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# Advances in the Synthesis of Aromatic Iodo-compounds

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The review presents a compilation of data on the iodination of aromatic compounds published during the last 10-20 years. The synthetic advantages of various methods of preparation of aromatic iodo-derivatives are examined and data concerning the mechanism of direct iodination are presented.
The bibliography includes 127 references.

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## I. INTRODUCTION

The expansion of the range of methods of organic synthesis involves both the discovery of new reactions and reagents and a deepening of our knowledge of the chemical properties of compounds already known. The latter applies fully to the chemistry of aromatic iodo-derivatives. For about 100 years, aryl iodides have been used in various organometallic syntheses, mainly in the Ullmann reaction (for the latest reviews on this reaction, see Fanta[1] and Goshaev et al.[2]). A new branch of this by no means complete field of study involves the condensation of copper acetylides with compounds containing a halogen attached to an unsaturated carbon atom (usually with aryl iodides). Further progress in this field is associated with the application of transition metal complexes, particularly palladium complexes (see the relevant reviews[3-6]). Summarising the reactions of halides in the presence of palladium salts, Heck[7] noted the enhanced and frequently uniquely high reactivity of the iodo-derivatives.

One must note the elegant method of generating aryl radicals in the photolysis of aryl iodides discovered by Kharasch and co-workers[8,9]. It must be emphasised that the reaction between aryl iodides and styrenes leads to stilbenes, which are the starting materials for the synthesis (by photochemical dehydrocyclisation) of a wide variety of compounds containing the phenanthrene fragment[10].

It is to be expected that further studies will expand still more the applications of aromatic iodo-derivatives in organic synthesis. One of the causes which has retarded a more extensive involvement of aryl iodides in practical organic synthesis has been the lack of simple and reliable methods of their preparation; the main method for the synthesis of the majority of aryl iodides up to the 1950s involved a multistage synthesis based on the Sandmeyer reaction. However, the studies in the last 10–20 years have led to the discovery of new simple methods which have made aryl iodides quite easily available.

Whereas the methods of synthesis of aromatic bromo-, chloro-, and fluoro-derivatives have been widely described in monographs and have been published periodically in journal reviews, there are no similar publications devoted to aromatic iodo-derivatives with the exception of a short chapter in a monograph[11]. The main aim of this review is to draw the attention of chemists engaged in synthesis to the advances in the synthesis of aromatic iodo-derivatives.

The known methods of synthesis of aryl iodides can be divided into two large groups: direct iodination based on the direct formation of the carbon–iodine bond on substitution of aromatic compounds and indirect iodination involving the initial substitution of hydrogen in the aromatic substrate by an atom or group with its subsequent replacement by iodine. The entire experimental data are examined henceforth on the basis of this classification.

## II. DIRECT IODINATION

The vast majority of aromatic compounds, with the exception of a series of amines and phenols whose reactions are not considered in this review, do not interact with molecular iodine in the absence of oxidants. The set of oxidants used in direct iodination reactions was extremely limited up to the 1950s, but studies in recent years have greatly increased their number, which has led to the development of simple and reliable methods of synthesis of iodo-derivatives of different classes.

### 1. Iodination by the Tronov–Novikov Method

At the beginning of the 1950s, Tronov and Novikov showed that the iodination reaction can be successfully carried out in acetic acid in the presence of nitric and sulphuric acids as oxidants[12-14]. In the course of numerous experiments, it was established that the best results are obtained when mixtures of nitric ($d = 1.4$) and sulphuric ($d = 1.84$) acids are employed. This method was subsequently extended to a wide range of aromatic substrates[15-18] including benzene and its homologues, polynuclear aromatic compounds, oxygen-containing aromatic compounds (ethers, aldehydes, ketones, and carboxylic acids) and aromatic compounds of other classes.

In iodination by the Tronov–Novikov method, the organic substrate is usually dissolved in glacial acetic acid, finely ground iodine is added, and then a mixture of nitric and sulphuric acid is added dropwise with intense stirring (at temperatures ranging from room temperature to the boiling point of glacial acetic acid). In the iodination of reactive aromatic compounds, the acid mixture is diluted with acetic acid[19]. Sometimes, when the reaction is carried out at an elevated temperature, it is useful to add several millilitres of carbon tetrachloride to the reaction mixture in order to wash off the subliming iodine. The reaction is accompanied by the evolution of nitrogen oxides; it can be followed visually from the disappearance of iodine. In order to isolate the reaction products, the reaction mixture is diluted with water in most cases, and the iodo-derivative formed is filtered off.

