved by the thermal decomposition of iodide salts to iodo compounds.[2,20] In the present work the only

$$\mathrm{Ar_2I^+I^-} \xrightarrow{\text{heat}} 2\mathrm{ArI} \qquad (O)$$

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TABLE IV

UNSYMMETRICAL DIPHENYLIODONIUM SALTS BY VARIATIONS OF REACTION D[a]

Subst.[b]	X^-	M.p., °C.	Solvent	%	Eq.[a]	Ratio[c]	°C. (hr.)	Ref.
None	Br	208	......	74	1a	6.2	0–10 (1), 20 (24)	2*
		207	Water–acetic acid	54	4s	8	0–10 (3)	
2-NO$_2$	Cl[d]	161–162	Methanol	60	1s	2.1	0–5 (1), 20 (4)	V
	Br	144–145	......	10				V
	Br[e]	143	Water	75	1s	2	5 (1), 20 (3)	2,* V
	Br	150–151[f]	Methanol	61	1s	2.1	0–5 (1), 20 (4)	V
3-NO$_2$	I	102	......	79	5s, N	12.5	20 (2)	V, exptl.
	Br	172–175[e]	Water	62	1s	2	20 (3)	2,* V
		172–175[e]	Water	96	1a	1.8	20 (2)	2,* V
		197–198	Water	98	1s	2	20 (3)	V
		181–182	......	58	5s, M	12.5	10 (1), 20 (1)	V
	I	136[h]	......	19	5s, M	12.5	10 (1), 20 (1)	2, 3, V
	I	145–146[g]	DMF–methanol	78	5s, M	6.25	−20 to −10 (1), 0 (3)	2, 3, V
4-NO$_2$	Br[e]	149	......	41	1s	2	−30 (1), 0 (1)	V, exptl.
	I	127–128	......	2				V, exptl.
	Br	149–150	......	24	4s	2	−20 (0.5), 0 (1)	V
	I	127–128	......	12				V
	I[h]	143–146	......	53	5s, N	12.5	20 (1.5)	V
2-COOH	I[i]	140–142	......	39	5s, N	3.75	−10 (1), 0 (3)	
3-COOH	I[i]	151–152	Water–methanol	55	5s, N	3.75	−10 (1), 0 (3)	
4-COOH	I[i]	155–160	Methanol	69	5s, N	3.75	−10 (2), 0 (3)	Exptl.
4-F	Br[j]	188	......	27	1s	2	−25 (1), 20 (1)	
	I	143	......	12				
2-Cl	Br[k]	153	Formic acid	34	1s	1.1	0 (0.5)	
3-Cl	Br[k]	164[l]	Formic acid	92	1s	1.1	0 (0.5)	6
4-Cl	Br[k]	169	Formic acid	50	1s	1.1	0 (0.5)	
3-Br	Br[m]	161[n]	......	25	1s	2.3	−25 (1)	7
4-Br	Br[m]	175	......	43	1s	2	−5 to 0 (1)	
	I	118	......	1.4				
2-CH$_3$	Br[o]	167	Water	40	1a	1.1	15 (1)	
3-CH$_3$	Br[o]	180[p]	Water	52	1a	1.1	15 (1)	12
4-CH$_3$[q]	Br[e,o]	176–177	Water	58	1a	1.2	25 (1)	
2-CH$_3$O	Br[r]	175	Water	51	1a	1.1	15 (1)	
4-CH$_3$O	Br[r]	185[s]	Water	72	1a	1.2	25 (0.5)	2, 16, V
		191–192[s]	Methanol	51	1a	1.2	15 (2)	2, 16, V
4-CH$_3$O	I	168–169[s]	DFM–methanol	84	1a	1.2	15 (2)	V
	CF$_3$CO$_2$	164–166	Benzene	92	3t	1.5	−20 (1), 0 (12), 20 (48)	Exptl.
		160–162	Benzene	57	1a	1	−10 to 0 (12), 20 (4)	
3-CH$_3$CONH	I	155–157	Methanol	40	5s, M	13	0 (1), 20 (72)	
4-CH$_3$CONH[q]	Br	188–189[u]	......	23	1a	2	−25 (1)	13, exptl.
	I[t]	168	......	20	5s	12.5	−10 (0.5), 5 (2)	
3-NO$_2$-4′-CH$_3$CONH	I[v]	172–173	......	52	5s, N	1.25	10–25 (43)	
4-NO$_2$-4′-CH$_3$CONH	I	125–130	Methanol–Cellosolve	63	5s, N	1.25	10–25 (43)	

[a] Column headings have the same meanings as in Table I (q.v.). In addition the numbers under Eq. refer to the variation of reaction D in text, while the small letter specifies the medium (a, acetic acid–acetic anhydride–sulfuric acid; s, sulfuric acid; t, trifluoroacetic acid–acetic anhydride) and large letters refer to reactions in text concerned with the oxidation. Thus, 5s, M refers to reaction D-5 run in sulfuric acid after oxidation by reaction M. [b] Substituent in iodine-containing reagent unless otherwise noted; in all cases the nitro group is in the iodine-containing reagent. [c] Mole ratio of Ar′H to iodine-containing compound. [d] Compare salt of m.p. 164–165° (Table V). [e] *Anal.* Calcd. for $C_{12}H_9BrINO_2$: Br^-, 19.68. Found: Br^-, (2-NO$_2$) 19.60; (3-NO$_2$) 19.58; (4-NO$_2$) 19.54. [f] The m.p. varied with the rate of heating for samples inserted at 135°: 146–147° (1°/min.); 151° (4°/min.). [g] M.p.'s reported: 144.5–146° (ref. 2) and 153° (ref. 3). [h] *Anal.* Calcd. for $C_{12}H_9I_2NO_2$: C, 31.78; H, 2.00. Found: C, 32.01; H, 2.13. [i] *Anal.* Calcd. for $C_{12}H_{10}I_2O_2$: C, 34.45; H, 2.21. Found: C, 34.40; H, 2.28 (2-COOH); C, 34.69; H, 2.40 (3-COOH); C, 34.37; H, 2.35 (4-COOH). [j] *Anal.* Calcd. for $C_{12}H_9BrFI$: Br^-, 21.09. Found: Br^-, 20.97, 21.02. [k] *Anal.* Calcd. for $C_{12}H_9BrClI$: Br^-, 20.21. Found: Br^-, 20.13 (2-Br), 20.08 (3-Br), 20.19 (4-Br). [l] M.p. 164° reported (ref. 6). [m] *Anal.* Calcd. for $C_{12}H_9Br_2I$: Br^-, 18.17. Found: Br^-, 17.96, 18.02 (3-Br); 18.13, 18.15 (4-Br). [n] M.p. 169° reported (ref. 7). [o] *Anal.* Calcd. for $C_{13}H_{12}BrI$: Br^-, 21.31. Found: Br^-, 21.15 (2-CH$_3$), 21.19 (4-CH$_3$). [p] M.p. 193° reported (ref. 12). [q] Substituent in Ar′H; *cf.* footnote *b*. [r] *Anal.* Calcd. for $C_{13}H_{12}BrIO$: Br^-, 20.44. Found: Br^-, 20.37 (2-CH$_3$O), 20.40 (4-CH$_3$O). [s] M.p.'s reported: Br^-, 180° (ref. 16) and 185° (ref. 2); I^-, 162.5–163.5° (ref. 2) and 175° (ref. 16). [t] *Anal.* Calcd. for $C_{14}H_{13}I_2NO$: C, 36.12; H, 2.87. Found: C, 36.12; H, 2.87. [u] M.p. 183° reported (ref. 13). [v] *Anal.* Calcd. for $C_{14}H_{12}I_2N_2O_3$: C, 32.99; H, 2.35. Found: C, 33.34; H, 2.35.

