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# [A022] Facile Syntheses of Symmetrical Diaryliodonium Salts from Various Arenes, with Sodium Metaperiodate as the Coupling Reagent in Acidic Media

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**Abstract:** Easy, cheap, safe and effective preparative procedures to obtain symmetrical diaryliodonium bromides (in 15-88% crude yields) from various arenes are presented in this paper. A novel method for preparing iodosyl sulfate (Chrétien's reagent) is given. Several crude diaryliodonium bromides were readily *oxidatively* metathesized with 30% aq. $H_2O_2$ and 40% aq. $HBF_4$ (in acetone, used both as a solvent and "halogen scavenger") to give pure diaryliodonium tetrafluoroborates in 64-85% yields.

**Key words:** symmetrical diaryliodonium salts, arenes, sodium metaperiodate, iodosyl sulfate, oxidative anion metatheses

Symmetrical and unsymmetrical diaryliodonium salts, $Ar_2I^+X^-$ and $Ar(Ar')I^+X^-$, represent an important and best investigated class of aromatic iodine(III) derivatives. They are used in organic synthesis as arylating reagents. Some of them display a biological activity, and some are widely used as efficient catalysts for radiation initiated polymerisation. Generally, their reactivity is less pronounced than that of other hypervalent iodine(III) compounds. They are solid compounds, mostly stable towards heat (particularly those with substantially nonnucleophilic counterions), oxygen, and humidity; they are mildly light-sensitive and should be stored in the dark, without refrigeration.[1]

There is a multitude of different published methods for the preparation of various diaryliodonium salts, and the relevant literature is still quickly expanding.[1] In our opinion, some of these methods are costly and cannot be easily adopted in common organic laboratories - but it is still possible and desirable to devise some new preparative procedures, which would be easy, cheap, safe, and effective. We hope that a novel method reported in this paper may fulfil, at least in part, these expectations.

One of the most important applications of diaryliodonium salts is their use in the arylation of organic and inorganic nucleophiles,[1b,c] including the fluoride anion, which results in the formation of aromatic fluorides.[2] In several of such reactions relatively drastic conditions may be necessary, especially for the least reactive heterocyclic iodonium salts. The search for optimum conditions is often desirable even for well established reactions, by applying new findings concerning the use of specific solvents, catalysts or radical traps.[1f] If the ionic mechanism is evidently prevailing, e.g. when some iodonium salts with definitely nucleophilic counterions are thermally decomposed, then there are displayed practically important differences in the reactions of symmetrical and unsymmetrical iodonium salts:

$$Ar_2I^+X^- \xrightarrow{\triangle}$$
$$\longrightarrow \textbf{ArX} + ArI$$
(*two products to be resolved*)

(1)

$$Ar(Ar')I^+X^- \xrightarrow{\triangle}$$
$$\longrightarrow \textbf{ArX} + Ar'X + ArI + Ar'I$$
(*four products to be resolved*)

(2)

However, in the latter case (Eq. 2) the chemoselective reactions are often encountered (which may increase the amount of a desirable **ArX** in the four-component final reaction mixture): e.g. in the case of a thermal decomposition of 4-anisyl(phenyl)iodonium bromide, the decomposition may lead either to 4-iodoanisole and bromobenzene or to 4-bromoanisole and iodobenzene. Actually, at least 87% and possibly more of the thermal decomposition followed the first reaction path. Sandin[3] explained this result us follows: "the decomposition occurred in such a way that the more electronegative radical (4-anisyl) remained attached to the iodine atom". Nevertheless, the use of the symmetrical diaryliodonium salts in various arylation reactions is simpler and practically more convenient.[4]

Beringer and co-workers[5] devised three the most popular methods for preparing symmetrical diaryliodonium salts from corresponding arenes:

(A) Coupling of two identical aromatic compounds with iodosyl sulfate in sulfuric acid:

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

(3)

ArH = benzene, four halogenobenzenes, nitrobenzene, 4-nitroanisole and methyl 4-tolyl sulfone. The yields were over 50% except with the last compound. For preparing iodosyl sulfate (named there erroneously: iodyl sulfate) they mostly used the following reaction:

$$2 I_2 + 6 NaIO_3 + 11 H_2SO_4 \longrightarrow$$
$$\longrightarrow 5 (IO)_2SO_4 + 6 NaHSO_4 + 8 H_2O \tag{4}$$

