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ORGANIC POLYVALENT IODINE COMPOUNDS

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CONTENTS

I. Introduction 243
II. Preparation 244
  A. Iodo Dihalides 244
  B. Iodo Dicarboxylates 245
  C. Miscellaneous Iodo Disalts 245
  D. Iodoso Compounds 245
  E. Iodonium Salts 246
  F. Triaryliodine Compounds 248
  G. Iodoxy Compounds 248
  H. Iodyl Salts 249
III. Properties 249
  A. Iodo Dihalides 249
  B. Iodo Dicarboxylates 253
  C. Miscellaneous Iodo Disalts 254
  D. Iodoso Compounds 255
  E. Iodonium Salts 256
  F. Iodoxy Compounds 259
IV. Bonding and Structures 260
  A. Iodo Dihalides 260
  B. Iodoso Compounds 262
  C. Iodonium Salts 262
  D. Iodoxy Compounds 262
  E. Spectral Data 263
V. References 264

I. INTRODUCTION

A large class of organic compounds is known containing iodine in the (III) or (V) state. Such compounds were first described in 1885 by Willgerodt (189) who summarized the early work up to 1914. Sandin (171) reviewed the literature to 1942. Beringer and Gindler (37) made an exhaustive tabulation of the physical and chemical properties of, and references to, all compounds of this class known to 1956. The present review is primarily concerned with developments since these surveys were published. Only compounds containing one or more carbon–iodine bonds are considered; excluded are compounds with iodine bonded only to atoms other than carbon, and molecular complexes of iodine.

Organic polyvalent iodine compounds may be classified into five types. General formulas, with some specific examples to illustrate the preferred *Chemical Abstracts* names, are

(1) Iodine(III) compounds with *one* carbon–iodine bond.

(a) Iodo disalts, RIX_2

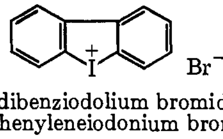
$C_6H_5SO_2CH_2ICl_2$	CH_3ICl_2	*p*-$CH_3C_6H_4I(OCOCH_3)_2$
phenyl iodomethylsulfone dichloride	iodomethane dichloride	*p*-iodotoluene diacetate

(b) Iodoso compounds, RIO

m-OIC_6H_4IO
m-diiodosobenzene

(2) Iodine(III) compounds with *two* carbon–iodine bonds on the same iodine atom, RIR′X.

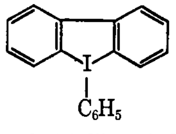
$(C_6H_5)_2ICl$
diphenyliodonium chloride



dibenziodolium bromide
(biphenyleneiodonium bromide)

(3) Iodine(III) compounds with *three* carbon–iodine bonds on the same I atom.

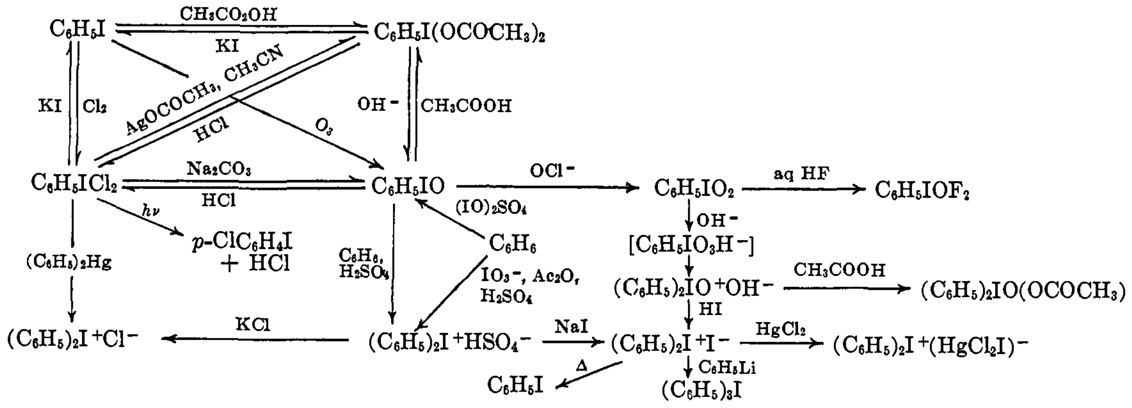
$(C_6H_5)_3I$
triphenyliodine



5-phenyl-5H-dibenziodole
(phenylbiphenyleneiodine)

CHART I

INTERCONVERSIONS OF ARYL POLYVALENT IODINE COMPOUNDS



(4) Iodine(V) compounds with *one* carbon–iodine bond.

$C_6H_5IO_2$ iodoxybenzene

$C_6H_5IOF_2$ iodosobenzene difluoride

(5) Iodine(V) compounds with *two* carbon–iodine bonds on the same I atom.

$(C_6H_5)_2IO(OCOCH_3)$ diphenyliodyl acetate

Most of the known, stable compounds in each of these classes contain an aromatic R group; in fact, only in groups 1a and 2 have nonaromatic derivatives been prepared. Examples of interconversions among the five classes are shown in Chart I.

II. PREPARATION

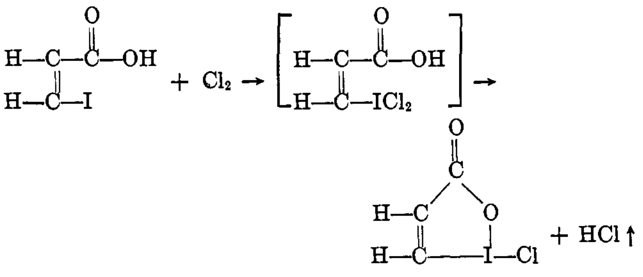
A. IODO DIHALIDES

Passing dry chlorine into a solution of aromatic iodo compound (123) or an α-iodomethylsulfone (60) in virtually any organic solvent causes appreciable formation of an iodo dichloride. The reaction is reversible; the kinetics and equilibrium of the reaction will be discussed in section IIIA of this review. The synthesis of iodoaryl dichlorides is best carried out in chloroform solution, low-boiling petroleum ether being added to precipitate the dichloride if crystallization is not spontaneous. Prior to use, dichlorides should be recrystallized from chloroform, as they undergo a light-catalyzed decomposition on standing.

$$C_6H_5I + Cl_2 \rightleftarrows C_6H_5ICl_2$$

$$C_6H_5ICl_2 \xrightarrow{h\nu} p\text{-}ClC_6H_4I + HCl\uparrow$$

Iodoalkyl dichlorides have been prepared from the iodoalkane and chlorine at −196° (183). Iodomethane dichloride, the most stable of this series, decomposes at −30° to chloromethane and iodine monochloride. Higher homologs decompose above liquid air temperature. Stable dichlorides of simple substituted olefins have been obtained (181), *e.g.*, $ClCH{=}CHICl_2$. Likewise, addition of chlorine to β-iodoacrylic acid and β-iodofumaric acid gives products (183) which lose hydrogen chloride, forming stable products containing polyvalent iodine in a ring.



A few iodo difluorides have been prepared, which are of the aryl series. Treatment of *p*-iodosotoluene with 46% hydrofluoric acid in acetic acid gave a solution from which *p*-iodotoluene difluoride was recovered on addition of water (69). The dry solid was redissolved in chloroform and was kept in solution for 2 or 3 days without appreciable etching of glass vessels by liberated hydrogen fluoride. Equal weights of iodosobenzene and 40% hydrofluoric acid containing potassium hydrogen fluoride were mixed in chloroform and treated with chloroform saturated with dry hydrogen fluoride. The resulting solution of iodobenzene difluoride was used directly as a fluorinating agent (87). An alternate procedure involved the electrolysis of an acetonitrile solution of silver(I) fluoride and iodobenzene using platinum electrodes at 4–6 v, and a current density of 50 ma/cm² (173). A good yield of iodobenzene difluoride was obtained at the anode under these conditions, but at higher current densities the solvent was attacked.

$$p\text{-}CH_3C_6H_4IO + 2HF \rightarrow p\text{-}CH_3C_6H_4IF_2 + H_2O$$

$$C_6H_5I + 2F^- \rightarrow C_6H_5IF_2 + 2e^- \quad \text{(at anode)}$$

Only one report of the preparation of iodo dibromides has been published. In 1905, Thiele and Peter (182) claimed to have isolated iodomethane dibromide and iodobenzene dibromide. They also speculated on the existence of iodo diiodides, but no such compounds have been reported.

B. IODO DICARBOXYLATES

Iodobenzene diacetate is most easily prepared by stirring iodobenzene in a 40% acetic acid solution of peracetic acid (145). If commercial 40% peracetic acid is unavailable, a suitable reagent can be prepared by stirring 30% hydrogen peroxide and glacial acetic acid for 8–10 hr. Alternatively, the less soluble iodo diacetate can be precipitated from acetic acid solutions of the corresponding dichloride or iodoso compound. Addition of iodobenzene dichloride to silver acetate suspended in acetonitrile yields silver chloride and iodobenzene diacetate (1). The latter is soluble in the acetonitrile and is obtained by freeze-drying the solution at −40°.

$$CH_3COOH + CH_3CO_3H + C_6H_5I \rightarrow C_6H_5I(OCOCH_3)_2 + H_2O$$

Iodo dibenzoates are conveniently prepared in the same manner as diacetates, preferably using perbenzoic acid and the iodo compound. Other iodo dicarboxylates must be prepared by fractional precipitation from acetic acid solution, due to the unavailability of corresponding peroxy acids.

C. MISCELLANEOUS IODO DISALTS

Heretofore, iodo dinitrates, chromates, sulfates, hydrogen sulfates, etc., were prepared by addition of the appropriate acid to an acetic acid solution of the iodo dichloride or the iodoso compound (171). Fractional precipitation of the salts could not, of course, be used to prepare sensitive salts which decompose in strong acids. Recently it was found that a number of these salts can be prepared conveniently under much less severe conditions, namely by double displacement in acetonitrile solution (1).

$$C_6H_5ICl_2 + 2AgX \rightarrow C_6H_5IX_2 + 2AgCl\downarrow$$

A suspension or solution of silver salt is added to iodobenzene dichloride solution, the silver chloride filtered, and the soluble iodo salt recovered by freeze-drying the solution at −40°. This technique appears to hold great promise, especially as sensitive highly substituted salts, hitherto not isolated, should be able to be prepared by the method. Table I lists products of displacement of iodobenzene dichloride by a number of silver salts. It will be noted that some iodo salts are evidently unstable even at −40°, including the previously reported iodobenzene dibromide.

D. IODOSO COMPOUNDS

Only aryliodoso compounds, ArIO, are known. Presumably conjugation with an aromatic ring is essential to the stability of the I–O bond. Aryliodoso compounds should be prepared and used when fresh, as they disproportionate on standing.

TABLE I

DOUBLE DISPLACEMENT ON IODOBENZENE DICHLORIDE IN ACETONITRILE

Salt	Product	Salt	Product
$AgOCOCH_3$	$C_6H_5I(OCOCH_3)_2$	Ag_2CO_3	$C_6H_5IO + CO_2$
$AgOCOCF_3$	$C_6H_5I(OCOCF_3)_2$	Ag_2O	Decomposition
$AgNO_3$	$C_6H_5I(NO_3)_2 \cdot C_6H_5ICl_2$	AgN_3	$C_6H_5I + N_2$
Ag_2CrO_4	$C_5H_5ICrO_4$	$AgCN$	$C_6H_5I + (CN)_2$
Ag_2SO_4	$C_6H_5ISO_4$	$AgCNO$	$C_6H_5I + (CNO)_x$ (decomp)
$Ag_2C_2O_4$	$C_6H_5IO + CO_2$	$AgSCN$	$C_6H_5I + (SCN)_x$
$AgONO$	$C_6H_5IO + NO_2$	$AgBr$	$C_6H_5I + Br_2$
$AgNO_2$	$C_6H_5IO + N_2O_3$	AgI	$C_6H_5I + I_2$

$$2C_6H_5IO \rightarrow C_6H_5I + C_6H_5IO_2$$

This reaction, rather slow at room temperature, proceeds readily at 100° and is occasionally used to prepare iodoxy compounds (187).

Iodoso compounds are prepared by the following methods. (a) Silver oxide, alkali hydroxides or carbonates, or alkaline earth carbonates effect hydrolysis of iodo disalts in aqueous solution by a reversible process (123, 189).

$$C_6H_5ICl_2 + 2OH^- \rightarrow C_6H_5IO + 2Cl^- + H_2O$$

(b) Direct oxidation of the iodo compound has been effected using fuming nitric acid (130), potassium permanganate in dilute sulfuric acid (12), ozone (78), peracetic acid (9, 45) followed by hydrolysis, potassium persulfate (108), and presumably other oxidants.

$$C_6H_5I + O_3 \rightarrow C_6H_5IO + O_2\uparrow$$

(c) Iodosyl sulfate, $(IO)_2SO_4$, effects aromatic substitution giving the iodoso compound from the parent hydrocarbon (127).

$$2C_6H_6 + (IO)_2SO_4 \rightarrow 2C_6H_5IO + H_2SO_4$$

The reagent is conveniently prepared by the combination of iodine, an iodate, and sulfuric acid (92).

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

In the absence of excess sulfuric acid, 50–60% yields of iodoso compounds were obtained in the following reactions (120).

$$2C_6H_5NO_2 + (IO)_2SO_4 \rightarrow 2m\text{-}O_2NC_6H_4IO + H_2SO_4$$

$$2C_6H_5COOH + (IO)_2SO_4 \rightarrow 2m\text{-}HOOCC_6H_4IO + H_2SO_4$$

$$2C_6H_5SO_3H + (IO)_2SO_4 \rightarrow 2m\text{-}HSO_3C_6H_4IO + H_2SO_4$$

The aryl compounds in amounts of 40–50% were accounted for as iodonium salts formed in a slow acid-catalyzed decomposition (80).

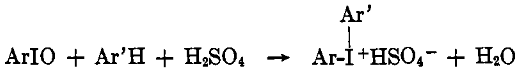
$$ArH + ArIO + H_2SO_4 \rightarrow Ar_2I^+HSO_4^- + H_2O$$

(d) Displacement of iodobenzene dichloride with silver nitrite, oxalate, or carbonate in acetonitrile gave iodosobenzene (*cf.* Table I) (1).

E. IODONIUM SALTS

A large number of specific syntheses have been described for the preparation of iodonium salts, but six methods are generally useful and thus deserve special description (30, 61).

(a) Iodo disalts, iodoso and iodoxy compounds, undergo acid-catalyzed condensation with aromatic hydrocarbons, giving the mixed iodonium salts (27).

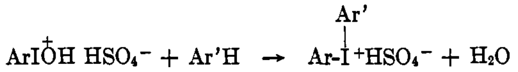


$$ArIO + Ar'H + H_2SO_4 \rightarrow Ar\text{-}\overset{\overset{Ar'}{|}}{I}{}^{+}HSO_4^{-} + H_2O$$

It was proposed that the reaction proceeds by a two-step mechanisms First, protonation of the iodoso compound gives

$$ArIO + H_2SO_4 \rightarrow ArI^{+}OH\ HSO_4^{-}$$

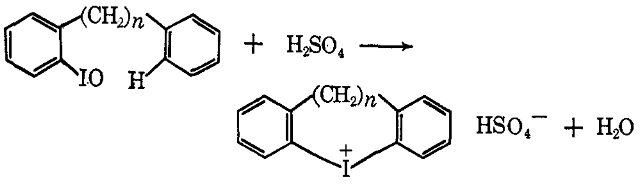
Second, this cationic species effects electrophilic substitution of the hydrocarbon



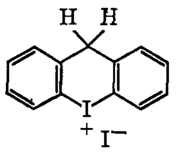
$$Ar\overset{+}{I}OH\ HSO_4^{-} + Ar'H \rightarrow Ar\text{-}\overset{\overset{Ar'}{|}}{I}{}^{+}HSO_4^{-} + H_2O$$

Condensation of benzene with *o*- and *m*-nitroiodosobenzene in the presence of sulfuric acid gave 2- and 3-nitrodiphenyliodonium hydrogen sulfates (27) as the products. With *n*-butylbenzene, 2- and 3-nitrophenyl-(*n*-butylphenyl)iodonium hydrogen sulfates were the primary products. In trifluoroacetic acid, the same products were obtained as the trifluoroacetate salts.

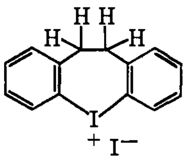
Ring closure of a series of iodoso compounds in sulfuric acid was effected (53) by the same general type of reaction.



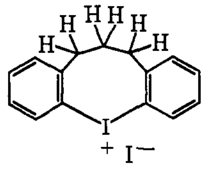
Yields of 99% dibenziodolium hydrogen sulfate (*n* = 0), 95% of 10H-dibenz[*b,e*]iodininium iodide (I) (*n* = 1), 60% of 10,11-dihydrodibenz[*b,f*]iodopinium iodide (II) (*n* = 2), and 70% of 6,7-dihydro-5H-dibenz[*b,g*]iodocinium iodide (III) (*n* = 3) were obtained; the lowest return corresponding to the product containing a seven-membered ring.