iodonium salts so treated were symmetrical and thus gave only one product. The data on decompositions which gave solid iodo compounds are given in Table VI.

TABLE V

PREPARATION OF DIPHENYLIODONIUM SALTS BY METATHESIS[a]

Substituents	Anion	M.p., °C.	%	Other product[b]	Solvents		Ref.
					Reaction	Crystallization	
None	BF_4	151–153[c]	84	AgCl	Water	Water	30, exptl.
	$B(C_6H_5)_4$	193–195[c]	~100	NaCl	Water	DFM–acetonitrile	26
	ClO_4[d]	173–174[c]	34	HCl	Water	Water	25
	$C_6H_5SO_3$[e]	178–182	68	$PbCl_2$	Methanol	2-Propanol	Exptl.
	$C_7H_7SO_3$[f]	178–181	69	$PbCl_2$	Methanol	2-Propanol	Exptl.
	$C_6H_2Br_3SO_3$[g]	191–193	75	HCl	Methanol–water	Methanol–water	27
2-NO_2	Cl[h]	164–165	~80	NH_4NO_3	Water	....	IV
	Br[i]	148–149[j]	~80	$NaNO_3$	Water	....	2, IV
	I	106–107	89	KCl	Water	....	IV, exptl.
	NO_3[k]	180–181	..	AgI	Methanol	Methanol–water	
3-NO_2	Cl[h]	192–193[l]	~80	NH_4NO_3	Water	....	
	Br[i]	186–187[l]	~80	$NaNO_3$	Water	....	2, IV
	I[m]	146–148	86	KCl	Water	....	IV
		148–149[l]	..	KNO_3	Water		
	NO_3[k]	183–185	..	AgI	Methanol	Methanol–water	
4-NO_2	Cl[h]	160–161	~80	NH_4NO_3	Water	....	
	Br[i]	166–167	~80	$NaNO_3$	Water	....	IV, exptl.
	I[m]	143–145	~90	$C_7H_7SO_3K$	Water	Water	IV, exptl.
		143–146		KNO_3	Water	....	IV, exptl.
	NO_3[k]	163–165	..	AgI	Methanol	Methanol–water	
	$C_7H_7SO_3$[n]	190–193	78	$PbBr_2$	Methanol	Ethanol–water	
3,3′-$(NO_2)_2$	Cl	217[p]	~90	NH_4HSO_4	Water	DMF–water	I, exptl.
	Br	210[p]	~90	$NaHSO_4$	Water	....	2, I, exptl.
	I	149–150[p]	~90	$KHSO_4$	Water	....	
4,4′-F_2	I	181	81	KCl	Water	....	I
4,4′-Cl_2	Cl[o]	210[q]	94	NH_4HSO_4	Water	DMF	4, I, exptl.
	Br[r]	187–188[q]	~90	$NaHSO_4$	Water	Methanol	4, I
	I[s]	157–159[q]	~90	$KHSO_4$	Water	Methanol	4, I
4,4′-Br_2	Cl	212[t]	72	NH_4HSO_4	Water–methanol	DFM	5, I
	Br	195–196[t]	93	$NaHSO_4$	Water–methanol	....	
	I[u]	166–167[t]	~100	$KHSO_4$	Water–methanol	DMF	
$(CH_3)_6$[v]	Picrate	161–163	96	NaCl	Water	....	II
4-CH_3O	Br[w]	215–218[x]	87	$F_3CCO_2NH_4$	Water	Water	2, 16, IV
	I[y]	204–208[x]	~100	F_3CCO_2K	Water	DMF–methanol	2, 16, IV
4,4′-$(CH_3O)_2$	Cl	211–212	81	$F_3CCO_2NH_4$	Water	....	III, exptl.
	Br[z]	239–243[aa]	70	F_3CCO_2K	Water	Water	III, exptl.
	I[bb]	202–206[aa]	~100	F_3CCO_2K	Water	DMF–methanol	III, exptl.
4,4′-$(CH_3CO_2)_2$	I	213	80	KCl	Water	Methanol	III
2,2′-$(CH_3O)_2$	Cl	206	90	NH_4HSO_4	Water	....	
5,5′-$(NO_2)_2$	Br[cc]	206	90	$NaHSO_4$	Water	....	
	I	145–147	90	$KHSO_4$	Water	....	
4-NO_2-4′-CH_3CONH	NO_3[dd]	150–153	..	AgI	Methanol	Methanol	