(B) Coupling of two identical aromatic compounds with an iodate in $AcOH/Ac_2O$/conc. $H_2SO_4$ anhydrous mixtures:

$$2 ArH + IO_3^- + 2 H_2SO_4 + 2 Ac_2O \longrightarrow$$
$$\longrightarrow Ar_2I^+ + 2 HSO_4^- + 4 AcOH + [O] \tag{5}$$

ArH = benzene, toluene, mesitylene, $t$-butylbenzene, $n$-dodecylbenzene, cyclohexylbenzene, anisole, acetanilide and succinanil. The yields varied from 9 to 88%; the reaction with anisole went in poor yield. If the temperature of a reaction mixture was not kept below 15 $^{\circ}$C during the addition of $H_2SO_4$ and for some hours thereafter, a vigorous, exothermic reaction might occur. It may be that in such instances the iodate was affecting a deep-seated oxidation of the aromatic compound.

(C) Coupling of two identical aromatic compounds with an iodine(III) acylate in the presence of an acid:

$$2 ArH + I(OCOR)_3 + HX \longrightarrow$$
$$\longrightarrow Ar_2I^+X^- + 3 RCOOH \tag{6}$$

X = anisole, toluene and acetoxybenzene. The yields varied from 11 to 58%. Anisole yielded a product with iodine(III) acetate and acetic acid, but most work has been done with iodine(III) trifluoroacetate and $CF_3COOH$. With less reactive toluene, a stronger acid as $H_2SO_4$ was needed.


In contrast to the Beringer's simple procedures, the other reported methods[1,6] are mostly devoid of such preparative simplicity, albeit they are unique for certain specific purposes:

(D) Some lithiated arenes or heteroarenes readily reacted with *trans*-1-chloro-2-(dichloroiodo)ethylene to form symmetrical aromatic iodonium salts, with elimination of acetylene. The same method was applied to obtain bis(2-naphthyl) and bis(9-anthryl)iodonium chlorides.[7]

(E) By reacting (trifluorosilyl)arenes with $IF_3$ in the presence of $BF_3$, several symmetrical diaryliodonium salts were synthesized.[8]

(F) By reacting arenediazonium chlorides with $HgI_2/KI$ in aqueous solutions, the unstable intermediates, arenediazonium iodomercurates, slowly decomposed to give diaryliodonium iodomercurates, along with iodoarenes and biphenyl derivatives (that confirms the radical mechanism of the reaction).[9]

(G) (Dicyano)iodonium triflate, $(NC)_2I^{+-}OTf$, generated in situ, readily reacts with stannylated derivatives of arenes and heteroarenes under very mild conditions to afford the respective symmetrical iodonium salts in good yield.[1e]
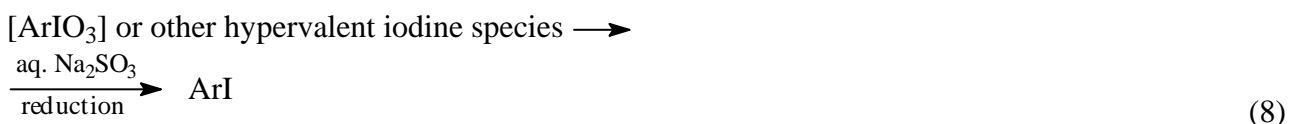
(H) Iodosyl triflate, $O=IOTf$, and iodosyl fluorosulfate, $O=IOSO_2F$, readily react with arenes and trimethylsilylarenes under mild conditions to afford symmetrical iodonium triflates, $Ar_2I^{+-}OTf$, or hydrogensulfates, $Ar_2I^{+-}OSO_3H$.[1e] Naumann and co-workers[10] used a similar procedure for the preparation of bis(pentafluorophenyl)iodonium triflate, $(C_6F_5)_2I^{+-}OTf$, from iodine(III) trifluoroacetate, pentafluorobenzene and triflic acid, $CF_3SO_3H$.