Iodobenzene (80%), 2-iodo-*p*-xylene (87%), 2,5-di-iodo-*p*-xylene (85%), iodomesitylene (88%), iododurene (100%), di-iododurene (88%), di-iodomesitylene (80%), tri-iodomesitylene (63%), iodopentamethylbenzene (87%), 4,4′-di-iodobiphenyl (68%), 2,7-di-iodofluorene (50%), 2,7-di-iodofluorenone (75%), 2,7-di-iodophenanthrenequinone (50%), 2-iodofluorenone-5-carboxylic acid (65%), as well as many other aromatic iodo-compounds have been obtained by this method.

Iodonitro-derivatives are formed as side products at elevated temperatures[20], which suggested a "single-stage" reaction for the introduction of iodine and nitro-groups into aromatic compounds[21]; studies of the isomeric composition of the products led to the conclusion that iodination takes place initially and is followed by nitration[22]. 4-Iodonitrobenzene (46%), 2-iodo-5-nitro-*p*-xylene (45%), 4-iodo-4′-nitrobiphenyl (50%), and 2-iodo-7-nitrofluorene (61%) have been synthesised successfully by this method[22–25].

Further studies of the oxidative side processes will probably lead to the development of new useful methods, as can be seen from the synthesis of 4,4′-di-iodobenzophenone in 40% yield on iodination of diphenylmethane[26].

### 2. Iodination in the Presence of Iodic and Periodic Acids

Although iodination in the presence of iodic acid has been known for more than 100 years (see, for example, Kekulé [27]), the extensive possibilities of this reagent as an oxidant in the iodination of a large number of aromatic substrates were demonstrated only in 1960.[28] Subsequently, this reagent was used in the iodination of *p*-xylene and durene[29]. The method is convenient for the iodination of fluorene whose molecule contains the readily oxidisable methylene group[30]; it proved useful also in the iodination of methylated polyphenylenes[31–33].

Periodic acid dihydrate is used in the iodination of alkylbenzenes[34–36]. In particular, satisfactory results have been obtained in the presence of this oxidant in the monoiodination of mesitylene, durene, pentamethylbenzene, 5-t-butyl-1,3-dimethylbenzene, 4-t-butyl-1,2-dimethylbenzene, and even 5-t-butyl-1,2,3-trimethylbenzene, 1,2,4,5-tetraisopropylbenzene, and *p*-di-t-butylbenzene. A critical examination of the methods of synthesis of iodo-derivatives of alkylbenzene led to the conclusion[37] that the above procedure is the most suitable for the introduction of one and two iodine atoms into the alkylbenzene molecule. The efficiency of periodic acid in the iodination of unsubstituted polyphenylenes[38,39], fluoranthene[40], and acenaphthene[41] has been demonstrated.

### 3. Iodination in the Presence of Peracetic Acid

It was shown in the middle 1960's [42–46] that peracetic acid is an effective oxidant in direct iodination. The method was extended to a wide range of aromatic substrates; particularly good results were obtained for atomatic compounds containing electron-donating substituents.

The study of the reaction mechanism led to the hypothesis that acetyl hypoiodite and its protonated form are the source of electrophilic iodine[44]. Autocatalysis in the iodination of benzene homologues with electron-donating substituents was noted and the authors explained it by the oxidation of the iodo-derivatives formed initially by the corresponding iodoso-derivatives or their acetates in accordance with the following scheme:

$$ArI + CH_3CO_3H \rightarrow ArIO + CH_3CO_2H ,$$
$$ArIO + 2CH_3CO_2H \rightarrow ArI(OCOCH_3)_2 + H_2O .$$

The polyvalent iodine compounds formed are effective oxidants in the oxidation of iodine to acetyl hypoiodite:

$$ArI(OCOCH_3)_2 + I_2 \rightarrow ArI + 2CH_3COO^{\oplus}I^{\oplus}$$

This hypothesis was confirmed by the successful iodination of *m*-xylene in warm acetic acid in the presence of iodosobenzene or phenyliodoso acetate†.