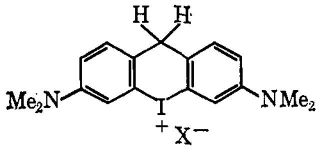
I



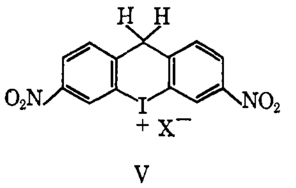
II



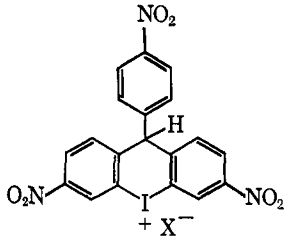
III



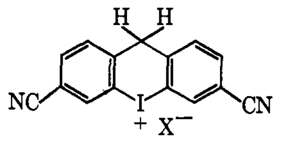
IV



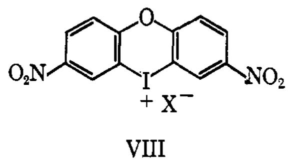
V



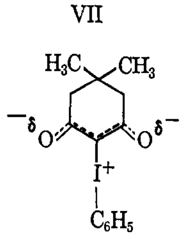
VI



VII



VIII



IX

Phosphorus(V) oxide in petroleum ether was also shown to be an effective acid catalyst (40); condensation of iodosobenzene with benzene in this solution at 0° gave, on hydrolysis, good yields of diphenyliodonium iodide.

(b) In sulfuric acid, iodosyl sulfate effects direct condensation with aromatic hydrocarbons (117, 151). Iodosyl sulfate was first prepared by thermal decomposition of iodine pentoxide in sulfuric acid, or by reaction of iodine pentoxide with iodine (151).

$$2I_2 + 3I_2O_5 + 5H_2SO_4 \rightarrow 5(IO)_2SO_4 + 5H_2O$$

Beringer and co-workers (30) found a simpler synthesis, involving merely the stirring of iodine with an iodate salt.

$$2I_2 + 6IO_3^{-} + 11H_2SO_4 \rightarrow 5(IO)_2SO_4 + 6HSO_4^{-} + 8H_2O$$

A third, little-explored method for iodosyl sulfate involves oxidation of iodine with nitric acid.

$$I_2 + 3HNO_3 + 8H_2SO_4 \rightarrow (IO)_2SO_4 + 3NO^{+} + 4H_3O^{+} + 7HSO_4^{-}$$

A suspension of iodosyl sulfate in sulfuric acid is most conveniently added to the hydrocarbon at about 5°, as the proposed first step is quite exothermic.

$$2ArH + (IO)_2SO_4 + H_2SO_4 \rightarrow 2Ar\overset{+}{I}OH + 2HSO_4^{-}$$

The second, supposedly slower reaction is clearly the same as that in method a above.

$$ArH + Ar\overset{+}{I}OH \rightarrow Ar_2I^{+} + H_2O$$

Hwang and co-workers (90–92) prepared several previously unreported iodolium salts by ring closure of substituted methanes and one ether. Compound IV, 3,7-bis(dimethylamino)-10H-dibenz[*b,e*]iodininium iodide dihydriodide, was isolated in 77% yield from the condensation of bis(*p*-dimethylaminophenyl)methane. Numerous derivatives were prepared and characterized. From 4,4′-dinitrodiphenylmethane, an 85% yield of

3,7-dinitro-10H-dibenz[*b,e*]iodininium iodide (V) was obtained. Similar condensations of tris(*p*-nitrophenyl)methane, bis(*p*-cyanophenyl)methane, and bis(*p*-nitrophenyl) ether formed, respectively, 76% of 3,7-dinitro-10-(*p*-nitrophenyl)-10H-dibenz[*b,e*]iodininium iodide (VI), 81% of 3,7-dicyano-10H-dibenz[*b,e*]iodininium iodide (VII), and an unspecified yield of 3,6-dinitrophenoxiodinin-5-ium iodide (VIII). Attempts to prepare the sulfur analog of VIII by condensation of bis(*p*-nitrophenyl)sulfide were unsuccessful, bis(*p*-nitrophenyl) sulfone instead being obtained.

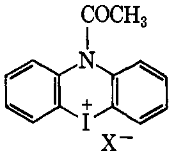
The salts were isolated as hydrogen sulfates or as iodides. From these, numerous salts were prepared, as both simple and complex organic derivatives. In Table II are given the melting points of the principal salts prepared, all of which decompose at their melting points. All are insoluble in water and organic solvents, but soluble in 85% formic acid, from which they were recrystallized. The effect of each of the salts on the growth of *Bacillus subtilis* was measured.

TABLE II

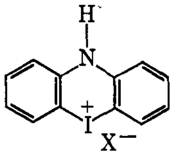
DECOMPOSITION POINTS (IN °C) OF COMPLEX IODONIUM SALTS IV–VIII

Compound	Cl^-	Br^-	I^-	SCN^-	HSO_4^-
IV	197.5	197.5	195	153.5	...
V	211.5	217.5	164	167–168	217.5
VI	176.5	178.5	151–152	185–187	237
VII	233	214–215	177–178	207–209	236
VIII	246	245	160	167–168	232

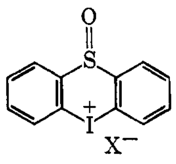
Beringer, Kravetz, and Topliss (39a) recently published the results of some attempts to prepare iodonium salts containing iodine and oxygen, sulfur, or nitrogen in six-membered rings, and salts containing iodine in five-, six-, and seven-membered rings. Three general methods were used: (i) reaction of a 4,4′-disubstituted diphenyl compound with iodosyl sulfate in sulfuric acid; (ii) oxidation of an iodo compound with hydrogen peroxide or potassium persulfate, followed by treatment with sulfuric acid to effect cyclization; (iii) nitration of a heterocyclic iodonium cation. Metathesis of the salt originally obtained allowed isolation of the desired compound. High yields of dibenzolium compounds and 10H-dibenz[*b,e*]iodonium salts were obtained using method i, with the exception of products which were electronically and sterically unfavored. Phenoxiodonium salts such as VIII were prepared by method ii, the reaction being carried out at −45° in a large excess of sulfuric acid; VIII was also obtained by nitration of the unsubstituted phenoxiodonium cation. A 50% yield of the 10-acetylphenoxiodonium cation IXa was obtained from N-acetyl-2-iododiphenylamine by method ii using potassium persulfate; when hydrogen peroxide in acetic acid was used, no iodonium salt was formed. The phenaziodonium cation IXb was obtained by hydrolysis of IXa in 20% sulfuric acid. While the sulfur analog of VIII could not be prepared, the sulfoxide analog 10-oxidophenothiiodonium cation IXc was obtained in 17% yield by treatment of the iodo compound with hydrogen peroxide in an acetic–sulfuric acid mixture at 5–10°.



IXa



IXb



IXc

(c) Iodine(III) acylates are conveniently prepared by the method of Fichter and Stern (90), which employs a mixture of iodine and trifluoroacetic acid in a nitric acid–acetic anhydride solution.

$$2I_2 + 12CF_3COOH + 9(CH_3CO)_2O + 6HNO_3 \rightarrow 4I(OCOCF_3)_3 + 18CH_3COOH + 2N_2O_3\uparrow$$

Iodine acylates react with aromatic hydrocarbons in an acid-catalyzed condensation.

$$2ArH + I(OCOCF_3)_3 + HX \rightarrow Ar_2I^+X^- + 3CF_3COOH$$

Condensation of thiophene in trifluoroacetic acid with iodine trifluoroacetate gave 2,2′-dithienyliodonium trifluoroacetate, which was recrystallized and obtained as the iodide in 67% yield. Mixtures of benzene and thiophene were condensed with iodine trifluoroacetate in acetic acid, and 2-thienylphenyliodonium trifluoroacetate was obtained as the primary product (24).

(d) Sodium or potassium iodate, in an acetic acid–acetic anhydride–sulfuric acid mixture, can be used to effect direct reaction with aromatic hydrocarbons, forming open-chain iodonium salts. The nature of the O radical produced in the reaction has not been determined (28).

$$2ArH + KIO_3 + H_2SO_4 + 2(CH_3CO)_2O \rightarrow Ar_2I^+HSO_4^- + 4CH_3COOH + KHSO_4 + [O]$$

(e) Iodine trichloride combines directly with organometallic compounds in a three-step reaction (26). Only in a few cases does reaction stop at the first step, for example the reaction of 2-chlorovinylmercury(II) chloride giving 2-chloroiodoethylene dichloride (49). Typically, reaction of iodine trichloride or of an iodoaryl dichloride with organometallic compounds gives an iodonium salt. The latter reaction can obviously be used to prepare a mixed iodonium salt, RIR'^+X^-. Organolithium compounds react with iodine trichloride, iodo dichlorides, or iodonium salts giving triaryliodine compounds (49).

$$RM + ICl_3 \rightarrow RICl_2 + MCl$$

$$RM + RICl_2 \rightarrow RIR^+Cl^- + MCl$$

$$RM + RIR^+Cl^- \rightarrow R_3I + MCl$$

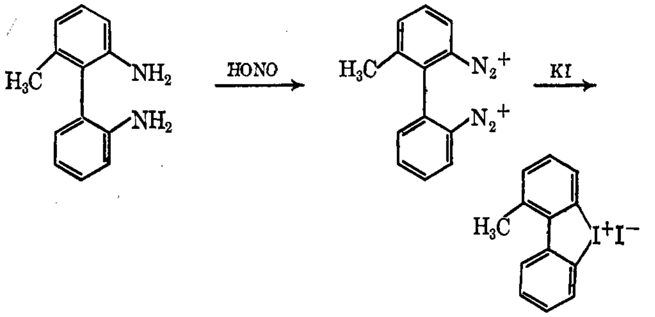
(f) A mixture of iodoso and iodoxy compounds undergoes base-catalyzed condensation, forming iodonium iodates, from which other iodonium salts can be obtained (27, 80, 123). A patent was issued (150) for

$$\mathrm{ArIO_2 + OH^- \rightleftarrows ArIO_3H^-}$$
$$\mathrm{Ar'IO + ArIO_3H^- \rightarrow ArIAr'^+IO_3^- + OH^-}$$

the production of diphenyliodonium salts by base hydrolysis of iodobenzene dichloride, followed by hypochlorite oxidation. The chloride salt was precipitated by addition of brine.

Among more important specific syntheses is the preparation of the enolate betaine IX from 5,5′-dimethyl-1,3-cyclohexanedione (dimedon) by reaction with iodobenzene difluoride (76) or diacetate (138), iodosobenzene (76), or diphenyliodonium hydroxide (136) in refluxing chloroform, acetone, or water. Spectral evidence for the structure shown was obtained. Similar reactions with 5-phenyl-1,3-cyclohexanedione gave an 82% yield of the analogous betaine (mp 134°) (139).

Cyclic iodonium salts were prepared as intermediates in the preparation of biphenylenes, by a modified Sandmeyer reaction (16). Apparently yields were low, as the reaction has not been reported elsewhere.

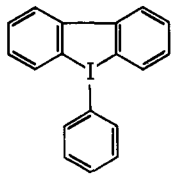


Solubility of iodonium salts in water decreases, in general, with increasing molecular weight of the anion for a given cation. Shaking an iodonium chloride with solutions of alkali bromide, iodide, thiocyanate, or nitrate precipitates these salts (53). Hydrogen sulfates are, however, usually more soluble than chlorides (150). Cyclic iodonium salts are generally insoluble in water and most organic solvents, but soluble in 85% formic acid (90). Ion-exchange techniques have also been used to obtain certain iodonium salts. An aqueous solution of diphenyliodonium bromide was passed through a column of Amberlite IRA-400 resin in the fluoride form. Treatment of the effluent with potassium borohydride solution at 0° gave a precipitate of diphenyliodonium fluoroborate (82). Diphenyliodonium fluoroborate (mp 110° dec) decomposed with a feeble explosion under vacuum; in air, a shattering detonation was observed. Addition of bismuth(III) iodide and potassium iodide to a solution of diphenyliodonium chloride precipitated the highly colored diphenyliodonium tetraiodobismuthate(III), $(C_6H_5)_2I^+BiI_4^-$ (152). It was claimed that formation of the salt could be detected in the presence of 0.1–0.3 μg of bismuth ion.

F. TRIARYLIODINE COMPOUNDS

Addition of an organolithium compound, for example, phenyllithium, to an iodonium salt in an inert solvent causes formation of a triaryliodine compound. Most such compounds are unstable and decompose immediately to free radicals which then react with one another. Two stable triaryliodine compounds have been reported. Addition of phenyllithium to diphenyliodonium iodide in ether at −80° gave a citron-yellow product, triphenyliodine (49). Addition of phenyllithium to dibenziodolium iodide in tetrahydrofuran, in the absence of air and moisture, gave a lemon-yellow solid, 5-phenyl-5H-dibenziodole (X).

The latter is insoluble in water and methanol, soluble in benzene, and decomposes explosively at 105°. Reaction of X with iodine gives dibenziodolium triiodide; with triphenylboron, X gives dibenziodolium tetraphenylborate (mp 195–196°) (190).



X

G. IODOXY COMPOUNDS

The simplest preparation of aryliodoxy compounds takes advantage of the slow disproportionation of aryliodoso compounds; steam distillation of the iodo compound from the mixture leaves the nonvolatile iodoxy substance. However, this is an uneconomical process as a 50% return of product is possible at best; half of the iodoso compound returns to the iodo state (123, 187).

Oxidation of iodo dichlorides or other disalts, or of iodoso compounds, is achieved using hypochlorite solution, generated by saturating cold aqueous base with chlorine gas (188).

$$\mathrm{C_6H_5ICl_2 + 2OCl^- \rightarrow C_6H_5IO_2 + 2Cl^- + Cl_2}$$
$$\mathrm{C_6H_5IO + OCl^- \rightarrow C_6H_5IO_2 + 2Cl^-}$$

Alkaline potassium permanganate solution effects oxidation of *o*-iodosobenzoic acid to *o*-iodoxybenzoic acid (79). Direct oxidation of the iodo compound also was achieved using Caro's reagent, peroxymonosulfuric acid (17, 128). Oxidation of iodobenzene was quantitative when a twofold excess of the acid was used;

$$\mathrm{C_6H_5I + 2H_2SO_5 \rightarrow C_6H_5IO_2 + 2H_2SO_4}$$

iodosobenzene was identified as an intermediate product.

Reaction of hot 46% hydrofluoric acid with an iodoxy compound gives an iodosoaryl difluoride (184). Little is known of the properties or reactions of these

$$\mathrm{ArIO_2 + 2HF \rightarrow ArIOF_2 + H_2O}$$

materials. Other salts of iodoxy compounds with acids and bases have been prepared, indicating that the class of compounds possesses some amphoteric character despite their extremely low solubility in virtually all solvents.

H. IODYL SALTS

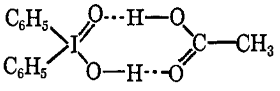
Iodoxybenzene behaves as a monobasic acid, forming a conjugate base in strongly alkaline solution.

$$C_6H_5IO_2 + OH^- \rightleftarrows C_6H_5IO_3H^-$$

The base quantitatively, and irreversibly, changes to diphenyliodyl hydroxide (128), a strong oxidizing agent, and one of the less stable members of this class of compounds.

$$2C_6H_5IO_3H^- \rightarrow (C_6H_5)_2IO^+OH^- + IO_3^- + OH^-$$

Addition of acetic or carbonic acid (aqueous solution of carbon dioxide) precipitates the corresponding acetate and carbonate salts. Dipole moment studies of the acetate (μ = 3.5–5 D.) indicate a cyclic structure for both salts (118).



III. PROPERTIES

A. IODO DIHALIDES

Iodo dichlorides are solids at room temperature, with the exception of the unstable alkyl salts. In the absence of a chromophoric group they are yellow crystalline materials. On standing they decompose, liberating hydrogen chloride; before use, iodo dichlorides should be recrystallized. Heating speeds both this

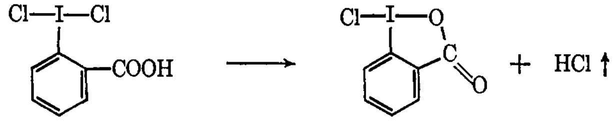
$$C_6H_5ICl_2 \rightarrow p\text{-}ClC_6H_5I + HCl\uparrow$$

reaction and the rate of dissociation to chlorine and the iodo compound. In some cases the latter is so great that the melting points of the dichloride and iodo compound are identical; in all cases melting points are a function of the rate of heating (37). The extent of decomposition of the iodo dichlorides is a function of substitution; electrophilic substituents decrease the electron density at the iodine atom, decreasing the strength of the I–Cl bond. Bekoe and Hulme (22) correlated this effect by comparing the change in melting point of a freshly prepared sample over a 0.5-hr period to the parent compound's dipole moment. Effects observed for a series of *para*-substituted salts are shown in Table III; those for *meta*- and *ortho*-substituted salts are in general similar, although some steric effects were observed. The *o*-methyl, tetramethyl, and pentamethyl salts are quite unstable, while the *o*-carboxyl salt on standing loses hydrogen chloride forming a stable heterocycle similar to the β-iodoacrylic acid derivative (3).

TABLE III

STABILITY OF IODOARYL DICHLORIDES AS A FUNCTION OF DIPOLE MOMENT OF ArI (22)

Compound	Change in mp, °C, 0.5 hr	Dipole moment, D., ArI
p-$NH_2C_6H_4ICl_2$	Rapid decompn	+2.8
p-$CH_3C_6H_4ICl_2$	2	+1.7
$C_6H_5ICl_2$	2	+1.3
p-$C_6H_5C_6H_4ICl_2$	2	+1.2
p-$IC_6H_4ICl_2$	1	0
p-$BrC_6H_4ICl_2$	1	−0.2
p-$ClC_6H_4ICl_2$	0	−0.4
p-$NO_2C_6H_4ICl_2$	0	−2.6



The solid-state decomposition of iodo dichlorides is light catalyzed (109) and can be minimized by keeping the sample in a dark, cool place. The author observed complete decomposition of the unsubstituted salt within 1–2 hr at 40°, under irradiation by a 275-w GE sun lamp.

Exner (60) has reported the preparation of dichlorides of some iodomethylsulfones, RSO_2CH_2I. Table IV lists the melting points of the salts and their parent compounds; as for the aryl derivatives, some lose chlorine, on heating, so rapidly that the two values are identical. All salts decompose at their melting points.