[a] Column headings have the same meanings as in Table I. [b] *Other Product* is that resulting from the metathesis besides the iodonium salt. [c] M.p.'s reported: BF_4^-, 136° (ref. 30); $B(C_6H_5)_4^-$, 195–196° (ref. 26); ClO_4^-, m.p.; 65° (ref. 25). [d] Explodes on grinding. [e] *Anal.* Calcd. for $C_{18}H_{15}IO_3S$: C, 49.33; H, 3.45; I, 28.95; S, 7.32. Found: C, 49.51; H, 3.69; I, 28.93; S, 7.32. [f] *Anal.* Calcd. for $C_{19}H_{17}IO_3S$: C, 50.45; H, 3.79; I, 28.06; S, 7.09. Found: C, 50.70; H, 4.03; I, 28.06; S, 7.40. [g] *Anal.* Calcd. for $C_{18}H_{12}Br_3IO_3S$: C, 33.03; H, 1.80; S, 4.73. Found: C, 33.28; H, 2.02; S, 4.73. [h] *Anal.* Calcd. for $C_{12}H_9ClINO_2$: C, 39.87; H, 2.51. Found: C, 39.98 (2-NO_2), 39.94 (3-NO_2), 40.08 (4-NO_2); H, 2.57 (2-NO_2), 2.48 (3-NO_2), 2.62 (4-NO_2). [i] *Anal.* Calcd. for $C_{12}H_9BrINO_2$: C, 35.47; H, 2.22. Found: C, 35.66 (2-NO_2), 35.57 (3-NO_2), 35.59 (4-NO_2); H, 2.26 (2-NO_2), 2.25 (3-NO_2), 2.22 (4-NO_2). [j] M.p. 143° reported (ref. 2). [k] *Anal.* Calcd. for $C_{12}H_9IN_2O_5$: C, 37.16; H, 2.32. Found: C, 37.43 (2-NO_2), 37.29 (3-NO_2), 37.54 (4-NO_2); H, 2.29 (2-NO_2), 2.17 (3-NO_2), 2.13 (4-NO_2). [l] M.p.'s reported: Cl^-, 185–185.5° (ref. 2), 170–172° (ref. 3); Br^-, 172–175° (ref. 2); I^-, 144.5–146° (ref. 2), 153° (ref. 3). [m] *Anal.* Calcd. for $C_{12}H_9I_2NO_2$: C, 31.78; H, 2.00. Found: C, 31.98 (3-NO_2), 32.01 (4-NO_2); H, 2.25 (3-NO_2), 2.13 (4-NO_2). [n] *Anal.* Calcd. for $C_{19}H_{16}INO_5S$: C, 45.88; H, 3.24. Found: C, 45.67; H, 3.48. [o] *Anal.* Calcd. for $C_{12}H_8Cl_3I$: Cl^-, 9.21. Found: Cl^-, 9.18. [p] M.p.'s reported: Cl^-, 203–205° (ref. 2), 214° (ref. 3); Br^-, 178–179° (ref. 2), 183–184° (ref. 3); I^-, 127–128° (ref. 2), 130.5° (ref. 3). [q] M.p.'s reported: Cl^-, 203–205° (ref. 2), 214° (ref. 3); Br^-, 178–179° (ref. 2), 183–184° (ref. 3); I^-, 127–128° (ref. 2), 130.5° (ref. 3). [r] *Anal.* Calcd. for $C_{12}H_8BrCl_2I$: C, 33.58; H, 1.86. Found: C, 33.44; H, 2.05. [s] *Anal.* Calcd. for $C_{12}H_8Cl_2I_2$: C, 30.22; H, 1.69. Found: C, 30.46; H, 1.98. [t] M.p.'s reported (ref. 5): Cl^-, 209°; Br^-, 194°; I^-, 160°; see also Table I. [u] *Anal.* Calcd. for $C_{12}H_8Br_2I_2$: I^-, 19.2. Found: I^-, 19.1. [v] 2,2′,4,4′,6,6′-Hexamethyldiphenyliodonium picrate. [w] *Anal.* Calcd. for $C_{13}H_{12}BrIO$: C, 39.92; H, 3.08. Found: C, 40.04; H, 4.01. [x] See Table IV. [y] *Anal.* Calcd. for $C_{13}H_{12}I_2O$: C, 35.64; H, 2.76. Found: C, 35.55; H, 2.88. [z] *Anal.* Calcd. for $C_{14}H_{14}BrIO_2$: C, 39.93; H, 3.35. Found: C, 40.19; H, 3.36. [aa] See Table II. [bb] *Anal.* Calcd. for $C_{14}H_{14}I_2O_2$: C, 35.92; H, 3.01. Found: C, 36.36; H, 2.98. [cc] *Anal.* Calcd. for $C_{14}H_{12}BrINO_6$: Br, 15.64. Found: Br, 15.48. [dd] *Anal.* Calcd. for $C_{14}H_{11}IN_3O_6$: C, 37.85; H, 2.50. Found: C, 37.62; H, 2.66.

TABLE VI

IODOBENZENES FROM SYMMETRICAL DIPHENYLIODONIUM SALTS[a]: Reaction O

Substituents	Melting points, °C. Found	Authentic	2ArI, %	Decomposition conditions
3-NO_2	39	38	76	150°, vacuum
4-Cl	56–57	56	73	100° (72), DMF
4-Br	92	92	85	Reflux, DMF
4-I	129–130	129	70	120°, vacuum
4-Succinimido	238	239	86	Reflux, DMF
2-CH_3O-5-NO_2	95–96	96	54	Reflux, 1:1 H_2O–HOAc
2-CH_3-5-CH_3SO_2	114–116	114–116[b]	..	110° (2)

[a] The column headings have the same meaning as in Table I. [b] M.p. determined by independent synthesis; see Experimental.

From other symmetrical diphenyliodonium salts liquid iodo compounds were obtained; these were characterized as benzoic acids. Thus, 4-fluoroiodobenzene and 4-*t*-butyliodobenzene were converted to Grignard reagents and carbonated to give 4-fluorobenzoic acid and 4-*t*-butylbenzoic acid, while 4-*n*-dodecyliodobenzene and 4-cyclohexyliodobenzene were oxidized to 4-iodobenzoic acid.

Purity of Iodonium Salts; Absence of Isomers.—In most cases the purity of the iodonium halides as determined by halide ion titration could be brought to 99-100% by one or two crystallizations. In some cases it was found that even after analytical purity was achieved, the melting point could be raised by further crystallization, possibly because of the removal of small amounts of isomers.

An effort was made to isolate a by-product isomer (such as a 2,4′-dichlorodiphenyliodonium salt) from the reaction of chlorobenzene with iodyl sulfate in sulfuric acid. It was felt that such an isomer might be found in the mother liquor after the bisulfate (obtained in 65% yield after dilution with water) had been removed. Addition of ammonium chloride gave 7% of a dichlorodiphenyliodonium chloride, m.p. 184–185°, which was fractionally crystallized. However, most of the material achieved the m.p. of 211°, characteristic of 4,4′-dichlorodiphenyliodonium chloride and the lower-melting fractions became too small to investigate further. In this case, then, substitution has occurred very largely *para* to the chlorine atom. Indeed, to date our efforts to isolate isomeric salts have been without success.