### 4. Iodination in the Presence of Variable-Valence Metal Chlorides

In 1970 a method was proposed for the direct iodination of aromatic compounds using bivalent copper chloride and an iodine donor ($I_2$, $AlI_3$, or $FeI_2.4H_2O$).[47] It was also found that the copper acetate–iodine system is effective for the iodination of azulene[48].

The effectiveness of antimony pentachloride as the oxidant in the oxidation of aromatic compounds in carbon tetrachloride was demonstrated in 1974.[49] It is of interest to note the very high yields of the *p*-isomers, which are respectively 98, 99, and 100% in the case of fluorobenzene, chlorobenzene, and bromobenzene.

### 5. Iodination by *N*-iodoamides

*N*-Iodosuccinimide is used successfully in the iodination of fluorene[50] (for the synthesis of the reagent, see Benson et al.[51]). The effectiveness of acid *N*-iodoamides in arene iodination reactions has been demonstrated[52–55]. These reactions are accelerated on catalysis by acids; particularly good results have been obtained using trifluoroacetic acid[55]. The authors believe that trifluoroacetyl hypoiodite is the source of electrophilic iodine in this process.

Trifluoroacetyl hypoiodite was probably first postulated as a source of electrophilic iodine by Henne and Zimmer[56], who demonstrated the effectiveness of the iodine/silver trifluoroacetate system in the iodination of aromatic compounds; an elegant method of synthesis of iodoveratrol was developed on the basis of this procedure[57]. In this reaction, iodine can be successfully replaced by chlorine iodide[58]. It has been shown that in the series of acetyl hypohalites, trifluoroacetyl hypohalites are the most powerful halogenating agents[59].

### 6. Iodination in the Presence of Phenyliodoso Trifluoroacetate#

An attempt at the coupled addition of iodine and trifluoroacetoxy-groups to the triple bond of tolane, by analogy with iodoacetoxylation by the iodine/phenyliodoso acetate system was made in 1979.[60] However, instead of the expected addition to the triple bond, tolane was oxidised to an α-diketone (benzil). It was found that the oxidation of diarylacetylenes to α-diketones is a general reaction[61]. Together with benzil, *p*-di-iodobenzene, formed as a result of the iodination of iodobenzene whose source was a molecule of phenyliodoso trifluoroacetate, was isolated from the reaction product[62]. Inorganic derivatives of polyvalent iodine (iodic and periodic acid) are widely used as oxidants in direct iodination reactions but organic derivatives of polyvalent iodine have not

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†Bis(acetato-*O*)phenyliodine (Ed.of Translation).

#Bis(trifluoroacetato-*O*)phenyliodine (Ed.of Translation).

been used until recently in preparative organic chemistry, although the possibility, in principle, of iodinating *m*-xylene in warm acetic acid using iodosobenzene or phenyl iodosoacetate was demonstrated as early as 1963.[44] Phenyliodosoacetate has no special advantages over more readily available oxidants in direct iodination reactions; when azobenzene is iodinated in the presence of phenyl iodosoacetate, 4-iodoazobenzene is formed only in insignificant yield[63].

A detailed study of iodination in the presence of phenyliodoso trifluoroacetate showed that, in contrast to phenyliodoso acetate, this reagent is very effective as an oxidant and makes it possible to introduce from one to three iodine atoms into the aromatic ring at room temperature[64–66]. It was found that the iodine/phenyliodoso trifluoroacetate system is effective in the iodination of not only benzenoid compounds but also certain heterocycles[67]. It was discovered that the bromine/phenyliodoso trifluoroacetate system is effective in the bromination of aromatic compounds[60]. Some data on the iodination of aromatic compounds by the iodine/phenyliodoso trifluoroacetate system at room temperature are presented in Table 1.