TABLE IV

MELTING POINTS OF IODOMETHYLSULFONE DICHLORIDES, $RSO_2CH_2ICl_2$

R	Mp, °C	
	RSO_2CH_2I	$RSO_2CH_2ICl_2$
Cyclohexyl	90	86–87
p-Tolyl	127	127
β-Naphthyl	139	97
n-Propyl	67	67–71
Phenyl	...	100–101

Physical and chemical properties of iodomethylsulfone chlorides are quite similar to those of iodoaryl dichlorides. Exner (60) explained their unexpected stability by observing that the steric effect of the α-sulfone group, known to be similar to that of the neopentyl group, would block S_N2 attack while polar effects of the same group would prevent S_N1 attack. By this reasoning, iodoethylsulfone dichlorides (β-ethylsulfone derivatives) should be much less stable than the methyl analogs; in fact, none could be prepared.

In aqueous solutions, iodo disalts are quantitatively reduced by potassium iodide. Titrating the liberated

$$ArIX_2 + 3I^- \rightarrow ArI + 2X^- + I_3^-$$

iodine with standard sodium thiosulfate gives the equivalent weight of the iodine compound, a fact frequently made use of in the analysis of these compounds

(142, 189). In alkaline medium the salts are reversibly hydrolyzed (186).

$$ArIX_2 + H_2O \rightleftharpoons ArIO + 2HX$$

In sodium or calcium hypochlorite solution, disalts and iodoso compounds are oxidized to iodoxy compounds (188).

$$ArIX_2 + 2OCl^- \rightarrow ArIO_2 + 2X^- + Cl_2$$

$$ArIO_2 + OCl^- \rightarrow ArIO_2 + Cl^-$$

Addition of certain silver salts, either in suspension or solution, to an acetonitrile solution of an iodo dichloride displaces silver chloride. Table I shows those compounds which have been isolated on freeze-drying the resulting solutions.

Perhaps the most useful property of the dichlorides, and of other disalts, is the ready homolytic cleavage of the I–X bond giving active radicals. For this reason considerable interest has developed in their use as synthetic reagents, while the use of iodobenzene dichloride and iodobenzene dibenzoate as polymerization catalysts has been considered (89, 167).

The potential uses of iodobenzene dichloride as a chlorinating agent were first observed by Garvey, Halley, and Allen (69). Addition of the dichloride to unsaturated hydrocarbons in refluxing ethylene dichloride gave the same products as chlorine addition, but the reaction was milder. Bloomfield (44) reported that addition of the dichloride to rubber in refluxing carbon tetrachloride took place with less than 4% substitution, and the reaction was quantitative. No change was noted on adding 1% of benzoyl peroxide, a radical initiator; however, on addition of hydroquinone, a free-radical inhibitor, 27% of substitution was observed and only 85% of the dichloride was consumed in 2 hr. From these data Bloomfield concluded that the reaction must take place by a free-radical mechanism. He suggested that after liberation of atomic chlorine, the reaction might proceed by the chain mechanism proposed (110) for sulfuryl chloride.

$$C_6H_5ICl_2 \rightarrow C_6H_5ICl\cdot + Cl\cdot \qquad \text{(Eq 1)}$$

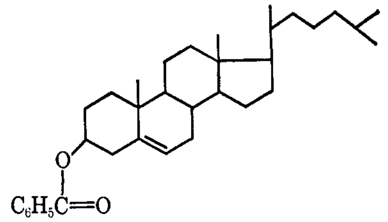
$$Cl\cdot + RH \rightarrow R\cdot + HCl \qquad \text{(Eq 2)}$$

$$R\cdot + C_6H_5ICl_2 \rightarrow RCl + C_6H_5ICl\cdot \qquad \text{(Eq 3)}$$

$$C_6H_5ICl\cdot \rightarrow C_6H_5I + Cl\cdot \qquad \text{(Eq 4)}$$

Ramakrishnan, Raghunath, and Pande (159) repeated Bloomfield's experiments and reported agreement with both the results and the proposed mechanism.

Berg and Wallis (23) obtained high yields of sterol dichlorides by the reaction of iodobenzene dichloride with steroid derivatives in refluxing carbon tetrachloride. For example, cholesteryl benzoate (XI) gave 80% over-all yield of cholesterol dichloride benzoate. Two of the four theoretically possible isomers were obtained. With chlorine only one isomer is obtained, but the product is an oil containing many by-products. The two isomers had very different physical properties, but their structures were not determined. On refluxing with zinc in acetic acid, both isomers gave the sterol benzoate, indicating a highly useful method of protecting double bonds during further synthesis; the olefin is recovered in high yield.



XI

Barton and Miller (21) studied the stereochemistry of cholesterol chlorination with chlorine and with iodobenzene dichloride. Chlorine was found to give the *trans*-5α,6β-dichlorocholestanol, while the products reported by Berg and Wallis were shown to be the *trans*-5α,6β and *cis*-5α,6α isomers. Initially Barton and Miller were unable to reproduce the earlier work and obtained only the *trans* isomer. It was discovered that two reactions are possible between a steroid double bond and iodobenzene dichloride; the first takes place more readily in the presence of small amounts of water. Table V shows the ratio of products obtained for three concentrations of water.

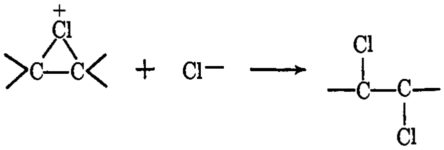
TABLE V

YIELDS OF *cis*- AND *trans*-DICHLOROCHOLESTANOL (21)

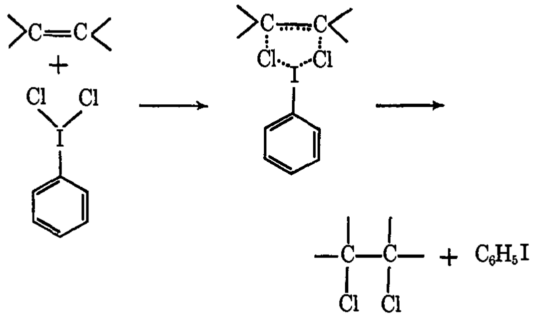
Ratio of cholesteryl benzoate:water	Yield, % *cis*	Yield, % *trans*
∞	83	15
7:1	22	60
1:1	9	64

$$C_6H_5ICl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- + C_6H_5I$$

$$Cl^- + HOCl + {>}C{=}C{<} \rightarrow$$



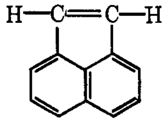
(Eq 5)



(Eq 6)

The first mechanism was easily confirmed, as no other ionic process is presumable. Evidence for the second path, in absence of water, is not so clear-cut. The authors felt that Bloomfield's evidence (44) for a free-radical mechanism was inconclusive, and showed only that an ionic mechanism was not possible under the conditions. Straight molecular addition, they stated, was more reasonable in that it guaranteed a *cis* configuration in the product.

Cristol, Stermitz, and Ramey (56) found that in the presence of *sym*-trinitrobenzene, a free-radical inhibitor, iodobenzene dichloride added to acenaphthylene (XII) in dry chloroform giving the *trans*- rather than the *cis*-dichloride predicted by a molecular addition mechanism. Chlorine gave exclusively the *cis*-dichloride, again the exact opposite of the predicted result. It was made clear, whatever the cause of the inverse effects, that if the reaction were a free-radical process, the attacking radical could not have been Cl· as suggested by Bloomfield. Low yields of the *trans* product were obtained, less than 10% in the absence of the radical inhibitor, and 28% when *sym*-trinitrobenzene was added. Thus not only do the results of the study appear inconclusive, but there is some doubt as to what the product of the *primary* reaction was. Summerbell and Lunk (180) found iodobenzene dichloride to be an exclusively *trans*-chlorinating agent, and found neither mechanism proposed by Barton and Miller acceptable (21).


XII

The confusion attending these reports has been rather well cleared; actually, three mechanisms play an important role in any description of iodo dichloride reactions. In the presence of water, reaction must proceed by the ionic mechanism as proposed by Barton and Miller. In the absence of water, both molecular addition and free-radical mechanisms have been observed and investigated.

Keefer and Andrews (102) studied zinc chloride catalyzed aromatic substitution with both chlorine and iodobenzene dichloride. In the latter case the rate of reaction was found to depend only on the rate of dissociation of dichloride, indicating the actual chlorinating agent to be molecular chlorine.

$$C_6H_5ICl_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C_6H_5I + Cl_2$$

$$ArH + Cl_2 \xrightarrow{k_3} ArCl + HCl$$

Assuming $k_3 >> k_f$, the reaction is initially first order in dichloride, but becomes of complex order as iodobenzene concentration increases. In acetic acid at 25°, $k_f/k_r = K_{eq} = 1.5 \times 10^{-3}$; $k_f = 0.144 \times 10^{-3}\ sec^{-1}$; the Arrhenius activation energy $E_a = 20.2$ kcal mole^{-1}; the enthalpy of activation $\Delta H^* = 9.9$ kcal mole^{-1}.

The rather interesting results of the above experiment led the authors to study dissociation of iodoaryl dichlorides systematically. Since all such compounds absorb strongly in the ultraviolet and visible, at a wavelength sufficiently removed from the chlorine bands to allow quantitative measurements of each band, spectrophotometric methods were used to obtain the following data. For iodobenzene dichloride, the rates k_f and k_r increase in the order $CCl_4 < CH_3NO_2 < CH_3COOH < CF_3COOH$; this was interpreted to indicate the transition state is more polar than the dichloride. The equilibrium constant increased as solvents were varied in the order $CH_3NO_2 < CH_3COOH < CCl_4$, which was interpreted to indicate that the dichloride is more polar than iodobenzene or chlorine. The rate of dissociation in carbon tetrachloride, benzene, or nitromethane is virtually zero in the dark, in the absence of a polar catalyst. No change was noted when hydrogen chloride, or traces of water were added, but when traces of both were added the rate rose to the same order of magnitude as that in acetic acid. In these solvents, the equilibrium constant is about ten times higher than that in acetic acid, but the enthalpy of activation is 9.8 kcal mole^{-1}, very close to that in the acid (2).

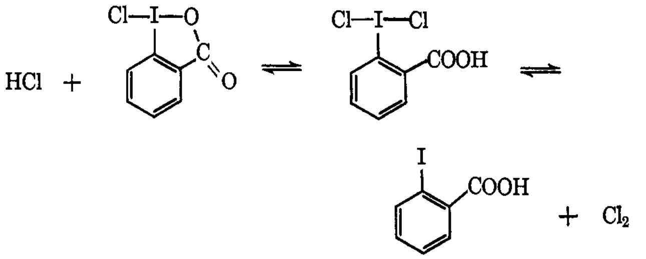
Exceptional reactivity was noted in trifluoroacetic acid (6). This was explained in terms of greater hydrogen bonding of the dichloride with the solvent (minimizing formation of molecular chlorine) and the formation of a unique species $C_6H_5I(OCOCH_3)Cl$ responsible for aromatic substitution (7). In support of the equilibrium step, strong inhibition of reactivity by hydrogen chloride was noted. Further, addition of acetic acid did not appreciably affect the dissociation equilibrium, but strongly inhibited substitution (105). The degree of inhibition was considered (106) a quantitative measure of solvating ability of the trifluoroacetic acid molecule; acetic and trifluoroacetic acids form a mixed dimer incapable of the equilibrium reaction with iodo dichlorides.

$$C_6H_5ICl_2 + CF_3COOH \rightleftharpoons C_6H_5I(OCOCF_3)Cl + HCl$$

As expected, aromatic substituents on the dichloride molecule have considerable effect on the rate and equilibrium of dissociation of iodo dichlorides. Electrophilic substituents increase the equilibrium constant, the order of effect being in general *ortho* > *meta* > *para* although all are of the same order of magnitude. In nitromethane at 25°, the ratio for chloroiodobenzene dichlorides is *ortho:meta:para ca.* 8:4:2 (104). Kinetic effects are somewhat more pronounced for *ortho*-substituted compounds due to steric effects (5); equilibrium is reached much more quickly, in general.

Dissociation data are in general incomplete due to experiment difficulties. Those available do not fit well to a Hammett $\sigma-\rho$ plot (103); solvation kinetics are quite subject to nonsystematic variation. The nature of the activated complex apparently varies with the solvent, for while the enthalpies of activation are similar in nitromethane and acetic acid, the Arrhenius activation energy in the former is much less than in the latter (3). Certain solvent mixtures, such as acetonitrile–nitromethane, were examined to evaluate the nature of solvation of dichlorides and activated complexes (107).

Iodoaryl dichlorides with nucleophilic substituents in the *ortho* position are very subject to thermal decomposition; *o*-carboxyl and *o*-carbomethoxy derivatives form heterocycles spontaneously with loss of hydrogen chloride, as described above. Understandably, a large *ortho* effect is observed both in equilibrium and kinetic measurements. Dissociation is believed to take place in the following manner (4).



Among such "internal nucleophiles," much more effective in promoting dissociation at the *ortho* position than at the *para* position, an order of such activity has been established (8). The value $k_f(ortho)/k_f(para)$ increased in the order $-CH_2OC_6H_5 < -CH_2OCOCH_3 < -CH_2OCH_3 < -COC_6H_5 < -COCH_3 < -OCOCH_3$. Recently the nitro group was shown to be an "internal nucleophile" for which the ratio of rate constants is 400–500 (95). By contrast, the rate constants for the *o*- and *p*-cyano group are similar.

Iodomethylsulfone dichlorides have been reported as being somewhat more highly dissociated than iodoaryl dichlorides (54); equilibrium constants lie in the range $10\text{–}40 \times 10^{-3}$. Otherwise, their kinetic behavior has been found to be analogous to that of the iodoaryl compounds.

In the presence of a polar catalyst, some chlorine is formed by equilibration with iodoaryl dichlorides. Aromatic substitution under these conditions will to some degree proceed by molecular addition of chlorine. In the absence of a polar catalyst, in nonpolar media, it is firmly established that free-radical reactions are characteristic of iodo dichlorides. Russell (168) studied aromatic solvent π-complexing of chlorine in the light-catalyzed reaction with 2,3-dimethylbutane. Relative reactivity ($k_{\text{tert}}/k_{\text{prim}}$) of most systems could be computed, assuming three reactive species were present. The species Cl· attacked both primary and tertiary hydrogen atoms, while ArCl· and Ar_2Cl· were assumed to abstract only tertiary atoms.

$$\text{relative reactivity} = k + k'[\text{Ar}] + k''[\text{Ar}]^2$$

In most solvents the value lay in the range 3–24 for a 4.0 *M* solution at 55°, and was a rather direct function of solvent basicity. The value for iodobenzene at 25° was 31, quite out of line by the above criteria. It was noted that yellow solid iodobenzene dichloride formed in a competing reaction. Russell explained both observations by proposing a competing, more rapid, radical reaction, the abstracting radical $C_6H_5ICl\cdot$ resulting from homolytic dissociation of the dichloride (169).

Recent studies of substitution reactions of iodobenzene dichloride have confirmed the existence of such a radical. The following mechanism was proposed for light- or heat-catalyzed substitution of iodobenzene dichloride (18). Reaction is initiated by homolytic

$$C_6H_5ICl_2 \rightarrow C_6H_5ICl\cdot + Cl\cdot$$

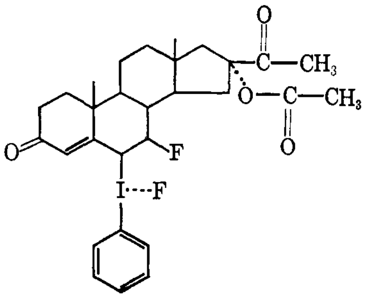
dissociation of the salt followed by a chain sequence.

$$C_6H_5ICl\cdot + RH \rightarrow R\cdot + HCl + C_6H_5I$$
$$R\cdot + C_6H_5ICl_2 \rightarrow C_6H_5ICl\cdot + RCl$$

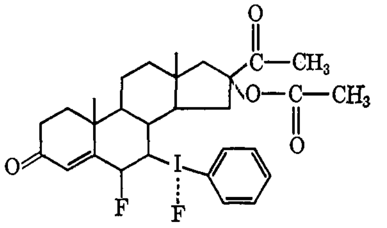
The important difference between this mechanism and that proposed by Bloomfield (44) is the manner in which the hydrogen atom is abstracted. Abstraction by chlorine atoms is known to proceed in a ratio tertiary: primary of 0.7:1, relative reactivity 4.2 (25°). In the light-catalyzed reaction of iodobenzene with 2,3-dimethylbutane, the ratio tertiary:primary was greater than 150:1, relative reactivity >900. Presumably in the presence of excess available tertiary hydrogen atoms, the radical does not abstract primary atoms.

Schreiber and Fernandez (174) attempted cleavage of triphenylmethylphenyl sulfide and triphenylmethylbenzyl sulfide using iodobenzene dichloride and iodobenzene diacetate; only triphenylmethyl chloride and triphenylmethylcarbinol, respectively, were obtained. Reaction of benzylphenyl sulfide (XIII) with iodobenzene dichloride gave a 70% yield of (α-chlorobenzyl)phenyl sulfide (175); reaction of dibenzyl sulfide formed (α-chlorodibenzyl) sulfide (XIV). With iodobenzene diacetate, XIII formed a sulfoxide in 51% yield.

Iodoaryl difluorides are white unstable solids; chloroform solutions are somewhat more stable and can be kept for 2 or 3 days without appreciable etching of the glass vessel. Holton, Cross, and Bowers (87) reported the reaction of such a solution of iodobenzene difluoride with a steroid, 17α-hydroxypregna-4,6-diene-3,20-dione acetate; the product was a phenyliodonium salt, having one of the structures XV or XVI.