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Experimental

Analytical Procedures.—Halide ions were determined argentimetrically with dichlorofluorescein or Eosyn Y as indicator for chloride ion and with dibromofluorescein as indicator for bromide and iodide ions. Some soluble salts were titrated potentiometrically with silver nitrate in 1:1 methanol–water using glass and silver electrodes. Some slightly soluble salts were dissolved with warming in 50% aqueous acetic acid, an excess of standard silver nitrate was added, and the excess was titrated with potassium thiocyanate, using a ferric alum indicator, or potentiometrically with hydrochloric acid. The purities of iodoso and iodoxy compounds were determined iodimetrically.[31] Other analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.; Dr. K. Ritter, Basel, Switzerland; and Drs. Weiler and Strauss, 164 Banbury Road, Oxford, England.

Melting Points.—As most iodonium salts decompose near their melting points, these depend strongly on the duration of heating. In general, after an approximate melting point was taken, a new sample was introduced about 10° below this point, and the temperature was raised 4–5° a minute. A Hershberg apparatus was used to take these capillary melting points.

The dependence of observed melting point on the method used in its determination is illustrated by the behavior of 4,4′-dimethyldiphenyliodonium bromide (prepared unequivocally by Joseph W. Dehn, Jr., in this Laboratory by treatment of *p*-tolyliodoso dichloride with *p*-tolyllithium at low temperature). After two crystallizations from water and two from methanol and after drying *in vacuo* at 100° for two hours the melting point taken in a capillary tube was 181–182° while that with a Fisher–John apparatus was 223–229°. The difference may have arisen from the capillary's acting as a condenser to keep the decomposition products, *p*-tolyl bromide and iodide, in contact with the iodonium salt while with the Fisher–Johns apparatus these decomposition products may escape.

Starting Materials. Aromatic Compounds.—Benzene, nitrobenzene, the halogenobenzenes, toluene, mesitylene, *n*-dodecylbenzene, cyclohexylbenzene, aniline and anisole were commercial products redistilled before use. 4-Nitroanisole was obtained from Distillation Products, Inc. Methyl *p*-tolyl sulfone was prepared by the method of Otto.[32] Succinanil was made from aniline.[33]

Iodo Compounds.—Iodobenzene, the iodotoluenes, the chloroiodobenzenes, the nitroiodobenzenes, the iodobenzoic acids and 2- and 4-iodoanisoles were obtained from Distillation Products, Inc. 4-Iodaniline was made from aniline[34] and converted to 4-iodoacetanilide. 4-Iodoaniline with succinic anhydride in benzene[33] gave 4-iodosuccinanilic acid, m.p. 215° (from methanol–water), which on further treatment with acetyl chloride gave **4-iodosuccinanil**, m.p. 239° (from dimethylformamide–water), previously reported[35] m.p. 86°.

Anal. Calcd. for $C_{10}H_8INO_2$: C, 39.89; H, 2.67; N, 4.65. Found: C, 40.09; H, 2.48; N, 4.85.

Methyl 3-iodo-4-methylphenyl sulfone was prepared by the following sequence of reactions.[36] Methyl *p*-tolyl sulfone with mixed sulfuric and fuming nitric acids at 5–10°, then room temperature for an hour, gave 77% of **methyl 3-nitro-4-methylphenyl sulfone**, m.p. 118–121° (from methanol). Reduction of this nitro compound with iron filings and hydrochloric acid gave 43% of **methyl 3-amino-4-methylphenyl sulfone**, m.p. 117–118° (from methanol). The diazotized amine was treated with potassium iodide to give **methyl 3-iodo-4-methylphenyl sulfone**, m.p. 114–116°, after chromatographing on alumina and crystallizing from benzene–heptane.

Iodoso- and Iodoxybenzenes.—By treatment with chlorine in cold, dry chloroform the iodobenzenes were converted in 81–96% yields to iodosobenzene dichlorides,[37] which were hydrolyzed in 68–91% yields to iodosobenzenes.[31] It was found advantageous to wash the crude, wet iodoso compounds with acetone rather than with the more usual chloroform. The purity of these compounds was assayed iodimetrically[31] and was generally 98–100%.

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(31) I. Masson, E. Race and F. E. Pounder, *J. Chem. Soc.*, 1669 (1935); H. J. Lucas, E. R. Kennedy and M. W. Formo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 483.

(32) R. Otto, *Ber.*, **18**, 154 (1885).

(33) L. F. Fieser, "Experiments in Organic Chemistry," third ed., D. C. Heath and Co., Boston, Mass., 1955, p. 105.

(34) R. Q. Brewster, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 347.

(35) A. Sanna, *Gazz. chim. ital.*, **57**, 761 (1927).

(36) J. P. Moran, Jr., B.S. Thesis, Polytechnic Institute of Brooklyn, 1956.

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

4-Nitroiodosobenzene dichloride was oxidized with sodium hypochlorite by the method of Formo and Johnson[38] in 86% yield to **4-nitroiodoxybenzene**, m.p. 216° (explodes), reported[39] m.p. 216° (explodes).

Benzenesulfonic Acids.—Benzenesulfonic and *p*-toluenesulfonic acids and sodium *m*-aminobenzenesulfonate were used as received from Distillation Products, Inc. 2,4,6-Tribromobenzenesulfonic acid was prepared as follows. To a solution of 55.25 g. (0.25 mole) of sodium *m*-aminobenzenesulfonate in 700 ml. of water 120 g. (41.25 ml., 0.75 mole) of bromine was added slowly at 25°, with additional stirring for 30 minutes. The precipitate from the cold (5°) solution was recrystallized from water to give 95 g. (95%) of **2,4,6-tribromo-3-aminobenzenesulfonic acid**, dried at 110°; no m.p., dec. at about 350°; neutralization equivalent 407 (theoretical, 409.9). This tribromo acid was added slowly to 10 g. of sodium nitrite in 300 ml. of ethanol. After gas evolution was complete, the solution was chilled to give the orange **2,4,6-tribromo-3-benzenediazoniumsulfonate**. The moist inner salt was suspended in 150 ml. of ethanol and 150 ml. of hypophosphorous acid and heated until nitrogen evolution ceased. The product separating from the chilled reaction mixture was recrystallized from water (decolorizing carbon) to give 85 g. (0.215 mole, 86%) of **2,4,6-tribromobenzenesulfonic acid**, m.p. 95–100°, reported[40] m.p. 95°; neutralization equivalent 417 (theoretical, 412.9).