**Table 1.** Iodination in the presence of phenyliodoso trifluoroacetate.[66]

| Aromatic substrate | Aryl iodide | Yield, % |
|---|---|---|
| Benzene | Iodobenzene | 72 |
| *o*-Xylene | 4,5-Di-iodo-*o*-xylene | 55 |
| *m*-Xylene | 4,6-Di-iodo-*m*-xylene | 77 |
| *p*-Xylene | 2,5-Di-iodo-*p*-xylene | 65 |
| Mesitylene | Tri-iodomesitylene | 84 |
| Durene | Di-iododurene | 52 |
| Diphenylmethane | 4,4'-Di-iododiphenylmethane | 52 |
| Triphenylmethane | 4,4',4''-Tri-iodotriphenylmethane | 32 |
| Biphenyl | 4,4'-Di-iodobiphenyl | 87 |
| *p*-Terphenyl | 4,4''-Di-iodo-*p*-terphenyl | 93 |
| Chlorobenzene | 1-Chloro-4-iodobenzene | 61 |
| Bromobenzene | 1-Bromo-4-iodobenzene | 63 |
| Iodobenzene | 1,4-Di-iodobenzene | 73 |
| Diphenyl ether | Di(4-iodophenyl) ether | 79 |
| Fluorenone | 2,7-Di-iodofluorenone | 51 |
| Biphenyl-4-carboxylic acid | 4-Iodobiphenyl-4'-carboxylic acid | 81 |
| Fluorene-9-carboxylic acid | 2,7-Di-iodofluorene-9-carboxylic acid | 70 |
| Methyl fluorene-9-carboxylate | Methyl 2,7-di-iodofluorene-9-carboxylate | 52 |
| Diphenylene oxide | 3,6-Di-iododiphenylene oxide | 59 |

On the basis of the data obtained in a $^{19}F$ NMR study of the iodination of arenes in carbon tetrachloride at room temperature, trifluoroacetyl hypoiodite has been proposed as the iodinating agent:

$$C_6H_5I(OCOCF_3)_2 + I_2 \rightleftarrows C_6H_5I + 2F_3CCOOI;$$
$$ArH + F_3CCOOI \rightarrow ArI + F_3CCOOH\ .$$

It was established that phenyl iodosotrifluoroacetate, prepared beforehand, must be used in the reaction. It can be generated in the reaction mixture *in situ* from phenyl iodosoacetate and trifluoroacetic acid[66].

The iodination reaction takes place at room temperature with aromatic substrates which are not oxidised under the experimental conditions and are more reactive in electrophilic substitution reactions than iodobenzene. The attempt to iodinate nitrobenzene, benzoic acid, and benzophenone led only to *p*-di-iodobenzene as a consequence of the iodination of the iodobenzene formed from phenyliodoso trifluoroacetate.

### 7. Iodination of Polymers

Reagents on a polymeric support have been recently introduced into practical organic synthesis. From this standpoint, iodine-containing polymers are of special interest since iodine can be readily substituted by another functional group or a reagent with polyvalent iodine can be formed. Compounds containing the iodosochloride [aryliodine dichloride] group in the benzoic acid residue, joined by an ester linkage to a steroid molecule[69], or an iodosofluoride [aryliodine difluoride] group in a polymeric molecule[70], have been used successfully in the selective halogenation of organic compounds. Polystyrene can be iodinated in the presence of iodic acid[71] or iodine pentoxide[72] as oxidants but iodination in the presence of phenyliodoso trifluoroacetate is a more convenient method[73].

### 8. Introduction of Polyvalent Iodine into the Aromatic Ring

The introduction of the iodo-group into the aromatic molecule on treatment with iodic and sulphuric acids can be classified as a variety of the direct iodination reaction[74]. Together with benzene, halogenobenzenes, benzoic acid, and nitrobenzene can enter into this reaction. The reduction of iodo-derivatives leads to the corresponding aryl iodides. On treatment with iodine tris(trifluoroacetate), it is possible to introduce the $(CF_3COO)_2I$ group[75]. The reduction of aryliodoso trifluoroacetates leads to aryl iodides. Many problems involving the mode of substitution in the benzene ring can be solved in this field. Whereas iodine is *ortho-para* directing, polyvalent iodine exhibits a powerful *meta*-directing effect.

## III. INDIRECT IODINATION

The reaction involving the replacement of the amino-group by iodine via diazonium salts has still not lost its importance especially when the amine is commercially available or it is necessary to synthesise an iodide having a specific structure without admixtures of other isomeric iodo-derivatives. The diazotisation of aniline in the presence of iodine[76], which makes it possible to obtain *p*-di-iodobenzene, probably via an intermediate aniline iodination stage, can be classified as a reaction of this type. In this connection it is necessary to point out a publication[77] whose authors claim that the synthesis of iodo-derivatives with the aid of diazonium salts in the presence of crown-ethers has advantages over the classical version of the Sandmeyer reaction. It is of interest to note the thermal stability of aryl iodides; the thermolysis of aryl bromides in the presence of iodine can serve as a preparative method of synthesis of iodo-derivatives[78].