XV

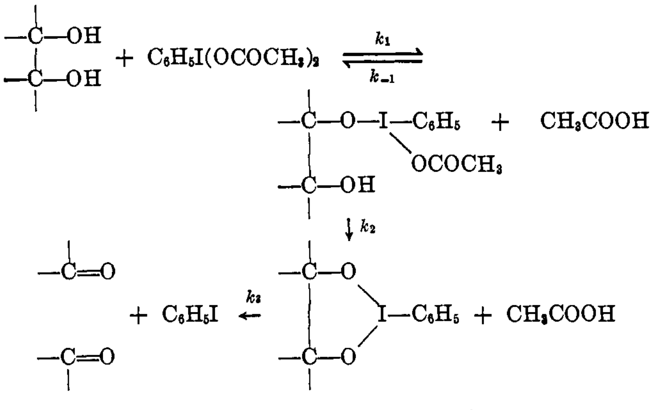


XVI

B. IODO DICARBOXYLATES

Iodoaryl diacetates are generally white or yellow salts melting at 80–150°. The observed dipole moment in benzene solution of the unsubstituted iodobenzene diacetate is 4.9 D. (118). Iodobenzene diacetate and dipropionate were shown not to be appreciably ionized in a number of solvents (97).

Two types of reactions of diacetates with organic substrates are observed: oxidation and substitution. Acetic acid solutions of iodobenzene diacetate behave in a manner very similar to lead tetraacetate, a selective oxidizing and methylating agent. Fission of 1,2-glycols forms ketones or aldehydes according to the proposed mechanism (55), similar to that for lead tetraacetate cleavage.



The second step was found to be rate determining, according to the second-order over-all rate equation

$$\text{rate} = k_2[\text{glycol}][C_6H_5I(OCOCH_3)_2]$$

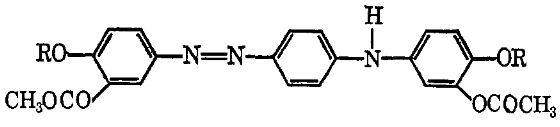
The kinetics agreed with those observed for lead tetraacetate fission, justifying the similar mechanism: rate constant $k_2 = 0.66 \times 10^{-3}$ (24.8°), $E_a = 21.3$ kcal mole^{-1}, and $\Delta H^* = 20.7$ kcal mole^{-1} (25°). The introduction of electrophilic substituents into the iodoaryl ring increased the rate of fission, while nucleophilic substituents decreased it.

An interesting application of glycol cleavage to biological materials is the use of the reaction (120) as a histological pretreatment, for the fission of 1,2-tissue glycols prior to staining with leucofuschin. *p*-Nitro- and *p*-methyliodobenzene diacetates, as well as iodobenzene diacetate and lead tetraacetate, were found suitable for the procedure.

Iodobenzene diacetate effects oxidation of primary aromatic amines. In benzene or acetic acid solutions, aniline, *o*-, *m*-, and *p*-toluidine, *o*-, *m*-, and *p*-chloraniline, *o*-anisidine, *m*- and *p*-nitroaniline, and α-naphthylamine formed the corresponding azo compounds (146). A mechanism was proposed similar to that postulated for the glycol fission above.

$$\begin{aligned} &2ArNH_2 + 2C_6H_5I(OCOCH_3)_2 \rightleftharpoons \\ &\qquad 2C_6H_5I{<}^{OCOCH_3}_{NHAr} + 2CH_3COOH \\ &\qquad\qquad \downarrow \\ &\qquad 2C_6H_5IOCOCH_3 + ArNHNHAr \\ &\qquad\qquad \downarrow \\ &\qquad 2C_6H_5I + 2CH_3COOH + ArN{=}NAr \end{aligned}$$

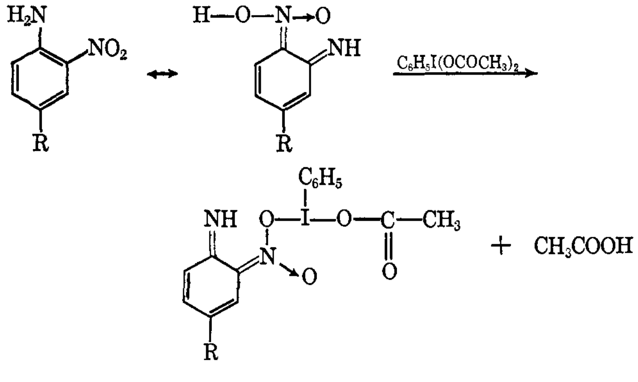
β-Naphthylamine formed primarily 1,2,6,7-dibenzophenazine and a product of empirical formula $C_{25}H_{20}O_5N_2$ (146). Oxidation of *p*-anisidine (4-methoxyaminobenzene) and *p*-phenetidine (4-ethoxyaminobenzene) gave mixtures of products: 4,4′-dialkoxybenzenes (5 and 6%, respectively), tetra-*p*-alkoxyazophenines (1%), *p*-benzoquinone di-*p*-alkoxyphenylimines (16 and 12%), and (11 and 5%) of



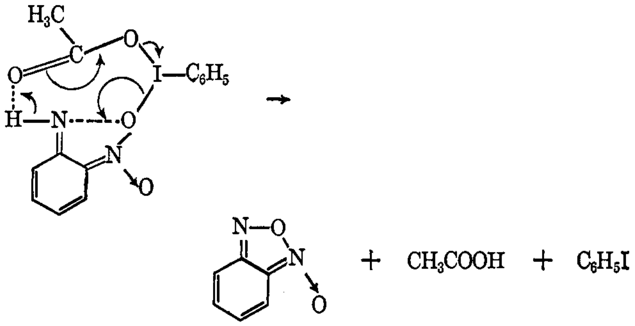
R = CH_3, C_2H_5

from the condensation of three molecules of starting material (132).

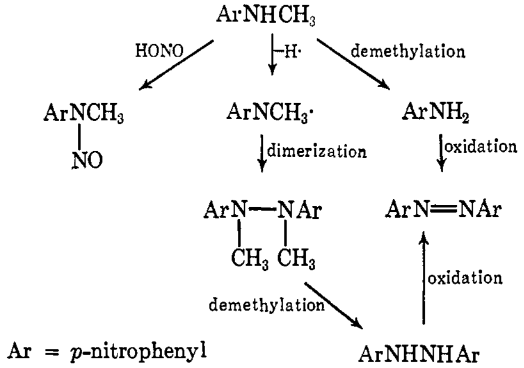
para-Substituted *o*-nitroanilines form benzofurazan oxides in benzene, but give good yields of *ortho* azo compounds from acetic acid solution (20). In benzene, yields of 90–93% of the oxides were obtained (R = CH_3, Cl, OCH_3, OC_2H_5) (147). The mechanism of this



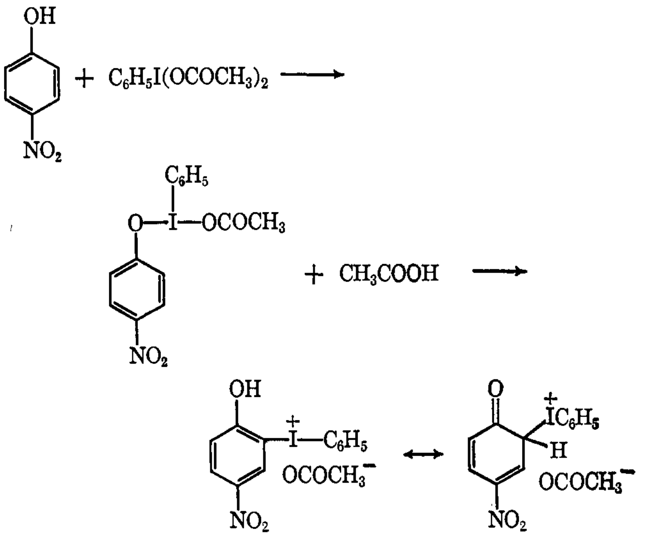
reaction was postulated as an attack of the diacetate on the ketimine tautomer of the substituted aniline followed by intramolecular cyclization (147).



p-Nitro-N-methylaniline undergoes deep-seated oxidation and extensive demethylation on treatment with iodobenzene diacetate (133). Among products obtained were *p*-nitro-N-nitroso-N-methylaniline, 4,4′-dinitroazobenzene, its N,N′-dimethyl derivative, and *p*-nitroaniline. The pathways indicated below were postulated on the basis of known reactions; nitrous acid is assumed to be a product of oxidation.



Iodobenzene diacetate reacts with phenols giving primarily products of a resinous nature. Among secondary products is an *o*-iodonium salt, for the formation of which the following mechanism was proposed (66, 178).



Lead tetraacetate is a useful methylating agent (62–64). Sandin and McCormack found that iodobenzene diacetate in hot acetic acid solution is equally good for this purpose, *e.g.*, a 20% yield of 1,3,5-trinitro-2,4-dimethylbenzene (trinitro-*m*-xylene) was obtained from 1,3,5-trinitrobenzene and the diacetate (172). A free-radical mechanism was proposed to account for the product; the diacetate decomposes at 160° to ethane, methane, carbon dioxide, and iodobenzene.

$$C_6H_5I(OCOCH_3)_2 \rightarrow C_6H_5I + 2(OCOCH_3)\cdot \qquad \text{(Eq 7)}$$

$$2(OCOCH_3)\cdot \rightarrow 2CH_3\cdot + 2CO_2\uparrow \qquad \text{(Eq 8)}$$

$$2CH_3\cdot + ArH \rightarrow ArCH_3 + CH_4\uparrow \qquad \text{(Eq 9)}$$

At room temperature in acetic acid solution the iodoaryl diacetates are useful acetoxylating agents, substituting at the *meta* position of N-arylacetamides bearing nucleophilic groups at the *para* position (19). (The acetoxyl radical produced in Eq 7 above is trapped before it can dissociate by reaction 8.) The rate constant increased and the activation energy decreased with nucleophilic substitution in the N-arylacetamide nucleus; the opposite effects were noted when electrophilic substituents were placed on the ring (99). Small erratic changes were noted when substituents were introduced into the iodoaryl ring and no reaction took place in benzene. In acetic acid, the rate increased by 40% when 1% of water was added, but no change in E_a was noted. From these observations the authors inferred that the transition state must be more polar than the reactants (98).

Lead tetrabenzoate is a convenient phenylating agent (83); thus it was reasoned (84) that iodobenzene dibenzoate might be an equally satisfactory reagent for this purpose. In fact, at 105° in pyridine, the same distribution of phenylpyridines was obtained in each case and in the presence of benzoyl peroxide, indicating a similar free-radical mechanism in all three reactions. Probably the path is like that proposed for the generation of methyl radicals from iodobenzene diacetate (84). General phenylation of aromatic and heterocyclic compounds by iodobenzene dibenzoate was reported. Reaction with nitrobenzene gave a ratio of *o*-, *m*-, and *p*-nitrodiphenyls of 58:9:33 (85, 124) while *p*-dichlorobenzene afforded mostly 2,5-dichlorodiphenyl (101).

C. MISCELLANEOUS IODO DISALTS

A large number of iodo disalts are known, but their reactions and properties are very poorly reported. Many have been isolated only once. The interested reader is referred to Beringer and Gindler's extensive tabulation (37) in which a reference is given, for each known compound, to the original literature. Patents have been obtained for the use of certain nitrobenzoate iodo disalts for use as biological toxicants, oxidizing agents, and motor fuel additives (131).

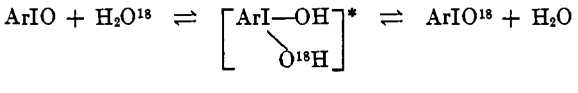
Addition of poly(*p*-iodostyrene) in chloroform to a chloroform solution of chlorine gave poly(*p*-iodostyrene dichloride) (143) which could be used directly as a chlorinating agent, or hydrolyzed to poly(*p*-iodosostyrene). This compound disproportionated on heating to the iodo compound and poly(*p*-iodoxystyrene). Unfortunately, no further report has been published on the preparation and properties of these interesting compounds.

D. IODOSO COMPOUNDS

Iodosoaryl compounds are in general pale yellow solids which behave as anhydrides of the hypothetical dibasic acid $ArI(OH)_2$. They decompose explosively on melting and on addition of acids or bases form salts of limited stability.

$$ArIO + H_3O^+ \rightleftharpoons Ar\overset{+}{I}OH + H_2O$$
$$ArIO + OH^- \rightleftharpoons ArIO_2H^-$$

Exchange studies of iodosobenzene and H_2O^{18} showed 30% exchange in neutral solution and 60% in basic



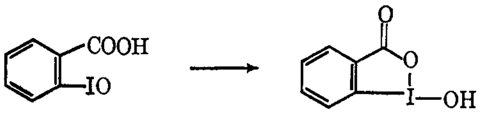
$$ArIO + H_2O^{18} \rightleftharpoons \left[ArI\begin{matrix}—OH \\ \diagdown O^{18}H\end{matrix}\right]^* \rightleftharpoons ArIO^{18} + H_2O$$

solution; *p*-iodosobenzoic acid underwent 30% exchange in neutral solution (73).

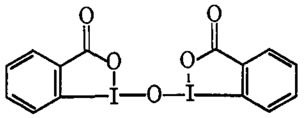
Diphenyliodonium hydroxide is formed by shaking equivalent weights of iodosobenzene and iodoxybenzene with silver oxide in water (81). The mechanism of this reaction has been doubly confirmed by radioactive tracer studies (13, 46).

$$ArI^{131}O + ArIO_2 + AgOH \rightarrow Ar_2I^{131+}OH^- + AgIO_3$$
$$ArIO + ArI^{131}O_2 + AgOH \rightarrow Ar_2I^+OH^- + AgI^{131}O_3$$

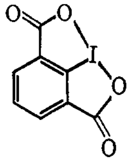
As previously noted, an *o*-carboxyl group exerts a large *ortho* effect on the iodo function; it in turn is strongly affected. Thus the p*K* of *o*-iodosobenzoic acid is larger than that of the *meta* or *para* salts, and simple esters have not been prepared of the former. As proposed for *o*-iodobenzene dichloride, it is probable that a five-membered 1-substituted 1,2-benziodoxolin-3-one ring is formed (15a). Evidence for this includes: lack of characteristic iodoso compound odor; stability in hot water or ethanol; formation of a monoacetate rather than a diacetate; and the weakness of the acid ($K = 6 \times 10^{-7}$ *vs.* 1.3×10^{-3} for *o*-iodobenzoic acid, 6×10^{-5} for benzoic acid). Infrared spectral evidence, also presented, includes appearance of the carbonyl band at 1650–1615 cm^{-1} for a series of 1-substituted 1,2-benziodoxolin-3-ones compared to 1760–1690 cm^{-1}, characteristic of the carboxyl group.



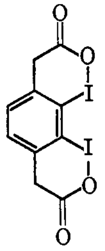
Treatment of *o*-iodosobenzoic acid with hydrogen chloride in methanol at 0° gives an anhydride (79), in accord with the above structure.



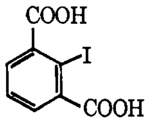
ortho-Dicarboxylated iodo salts are even more subject to lactone formation than are the monosubstituted compounds. Compound XVIa was obtained in 76% yield from the room temperature oxidation of 2-iodoisophthalic acid (XVIc) in an acetic acid–acetic anhydride solution containing excess peracetic acid (1a). Lactone XVIb was formed in 58% yield from 2-iodo-*m*-benzenediacetic acid (XVId) under similarc onditions.



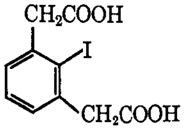
XVIa



XVIb



XVIc

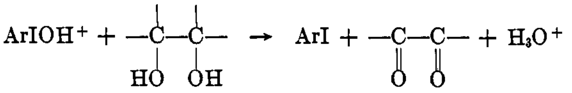


XVId

Reactions of iodoso compounds are otherwise similar to those of the iodo diacetates, owing to the ready interconversion in acid or basic solutions of salt and iodoso forms. The most characteristic application of iodoso compounds to synthesis has been their use as oxidizing agents. Biological preparations, *e.g.*, 3-phosphoglyceraldehyde dehydrogenase (158, 176), were oxidized to indeterminate products by iodosobenzene. The kinetics of oxidation of L-ascorbic acid by *o*-iodosobenzoic acid in nonbuffered aqueous solution were first order in each reactant, and the reaction was found to be catalyzed by cupric and ferric ions, as well as subject to general acid catalysis (47). It was proposed that, in a fast first step, the iodoso compound is protonated;

$$ArIO + H_3O^+ \rightleftharpoons ArIOH^+ + H_2O$$

in the rate-determining second step, oxidation is effected.



$$ArIOH^+ + \underset{HO}{\overset{|}{—C}}\underset{OH}{\overset{|}{—C—}} \rightarrow ArI + \underset{O}{\overset{}{—\underset{\|}{C}}}\underset{O}{\underset{\|}{—C—}} + H_3O^+$$

Reaction is instantaneous with *m*- or *p*-iodosobenzoic acid; with *o*-iodoxybenzoic acid, the ascorbic acid is oxidized but iodosobenzoic acid, rather than iodobenzoic acid, is formed.

Base-catalyzed condensation of iodoso compounds was shown to occur with any substance capable of forming a nucleophilic anion. With phenol, resorcinol, and cyclopentadiene, tars were produced (140). Unstable or metastable enolate betaines were obtained from reactions of iodoso compounds with indandione, malonic, or acetoacetic esters, pyrrole, indole, etc. As previously described, a stable enolate betaine was obtained on reaction with dimedon.