(I) Bis(pentafluorophenyl)iodonium chloride was prepared from either $C_6F_5Li$ or $(C_6F_5)_2Cd$ by reacting them with (dichloroiodo)pentafluorobenzene.[8]


In our former works[11] we used $I_2/NaIO_4$ or $KI/NaIO_4$ systems in strongly acidic media to oxidatively iodinate various aromatics. Recently,[12] we presented a novel aromatic iodination method, with sodium metaperiodate used as the only iodinating reagent. In fact, we had tried there to synthesize unknown so far periodylarenes as follows:
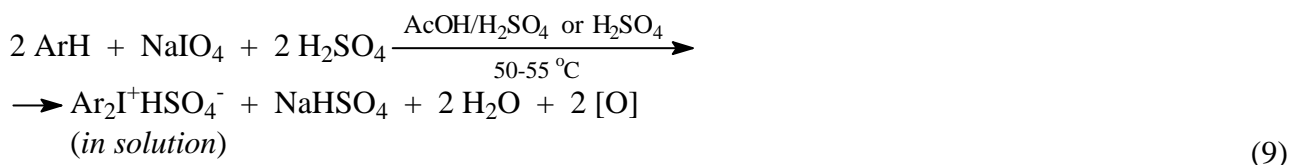
$$ArH + NaIO_4 + H_2SO_4 \longrightarrow$$
$$\longrightarrow [ArIO_3] + NaHSO_4 + H_2O$$

(7)

In spite of our numerous attempts, we could not isolate from the final reaction mixtures any such expected $ArIO_3$ intermediate. In our opinion, the postulated transient $ArIO_3$ species, probably present momentarily in the reaction mixtures, would quickly decompose in the anhydrous $AcOH/Ac_2O/conc.$ $H_2SO_4$ medium used for the reactions to form more stable iodine(III) intermediates, $ArI(OSO_3H)_2$, probably along with the formation of peracetic acid and/or peroxomonosulfuric acid. Such strongly hygroscopic compounds as $I_2(SO_4)_3$, $I(OSO_3H)_3$, $ArISO_4$ and $ArI(OSO_3H)_2$ are stable in anhydrous and strongly acidic media; they are discussed elsewhere[13] and are referred to the literature. When the final reaction mixtures were poured into an excess of aqueous $Na_2SO_3$ solution (a reductant), we isolated iodoarenes in 27-88% yields:

$$[ArIO_3] \text{ or other hypervalent iodine species} \longrightarrow$$
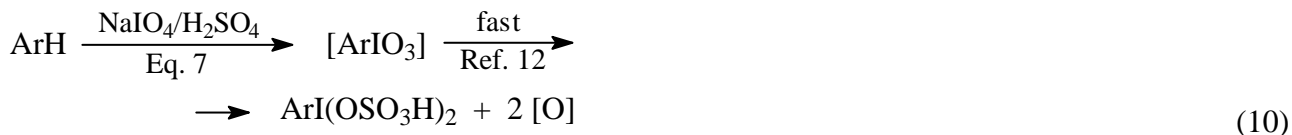$$\xrightarrow[\text{reduction}]{\text{aq. } Na_2SO_3} ArI$$

(8)

which confirmed that the stable C-I bond is formed in the said reactions (Eq. 7).


Thus, taking into account the former results visualized in Eqs 5 and 7, we have devised a novel method for preparing the symmetrical diaryliodonium salts from various arenes, with sodium metaperiodate, $NaIO_4$, as the effective coupling reagent acting in strongly acidic media:

$$2\ ArH\ +\ NaIO_4\ +\ 2\ H_2SO_4 \xrightarrow[50\text{-}55\ ^oC]{AcOH/H_2SO_4\ or\ H_2SO_4}$$

$$\longrightarrow Ar_2I^+HSO_4^-\ +\ NaHSO_4\ +\ 2\ H_2O\ +\ 2\ [O]$$
(*in solution*)

(9)

Possibly, the reactions undergo as follows:

$$ArH \xrightarrow[Eq.\ 7]{NaIO_4/H_2SO_4}\ [ArIO_3] \xrightarrow[Ref.\ 12]{fast}$$

$$\longrightarrow ArI(OSO_3H)_2\ +\ 2\ [O]$$

(10)

$$ArI(OSO_3H)_2\ +\ ArH\ (in\ excess) \xrightarrow[coupling]{acidic}$$

$$\longrightarrow Ar_2I^+HSO_4^-\ +\ H_2SO_4$$

(11)