Since, together with primary aromatic amines, aromatic carboxylic acids are the most readily available functional derivatives, the potential possibility of replacing the carboxy-group by iodine is of undoubted interest. A number of methods for the replacement of the carboxy-group (in the form of various derivatives) by iodine have been developed in recent years and will be considered below. Striking advances in the synthesis of aryl iodides were associated with the application of organometallic compounds, particularly thallium derivatives. In addition, reactions involving the decomposition of organic compounds of polyvalent iodine, leading to aryl iodides, have been examined; a series of effective methods of synthesis of polyvalent iodine compounds, which have led to the use of these previously exotic compounds as intermediates in the preparative synthesis of aromatic iodo-derivatives, have also been developed.

### 1. The Replacement of the Carboxy-Group by Iodine

The catalytic decarbonylation of aromatic carboxylic acid iodides to the corresponding aryl iodides by tris(triphenylphosphine)rhodium chloride was described in 1968.[79] *o*-Diiodobenzene, *o*-chloroiodobenzene, and *m*-di-iodobenzene, which are difficult to obtain by direct iodination, have been obtained in satisfactory yields by the above method. The reaction proceeds under mild conditions and gives rise to high yields of the iodide. The discovery of a relatively simple method of synthesis of aroyl iodides from the corresponding aroyl chlorides and sodium iodide[80] undoubtedly makes the decarbonylation reaction valuable in practice.

It is known that the thermolysis of aroyl peroxides in the presence of iodine can serve as a preparative method of synthesis of aryl iodides; particularly good results have been obtained using the peroxides of nitrobenzoic acids[81].

The Borodin–Hunsdieker reaction has not found extensive applications in the synthesis of aryl iodides but it should be noted that the photolysis of naphthoic acids in the presence of lead tetra-acetate and iodine has led to the corresponding iodonaphthalenes in high yields[82].

### 2. The Synthesis of Iodo-derivatives Via Organothallium Compounds

As early as the 1940's, Gilman observed[83] that organothallium compounds can be obtained with the aid of thallium trichloride. However, this reaction did not find applications in organic synthesis, probably as a consequence of the insignificant yield and severe conditions. In the 1950's Glushkova and Kocheshkov discovered the reaction involving the direct introduction of thallium into aromatic compounds by thallium tri-isobutyrate at 95–115 °C with formation of arylthallium di-isobutyrates[84–87]; they also demonstrated the ease of the cleavage of the thallium–carbon bond by molecular iodine with formation of iodo-derivatives. However, this reaction has not found synthetic applications, probably because of the difficulties in the introduction of thallium into deactivated aromatic compounds owing to the low electrophilicity of thallium tri-isobutyrate.

In 1969 McKillop and co-workers[88] showed that thallium tris(trifluoroacetate) is an excellent reagent for the introduction of thallium into organic substrates. It may be noted that the method of synthesis of thallium tris(trifluoroacetate) quoted in the well-known book by Fieser and Fieser[89] cannot be reproduced. Fieser and Fieser apparently based their description on a brief communication[88] where it was not stated that a small amount of water is essential for the preparation of thallium tris(trifluoroacetate) from thallium oxide and difluoroacetic acid; this was noted in a subsequent more detailed publication[91]. It has been established[90,91] that treatment of arylthallium bis(trifluoroacetate) with an aqueous solution of potassium iodide constitutes a very simple method of synthesis of aryl iodides:

$$ArH \xrightarrow{Tl(OCOCF_3)_3} ArTl(OCOCF_3)_2 \xrightarrow{KI} ArI$$

Substitution by thallium is usually carried out in trifluoroacetic acid; in the case of substrates sensitive to the action of acids, it is possible to employ acetonitrile. Aromatic compounds are usually substituted by thallium in the course of several minutes at room temperature but deactivated substrates require heating with thallium tris(trifluoroacetate) in boiling trifluoroacetic acid. Some data on the synthesis of aryl iodides via organothallium compounds are listed in Table 2.