E. IODONIUM SALTS

Predictions made from structural data regarding reactivity of the I–X bond in iodonium salts agree well with observations. Halides readily undergo homolytic fission, while fluoroborates react by a heterolytic electron-transfer mechanism. Iodonium halides are thus excellent arylating agents, undergo photochemical and thermal cleavage under relatively mild conditions, and react readily with organometallic compounds. Reactions of iodonium salts may be subclassified and will be treated according to the following scheme.

1. Reactions with Metal Salts

Reutov and co-workers investigated a large number of reactions between diaryliodonium salts and metal chlorides. Double salts formed from which organometallic compounds were obtained on reduction by finely divided metal.

$$\begin{array}{r} x\mathrm{ArIAr'Cl} + \mathrm{MCl}_y \rightarrow (\mathrm{ArIAr'})_x\mathrm{MCl}_{y+x} \\ \downarrow 2x/z\mathrm{M'} \\ \mathrm{Ar}_x\mathrm{MCl}_{y-x} + \mathrm{Ar'I} + 2x/z\mathrm{M'Cl}_z \end{array}$$

Mercury, thallium, tin, arsenic, antimony, and bismuth have been used successfully as M, M′, or both (155, 166). Electrophilic substituents on the aryl ring inhibited formation of the double salt. A mixed iodonium salt always cleaved with the more electronegative group going to the metal (160). When the metal

$$p\text{-}\mathrm{CH_3OC_6H_4IC_6H_5{}^+HgCl_3{}^-} + \mathrm{Hg^0} \rightarrow \mathrm{C_6H_5HgCl} + p\text{-}\mathrm{CH_3OC_6H_4I} + \mathrm{HgCl_2}$$

powder was added to the double salt at, or slightly above, room temperature, moderate to high yields of the organometallic compounds were obtained (153, 156, 165). Changing the reducing metal, or the solvent, affected the yield obtained from a given double salt. In acetone, reduction of diphenyliodonium chloromercurate(II) with mercury, iron, or zinc, gave 34% yield of phenylmercury(II) chloride. Reduction with copper gave 16% yield; no reaction was noted with silver. In ethanol, the same reduction gave 21% yield with iron, 9% with copper, and only traces of product with zinc (164).

Reduction of $\mathrm{R_2I^+SbCl_4{}^-}$ (R = $\mathrm{C_6H_5}$, p-$\mathrm{ClC_6H_4}$, p-$\mathrm{BrC_6H_4}$, p-$\mathrm{IC_6H_4}$, or p-$\mathrm{H_3CC_6H_4}$) in acetone with powdered antimony (161) gave a mixture of $\mathrm{R_2SbCl}$, $\mathrm{R_2SbCl_3}$, and $\mathrm{R_3SbCl_2}$ in 50–70% over-all yield. Treatment of diphenylantimony(V) chloride in 5 *N* hydrochloric acid with diphenyliodonium chloride gave $\mathrm{(C_6H_5)_2SbCl_3 \cdot (C_6H_5)_2ICl}$ (154). Reduction with zinc dust in acetone followed by acid extraction gave a 50% yield of triphenylantimony(V) chloride. Tris(p-methylphenyl)antimony(V) chloride, tris(3,5-dimethylphenyl)antimony(V) chloride, and tris(p-bromophenyl)antimony(V) chloride were obtained in a similar manner. Likewise, several mixed arylantimony(V) chlorides were prepared (163).

2. Arylation of Nucleophiles

On standing, or on refluxing in organic solvents, iodonium salts undergo a slow decomposition. In re-

$$\mathrm{ArIAr'^+X^-} \rightarrow \mathrm{ArI} + \mathrm{Ar'X}$$

fluxing dilute base, diphenyliodonium bromide decomposed in a few days to bromobenzene and iodobenzene (25). In N,N′-dimethylformamide, decomposition of diphenyliodonium chloride was rapid and first order until 90% of the salt had been consumed (35). The rate was depressed by addition of polar salts. In ethylene glycol the reaction was first order but slow, but in aqueous solution it was second order and very slow (35, 43). First-order rate constants increased in the order glycol < DMF < nitrobenzene < benzene. Catalysis by copper salts was observed with Cu(I) being more effective than Cu(II) in this respect. Catalysis was more pronounced in glycol and water than in DMF. It was proposed that in less polar solvents, ion-pair formation was responsible for the increased rate. In polar media, nucleophilic displacement on the 1-carbon was proposed. The possibility of solvolysis intermediates in water and glycol was discussed. As expected for the proposed nucleophilic displacement, rates of decomposition of substituted diphenyliodonium bromides decreased in the order 2-$\mathrm{NO_2}$ > 4-$\mathrm{NO_2}$ > 3-$\mathrm{NO_2}$ > H > t-$\mathrm{C_4H_9}$ > cyclohexyl > $\mathrm{CH_3}$ > F > $\mathrm{CH_3O}$ (29).

Diphenyliodonium halides react with bases and nucleophiles giving phenyl derivatives (36, 71). Both nucleophilic displacements and electron-transfer mechanisms are observed in such reactions. Reaction with hydroxide and phenoxide ions in dioxane–water mixtures was found to be second order except in low water concentrations, where the order decreased. Reaction of hydroxide is very sensitive to traces of peroxides, while the phenoxide reaction is insensitive. En-

$$\mathrm{(C_6H_5)_2I^+ + OH^-} \rightarrow \mathrm{C_6H_5OH + C_6H_5I}$$

$$\mathrm{(C_6H_5)_2I^+ + OC_6H_5{}^-} \rightarrow \mathrm{(C_6H_5)_2O + C_6H_5I}$$

thalpies of activation are, respectively, 28.8 and 24.7 kcal $\mathrm{mole^{-1}}$. Entropies of activation, respectively, are 20.1 and 0.6 eu. Direction of cleavage of mixed salts was found to be insensitive to the anion, solvent, nature of substituents, or catalyst. Catalysis by Cu(I) and Cu(II), acid, oxygen, and diphenyliodonium hydroxide was observed (38, 48). A free-radical mechanism was proposed, initiated by formation of an unstable *covalent* hydroxide which cleaved to one or more alter-

$$\mathrm{RIR'^+ + 2H_2O} \rightarrow \mathrm{(RIR'OH) + H_3O^+}$$

nate radical pairs.

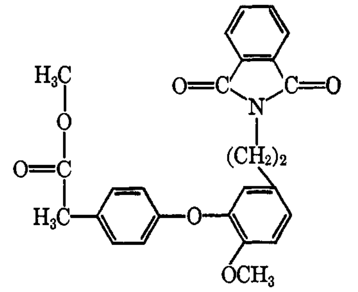
$$(RIR'OH) \rightarrow RI + \overline{R'\cdot + OH\cdot} \rightarrow RI + R'OH$$

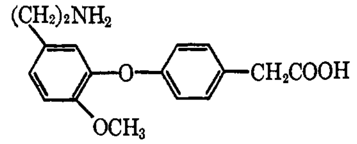
$$\text{or} \quad \overline{RIR'\cdot + OH\cdot}$$

$$\text{or} \quad \overline{R\cdot + R'\text{—}IOH\cdot}$$

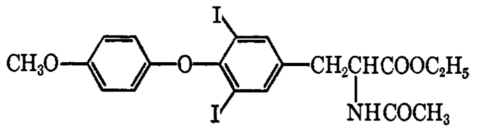
What is thought to have been a covalent hydroxide intermediate was isolated from dibenziodolium salt solutions as a hydrate which lost water at 75° giving a pale yellow-and-brown anhydrous compound (74).

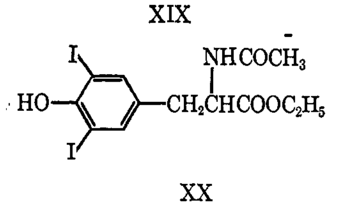
Application of this reaction to synthesis has been rather successful. Diphenyliodonium bromide, treated with phenols and phenoxides, gave diaryl ethers (170), and 8-hydroxyquinoline afforded 8-phenoxyquinoline. Ethers such as XVII and XVIII were prepared by reaction of phenoxides with symmetrically substituted iodonium salts (57).


XVII


XVIII

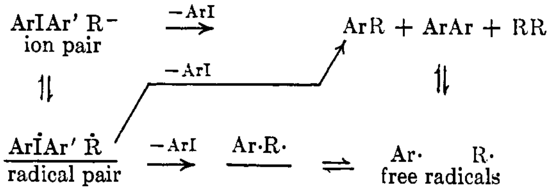
Likewise, in the preparation of 3,5-dihalogenated thyroxines, the ether XIX was prepared by refluxing bis(4-methoxyphenyl)iodonium bromide in methanol with sodium methoxide and the phenoxide XX (86).


XIX


XX

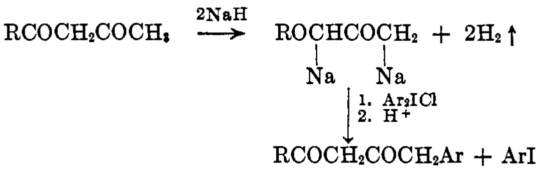
Diaryl ethers were prepared from 4-hydroxyphenoxyacetic acid and several 3,5-disubstituted thyronines (58). Nucleophilic displacement by methoxide ion on closed-ring iodonium cations is less favorable than on the open-chain analogs; 2-methoxy-2'-iododiphenyl could not be prepared by displacement of methoxide ion on dibenziodolium sulfate (68). An indirect reaction scheme was used to obtain the product.

5,5-Dimethylcyclohexane-1,3-dione (dimedon) underwent reaction with iodonium salts at the 2-position, giving 71–85% of the 2,2-diphenyl derivative in *t*-butyl alcohol containing sodium *t*-butoxide (33). Under similar conditions, phenyl derivatives of substituted malonic and oxaloacetic esters were obtained (32). While only 28–70% yields were obtained, it was speculated that these could be improved by refinement of the synthetic technique. Arylation was repressed in methanol, ethanol, and 2-propanol due to side reactions, for example, dehydration of the solvent. Accordingly, *t*-butyl alcohol was preferable as a solvent, as it is quite unreactive to free radicals. The mechanism proposed for phenylation of these compounds involved radical-pair formation (31).



A similar mechanism was proposed for the arylation of 1,3-indandiones. The radical process in this reaction was suggested by the observation (34) that addition of oxygen to the system reduced the yield from 93 to 53%.

β-Diketones were arylated in the γ position, in liquid ammonia (77). Table VI lists products obtained by the following reaction sequence.



$$RCOCH_2COCH_3 \xrightarrow{2NaH} RO\underset{Na}{C}HCO\underset{Na}{C}H_2 + 2H_2\uparrow \xrightarrow{1.\ Ar_2ICl;\ 2.\ H^+} RCOCH_2COCH_2Ar + ArI$$

TABLE VI

ARYLATION OF β-DIKETONES BY ARYLIODONIUM CHLORIDES

R	Ar	$RCOCH_2COCH_2Ar$
CH_3	C_6H_5	$CH_3COCH_2COCH_2C_6H_5$
C_6H_5	C_6H_5	$C_6H_5COCH_2COCH_2C_6H_5$
n-C_3H_7	C_6H_5	n-$C_3H_7COCH_2COCH_2C_6H_5$
n-C_5H_{11}	C_6H_5	n-$C_5H_{11}COCH_2COCH_2C_6H_5$
n-C_7H_{15}	C_6H_5	n-$C_7H_{15}COCH_2COCH_2C_6H_5$
CH_3	p-ClC_6H_4	$CH_3COCH_2COCH_2C_6H_4Cl$
C_6H_5	p-$H_3CC_6H_4$	$C_6H_5COCH_2COCH_2C_6H_4CH_3$
n-C_5H_{11}	p-$H_3CC_6H_4$	n-$C_5H_{11}COCH_2COCH_2C_6H_4CH_3$

3. Heterolytic Fission

Purely ionic iodonium salts, for example, the fluoroborates, cannot undergo nucleophilic displacement in the manner of chlorides and bromides. With oxygen bases, such as hydroxide and phenoxide, they give the same products in either case. Nitrogen, phosphorus,

$$(C_6H_5)_2I^+BF_4^- + C_6H_5OH \rightarrow (C_6H_5)_2O + C_6H_5I + HBF_4$$

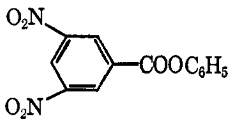
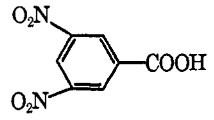
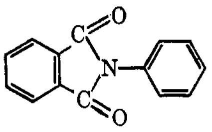
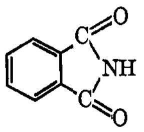
and other group V and VI bases, on the other hand, give oxonium salts rather than carbon-substituted products (for example, 2-phenylpyridine).

$$(C_6H_5)_2I^+BF_4^- + C_5H_5N: \rightarrow C_5H_5NC_6H_5^+BF_4^- + C_6H_5I$$

The products obtained in reactions of diphenyliodonium fluoroborate with miscellaneous bases are listed in Table VII (141).

TABLE VII

PRODUCTS OF REACTION OF DIPHENYLIODONIUM FLUOROBORATE WITH BASES

Base	Product
$:N(CH_3)_3$	$C_6H_5N(CH_3)_3{}^+BF_4^-$
$:NC_5H_5$	$C_6H_5NC_5H_5{}^+BF_4^-$
$:P(C_6H_5)_3$	$(C_6H_5)_4P^+BF_4^-$
$:As(C_6H_5)_3$	$(C_6H_5)_4As^+BF_4^-$
$:Sb(C_6H_5)_2$	$(C_6H_5)_3Sb^+BF_4^-$
$:S(C_6H_5)_2$	$(C_6H_5)_3S^+BF_4^-$
$:Se(C_6H_5)_2$	$(C_6H_5)_3Se^+BF_4^-$
C_6H_5OH	$(C_6H_5)_2O$
C_6H_5COOR	$C_6H_5COOC_6H_5$ (R = CH_3, C_2H_5)
	
$(C_6H_5)_2NH$	$C_6H_5NH_2$
$(C_6H_5)_3N:$	$(C_6H_5)_2NH$
	

4. *Photolytic and Thermal Cleavage*

Iodonium salts slowly decompose on standing by what are believed to be intramolecular rearrangements. Diphenyliodonium chloride forms iodobenzene and chlorobenzene; dibenziodolium iodide, heated at the decomposition point, gives 2,2′-diiodobiphenyl; and 3,6-dinitrophenoxiodinin-5-ium iodide forms bis(2-iodo-4-nitrophenyl) ether (90, 92).

In chloroform or benzene solutions at room temperature, diphenyliodonium fluoride, chloride, or bromide did not decompose on irradiation with ultraviolet light; however, the iodide formed diphenyliodonium triiodide, iodine, and benzene (93). In carbon tetrachloride, ether, or cyclohexane, no reaction was observed. The behavior of 4,4′-difluorodiphenyliodonium salts and dibenziodolium salts was found to be similar; the iodides decomposed but the chlorides, fluorides, and bromides did not. The enolate betaine of dimedon (IX) decomposed to iodobenzene and the phenyl ether of 2-iododimedon (135, 137). The reaction was complete in 2 hr in water, 1 hr in toluene, and 15 min in pyridine.

Diphenyliodonium chloride and fluoroborate undergo light-catalyzed reactions with triphenylphosphine (157).

$$(C_6H_5)_2ICl + (C_6H_5)_3P: \xrightarrow{h\nu} (C_6H_5)_4P^+Cl^- + C_6H_5I$$

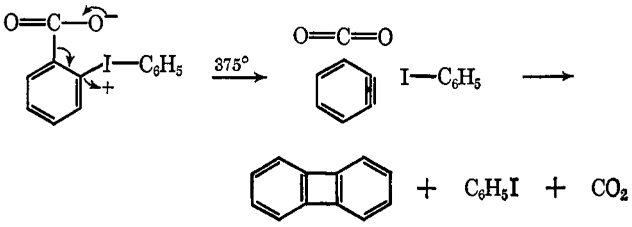
This reaction is distinct from, and faster than, dark reactions taking place by nucleophilic attack. The addition of radical scavengers inhibit the former, without affecting the latter. Yields of tetraphenylphosphonium salts were 56% of the chloride and 45% of the fluoroborate. In a later study equimolar mixtures of iodonium fluoroborate and triphenylphosphine were allowed to react in acetone, under irradiation by a mercury vapor lamp.

$$(RC_6H_4)_2I^+BF_4^- + (C_6H_5)_3P: \xrightarrow{h\nu} (RC_6H_4)P(C_6H_5)_3{}^+BF_4^-$$

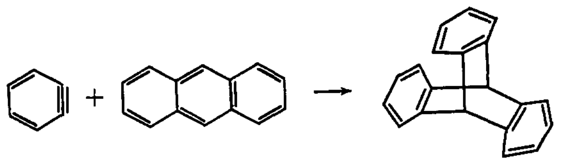
Yields of 85 (R = H), 49 (R = p-CH_3O), 61 (R = p-Cl), 51 (R = m-NO_2), and 47% (R = m-$COOC_2H_5$) (in methanol) were obtained in 6–10 hr (153a).

Removal of two *ortho* substituents from a benzene nucleus gives the highly reactive intermediate benzyne, C_6H_4. One of the more successful methods of accomplishing this reaction uses an iodonium betaine, 2-phenyliodonium benzoate [*Chemical Abstracts* preferred name, (o-carboxyphenyl)phenyliodonium hydroxide, inner salt]. This salt is easily prepared by adding potassium persulfate to a sulfuric acid solution of o-iodobenzoic acid. The mixture is allowed to react, benzene is added, and the resulting product is poured over ice and made strongly alkaline. From the chloroform extract of this mixture, the salt (mp 220.5–221° dec) was isolated in 84% yield (40, 119).