A chosen arene (2.6 equivalents; 30% excess) was dissolved or suspended in a definite volume of glacial AcOH/conc. $H_2SO_4$ mixture or in neat conc. $H_2SO_4$ (Table 1), and the stirred mixture was warmed up to 50-55 $^oC$. $NaIO_4$ (one equivalent) was slowly added portionwise within 1.5 hour, with stirring and keeping the given temperature. The stirring was continued for a further 3 hours while keeping the temperature at 50-55 $^oC$. The reactions were quenched by pouring the cooled final reaction mixtures into stirred ice-water. The precipitates were collected by filtration and rejected, the cold filtrates were extracted fourfold with diethyl ether to remove the unreacted arenes (the ethereal extracts were discarded). To the remaining aqueous solutions, an aqueous KBr solution (in excess) was added with stirring:

$$Ar_2I^+HSO_4^-\ (in\ solution)\ +\ aq.\ KBr\ (in\ excess) \longrightarrow$$

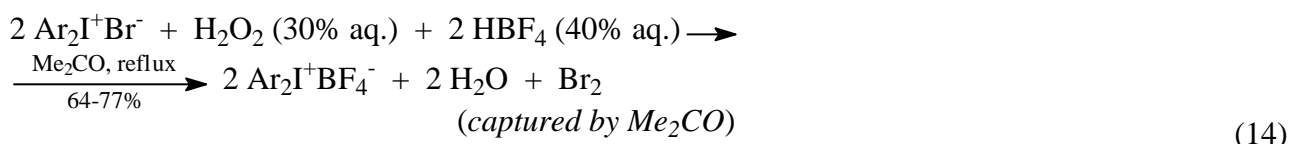$$\longrightarrow \downarrow Ar_2I^+Br^-\ +\ KHSO_4$$

(12)
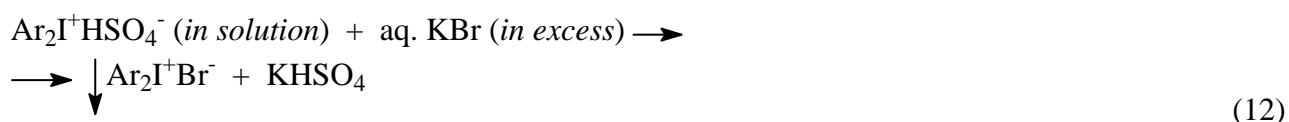
The precipitated diaryliodonium bromides, sparingly soluble in water, were collected by filtration, washed with cold water until the filtrates were neutral, and air-dried in the dark to obtain the desirable crude products in 15-88% yields (Table 1). They are sufficiently pure for further reactions. Small samples of the crude bromides were quickly recrystallized from boiling methanol to give pure analytical samples. There are repeated warnings in the literature[1d,3] that diaryliodonium halides are thermally unstable on prolonged heating, hence their recrystallizations should be carried out as quickly as possible from boiling solvents, followed by the immediate hot filtration neglecting the losses, and rapid cooling. More thermally stable iodonium salts, e.g. tetrafluoroborates, tosylates, trifluoroacetates, etc. can be recrystallized in usual way.

Next, for comparison, we have followed the Beringer's procedure[5] shown in Eq. 3, but we had previously prepared a suspension of iodosyl sulfate (iodous sulfate, Chrétien's reagent)[13,14] in conc. $H_2SO_4$ using a novel method for its preparation:

$$4\ I_2\ +\ 6\ NaIO_4\ +\ 13\ H_3SO_4\ \longrightarrow$$
$$\longrightarrow\ \downarrow 7\ (IO)_2SO_4\ +\ 6\ NaHSO_4\ +\ 10\ H_2O$$

(13)

Stoichiometric amounts of powdered diiodine and next $NaIO_4$ were suspended in conc. $H_2SO_4$, and the stirred mixture was heated at 70-75 $^oC$ for one hour. To the cooled suspension of yellow $(IO)_2SO_4$, acetic anhydride was slowly added dropwise with stirring, followed by a 30% excess of chosen arene. The stirring was continued at room temperature for 20-55 hours; for more details see the experimental part and Table 2. The reactions shown in Eq. 3 were quenched by pouring the final reaction mixtures into ice-water, and the following workups were the same as above to obtain the crude diaryliodonium bromides in 25-70% yields. Small samples of the crude bromides were quickly recrystallized from boiling methanol to afford the purified analytical samples.