**Table 2.** Synthesis of aromatic iodo-derivatives via organothallium compounds.

| Aromatic Substrate | Aryl iodide | Yield, % | Refs. |
|---|---|---|---|
| Benzene | Iodobenzene | 96 | [91] |
| Benzene* | 1,4-Di-iodobenzene | 89 | [92] |
| Benzene* | 1,2,4-Tri-iodobenzene | 70 | [92] |
| Benzene* | 1,2,4,5 Tetraiodobenzene | 41 | [92] |
| t-Butylbenzene | 1-t-Butyl-4-iodobenzene | 93 | [91] |
| *o*-Xylene | 4-Iodo-1,2-dimethylbenzene | 98 | [91] |
| *m*-Xylene | 4-Iodo-1,3-dimethylbenzene | 100 | [91] |
| *p*-Xylene | 2-Iodo-1,4-dimethylbenzene | 91 | [91] |
| Mesitylene | Iodomesitylene | 94 | [91] |
| Mesitylene* | Di-iodomesitylene | 92 | [92] |
| Mesitylene* | Tri-iodomesitylene | 82 | [92] |
| Biphenyl | 4-Iodobiphenyl | 70 | [91] |
| Naphthalene | 1-Iodonaphthalene | 60 | [91] |
| Benzoic acid | 2-Iodobenzoic acid | 76 | [91] |
| *p*-Toluic acid | 2-Iodo-4-methylbenzoic acid | 75 | [93] |
| Anisole | 4-Iodoanisole | 75 | [91] |
| 10,10-Dimethylanthrone | 1-Iodo-10,10-dimethylanthrone | 29 | [94] |
| Dibenzosuberone | 4-Iododibenzosuberone | 71 | [94] |
| Trifluoromethylbenzene | 3-Iodo-1-trifluoromethylbenzene | 54 | [91] |
| 2,3,5,6-Tetrafluoroanisole** | 2,3,5,6-Tetrafluoro-4-iodoanisole | 39 | [95] |
| 2,3,5,6-Tetrafluorotoluene** | 2,3,5,6-Tetrafluoro-4-iodotoluene | 77 | [95] |
| 1,3,4,5-Tetrafluorobenzene** | 2,4,5,6-Tetrafluoro-1-iodobenzene | 77 | [95] |
| Pentafluorobenzene** | Pentafluoroiodobenzene | 67 | [95] |
| Azobenzene | 2-Iodoazobenzene | 55 | [96] |
| Azobenzene | 2,2'-Di-iodoazobenzene | 36 | [96] |

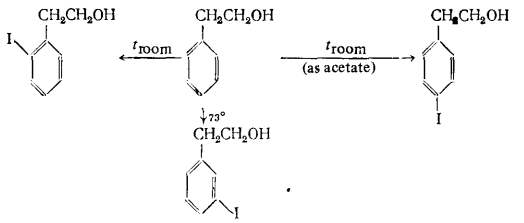
*Iodination in the presence of thallium tris(trifluoroacetate).

**Thallation with thallium tris(trifluoromethanesulphonate).

Glushkova and Kocheshkov[87] noted in an early study the absence of polythallation products when thallium tri-isobutyrate is used. McKillop and co-workers indicated only one instance of polythallation[97]. Studies of substitution by thallium with the aid of thallium tris(trifluoroacetate) showed that, under severe conditions, it is possible to introduce two bis(trifluoroacetoxy)thallium groups into the aromatic ring; after decomposition with potassium iodide, the corresponding di-iodo-derivatives were obtained in an insignificant yield[98]. Deacon and Tunaley[95] showed that thallium tris(trifluoromethanesulphonate) is more electrophilic than thallium tris(trifluoroacetate); with its aid, it is possible to substitute by thallium many deactivated substrates which do not react with thallium tris(trifluoroacetate). Treatment of the thallium compound with an aqueous solution of sodium iodide leads to the corresponding iodides. Substitution by thallium using thallium tris(trifluoroacetate) with subsequent treatment by potassium iodide is used solely for the preparative synthesis of monoiodoarenes. On the other hand, the interaction of aromatic compounds with molecular iodine in the presence of thallium tris(trifluoroacetate) as the oxidant[92] can serve as a method of preparative synthesis of polyiodo-derivatives. Mono-, di-, tri-, and tetra-iodo-derivatives of benzene have been obtained by this method in high yields.