Synthesis of Diphenyliodonium Salts. Reaction A (Iodyl Sulfate in Sulfuric Acid).—As reported,[2] iodyl sulfate was found to be conveniently prepared by vigorously stirring stoichiometric amounts of iodine and sodium or potassium iodate in concentrated sulfuric acid (reaction F); an alternate oxidation of iodine with nitric acid (reaction G) follows. To a vigorously stirred solution of 12.7 g. (50 mmoles) of iodine, 25.4 ml. of 30% fuming sulfuric acid and 20 ml. of concd. sulfuric acid there was added dropwise a solution of 7.4 ml. of 90% fuming nitric acid, 3.7 ml. of 30% fuming sulfuric acid and 3.7 ml. of concd. sulfuric acid. The mixture was stirred at 70–80° for 1.5 hours, during which time the iodine color disappeared and yellow crystals of **iodyl sulfate** formed (50 mmoles of iodyl sulfate). If the disappearance of the iodine color was not complete, additional nitric acid was added dropwise.

The preparation of iodonium salts with iodyl sulfate and benzene,[2] nitrobenzene,[2] benzoic acid[2] and chlorobenzene[18] has been previously reported. Improved preparations from nitrobenzene and chlorobenzene are now given; repetition of the reaction with benzoic acid under a variety of conditions gave products that could not be satisfactorily purified.

3,3′-Dinitrodiphenyliodonium Salts.—To a stirred suspension of 380 mmoles of iodyl sulfate in 400 ml. of concentrated sulfuric acid there was added at 10° over two hours 196.8 g. (1.6 moles) of nitrobenzene. After the mixture had been stirred at room temperature for 24 hours and at 45° for 36 hours, it was diluted at 5° with one liter of cold water. The precipitate was washed with water and dried to give 190 g. (406 mmoles, 54%) of crude 3,3′-dinitrodiphenyliodonium bisulfate, m.p. 163–166°. Four crystallizations from methanol raised the m.p. to 194–195°; m.p.'s previously reported: 165–167° (ref. 2), 168.5° (ref. 3). From the combined mother liquors there was obtained by the addition of aqueous sodium bromide 59 g. (130 mmoles, 17%) of **3,3′-dinitrodiphenyliodonium bromide**, m.p. 177–178°, m.p. 178–179° previously reported.[2]

Addition of dilute hydrochloric acid to a hot solution of pure 3,3′-dinitrodiphenyliodonium bisulfate gave colorless **3,3′-dinitrodiphenyliodonium chloride**, m.p. 214–215° after crystallization from aqueous dimethylformamide; m.p. 214° previously reported.[3] In a similar manner aqueous sodium bromide precipitated **3,3′-dinitrodiphenyliodonium bromide**, pale yellow crystals of m.p. 182–183° after crystallization from dimethylformamide; see m.p.'s above.

4,4′-Dichlorodiphenyliodonium Salts.—To a stirred, cold suspension of 50 mmoles of iodyl sulfate in sulfuric acid (see above) 25.4 ml. (250 mmoles) of chlorobenzene was added dropwise over 30 minutes. The reaction mixture was stirred at room temperature for 12 hours and at 45° for two hours, cooled to 5° and treated with 100 ml. of water and 10 ml. of ether at this temperature. On refrigeration overnight the mixture deposited a solid, which was crystallized from methanol to give 27 g. (60 mmoles, 60%) of **4,4′-dichlorodiphenyliodonium bisulfate**, m.p. 178–181°. Recrystallization raised the m.p. to 193°, neutralization equivalent 445 (theoretical, 447). This salt was soluble in water, methanol and ethanol but insoluble in isopropyl alcohol and in ether. The combined filtrates were decolorized with carbon, extracted with ether and treated with 25 ml. of concd. hydrochloric acid. The precipitate after washing and drying was 2.8 g. (7.3 mmoles, 7.3%) of crude **4,4′-dichlorodiphenyliodonium chloride**, m.p. 184–185°. One crystallization from acetonitrile and two from dimethylformamide raised the m.p. to 211°, reported[4] m.p. 202°. This salt was soluble in formic acid and in 2-pyrrolidone but insoluble in water, methanol and ether.

Anal. Calcd. for $C_{12}H_8Cl_3I$: Cl^-, 9.21. Found: Cl^-, 9.18.

Reaction B (an Iodate in Acetic Acid–Acetic Anhydride–Sulfuric Acid).—Symmetrical iodonium salts have been previously prepared from benzene,[2,20,21] toluene,[2] acetanilide[2] and anisole.[2] Reported below are the isolation of the very soluble iodonium bisulfate from benzene, improved preparations of salts from toluene and acetanilide and new salts from cyclohexylbenzene, *n*-dodecylbenzene and succinanil. (For a new, improved method of preparing iodonium salts from anisole see later in Experimental under Reaction C.[19b])

Diphenyliodonium Bisulfate.—To a well-stirred mixture of 55.5 ml. (0.625 mole) of benzene, 50 ml. of acetic anhydride and 53.5 g. (0.25 mole) of potassium iodate there was added below 5° a cold solution of 35 ml. of concd. sulfuric acid and 50 ml. of acetic anhydride over 8 hours. The reaction mixture was stirred for an additional 4 hours at 0–5° and at room temperature for 48 hours, cooled to 5°, and treated with 300 ml. of ether. The precipitate was washed with ether and crystallized from methanol (activated carbon) to give 50.7 g. (0.134 mole, 54%) of **diphenyliodonium bisulfate** of 96% purity, as indicated by conversion of an aliquot of diphenyliodonium iodide. Two crystallizations from methanol raised the m.p. to 164–166°; neutralization equivalent 378 (theoretical, 378).

4,4′-Dimethyldiphenyliodonium Salts.—After the reaction had been run as previously described,[2] inorganic salts were removed and washed with acetic acid to give a total volume of 205 ml., which was divided into two portions. After one portion has been diluted with 100 ml. of water, the mixture was extracted with ether and treated with a few mg. of sodium sulfite and 10 g. of sodium bromide in 50 ml. of water. The chilled solution gave two crops, totaling 10.8 g. (60%) of crude **4,4′-dimethyldiphenyliodonium bromide**, m.p. 169–173°. Crystallization from 3:1 methanol-water raised the m.p. to 171–173°; reported m.p.'s: 178° (ref. 8), 205–207° (ref. 2); see Table II and discussion under Melting Points.

Anal. Calcd. for $C_{14}H_{14}BrI$: Br^-, 20.54. Found: Br^-, 20.36.