It has been observed[1,15] that the best arylation yields of the nucleophilic bases are achieved by applying the symmetrical diaryliodonium salts with substantially nonnucleophilic counterions, viz. tosylates, triflates, hydrogensulfates, etc. Beringer and co-workers[15] have observed the superior yields with diphenyliodonium tetrafluoroborate in the phenylation of organic and inorganic bases. The sparingly soluble bromides or iodides were often nearly quantitatively precipitated out from hot solutions or suspensions of more soluble diaryliodonium hydrogensulfates or chlorides by the solutions of cheap sodium, potassium, ammonium or calcium salts with an appropriate counterion. However, a considerable number of necessary diaryliodonium salts were only attainable from the corresponding halides or hydrogensulfates by using costly and toxic lead(II), silver and barium salts, e.g. silver tetrafluoroborate, trifluoroacetate and nitrate or lead(II), silver or barium organosulfates or organocarboxylates, or otherwise. These anion metatheses are reviewed in Ref. 1b, p 1285 as well as in Ref. 5. In our former papers[16] we have reported on various *oxidative* anion metatheses (in methanol) in the crude diaryliodonium bromides, iodides or chlorides, previously obtained in our laboratory, which produced the corresponding pure diaryliodonium tetrafluoroborates, tosylates, trifluoroacetates, hydrogensulfates, nitrates, and triflates in 54-86% yields; for more details see our review,[17] pp 1361-1365. However, dr. Pawel Kazmierczak has observed that *acetone* used as the solvent of choice in the oxidative anion metatheses of crude diaryliodonium bromides and chlorides may act itself as a very efficient "halogen scavenger", hence the addition of cyclohexene to the reaction mixtures[16] is not necessary; see p 1363 in Ref. 17. It is due to a small amount of very reactive *enol form*, which in strongly acidified acetone solutions is very quickly equilibrated with the preponderant keto form. His finding has not been exploited in our laboratory up to now. In the present work we have applied this modified method to oxidatively metathesize six crude symmetric diaryliodonium bromides to the corresponding pure tetrafluoroborates in 64-85% yields (Table 3); for more details see the experimental section.

$$2\ Ar_2I^+Br^- + H_2O_2\ (30\%\ aq.) + 2\ HBF_4\ (40\%\ aq.) \longrightarrow$$

$$\xrightarrow[\text{64-77\%}]{\text{Me}_2\text{CO, reflux}} 2\ Ar_2I^+BF_4^- + 2\ H_2O + Br_2$$

*(captured by Me₂CO)*

$$(14)$$

Melting points of the purified tetrafluoroborates thus obtained were compared, if possible, with the respective literature data. In this way the chemical structures of some initial bromides (Tables 1 and 2) were additionally confirmed. Further supporting evidences were obtained by elemental analyses (I%) of the purified symmetrical diaryliodonium bromides and tetrafluoroborates as well as by their $^1$H and $^{13}$C NMR solution spectra (not shown here) compared with the respective spectra of authentic samples[16,18] and/or theoretically computed NMR spectra.

Summing up, in this paper we present a novel, easy and effective method for preparing a number of symmetrical diaryliodonium bromides (Table 1). The same bromides were obtained, for comparison, by the modified Beringer's procedure[5] (Table 2) in which the intermediate iodosyl sulfate (Chrétien's reagent) was prepared by a novel method. Several crude symmetrical diaryliodonium bromides were readily *oxidatively* metathesized to give the respective pure diaryliodonium tetrafluoroborates (Table 3).

All organic and inorganic reagents and solvents were commercial products (Aldrich, Lancaster) and were used without further purification. The melting points of the freshly recrystallized iodonium salts are uncorrected (they were measured in the way reported in Ref. 5) and are compared, if available, with the literature data (Tables 1-3). They were microanalyzed (%I ± 0.3), and finally their $^1$H and $^{13}$C NMR spectra (not shown here) were recorded at r.t. with a Brucker Avance DMX 400 MHz spectrometer, next compared with the same spectra of authentic samples[16,18] and/or theoretically computed spectra. Elemental iodine (diiodine) should be finely powdered to facilitate its dissolution in the reaction mixtures. Microanalyses were carried out at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw.