In the absence of trapping agents, sharp thermal cleavage of the betaine is observed at 375° giving biphenylene as the major product. The same reaction



was observed in flash photolysis, at 325°, and in the presence of anthracene, 23% of tryptycene obtained, indicating that benzyne most assuredly was formed. When the latter reaction was carried out in presence of a fourfold excess of the betaine, 90% of the anthracene was converted to tryptycene.



Other trapping agents behaved in the same manner, suggesting that pyrolysis of 2-phenyliodonium benzoate is a useful and practical method of preparing benzyne (39).

5. *Electrochemistry*

Iodonium salts function in general as neutral salts. 2-Phenyliodonium benzoate, however, gives the titration curve of a strong acid; the pK was computed to be 3.5. 4-Phenyliodonium benzoate has a pK of 4.6, and the 3-salt, a pK of 5.5. Differences in the pK values were attributed (42) to electrostatic and inductive effects. Hammett σ values calculated for the hydroxydiphenyliodonium cation were 0.85 (*meta*) and 0.71 (*para*). Analogous values for the aminodiphenyliodonium cation were calculated to be 0.98 and 1.06, respectively. The explanation offered for these values was that a group at the *para* position must be conjugated with the iodine atom.

Little is really known of electrochemical processes in the iodonium salt series, except that probably the diphenyliodine radical is involved. Polarography at the dropping mercury electrode has been reported, but the results have been contradictory (51, 52). First reports indicated a mechanism involving formation of an arylmercury intermediate. Later reports stated that no arylmercury intermediates, products, or logical remnants could be isolated; therefore this mechanism could not be correct. The following mechanism was proposed (14, 15) to explain the three observed waves (a fourth "extraneous" wave was considered "surface-limiting").

$$\begin{aligned} \mathrm{RIR^+ + e^-} &\rightarrow \mathrm{RI R\cdot} \\ \mathrm{RIR^+ + H^+ + 2e^-} &\rightarrow \mathrm{RI + RH} \\ \mathrm{RIR^+ + H^+ + 4e^-} &\rightarrow \mathrm{RH + R^- + I^+} \quad \text{(slow)} \\ \mathrm{R^- + H^+} &\rightarrow \mathrm{RH} \quad \text{(fast)} \end{aligned}$$

6. *Biocidal Applications*

Positive iodine compounds have, in general, good oxidizing power and as a result certain biocidal properties generally ascribed to "iodine"—tinctures, preparations, and complexes— are found in the iodonium series. Bis(3,4-dichlorophenyl)iodonium chloride and bis(2,4-dichlorophenyl)iodonium sulfate were evaluated as bacteriocides; the latter proved most effective against gram-negative bacteria (70). A number of substituted diaryliodonium chlorides were found to be inert to type A influenza virus, although it was reported that ring chlorination increased the activity in this respect (148, 149). Diphenyliodonium salts were found to have active spermicidal properties, killing instantaneously in aqueous solutions of 0.5% or less (88).

F. IODOXY COMPOUNDS

1. *Reactions*

Iodoxybenzene is a white solid which neither melts nor vaporizes below 230° but explodes on contact with a hot wire. Extreme care should be used in heating, compressing, or grinding iodoxy compounds, as heat or impact is known to detonate compounds of the series. Their use as explosives is precluded, however, by their rather low brisance.

Iodoxy compounds are very slightly soluble in water and insoluble in organic solvents. They are weak monobasic acids; the pK for iodoxybenzene, as measured by conductivity methods, is 10.4 (128). The free

$$\mathrm{C_6H_5IO_2 + 2H_2O \rightleftharpoons H_3O^+ + C_6H_5IO_3H^-}$$

base changes rapidly, and irreversibly, in cold alkali to diphenyliodyl hydroxide, a strong oxidizing agent.

$$\mathrm{2C_6H_5IO_3H^- \rightarrow (C_6H_5)_2IO^+OH^- + IO_3^- + OH^-}$$

Diphenyliodyl hydroxide reacts with most oxidizible ions, being reduced to a diphenyliodonium salt.

$$\mathrm{(C_6H_5)_2IO^+OH^- + 3Cl^- \rightarrow (C_6H_5)_2I^+Cl^- + Cl_2 + 2H_2O}$$

These compounds exhibit amphoteric properties to a marked degree. In acid, they act as weak bases despite their low solubility.

$$\mathrm{C_6H_5IO_2 + H_3O^+ \rightleftharpoons C_6H_5IO_2H^+ + H_2O}$$

2. *Electrochemistry*

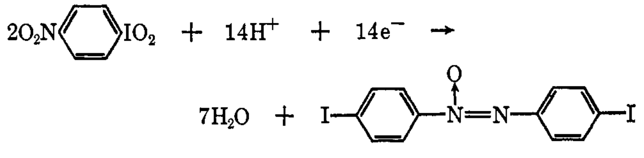
The strong oxidizing powers of iodoso and iodoxy compounds have drawn a good deal of attention to their possible electrochemical application. Grossman (75) described an iodosobenzene–iodoxybenzene electrode for pH determination.

$$\mathrm{C_6H_5IO + 2OH^- \rightleftharpoons C_6H_5IO_2 + H_2O + 2e^-}$$

With a view to application in magnesium and aluminum dry cells, electrochemical characterization of iodoso and iodoxybenzene, iodobenzene diacetate, and diphenyliodonium chloride was carried out (72). Performance efficiencies and current–voltage curves were plotted for the basic reactions.

$$\begin{aligned} \mathrm{C_6H_5IO + H_2O + 2e^-} &\rightarrow \mathrm{C_6H_5I + 2OH^-} \\ \mathrm{C_6H_5IO_2 + 2H_2O + 4e^-} &\rightarrow \mathrm{C_6H_5I + 4OH^-} \end{aligned}$$

King (116) studied the reduction of nitroiodosobenzenes, and nitroiodoxybenzenes in 1 M magnesium bromide solution, using a graphite–acetylene black cathode, and a zinc plate anode. A constant current of 0.5 amp was used; the reaction was judged complete when the first bubbles of hydrogen were noted at the cathode. *ortho*-Substituted compounds were reduced to *o*-iodonitrobenzene with 61.8 (iodoso) and 44.6% (iodoxy) efficiency, *meta* derivatives were reduced to 3,3′-diiodoazoxybenzene with greater than 80% efficiency, while *para*-substituted compounds formed the 4,4′-analog with like efficiency. Steric effects, which prohibit the formation of 2,2′-diiodoazoxybenzene, account for the difference in product. Premature evolu-



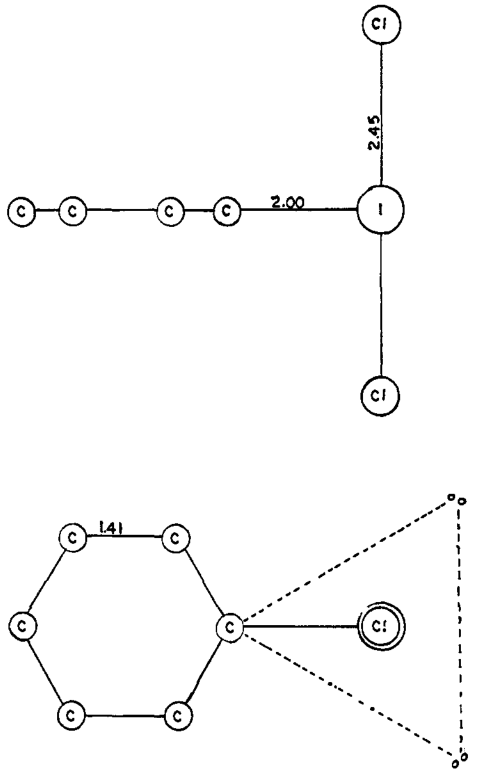


Figure 1.—Molecular structure of iodobenzene dichloride.

tion of hydrogen explains the low efficiency in the *ortho*-substituted systems. King established from these experiments that introduction of an electron-withdrawing group, such as the nitro substituent, increased the stability of iodoso and iodoxy compounds and made their reduction potential more negative.

Polarographic studies of iodoso- and iodoxybenzene at the dropping mercury electrode were made by two groups, independently (50, 65). Two irreversible waves are observed; $E_{1/2} = -0.88$ and -1.65 v. The first is thought to be due to reduction of iodoso- or iodooxybenzene to iodobenzene; it is independent of pH.

$$C_6H_5IO_2 + 2H_2O + 4e^- \rightarrow C_6H_5I + 4OH^-$$

The second, pH dependent, wave is believed to be due to reduction of iodobenzene to benzene.

$$C_6H_5I + H^+ + 2e^- \rightarrow C_6H_6 + I^-$$

No essential difference is noted between the polarograms of iodosobenzene and iodoxybenzene, except for the number of electrons in the first step.

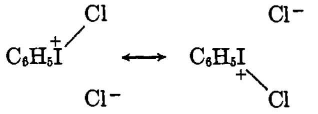
IV. BONDING AND STRUCTURES

A. IODO DIHALIDES

Any structure proposed for iodo dichlorides and difluorides must explain the ready fission observed for the iodine–halogen bond and the relative inertness of the C–I bond. Early investigators proposed the ionic structure, $C_6H_5ICl^+Cl^-$, for iodobenzene dichloride on the basis of its reaction with phenylmagnesium bromide. However, conductivity measurements and molecular weight determination showed that any dissociation is strictly molecular (96, 191). Le Fevre and Le Fevre

$$C_6H_5ICl_2 \rightleftharpoons C_6H_5I + Cl_2$$

(118) determined the dipole moment of iodobenzene dichloride in benzene solution to be 2.6 D. They assumed a trigonal planar structure and proposed on the basis of the dipole moment that a partial ionic hybrid was a likely structure.



$$C_6H_5\overset{+}{I}\text{–}Cl \; Cl^- \longleftrightarrow C_6H_5\overset{+}{I}\text{–}Cl \; Cl^-$$

Rather fortunately for anyone attempting to describe the bonding in iodo dichlorides, X-ray structure determinations have been reported for two compounds in the series. Archer and van Schalkwyk (11) studied the molecular and crystal structure of iodobenzene dichloride using long needles grown from carbon tetrachloride solution. Weissenberg and rotation photographs using Mo Kα and Cu Kα radiation were used to establish the atomic coordinates. The unit cell was found to contain eight molecules. The calculated density, 2.19 g cm^{-3}, agreed with the experimentally determined density, 2.2 g cm^{-3}. The molecule is T-shaped, containing a linear, symmetrical, Cl–I–Cl group almost perpendicular ($86 \pm 1°$) to the plane of the ring (Figure 1). The authors stated that the molecule must thus have a trigonal-bipyramidal structure, the ring and two lone pairs on the equatorial positions, the chlorine atoms at the apices. Here it is of interest to note the similarity of both structure and chemical properties to the diarylselenium dihalides (126). The I–Cl bond length, 2.54 A, is greater than the sum of the normal covalent radii, 2.32 A (144), which would indicate that the bond dissociation energy might be considerably less than the "normal single bond energy," 57.5 kcal mole^{-1}.

The I–Cl intermolecular distance of closest approach is 3.40 A, much less than the sum of ionic radii, 4.00 A (144). The investigators proposed that resulting interactions must represent a major bonding force in the crystal. The crystal is monoclinic, of space group $B2_1/a$, $a = 15.6$, $b = 5.45$, $c = 19.6$ A, $\beta = 90° 30'$; or, alternatively of space group $P2_1/a$, $a = 15.6$, $b = 5.45$, $c = 12.3$ A, $\beta = 128° 30'$. The cleavage plane is (001); Figure 2 shows the structure of the iodobenzene dichloride lattice projected onto the (010) plane.

In order to check these data, Bekoe and Hulme (22) investigated the structure of *p*-chloroiodobenzene dichloride. The molecular structure was reported to be the same as that of the unsubstituted salt, except that the angle of the linear Cl–I–Cl group to the plane of the ring was much less than 90°. No bond lengths were determined, nor were the angles established precisely. The

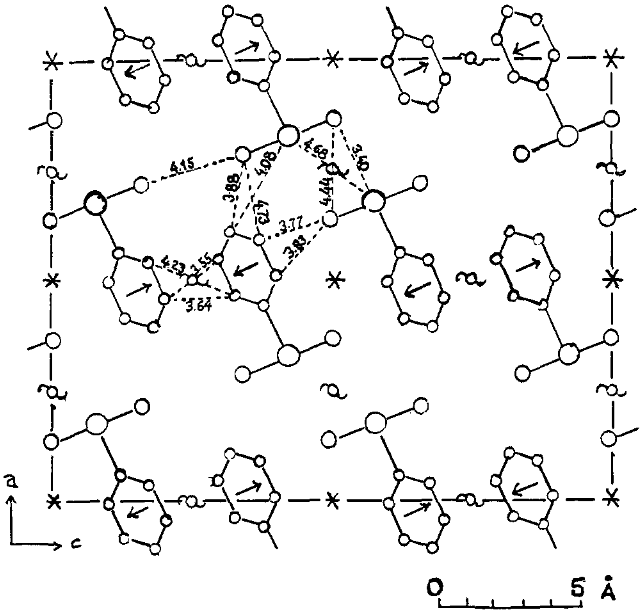


Figure 2.—Crystal structure of iodobenzene dichloride.

crystal is triclinic, containing two molecules per unit cell, the calculated density is 2.31 g cm^{-3}, and the space group is P$\bar{1}$, a = 10.1, b = 4.13, c = 11.0 A, α = 96° 42′, β = 107° 27′, γ = 91° 12′.

It has been inferred (21) from these *solid-state* structural data, that dsp^3 or d^{3}sp hybridization occurs in the iodine atom bonds. Resonance with the electron-withdrawing chlorine substituent in the *para* position increases the sp^2 character of the bonds in the plane of the ring, the same argument continues. By the same token the more highly electron-withdrawing *p*-nitro-substituted iodo dichloride should have a planar structure, almost exclusively sp^2 hybridized.

Such inferences and arguments are dangerous and misleading. They are merely *one* explanation of the observed conformation in the solid state, and assume that there must be a large barrier to rotation about the C–I bond. If this barrier were in fact very low, as is possible, the angle of the Cl–I–Cl group to the benzene ring would be only a function of greatest packing efficiency. The *p*-chlorine, being considerably larger than a *p*-hydrogen, would decrease the packing efficiency and the preferred orientation might be at less than 90°, as observed. A planar nitro group could influence packing, likewise, so that the most efficient conformation might be a planar one.

A directly measured value of the barrier to rotation about the C–I bond might easily be obtained by microwave spectroscopic techniques. Unfortunately no such data have been reported. However, it was noted that there is very little difference in equilibrium or rate constants for dissociation of *meta*- and *para*-substituted dichlorides, even for strongly interacting substituents. To check these observations (2–8, 54, 102–107), an F^{19} nmr study was made of *m*- and *p*-fluoroiodobenzene dichloride (125). Nearly zero difference in the chemical shifts of these compounds was noted; by Taft's correlation, a negligible resonance interaction with the ring is implied. On the other hand, the group exerts a large inductive effect, in the form of electron withdrawal. From the chemical shift difference between the dichlorides and the corresponding fluoroiodo compounds, the inductive contribution to the reactivity constant was calculated to be 1.3. This observation lends a good deal of weight to the alternate hypothesis, as if there were interaction between the aromatic π cloud and empty iodine d orbitals, there would be a rather large resonance interaction observed in the nmr spectrum. The effect of various substituents on the stability of iodoaryl dichlorides is in all cases equally well explained by purely inductive interaction, as by resonance effects.

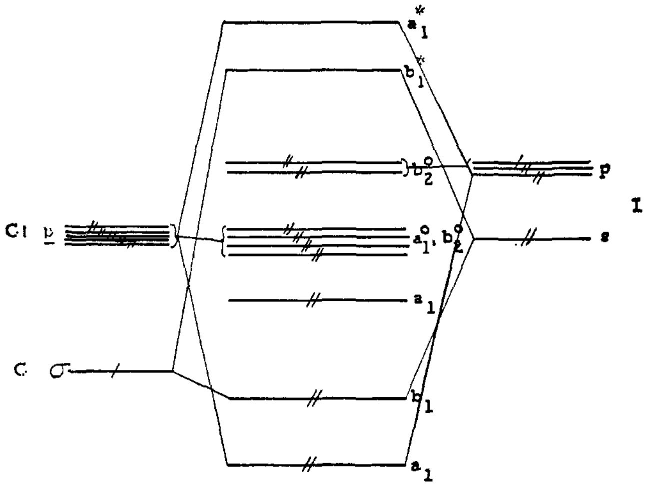


Figure 3.—Molecular-orbital diagram for iodobenzene dichloride.

Molecular-orbital description of bonding in iodobenzene dichloride may be undertaken on a qualitative basis. It will be assumed that no π interaction is observed between the ring and the iodine atom. The C–I bond and the two lone pairs on iodine are described by a planar LCAO–MO such as the following.

$$\begin{aligned} &\text{(antibonding)} & \psi_1 &= c_1\sigma_C - c_2p_z(\text{I}) \\ &\text{(bonding)} & \psi_2 &= c_1\sigma_C + c_2p_z(\text{I}) \end{aligned}$$

The linear Cl–I–Cl bond may be described by the following LCAO–MO.

$$\begin{aligned} &\text{(antibonding)} & \psi_3 &= c_3(p_a + p_b) + c_4p_x(\text{I}) \\ &\text{(nonbonding)} & \psi_4 &= c_5(p_a - p_b) \\ &\text{(bonding)} & \psi_5 &= c_3(p_a + p_b) - c_4p_x(\text{I}) \end{aligned}$$

Not involved in bonding are four p electrons on each chlorine atom. A splitting diagram may be drawn using arbitrarily chosen energy levels; qualitative agreement with experimental data is reached, but no quantitative agreement is claimed.