The other half of the reaction mixture was treated similarly with water, ether and sodium sulfite and was diluted to 450 ml. with water. Addition of 10 g. of potassium iodide in 50 ml. of water gave 13 g. (64%) of crude **4,4′-dimethyldiphenyliodonium iodide**, m.p. 149–151°. Recrystallization from methanol raised the m.p. to 162–163°; reported m.p.'s: 143–156°, depending on the rate of heating (ref. 9), 146° (ref. 8), 172–174° (ref. 2); see Table II.

A similar preparation gave after hydrolysis and treatment with ammonium chloride 53% of crude **4,4′-dimethyldiphenyliodonium chloride**, m.p. 150–155°. Repeated crystallizations from methanol raised the m.p. to 185–186°; reported m.p.'s: 178° (ref. 8), 193° (ref. 9).

Anal. Calcd. for $C_{14}H_{14}ClI$: C, 48.79; H, 4.09. Found: C, 48.93; H, 4.09.

Both the chloride and bromide prepared above when crystallized from 4:1 dioxane–water gave salts which contained dioxane in the proportion $2R_2IX \cdot C_4H_8O_2$.

Anal. Calcd. for $C_{32}H_{36}Cl_2I_2O_2$ (4,4′-dimethyldiphenyliodonium chloride dioxanate): C, 49.47; H, 4.67; Cl^-, 9.13. Found: C, 49.41; H, 4.67; Cl^-, 9.14. Calcd. for $C_{32}H_{36}Br_2I_2O_2$ (bromide dioxanate): Br^-, 18.45. Found: Br^-, 18.5.

The infrared spectrum of the dioxanate of the chloride showed bands of 11.2 and 11.48 μ which are present in dioxane itself but which are not present in the free chloride.

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[38] M. W. Formo and J. R Johnson, ref. 37, p. 486.

[39] C. Willgerodt, *J. prakt. Chem.*, [2] **33**, 160 (1886).

[40] R. Bassman, *Ann.*, **191**, 208 (1878).

4,4′-Dicyclohexyldiphenyliodonium Salts.—The reaction was run as described above for diphenyliodonium bisulfate but on a 0.1-mole basis and with benzene replaced by a molar equivalent of cyclohexylbenzene. After addition of 200 ml. of water, the reaction mixture was extracted with three 100-ml. portions of ether. Acetone (250 ml.) was added to the combined ether extracts, which was then divided into two portions. These were treated with concentrated solutions of sodium bromide and potassium iodide to give, after washing with water and acetone and crystallization from methanol, 35% of 4,4′-**dicyclohexyldiphenyliodonium bromide**, m.p. 175°, and 38% of 4,4′-**dicyclohexyldiphenyliodonium iodide**, m.p. 159–160°.

Anal. Calcd. for $C_{24}H_{30}BrI$: C, 54.87; H, 5.76; Br$^-$, 15.22. Found: C, 54.38; H, 5.77; Br$^-$, 15.1.

The iodide was slightly soluble in cold benzene (~0.8 g./100 ml.) and in hot acetone (~2.6 g./100 ml.) and more soluble in hot methanol (~8.3 g./100 ml.).

4,4′-Di-*n*-dodecyldiphenyliodonium Salts.—To a well-stirred mixture of 14.76 g. (60 mmoles) of *n*-dodecylbenzene, 5.35 g. (25 mmoles) of potassium iodate, 70 ml. of acetic acid and 20 ml. of acetic anhydride kept below 10° there was added over 10 minutes a cold mixture of 15 ml. of acetic acid and 12 ml. of sulfuric acid. After the mixture had been stirred overnight at room temperature, 100 ml. of water was added, and the mixture was extracted with three 50-ml. portions of ether. The combined extract was washed with water, treated with activated carbon and heated to remove most of the ether. A solution of 40 g. of sodium bromide in 60 ml. of water was added, and the mixture was cooled and stirred until crystallization occurred. The precipitate was crystallized three times from acetone to give 6.5 g. (9.3 mmoles, 37%) of 4,4′-**di-*n*-dodecyldiphenyliodonium bromide**, m.p. 93–96°.

Anal. Calcd. for $C_{36}H_{58}BrI$: Br$^-$, 11.46. Found: Br$^-$, 11.70.

Using the same procedure but with 20 g. of potassium iodide in 50 ml. of water as the precipitant, there was obtained, after two crystallizations from acetone, 7.8 g. (10.5 mmoles, 42%) of 4,4′-**di-*n*-dodecyldiphenyliodonium iodide**, m.p. 99–103°.

Anal. Calcd. for $C_{36}H_{58}I_2$: I$^-$, 17.04. Found: I$^-$, 17.16.

This iodide was slightly soluble in cold benzene (~1.5 g./100 ml.), ether and chloroform and was soluble in hot acetone, methanol and ethanol.

4,4′-Disuccinimidodiphenyliodonium Salts.—To a vigorously stirred solution of 52.6 g. (300 mmoles) of succinanil in 24 ml. of concd. sulfuric acid, 147 ml. of acetic acid and 48 ml. of acetic anhydride there was added 32.1 g. (150 mmoles) of potassium iodate at 20°. The reaction mixture was stirred at 70° for 23 hours and at room temperature for 12 hours and was then treated with 200 ml. of water and a concd. aqueous solution of 50 g. of potassium iodide. The precipitate was washed and dried *in vacuo* over potassium hydroxide pellets to give 79.2 g. (132 mmoles, 88%) of **4,4′-disuccinimidodiphenyliodonium iodide**, m.p. 178°. Crystallization from formic acid–acetic acid raised the m.p. to 184–185°.

Anal. Calcd. for $C_{20}H_{16}I_2N_2O_4$: I$^-$, 21.0. Found: I$^-$, 21.3.

This salt was soluble in hot formic acid but only slightly soluble in hot acetone, methanol, ethanol, tetrahydrofuran, dioxane and acetic acid.

Thermal decomposition of 7.0 g. (11.6 mmoles) of the above iodide in dimethylformamide gave 6.09 g. (20 mmoles, 86%) of 4-**iodosuccinanil**, m.p. 218–219°. Recrystallization from dimethylformamide raised the m.p. to 238°, reported[31] m.p. 86°. There was no depression of m.p. on admixture with an authentic sample prepared as described above under **Iodo Compounds**.

Succinanil was converted also in 43% yield to **4,4′-disuccinimidodiphenyliodonium chloride**, m.p. 207° (from formic acid), by a procedure similar to that given above for the iodide.