**Novel Procedure for Preparing Symmetrical Diaryliodonium Bromides from Arenes** (Table 1). A chosen arene (26 mmol; 30% excess) was dissolved or suspended either in conc. $H_2SO_4$ or in a glacial AcOH/conc. $H_2SO_4$ mixture (see Table 1 for the volumes used in the reactions) and the resulting mixture was warmed up, with stirring, to 50-55 $^o$C [only for isophthalic acid: to 70-75 $^o$C]. While keeping the same temperature, $NaIO_4$ (2.14 g, 10 mmol; 0% excess) was slowly added portionwise within 1.5 h. The stirring was continued at 50-55 $^o$C for 3 h [only for isophthalic acid: for 7 h at 70-75 $^o$C]. The cooled final reaction mixtures were poured into stirred ice-water (300 g). The precipitates were collected by filtration and rejected. The cold filtrates were extracted with

diethyl ether (4 x 50 mL) and the ethereal extracts (containing the unreacted initial arenes) were discarded. An aq. KBr solution (2.0 g, 16.8 mmol KBr dissolved in 10 mL $H_2O$) was added to the vigorously stirred remaining aq. solutions. After ca. 1 h, the precipitated diaryliodonium bromides were collected by filtration and were washed with cold water until the filtrates were neutral, dried preliminarily by the suction, and air-dried in the dark to give the crude products in 15-88% yields (Table 1). Small samples of the crude bromides were recrystallized from boiling MeOH as quickly as possible to give the purified analytical samples.

**Modified Procedure[5] for Preparing Symmetrical Diaryliodonium Bromides from Arenes** (Table 2).

Powdered diiodine (0.72 g, 2.84 mmol; 0% excess) and next $NaIO_4$ (0.92 g, 4.30 mmol; 0% excess) were suspended in stirred conc. $H_2SO_4$ (10 mL), and the vigorous stirring was continued for 1 h at 70-75 °C. Next, $Ac_2O$ (0-6 mL, see Table 2) was slowly added dropwise, with stirring, to the cooled suspension of yellow $(IO)_2SO_4$ in conc. $H_2SO_4$. A chosen arene (26 mmol; 30% excess) was added portionwise or dropwise, with stirring, and the stirring was continued at r.t. for 20 h [only for benzene: the stirring was continued firstly at r.t. for 2 h, and next at 50-55 °C for 1 h]. The final reaction mixtures were poured into stirred ice-water (300 g), and the following workups were quite the same as those in the former procedure. The air-dried diaryliodonium bromides were obtained in 25-70% crude yields (Table 2). Small samples of the crude bromides were quickly recrystallized from boiling MeOH to afford the purified analytical samples.

**Facile Oxidative Anion Metatheses in Crude Symmetrical Diaryliodonium Bromides to Give Pure Symmetrical Diaryliodonium Tetrafluoroborates** (Table 3); cf. Ref. 16.

A powdered crude diaryliodonium bromide (5 mmol) was suspended in $Me_2CO$ (15 mL), and next 40% aq. $HBF_4$ (1 mL, ca. 6 mmol $HBF_4$) and 30% aq. $H_2O_2$ (0.75 mL; ca. 7.5 mmol $H_2O_2$) were subsequently slowly added, with stirring. The stirred suspension was refluxed until the suspended bromide fully dissolved, and the boiling was continued for a further 15 min. The solvent was distilled off in a rotary evaporator. The semisolid residue was triturated with $Et_2O$ (15 mL). The solid precipitate was collected by filtration, washed with $Et_2O$, dried preliminarily by the suction, air-dried in the dark, and recrystallized from appropriate solvent to give the respective pure diaryliodonium tetrafluoroborate in the yield given in Table 3.

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**Table 1.** Crude yields for symmetrical diaryliodonium bromides, $Ar_2I^+Br^-$, synthesized from the respective arenes, ArH, with $NaIO_4$ as the coupling reagent in varied acidic media.