No structural data are available regarding any other iodo disalts. Probably the difluoride has a similar

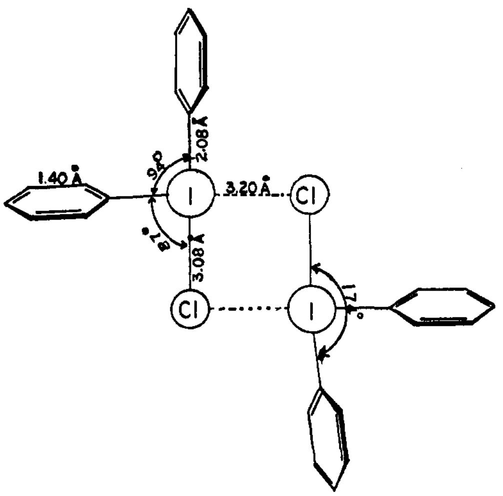


Figure 4.—Molecular configuration of diphenyliodonium chloride.

arrangement to the dichloride. It has been shown that iodo dicarboxylates are not ionized in solution (97). Salts such as the sulfate, nitrate, and trichloromercurate (II) must be ionized to some extent although I–O or I–Cl coordination must stabilize the salt to quite a degree. Salts such as the carbonate or nitrite, in which this coordination is evidently not possible, are unstable and decompose.

B. IODOSO COMPOUNDS

No X-ray structure determination has been completed for iodosobenzene or any aryliodoso compound. While it has been assumed that the C_1–I–O group is linear, there is no valid reason for this assumption. Bonding has been compared to that in the sulfoxides, namely formation of a "double bond," a polar link resulting from overlap of an empty iodine 5d orbital with the oxygen p_x orbital. Although this is probably a very good description of bonding in dimethyl sulfoxide, it fails to consider the relative sizes of sulfur and iodine. The 5d orbitals are so large that overlap with the oxygen p_x is difficult at best. In the absence of X-ray data or similar information, inference must be made from the iodoxy series, for which X-ray data are in existence. The dipole moment of iodosobenzene must be high, indicating a charged structure.

$$C_6H_5\overset{+}{I}—\overset{-}{O}$$

The electrostatic attraction, or some π overlap, shortens the I–O bond to about 1.60 A, somewhat less than the sum of normal single covalent radii, 2.00 A (144). While a "double bond" as such cannot form, some increase in the bond strength is indicated.

C. IODONIUM SALTS

Iodonium salts are, in general, ionic substances. Chlorides, bromides, and iodides possess some covalent character in a manner similar to that in the aryliodo dichlorides. Still, the halogen atoms are nonequivalent; only 1 g-equiv of silver iodide is precipitated when silver nitrate is added to an aqueous solution of diphenyliodonium iodide.

X-Ray data are available for diphenyliodonium chloride, iodide, fluoroborate, and trichloromercurate(II). The first two are isomorphous, and have a T-shaped structure as shown in Figure 4 (111–114); the molecules crystallize in pairs about the I–X bonds. It is of interest to note that, as in the iodo dichlorides, the I–Cl and I–I bonds are somewhat longer than normal covalent bonds, but shorter than the sum of ionic radii. Likewise, the corresponding intermolecular distances are notably less than the sums of the van der Waals radii; in fact, in diphenyliodonium iodide, the intra- and intermolecular I–I distances are equal, 3.34 A. Both the chloride and iodide crystals belong to space group C2/c, and contain eight molecules per unit cell. Lattice parameters are, for the chloride, $a = 20.81$, $b = 5.82$, $c = 20.26$ A, $\beta = 102° 34'$; for the iodide, $a = 22.08$, $b = 6.27$, $c = 20.42$ A, $\beta = 101°$.

Structures of the purely ionic fluoroborate salt and trichloromercurate (II) were determined. In the former the diphenyliodonium cation has an angular configuration, C_1–I–$C_1' = 94°$; the benzene rings are at an angle to the plane of these atoms. The crystal belongs to space group $P2_1/c$ and contains four molecules per unit cell. Lattice parameters are $a = 6.05$, $b = 12.80$, $c = 17.26$ A, $\beta = 97° 15'$. The crystal of the trichloromercurate(II) is based on infinite segments of the anion lattice $[HgCl_3]_\infty^-$. It belongs to space group $P2_12_12_1$ and contains four molecules per unit cell. Lattice parameters are $a = 13.5$, $b = 5.82$, $c = 18.60$ A (115, 179).

As a further reflection on bonding in iodonium salts, exchange studies of substituted diarylfluoroborates with I^{131}-labeled iodobenzene were conducted. All exchanged rapidly near their decomposition point, the nitro derivatives exchanging most slowly (162).

$$Ar_2I^+BF_4^- + C_6H_5I^{131} \rightleftharpoons ArI^{131}C_6H_5{}^+BF_4^- + ArI$$

Thus, as expected, the iodonium group acts as an electron-withdrawing function and is stabilized by electrophilic substituents on the ring.

D. IODOXY COMPOUNDS

Due to their insolubility in virtually all solvents, little is known of the solution properties of iodoxy compounds except that they form conjugate acids and bases. In the solid state, a good deal more is known of them as the structure of *p*-chloroiodoxybenzene was determined by X-ray methods. Crystals were grown from acetic acid for this purpose (10). The molecule is asymmetrical and nonplanar, as shown in Figure 5. The I–O bonds (1.60 and 1.65 A) are much shorter than the sum of normal covalent radii (2.00 A) (144), indicating some sort of multiple bonding. As in the dichlorides, the intermolecular distances of closest approach of iodine and oxygen, and of two oxygen atoms (2.87 and 2.62 A, respectively) are shorter than the sum of van der Waals radii (3.3 and 2.7–3.0 A). This must represent a major bonding force in the crystal. The crystal belongs to space group $P2_1/c_1$; lattice parameters are $a = 14.4$, $b = 6.50$, $c = 8.11$ A, $\beta = 98.6°$.

The asymmetry of the iodoxybenzene molecule makes a molecular-orbital description of its bonding extremely difficult. Analogies have been drawn to the sulfone bonding scheme, but, as for the iodosobenzene analogy to sulfoxides, the analogy fails to consider the difference in size between iodine and sulfur. Overlap of 5d iodine orbitals with $2p_x(O)$ is difficult at best. Possibly a charged structure including some π overlap would best describe the true bonding scheme.

E. SPECTRAL DATA

1. *Iodo Disalts and Iodoso Compounds*

Infrared spectra of iodo disalts and iodoso compounds are quite similar to those of the parent iodo compounds. For example, iodobenzene exhibits peaks at 1575, 1059, and 997 cm^{-1}. The dichloride shows an additional peak at 675 cm^{-1}; the iodoso compound exhibits an extra peak at 687 cm^{-1} (1). The former is assumed to be the I–Cl stretching frequency, the latter the I–O stretching band. The C–I stretching frequency, calculated to occur at 650 cm^{-1}, is not observed; it is probably strongly coupled to the ring. Force constants were calculated for the I–O bond in various iodoso and iodoxy compounds from their infrared spectra (67). The infrared spectra of *o*-, *m*-, and *p*-nitroiodosobenzenes were compared (116). The infrared spectra of *o*-, *m*-, and *p*-iodosobenzoic acids and other derivatives of iodobenzoic acid were recently discussed in light of the lactone structures assigned the *ortho* derivatives (15a).

Iodoaryl dihalides absorb strongly in the ultraviolet, and this fact was made extensive use of in the study of dissociation kinetics and equilibrium (2–8, 54, 102–107).

2. *Iodonium Salts*

Infrared spectra of iodonium salts in the region 4000–600 cm^{-1} (122) differ from those of the parent iodo compounds only by exhibiting absorptions due to interaction with the KBr matrix. Spectral studies, using infrared and Raman techniques in the region 400–200 cm^{-1}, confirmed the ionic nature of diphenyliodonium chloride, iodide, and fluoroborate (59, 100, 129).

Ultraviolet and visible absorption of iodonium cations is insensitive to the anion (94). No evidence for charge transfer could be found in the spectra of diphenyliodonium iodide or di(*p*-tolyl)iodonium iodide.

The spectrum of dibenziodolium cation is similar to that of fluorene. Introduction of a *p*-fluoro or *p*-methyl group to one ring caused small bathochromic shifts. This was attributed to resonance effects (41, 121), but could be explained by inductive interactions quite as well. The latter explanation agrees with observations previously made in the iodo dihalide system regarding resonance effects.

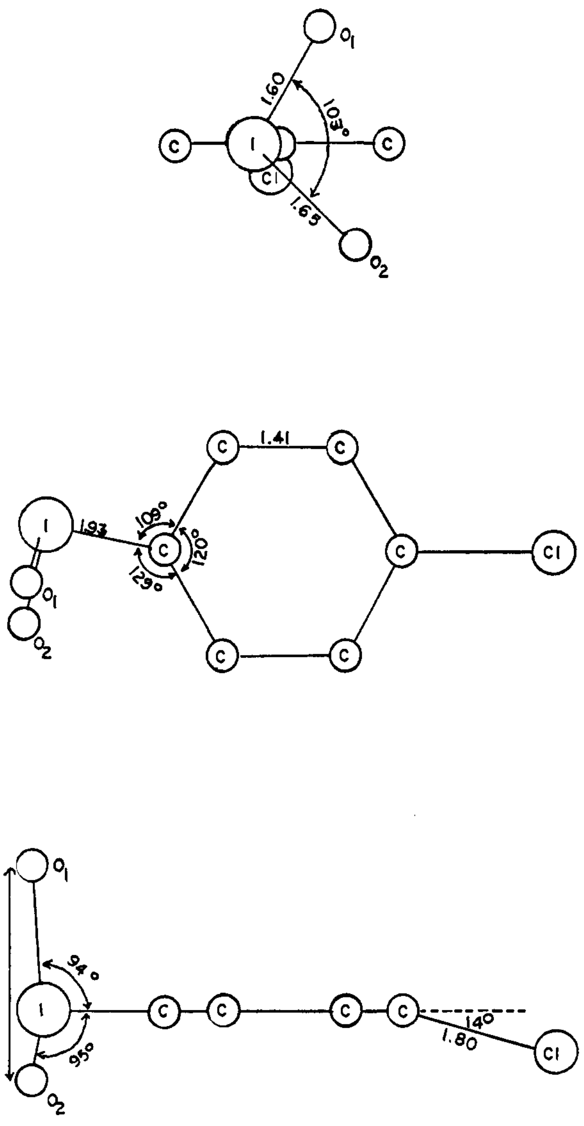
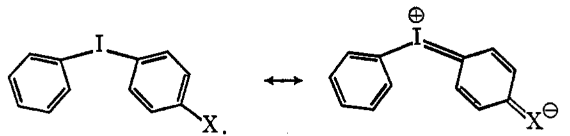


Figure 5.—Molecular structure of iodoxybenzene.



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V. REFERENCES

(1) Alcock, N. W., and Weddington, T. C., *J. Chem. Soc.*, 4103 (1963).
(1a) Agosta, W. C., *Tetrahedron Letters*, 2681 (1965).
(2) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **80**, 1723 (1958).
(3) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **81**, 2374 (1959).
(4) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **81**, 3218 (1959).
(5) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **81**, 5329 (1959).
(6) Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **82**, 3059 (1960).
(7) Andrews, L. J., Keefer, R. M., and Cotter, J. L., *J. Am. Chem. Soc.*, **84**, 793 (1962).
(8) Andrews, L. J., Spears, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **86**, 687 (1964).
(9) Arbuzov, B. A., *J. Prakt. Chem.*, **131**, 357 (1931).
(10) Archer, E. M., *Acta Cryst.*, **1**, 64 (1948).
(11) Archer, E. M., and van Schalkwyk, T. G. D., *Acta Cryst.*, **6**, 88 (1953).
(12) Askenasy, P., and Meyer, V., *Ber.*, **26**, 1354 (1893).
(13) Aten, J. B. Th., and Aten, A. H. W., Jr., *J. Am. Chem. Soc.*, **74**, 2411 (1952).
(14) Bachofner, H. E., Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1957.
(15) Bachofner, H. E., Beringer, F. M., and Meites, L., *J. Am. Chem. Soc.*, **80**, 4269, 4274 (1958).
(15a) Baker, G. P., Mann, F. G., Sheppard, N., and Tetlow, A. J., *J. Chem. Soc.*, 3721 (1965).
(16) Baker, W., Barton, J. W., and McOmie, J. F. W., *J. Chem. Soc.*, 2658 (1958).
(17) Bamberger, E., and Hill, A., *Ber.*, **33**, 533 (1900).
(18) Banks, D. F., Huyser, E. S., and Kleinberg, J., *J. Org. Chem.*, **29**, 3692 (1964).
(19) Barlin, G. B., and Riggs, N. V., *J. Chem. Soc.*, 3125 (1954).
(20) Barlin, G. B., Pausacker, K. H., and Riggs, N. V., *J. Chem. Soc.*, 3122 (1954).
(21) Barton, D. H. R., and Miller, E., *J. Am. Chem. Soc.*, **72**, 370 (1950).
(22) Bekoe, D. A., and Hulme, R., *Nature*, **177**, 1230 (1956).
(23) Berg, C. J., and Wallis, E. S., *J. Biol. Chem.*, **162**, 683 (1946).
(24) Beringer, F. M., Bachofner, H. E., Falk, R. A., and Lett, M., *J. Am. Chem. Soc.*, **80**, 4279 (1958).
(25) Beringer, F. M., Brierley, A., Drexler, M., Gindler, E. M., and Lumpkin, C. C., *J. Am. Chem. Soc.*, **75**, 2708 (1953).
(26) Beringer, F. M., Dehn, J. W., Jr., and Winicov, M., *J. Am. Chem. Soc.*, **82**, 2948 (1960).
(27) Beringer, F. M., Drexler, M., Gindler, E. M., and Lumpkin, C. C., *J. Am. Chem. Soc.*, **75**, 2702 (1953).
(28) Beringer, F. M., and Falk, R. A., *J. Am. Chem. Soc.*, **81**, 2997 (1959).
(29) Beringer, F. M., and Falk, R. A., *J. Chem. Soc.*, 4442 (1964).
(30) Beringer, F. M., Falk, R. A., Karniol, M., Lillien, I., Masulio, G., Mausner, M., and Sumner, E., *J. Am. Chem. Soc.*, **81**, 342 (1959).
(31) Beringer, F. M., and Forgione, P. S., *Tetrahedron*, **19**, 739 (1963).
(32) Beringer, F. M., and Forgione, P. S., *J. Org. Chem.*, **28**, 714 (1963).
(33) Beringer, F. M., Forgione, P. S., and Yudis, M. D., *Tetrahedron*, **8**, 49 (1960).
(34) Beringer, F. M., Galton, S. A., and Huang, S. J., *J. Am. Chem. Soc.*, **84**, 2819 (1962).
(35) Beringer, F. M., Geering, E. J., Kuntz, I., and Mausner, M., *J. Phys. Chem.*, **60**, 141 (1956).
(36) Beringer, F. M., and Gindler, E. M., *J. Am. Chem. Soc.*, **77**, 3203 (1955).
(37) Beringer, F. M., and Gindler, E. M., *Iodine Abstr. Rev.*, **3**(3) (1956).
(38) Beringer, F. M., Gindler, E. M., Rapoport, M., and Taylor, R. J., *J. Am. Chem. Soc.*, **81**, 315 (1959).
(39) Beringer, F. M., and Huang, S. J., *J. Org. Chem.*, **29**, 445 (1964).
(39a) Beringer, F. M., Kravetz, L., and Topliss, G. B., *J. Org. Chem.*, **30**, 1141 (1965).
(40) Beringer, F. M., and Lillien, I., *J. Am. Chem. Soc.*, **82**, 725 (1960).
(41) Beringer, F. M., and Lillien, I., *J. Am. Chem. Soc.*, **82**, 5135 (1960).
(42) Beringer, F. M., and Lillien, I., *J. Am. Chem. Soc.*, **82**, 5141 (1960).
(43) Beringer, F. M., and Mausner, M., *J. Am. Chem. Soc.*, **80**, 4635 (1958).
(44) Bloomfield, G. F., *J. Chem. Soc.*, 114 (1944).
(45) Boeseken, J., and Schneider, C., *Proc. Acad. Sci. Amsterdam*, **33**, 827 (1930); **35**, 1140 (1932).
(46) Bothner-By, A. A., and Vaughn, C. W., *J. Am. Chem. Soc.*, **74**, 4400 (1952).
(47) Caraway, W. T., and Hellerman, L., *J. Am. Chem. Soc.*, **75**, 5334 (1953).
(48) Caserio, M. C., Glusker, D. L., and Roberts, J. D., *J. Am. Chem. Soc.*, **81**, 336 (1959).
(49) Clauss, K., *Ber.*, **88**, 268 (1955).
(50) Colichman, E. C., *Anal. Chem.*, **25**, 1124 (1953).
(51) Colichman, E. C., and Maffei, H. P., *J. Am. Chem. Soc.*, **74**, 2744 (1952).
(52) Colichman, E. C., and Matschiner, J. T., *J. Org. Chem.*, **18**, 1124 (1953).
(53) Collette, J., McGreer, D., Crawford, R., Chubb, F., and Sandin, R. B., *J. Am. Chem. Soc.*, **78**, 3819 (1956).
(54) Cotter, J. L., Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.*, **84**, 4692 (1962).
(55) Criegee, R., and Beucker, H., *Ann. Chem.*, **541**, 218 (1939).
(56) Cristol, S. J., Stermitz, F. R., and Ramey, P. S., *J. Am. Chem. Soc.*, **78**, 4939 (1956).
(57) Crowder, J. R., Glover, E. E., Grundon, M. F., and Kaempfen, H. X., *J. Chem. Soc.*, 4578 (1963).
(58) Dibbo, A., Stephenson, L., Walker, T., and Warburton, W. K., *J. Chem. Soc.*, 2645 (1961).
(59) Epshtein, L. M., and Taroslavskii, N. G., *Dokl. Akad. Nauk SSSR*, **149**, 865 (1963); *Chem. Abstr.*, **59**, 4676*f* (1963).
(60) Exner, O., *Collection Czech. Chem. Commun.*, **24**, 3567 (1959).
(61) Falk, R. A., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1961.
(62) Fieser, L. F., and Chang, F. C., *J. Am. Chem. Soc.*, **64**, 2043 (1942).
(63) Fieser, L. F., Clapp, R. C., and Daudt, W. H., *J. Am. Chem. Soc.*, **64**, 2052 (1942).
(64) Fieser, L. F., and Oxford, A. E., *J. Am. Chem. Soc.*, **64**, 2060 (1942).
(65) Fornasari, E., Scarpa, M., and Lanza, P., *Atti Accad. Nazl. Lincei, Classe Sci. Fis. Mat. Nat.*, **14**, 70, 272 (1953).
(66) Fox, A. R., and Pausacker, K. H., *J. Chem. Soc.*, 295 (1957).
(67) Furlani, C., and Sartori, G., *Ann. Chim.* (Rome), **47**, 124 (1957).