Anal. Calcd. for $C_{20}H_{16}ClIN_2O_4$: C, 47.03; H, 3.16; Cl$^-$, 6.94; N, 5.48. Found: C, 46.88; H, 3.37; Cl$^-$, 6.85; N, 5.57.

The solubility of the chloride was similar to that of the iodide.

Reaction C (Iodine(III) Trifluoroacetate in Acetic Anhydride). 4,4′-**Dimethoxydiphenyliodonium Trifluoroacetate.**—To 7 ml. of acetic anhydride, cooled to about −15°, there was added with stirring 2.7 ml. of fuming nitric acid (sp. gr. 1.51). With the temperature kept below 20°, 2.5 g. (20 mmoles) of iodine and 4.7 ml. (61.2 mmoles) of trifluoroacetic acid were added. The mixture was stirred for one-half hour, during which time the temperature rose to 40–45°, the iodine dissolved completely, and nitrogen oxides were evolved. Solvent was removed by distillation at 1–2 mm. with the pot temperature kept below 40°. The oily, semi-solid residue of iodine(III) trifluoroacetate was dissolved in 15 ml. of acetic anhydride.

This solution was kept at −10° while a solution containing 8.7 ml. (80 mmoles) of anisole, 35 ml. of acetic anhydride and 5 ml. (66 mmoles) of trifluoroacetic acid was added in about 20 minutes. The reaction mixture was placed in a refrigerator overnight and then kept at room temperature for three hours. Removal of solvents at low temperature left an oil which gave crystals on treatment with 200 ml. of ether. Finally at 0°, the crystals were collected, washed with ether and dried to give 5.0 g. (55%) of crude 4,4′-**dimethoxydiphenyliodonium trifluoroacetate**.

This salt was twice crystallized from benzene (5 g./100 ml.) to yield 3.8 g. of white feathery needles of m.p. 134–136° dec. For halide salts see Table V.

Anal. Calcd. for $C_{16}H_{14}O_4F_3I$: C, 42.31; H, 3.11. Found: C, 42.60; H, 2.97.

Reaction D (An Iodoso or Iodoxy Compound with an Aromatic Compound). In Sulfuric Acid.—Previously reported[2] condensations are those of iodosobenzene with benzene, toluene and anisole, of 2-nitroiodosobenzene with benzene and of 3-nitroiodosobenzene with benzene and *n*-butylbenzene; see Table IV. Reported below is the condensation of 4-nitroiodosobenzene with benzene.

4-**Nitrodiphenyliodonium Salts.**—To a vigorously stirred slurry of 150 ml. of concd. sulfuric acid and 15.6 g. (0.2 mole) of benzene at −20 to −30° finely powdered 4-nitroiodosobenzene (26.5 g., 100 mmoles) was added over 45 minutes. Oxidizing power disappeared in an hour. After having been poured onto a kg. of ice, the reaction mixture was filtered to remove solids, shaken twice with 10 g. of activated carbon and treated with 20 g. of sodium bromide in 100 ml. of water. The precipitate was washed with water and with ether and dried to give 16.6 g. (41%) of 4-**nitrodiphenyliodonium bromide**, m.p. 149°.

Anal. Calcd. for $C_{12}H_9BrINO_2$: Br$^-$, 19.68. Found: Br$^-$, 19.53.

The combined mother liquors with potassium iodide gave 0.7 g. (1.5%) of 4-**nitrodiphenyliodonium iodide**, m.p. 128°; *cf.* material of m.p. 143–146° prepared by metathesis (Table V).

When the same condensation was run with 4-nitroiodoxybenzene (reaction D-4), somewhat lower yields were obtained; see Table IV.

In Acetic Acid–Acetic Anhydride–Sulfuric Acid.—Previously reported[2] condensations are those of iodosobenzene with benzene, toluene and anisole and of 3-nitroiodosobenzene with benzene; see Table IV. The condensation of iodosobenzene with acetanilide is reported below.

4-**Acetamidodiphenyliodonium Salts.**—To a vigorously stirred solution of 13.5 g. (100 mmoles) of acetanilide in 50 ml. of concd. sulfuric acid at −25° there was added dropwise a suspension of 11.0 g. (50 mmoles) of iodosobenzene in 40 ml. of acetic acid and 10 ml. of acetic anhydride. The reaction mixture was stirred for 30 minutes at −25°, allowed to warm to room temperature, poured onto 600 g. of ice and treated twice with activated carbon. A solution of sodium bromide (20 g.) was added, giving a precipitate which was washed and dried to yield 4.8 g. (23%) of 4-**acetamidodiphenyliodonium bromide**, m.p. 188–189°, reported[13] m.p. 174°.

Anal. Calcd. for $C_{14}H_{13}BrINO$: Br$^-$, 19.12. Found: Br$^-$, 18.94, 18.89.

In Acetic Anhydride–Trifluoroacetic Acid; 4-Methoxydiphenyliodonium Trifluoroacetate.—To a stirred solution of 7.2 g. (22.4 mmoles) of iodosobenzene diacetate in 20 ml. of acetic anhydride and 5.2 ml. (67.2 mmoles) of trifluoroacetic acid held at −20° there was added slowly a solution of 3.6 ml. (33 mmoles) of anisole in 15 ml. of acetic anhydride. After one hour at −20° and 12 hours at 0°, the reaction mixture was kept at room temperature for two days. After removal of solvents *in vacuo* below 70° the residual oil was treated with anhydrous ether at 0°. The crystals were collected, washed with cold anhydrous ether and dried to give 8.8 g. (20.8 mmoles, 92%) of **4-methoxydiphenyliodonium trifluoroacetate**, m.p. 166–169° (dec.) after two further crystallizations from benzene.

Anal. Calcd. for $C_{15}H_{12}F_3IO_3$: C, 42.47; H, 2.85. Found: C, 42.63; H, 2.95.

Reaction D-5 (Oxidation of an Iodo Compound Followed by Condensation).—No reactions of this type have been previously reported by this group; *cf.* Sandin and co-workers.[24] Reported below are the oxidation and condensation of a nitroiodobenzene and iodobenzoic acid to nitro- and carboxydiphenyliodonium salts.