It was found that benzoic acid is substituted by thallium in the *ortho*-position with an unusually high yield (~98%).[88] Further studies[99] established that many oxygen-containing compounds form complexes with the thallium salt in a preliminary step. If intramolecular attack can lead to the formation of a five- or six-membered transition state, then thallium attacks the available *ortho*-position. A similar

discovery was also made for azobenzenes[100]. The arene thallation reaction is reversible[99]; using thermodynamic and kinetic control and also bearing in mind the formation of complexes, it is possible to select conditions under which the required isomer is obtained with the maximum yield[101]:



Subsequently it was shown that diarylthallium trifluoroacetates, readily obtainable from arylthallium bis(trifluoroacetates) on treatment with triethyl phosphite or warm aqueous acetone, react with iodine to form the corresponding aryl iodides in very high yields[102]. This method can be regarded as a procedure for the conversion of aryl bromides or aryl chlorides into the corresponding iodides, since one of the methods of synthesis of diarylthallium compounds consists in the interaction of Grignard reagents with tervalent thallium salts (halides or carboxylates).[103]

### 3. The Synthesis of Aryl Iodides Via Organomercury Compounds

In 1974 Deacon and Farquharson[104] established that arenes give rise to polymercurated derivatives on fusion with mercury trifluoroacetate. Treatment of these compounds with a solution of bromine and potassium bromide in methanol constitutes an effective method for the synthesis of polybrominated arenes[105]. Polyiodoarenes are formed analogously in high yields on reaction with iodine and potassium iodide in dimethylformamide, while treatment of polymercuriarenes with molecular chlorine gave rise to polychloroarenes[106]. It has been shown that liquid solutions of potassium tri-iodide can be used for the preparation of polyiodo-derivatives[107], but there is a risk of a side reaction involving protolysis, as a result of which the iodo-derivatives obtained are sometimes contaminated and only mass spectrometry can serve as a criterion of their purity[86].

An alternative method of synthesis of polyiodoarenes[108] is based on the Jacobsen cross-reaction. In sulphuric acid, mono- or di-iodoarenes disproportionate with formation of polyiodoarenes. Since the initial iodo-derivatives can be readily obtained by one of the direct iodination methods described above, this reaction has acquired undoubted synthetic interest.

### 4. Decomposition of Organic Compounds of Polyvalent Iodine

It is known that the thermal decomposition of iodonium salts can be used as a preparative method of synthesis of aryl iodides (see, for example, Beringer et al.[109]). A similar method has been used successfully in the synthesis of *o*-iodobiphenyls, which are relatively difficult to obtain[110,111]. In 1966–67 Leffler and co-workers[112,113] showed that aryl iodosocarboxylates having the general formula $ArI(OCOR)_2$ are capable of undergoing thermal decomposition via a heterolytic mechanism with the intermediate formation of acyl hypoiodites, which are decarboxylated to the corresponding iodides:

$$ArI(OCOR)_2 \rightleftarrows \overset{\oplus}{ArI}OCOR\ \overset{\ominus}{RCOO} \rightarrow ArOCOR + (RCOOI) \xrightarrow{-CO_2} RI\ .$$

This reaction has been hardly investigated in its synthetic aspect, although phenyliodoso *o*-phenylbenzoate§ gives rise to *o*-iodobiphenyl in a moderate yield on thermolysis[114], while iodobenzene has been obtained in a low yield on photolysis of 2,4,6-trimethylphenyliodoso benzoate¶ in the presence of iodine[115].

The development of a simple and reliable method of synthesis of aryliodoso carboxylates+ [116] makes the preparation of aryl iodides by the decomposition of these compounds of potential synthetic value.

## IV. THE MECHANISM OF THE IODINATION OF ARENES

Although the number of publications on the mechanism of the iodination of arenes is much smaller than that of the communications devoted to the investigation of the mechanism of chlorination or bromination, they are quite sufficient to reject the erroneous hypothesis, migrating from textbook to textbook (see, for example, Nesmeyanov and Nesmeyanov[117]), that "hydrogen iodide reduces the iodobenzene obtained". It is known that iodobenzene does not change on heating with hydrogen iodide and red phosphorus for 5 h at 182 °C.[118]

Another widely held erroneous view is that Lewis acids do not catalyse the iodination reaction. It has been shown[47] that copper(II) chloride is an effective catalyst of this reaction.