(68) Fuson, R. C., and Albright, R. L., *J. Am. Chem. Soc.*, **81**, 487 (1959).

(69) Garvey, B. S., Halley, L. F., and Allen, C. F. H., *J. Am. Chem. Soc.*, **59**, 1827 (1937).

(70) Gershenfeld, L., and Kruse, C., *Am. J. Pharm.*, **121**, 343 (1949).

(71) Gindler, E. M., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1957.

(72) Glickman, R., and Morehouse, C. K., *J. Electrochem. Soc.*, **108**, 303 (1961).

(73) Gragerov, I. P., and Lewit, A. F., *Zh. Obshch. Khim.*, **33**, 544 (1963); *Chem. Abstr.*, **59**, 1506*h* (1963).

(74) Greidanaus, J. W., Rebel, W. J., and Sandin, R. B., *J. Am. Chem. Soc.*, **84**, 1504 (1962).

(75) Grossman, F., *Roczniki Chem.*, **7**, 567 (1927); *cf. Chem. Rev.*, **32**, 264 (1943).

(76) Gudriniece, E., Neilands, O., and Vanags, G., *Zh. Obshch. Khim.*, **27**, 2737 (1957); *Chem. Abstr.*, **52**, 7177*e* (1958).

(77) Hampton, K. G., Harris, T. M., and Hauser, C. R., *J. Org. Chem.*, **29**, 3511 (1964).

(78) Harries, C., *Ber.*, **36**, 2996 (1903).

(79) Hartmann, C., and Meyer, V., *Ber.*, **26**, 1727 (1893).

(80) Hartmann, C., and Meyer, V., *Ber.*, **27**, 426 (1894).

(81) Hartmann, C., and Meyer, V., *Ber.*, **27**, 502 (1894).

(82) Heal, H. G., *J. Inorg. Nucl. Chem.*, **16**, 208 (1961).

(83) Hey, D. H., Stirling, C. J. M., and Williams, G. H., *J. Chem. Soc.*, 2747 (1954).

(84) Hey, D. H., Stirling, C. J. M., and Williams, G. H., *J. Chem. Soc.*, 3693 (1955).

(85) Hey, D. H., Stirling, C. J. M., and Williams, G. H., *J. Chem. Soc.*, 1475 (1956).

(86) Hillman, G., U. S. Patent 2,886,592 (1959); *Chem. Abstr.*, **53**, 21699*d* (1959).

(87) Holton, P. G., Cross, A. D., and Bowers, A., *Steroids*, **2**, 71 (1963).

(88) Holzaepfel, J. H., Greenlee, R. E., Wyand, R. E., and Ellis, W. C., Jr., *Fertility Sterility*, **10**, 272 (1959); *Chem. Abstr.*, **54**, 25577*i* (1960).

(89) Hopff, H., and Metzler, H., German Patent 1,140,344 (1962); *Chem. Abstr.*, **58**, 5807*a* (1963).

(90) Hwang, W. K., *Sci. Sinica* (Peking), **6**, 123 (1957); *Chem. Abstr.*, **51**, 16476 (1957).

(91) Hwang, W. K., *Hua Hsueh Hsueh Pao*, **23**, 438 (1957); *Chem. Abstr.*, **52**, 16356 (1958).

(92) Hwang, W. K., Wang, C. H., and Chen, S. Y., *K'o Hsueh T'ung Pao*, **2**, 49 (1957); *Chem. Abstr.*, **53**, 4280 (1957).

(93) Irving, H., and Reid, R. W., *J. Chem. Soc.*, 2078 (1960).

(94) Irving, H., Turner, G. P. A., and Reid, R. W., *J. Chem. Soc.*, 2082 (1960).

(95) Jeffery, E. A., Andrews, L. J., and Keefer, R. M., *J. Org. Chem.*, **30**, 617 (1965).

(96) Johnson, J. R., in Gilman's "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p 1612.

(97) Johnson, W. D., and Riggs, N. V., *Australian J. Chem.*, **8**, 457 (1955).

(98) Johnson, W. D., and Riggs, N. V., *Australian J. Chem.*, **11**, 34 (1958).

(99) Johnson, W. D., and Riggs, N. V., *Australian J. Chem.*, **17**, 787 (1964).

(100) Juliusberger, F., Topley, B., and Weiss, J., *J. Chem. Soc.*, 1295 (1935).

(101) Karelsky, M., and Pausacker, K. H., *Australian J. Chem.*, **11**, 39 (1958).

(102) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **79**, 4348 (1957).

(103) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **80**, 277 (1958).

(104) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **80**, 5350 (1958).

(105) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **82**, 4547 (1960).

(106) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **83**, 376 (1961).

(107) Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.*, **84**, 3635 (1962).

(108) Kennedy, R. J., and Stock, A. M., *J. Org. Chem.*, **25**, 1901 (1960).

(109) Keppler, F., *Ber.*, **31**, 1136 (1898).

(110) Kharasch, M. S., and Brown, H. C., *J. Am. Chem. Soc.*, **62**, 925 (1940).

(111) Khotsyanova, T. L., *Kristallografiya*, **1**, 524 (1956).

(112) Khotsyanova, T. L., *Kristallografiya*, **2**, 51 (1957).

(113) Khotsyanova, T. L., *Dokl. Akad. Nauk SSSR*, **110**, 7 (1956); *Chem. Abstr.*, **52**, 4282*h* (1958).

(114) Khotsyanova, T. L., and Struchkov, Yu. T., *Zh. Fiz. Khim.*, **26**, 644, 669 (1952); *Chem. Abstr.*, **49**, 6684*e* (1952).

(115) Khotsyanova, T. L., and Struckhov, Yu. T., *Kristallografiya*, **2**, 384 (1957); *Chem. Abstr.*, **52**, 3457*e* (1958).

(116) King, M. V., *J. Org. Chem.*, **26**, 3323 (1961).

(117) Kinzer, G. W., U. S. Patent 2,878,283 (1959); *Chem. Abstr.*, **53**, 14058*e* (1959).

(118) Le Fevre, C. G., and Le Fevre, R. J. W., *J. Chem. Soc.*, 3373 (1950).

(119) Le Goff, E., *J. Am. Chem. Soc.*, **84**, 3786 (1962).

(120) Lhatka, J. F., *Stain Technol.*, **29**, 295 (1954); *Nature*, **174**, 882 (1954).

(121) Lillien, I., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1960.

(122) Lillien, I., *J. Chem. Soc.*, 4498 (1962).

(123) Lucas, H. J., and Kennedy, E. R., "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, pp 355, 482–485.

(124) Lynch, B. M., and Pausacker, K. H., *Australian J. Chem.*, **10**, 329 (1957).

(125) Maciel, G. E., *J. Am. Chem. Soc.*, **86**, 1269 (1964).

(126) McCullough, J. D., *Acta Cryst.*, **6**, 747 (1953).

(127) Masson, I., and Hanby, W. E., *J. Chem. Soc.*, 1699 (1938).

(128) Masson, I., Race, E., and Pounder, F. E., *J. Chem. Soc.*, 1669 (1935).

(129) Medlin, W. V., *J. Am. Chem. Soc.*, **57**, 1026 (1935).

(130) Meyer, V., and Wachter, W., *Ber.*, **25**, 2632 (1892).

(131) Miller, R. E., U. S. Patents 3,053,888 and 3,053,889 (1963); *Chem. Abstr.*, **58**, 6753*c*, 8983*e* (1963).

(132) Mitchell, J., and Pausacker, K. H., *J. Chem. Soc.*, 4502 (1954).

(133) Mitchell, J., and Pausacker, K. H., *Australian J. Chem.*, **10**, 460 (1957).

(134) Nefedov, V. D., Norseov, Yu. U., Savlevich, Kh., Sonotova, E. N., Toropova, M. A., and Khalkin, V. A., *Dokl. Akad. Nauk SSSR*, **144**, 806 (1962); *Chem. Abstr.*, **57**, 11062*f* (1962).

(135) Neilands, O., Vanags, G., and Gudriniece, E., *Zh. Obshch. Khim.*, **28**, 1201 (1958); *Chem. Abstr.*, **52**, 19988 (1958).

(136) Neilands, O., and Vanags, G., *Dokl. Akad. Nauk SSSR*, **129**, 337 (1959); *Chem. Abstr.*, **54**, 7703*f* (1960).

(137) Neilands, O., and Vanags, G., *Dokl. Akad. Nauk SSSR*, **130**, 90 (1960); *Chem. Abstr.*, **54**, 10897*d* (1960).

(138) Neilands, O., and Vanags, G., *Zh. Obshch. Khim.*, **30**, 510 (1960); *Chem. Abstr.*, **54**, 24469*b* (1960).

(139) Neilands, O., and Vanags, G., *Zh. Obshch. Khim.*, **31**, 146 (1961); *Chem. Abstr.*, **55**, 23386 (1961).

(140) Neilands, O., and Vanags, G., *Dokl. Akad. Nauk SSSR*, **141**, 872 (1961); *Chem. Abstr.*, **56**, 12715 (1962).

(141) Nesmeyanov, A. N., Makarova, L. G., and Tolstaya, T. P., *Tetrahedron*, **1**, 145 (1957).

(142) Nichol, J. C., and Sandin, R. B., *J. Am. Chem. Soc.*, **67**, 1307 (1945).

(143) Okawara, M., Kurusu, Y., and Imoto, E., *Kogyo Kagaku Zasshi*, **65**, 1647 (1962); *Chem. Abstr.*, **58**, 8051*d* (1963).

(144) Pauling, L., "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 225, 526.

(145) Pausacker, K. H., *J. Chem. Soc.*, 107 (1953).

(146) Pausacker, K. H., *J. Chem. Soc.*, 1989 (1953).

(147) Pausacker, K. H., and Scroggie, J. G., *J. Chem. Soc.*, 4499 (1954).

(148) Pershin, G. N., and Bogdanova, N. S., *Farmakol. i Toksikol.*, **25**, 209 (1962); *Chem. Abstr.*, **57**, 15605*e* (1962).

(149) Pershin, G. N., Bogdanova, N. S., Znaeva, K. I., and Kraft, M. Ya., *Farmakol. i Toksikol.*, **24**, 690 (1961); *Chem. Abstr.*, **58**, 12885*f* (1963).

(150) Pirkl, J., Czechoslovakian Patents 87,798 and 87,838 (1959); *Chem. Abstr.*, **54**, 9845*a* (1960).

(151) Plati, J. T., U. S. Patent 2,839,583 (1958); *Chem. Abstr.*, **52**, 16288*b* (1958).

(152) Potretz, H. A., and Rosen, J. M., *Anal. Chem.*, **21**, 1276 (1949).

(153) Ptitsyna, O. A., Kozlova, A. N., and Reutov, O. A., *Izv. Akad. Nauk SSSR*, 634 (1962); *Chem. Abstr.*, **57**, 15148*a* (1962).

(153a) Ptitsyna, O. A., Pudeeva, M. E., Bel'Kevich, N. A., and Reutov, O. A., *Dokl. Akad. Nauk SSSR*, **163**, 383 (1965); *Chem. Abstr.*, **63**, 11611*c* (1965).

(154) Ptitsyna, O. A., Reutov, O. A., and Ertel, G., *Izv. Akad. Nauk SSSR*, 285 (1961); *Chem. Abstr.*, **55**, 19841*h* (1961).

(155) Ptitsyna, O. A., Reutov, O. A., and Turchinskii, M. F., *Nauchn. Dokl. Vysshei Shkoly, Khim. i Khim. Tekhnol.*, 138 (1959); *Chem. Abstr.*, **53**, 17030*i* (1959).

(156) Ptitsyna, O. A., Reutov, O. A., and Turchinskii, M. F., *Dokl. Akad. Nauk SSSR*, **114**, 110 (1957); *Chem. Abstr.*, **52**, 10909 (1958).

(157) Ptitsyna, O. A., Turchinskii, M. F., Sidel'nikova, E. A., and Reutov, O. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1527 (1963); *Chem. Abstr.*, **59**, 15309*b* (1963).

(158) Rafter, G. W., *Arch. Biochem. Biophys.*, **67**, 267 (1957).

(159) Ramakrishnan, C. S., Raghunath, D., and Pande, J. B., *Trans. Inst. Rubber Ind.*, **30**, 129 (1954); *Chem. Abstr.*, **49**, 657*a* (1955); *Rubber Chem. Technol.*, **28**, 598 (1955); *Chem. Abstr.*, **49**, 16493*d* (1955).

(160) Reutov, O. A., "Theoretical Organic Chemistry, Kekulé Symposium, London, 1958," Butterworths, London, 1959, p 176.

(161) Reutov, O. A., and Ertel, G., *Chem. Tech.* (Berlin), **10**, 201 (1958); *Chem. Abstr.*, **52**, 20000*h* (1958).

(162) Reutov, O. A., Ertel, G., and Ptitsyna, O. A., *Dokl. Akad. Nauk SSSR*, **133**, 1108 (1960); *Chem. Abstr.*, **54**, 24478*c* (1960).

(163) Reutov, O. A., and Lovtsova, A. N., *Vestn. Mosk. Univ., Mekhan. i Khim.*, **13**, 191 (1958); *Chem. Abstr.*, **53**, 11283*h* (1959).

(164) Reutov, O. A., and Khu, K. V., *Dokl. Akad. Nauk SSSR*, **122**, 825 (1958); *Chem. Abstr.*, **53**, 4177*h* (1959).

(165) Reutov, O. A., Ptitsyna, O. A., and Stiazhkina, N. B., *Dokl. Akad. Nauk SSSR*, **122**, 1032 (1958); *Chem. Abstr.*, **53**, 4161*f* (1959).

(166) Reutov, O. A., Ptitsyna, O. A., and Turchinskii, M. F., *Dokl. Akad. Nauk SSSR*, **139**, 146 (1961); *Chem. Abstr.*, **56**, 3527 (1962).

(167) Richards, L. M., U. S. Patent 2,467,231 (1949); *Chem. Abstr.*, **43**, 5231*d* (1949).

(168) Russell, G. A., *J. Am. Chem. Soc.*, **80**, 4987 (1958).

(169) Russell, G. A., private communication.

(170) Sakai, S., Nakajima, K., Ihida, A., Ishida, I., and Saito, M., *Yakugaku Zasshi*, **82**, 1532 (1962); *Chem. Abstr.*, **58**, 13912*f* (1963).

(171) Sandin, R. B., *Chem. Rev.*, **32**, 249 (1943).

(172) Sandin, R. B., and McCormack, W. B., *J. Am. Chem. Soc.*, **67**, 205 (1945).

(173) Schmidt, H., and Meinert, H., *Angew. Chem.*, **72**, 109 (1960).

(174) Schreiber, K. C., and Fernandez, V. P., *J. Org. Chem.*, **26**, 2478 (1961).

(175) Schreiber, K. C., and Fernandez, V. P., *J. Org. Chem.*, **26**, 2910 (1961).

(176) Segal, H. L., and Boyer, P. D., *J. Biol. Chem.*, **204**, 265 (1953).

(177) Sharefkin, J. F., and Saltzmann, H., *Anal. Chem.*, **35**, 142 (1963).

(178) Siegel, A., and Antony, F., *Monatsh.*, **86**, 292 (1955).

(179) Struchkov, Yu, T., and Khotsyanova, T., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 821 (1960); *Chem. Abstr.*, **56**, 11028*g* (1962).

(180) Summerbell, R. K., and Lunk, L. C., *J. Am. Chem. Soc.*, **79**, 4802 (1957).

(181) Thiele, J., and Haakh, H., *Ann. Chem.*, **369**, 131 (1909).

(182) Thiele, J., and Peter, W., *Ber.*, **38**, 2842 (1905).

(183) Thiele, J., and Peter, W., *Ann. Chem.*, **369**, 119 (1909).

(184) Weinland, R. F., and Stille, W., *Ber.*, **34**, 2631 (1901).

(185) Willgerodt, C., *J. Prakt. Chem.*, [2] **33**, 154 (1886).

(186) Willgerodt, C., *Ber.*, **25**, 3494 (1892).

(187) Willgerodt, C., *Ber.*, **26**, 357, 1307, 1802 (1893).

(188) Willgerodt, C., *Ber.*, **29**, 1567 (1896).

(189) Willgerodt, C., "Die organischen Verbindungen mit mehrwertigem Jod," F. Enke, Stuttgart, 1914.

(190) Wittig, G., and Rieber, M., *Ann. Chem.*, **562**, 187 (1949).

(191) Zappi, E. V., and Cortelezzi, J., *Anales Asoc. Quim. Arg.*, **21**, 71 (1933); *cf. Chem. Rev.*, **32**, 270 (1943).