2-Nitrodiphenyliodonium Iodide.—To a solution of 5.0 g. (20 mmoles) of 2-nitroiodosobenzene in 100 ml. of concd. sulfuric acid there was added with stirring at 20–25° 6.0 g. (22 mmoles) of potassium persulfate and then 25 ml. of benzene. After further stirring for 1.5 hours, the reaction mixture was poured onto ice, the solid was removed by filtration, unreacted benzene was separated, and the solution was clarified by several treatments with activated carbon. Addition of aqueous potassium iodide gave an orange precipitate which on washing and drying gave 7.2 g. (17.4 mmoles, 79%) of **2-nitrodiphenyliodonium iodide**, m.p. 102°; see Table V for salt of m.p. 106–107°.

4-Carboxydiphenyliodonium Iodide.—To a solution of 10.0 g. (40 mmoles) of 4-iodobenzoic acid in 100 ml. of concd. sulfuric acid there was added with stirring 21.6 g. (80 mmoles) of potassium persulfate at −10° and then, after 15 minutes, 50 ml. of benzene at −20°. The mixture was stirred at −10° for 1 hour and at 0° for 3 hours and then was processed as in the preceding experiment to give 13 g. (28 mmoles, 69%) of crude **4-carboxydiphenyliodonium iodide**. After crystallization from methanol the product softened at 155–160° but finally melted at 265°; 4-iodobenzoic acid melts at 265°.

Anal. Calcd. for $C_{13}H_{10}I_2O_2$: C, 34.45; H, 2.21. Found: C, 34.37; H, 2.35.

Metathesis. Diphenyliodonium Fluoroborate.—To a solution of 44 g. (139 mmoles) of diphenyliodonium chloride in 800 ml. of water there was added at 60° 150 mmoles of silver fluoroborate (61.3 g. of Baker and Adamson solution: 47.75% $AgBF_4$, 3.58% HBF_4, 0.71% H_3PO_3). The precipitate of silver chloride was removed, and the filtrate was cooled and seeded. Alternate crystallization and concentration of mother liquors at 50 mm. pressure yielded 43.8 g. (120 mmoles, 86%) of **diphenyliodonium fluoroborate**, m.p. 134–136°. Recrystallization of 40 g. of this material from 125 ml. of water raised the m.p. to 136°, reported[30] m.p. 136°.

Diphenyliodonium Benzenesulfonate.—To a solution of 81 g. (260 mmoles) of diphenyliodonium chloride and 53 g. (300 mmoles) of benzenesulfonic acid monohydrate in 450 ml. of methanol boiling under reflux there was added in small portions 34.1 g. (130 mmoles) of lead carbonate. The reaction mixture was stirred at reflux for two hours and then for four hours at room temperature. After the removal of lead chloride from the chilled solution, the solution was concentrated to one-half the original volume, and one-half pound of ether was added with stirring. The first and second crops of crystals (96 g.) obtained from the cold solution were combined and recrystallized from a liter of isopropyl alcohol to give 76 g. (177 mmoles, 68%) of **diphenyliodonium benzenesulfonate**, m.p. 175–184°. This material was neutral to litmus paper and gave negative tests for lead and chloride ions. Two more crystallizations raised the m.p. to 178–182°.

Anal. Calcd. for $C_{18}H_{15}IO_3S$: C, 49.33; H, 3.45; I, 28.94; S, 7.32. Found: C, 49.51; H, 3.69; I, 28.93; S, 7.32.

Diphenyliodonium Tosylate.—In a similar manner there was obtained from 107.5 g. of diphenyliodonium chloride, 76 g. of *p*-toluenesulfonic acid monohydrate and 45.3 g. of lead carbonate in methanol 133 g. of crude product. This was crystallized from isopropyl alcohol to give 105.6 g. (69%) of **diphenyliodonium tosylate**, m.p. 176–184°, neutral to litmus and free of lead and chloride ions. Two further crystallizations raised the m.p. to 178–181°.

Anal. Calcd. for $C_{19}H_{17}IO_3S$: C, 50.45; H, 3.79; I, 28.06; S, 7.09. Found: C, 50.70; H, 4.03; I, 28.00; S, 7.40.

BROOKLYN 1, N. Y.

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

Diaryliodonium Salts. X. Catalysts and Inhibitors in the Reactions of Diphenyliodonium Ions with Anions and Hydroxylic Solvents[1]

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The retardation of the hydrolysis of the diphenyliodonium ion by acid and by chloride ion and the retardation of the reaction with chloride ion by acid have suggested: (a) that these reactions proceed by the reversible formation from the diphenyliodonium ion of an intermediate, (b) that the intermediates may be reconverted to diphenyliodonium ion by acid, and (c) that the intermediate may be hydrolyzed by water or react with chloride ion and water. Equations derived on the basis of these assumptions have been used to analyze the data. Oxygen was found to have little effect on the initial rates of these reactions but to affect the shapes of the curves; these effects have been discussed but cannot now be explained. The results of the hydrolyses of diphenyliodonium salts catalyzed by added cupric sulfate and run under oxygen, nitrogen and hydrogen do not fully distinguish between various mechanistic possibilities, including: (a) reversible formation and irreversible hydrolysis of a copper-containing intermediate and (b) reaction of the diphenyliodonium ion with copper(I) hydroxide. Indeed, our evidence allows both copper(I) and copper(II) species as catalysts but suggests that the copper(I) catalyst is more reactive. Some peroxide-catalyzed reactions of iodonium salts with ethers and alcohols also are discussed.

Introduction

About ten years after the discovery of the iodonium salts Büchner reported a preliminary study[2] of the decomposition of diphenyliodonium chloride and iodide to halogenobenzenes with heat and light. An earlier paper[3] of the present series reported on

$$C_6H_5I^+C_6H_5\ X^- \longrightarrow C_6H_5X + C_6H_5I \qquad (A)$$

further work in this field and commented on Büchner's findings.[4] In the present study the

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(1) This paper is taken largely from the master's thesis of Morris Rapoport and in smaller part from the doctoral dissertations of E. Melvin Gindler and Roy J. Taylor; see also Acknowledgments. Attention is directed to the recent substantial contribution to this field by M. C. Caserio, D. L. Glusker and J. D. Roberts (ref. 8).

(2) E. H. Büchner, *Koninklijke Akad. v. Wettenschappen te Amsterdam, Proc. Sec. Sci.*, **5**, 646 (1903) (in English).

(3) F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(4) Ref. 2: "Very small quantities of acid retard the reaction (with chloride ion) to a remarkable extent or bring it to a standstill; the presence of traces of iodine causes a regular fall in the reaction coefficient; a little of the free base (diphenyliodonium hydroxide) accelerates, on the other hand, the decomposition to a strong degree. The halogenobenzenes formed during the reaction appear to be inert."