Direct iodination is an electrophilic aromatic substitution reaction; the iodination of benzoic acid involves the formation of *m*-iodobenzoic acid in 75–80% yield, while the iodination of toluene gives rise to a mixture of *o*- and *p*-iodotoluenes. Electron-donating substituents accelerate the reaction, while electron-accepting substituents retard it. In the presence of sulphuric and nitric acids, the substrate is iodinated and not nitrated; on the other hand, when benzene is treated with iodine and much greater amounts of sulphuric and nitric acids than required for monoiodination, *p*-iodonitrobenzene is produced[120]. Consequently, the compound is initially iodinated and then nitrated; in the reverse order of reactions, the main product would have been the *m*-isomer. Benzene iodinated in the presence of nitronium tetrafluoroborate also gives rise to iodobenzene. It has been suggested that the iodine cation, formed with participation of the nitronium cation in accordance with the scheme

$$2H_2SO_4 + HNO_3 \rightarrow NO_2^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}\ ,$$
$$I_2 + 2NO_2^{\oplus} \rightarrow 2I^{\oplus} + 2NO_2\ .$$

functions as the iodinating agent. However, this hypothesis must be treated with caution, since the existence of the iodine cation as a kinetically independent species is possible only in highly acid media (for an exhaustive review, see Arotsky and Symons[119]).

It has been suggested that the formation of acyl hypoiodite is a source of electrophilic iodine in many direct iodination reactions[46,55,56] (see above).

It has been found that the reactivity of toluene in the iodination reaction by the Tronov–Novikov method is 9.5 times higher than that of benzene[120]; under the same conditions, the relative rate of nitration of toluene compared with the nitration of benzene is 8.22.

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§(*o*-phenylbenzoato-*O*)phenyliodine (Ed.of Translation).

¶(Benzoato-*O*)-2,4,6-trimethylphenyliodine (Ed.of Translation).

+(Carboxylato-*O*)aryliodine derivatives (Ed.of Translation).

In the iodination reactions investigated, the constant $\rho$ is negative and varies from −4.5 to −6.4; $\rho = -4.5$ for iodination in the presence of a mixture of sulphuric and nitric acids[120], $\rho = -6.27$ for electrochemical iodination[121], and $\rho = -6.4$ for iodination by the tri-iodine cation[122].

Bearing in mind the foregoing factors, iodic and periodic acids can be recommended as oxidants for the monoiodination of reactive substrates; particularly satisfactory results have been obtained in the iodination of alkylbenzenes by the Tronov–Novikov method. In order to introduce two iodine atoms into the aromatic ring, one may recommend iodination in the presence of phenyliodoso trifluoroacetate. Deactivated compounds are probably best iodinated by the Tronov–Novikov method or in the presence of silver sulphate; in the iodination by the former method, benzil is oxidised to iodobenzoic acid, while in the presence of silver sulphate it is successfully iodinated[123]. Satisfactory results have been obtained in many instances of the iodination of condensed aromatic hydrocarbons using iodic and periodic acids as oxidants, although the latter sometimes oxidises polynuclear aromatic compounds[124].

If it is necessary to obtain an iodo-derivative containing substituents in the molecule in positions which are difficult or even impossible to ensure by means of direct iodination, then the synthesis of aryliodides via organometallic compounds, particularly via organothallium compounds has to be recommended. In particular, the direct iodination of *p*-toluic acid in the presence of potassium permanganate leads to *m*-iodo-*p*-toluic acid (in 90% yield),[125] while the synthesis via an organothallium compound makes it possible to obtain *o*-iodo-*p*-toluic acid (in 75% yield);[93] whereas the direct iodination of azobenzene in the presence of phenyliodoso acetate leads to 4-iodoazobenzene (in an insignificant yield),[63] the synthesis via the organothallium compound makes it possible to obtain 2-iodoazobenzene (in 55% yield).[96]

Despite certain advances achieved in the synthesis of aryl iodides, the direct iodination of certain deactivated substrates, particularly six-membered nitrogen-containing aromatic heterocycles, remains problematical. New advances in direct iodination will probably be associated with the application of both new oxidants[125] and with the search for systems whereby hydrogen iodide can be removed from the reaction sphere by another procedure[126,127].

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