| Initial arene, ArH<br>**Product, $Ar_2I^+Br^-$** | Crude yield (%) for $Ar_2I^+Br^-$ | Acidic medium (mL) | Mp (°C)[a] for pure product |
|---|---|---|---|
| $C_6H_6$<br>**$(C_6H_5)_2I^+Br^-$** | 64 | $H_2SO_4$ (15)<br>AcOH (15) | 228-229 |
| $C_6H_5F$<br>**$(4-FC_6H_4)_2I^+Br^-$** | 62 | $H_2SO_4$ (20)<br>AcOH (10) | 238-239 |
| $C_6H_5Cl$<br>**$(4-ClC_6H_4)_2I^+Br^-$** | 88 | $H_2SO_4$ (20)<br>AcOH (10) | 199 |
| $C_6H_5Br$<br>**$(4-BrC_6H_4)_2I^+Br^-$** | 60 | $H_2SO_4$ (20)<br>AcOH (10) | 197 |
| $C_6H_5I$ | (b) | $H_2SO_4$ (20)<br>AcOH (10) | - |
| $C_6H_5CH_3$<br>**$(4-CH_3C_6H_4)_2I^+Br^-$** | 32 | $H_2SO_4$ (5)<br>AcOH (35) | 178-179 |
| $1,2-(CH_3)_2C_6H_4$<br>**$(3,4-(CH_3)_2C_6H_3)_2I^+Br^-$** | 28 | $H_2SO_4$ (5)<br>AcOH (35) | 187-188 |
| $1,3,5-(CH_3)_3C_6H_3$<br>**$(2,4,6-(CH_3)_3C_6H_2)_2I^+Br^-$** | 26 | $H_2SO_4$ (5)<br>AcOH (35) | 128 |
| $C_6H_5COOH$<br>**$(3-HOOCC_6H_4)_2I^+Br^-$** | 54 | $H_2SO_4$ (20) | 205-208 |
| $4-IC_6H_4COOH$ | (c) | $H_2SO_4$ (20) | - |
| $4-CH_3C_6H_4COOH$<br>**$(5-HOOC-6-CH_3C_6H_3)_2I^+Br^-$** | 80 | $H_2SO_4$ (20) | 198-200 |
| $4-CH_3OC_6H_4COOH$<br>**$(5-HOOC-6-CH_3OC_6H_3)_2I^+Br^-$** | 77 | $H_2SO_4$ (20)<br>AcOH (10) | 217-219 |
| $C_6H_5COOCH_3$<br>**$(3-CH_3OOCC_6H_4)_2I^+Br^-$** | 55 | $H_2SO_4$ (20) | 142-145 |
| $C_6H_5CONH_2$<br>**$(3-H_2NOOCC_6H_4)_2I^+Br^-$** | 53 | $H_2SO_4$ (20) | 208-209 |
| $C_6H_5SO_2NH_2$<br>**$(3-H_2NO_2SC_6H_4)_2I^+Br$** | 23 | $H_2SO_4$ (20) | 181-182 |
| $C_6H_5NO_2$<br>**$(3-O_2NC_6H_4)_2I^+Br^-$** | 42 | $H_2SO_4$ (20) | 178 |
| $1,3-(HOOC)_2C_6H_4$<br>**$(3,5-(HOOC)_2 C_6H_3)_2I^+Br^-$** | 15 | $H_2SO_4$ (20) | 269-270 |

a) Elemental analyses, I% ±0.3, and melting points (uncorrected) are related to the recrystallized products.

b) When iodobenzene was coupled to form the respective $Ar_2I^+Br^-$, then the major product thus formed was $(4-I-C_6H_4)(C_6H_5)I^+Br^-$, only admixed with the purported bis(4-iodophenyl)iodonium bromide (TLC, NMR). It is probably due to the prevailing *ipso* attack onto the C-I bond in iodobenzene by assumed hypervalent iodine coupling agent, $4-IC_6H_4I(OSO_3H)_2$, generated in the reaction mixture.

c) When 4-iodobenzoic acid was coupled to form the respective $Ar_2I^+Br^-$, then the major product thus formed was $(3-HOOC-6-IC_6H_3)(4-HOOCC_6H_4)I^+Br^-$, only admixed with the purported $(3-HOOC-6-IC_6H_3)_2I^+Br^-$ (TLC, NMR). It is probably due to the same reason explained above in the footnote b.

**Table 2.** Crude yields for symmetrical diaryliodonium bromides, $Ar_2I^+Br^-$, synthesized from the respective arenes, ArH, with iodosyl sulfate as the coupling reagent in anhydrous acidic media.

| Initial arene, ArH<br>**Product, $Ar_2I^+Br^-$** | Crude yield (%) for<br>$Ar_2I^+Br^-$ | $Ac_2O$ added<br>(mL) | Mp ($^o$C)[a]<br>for pure product |
|---|---|---|---|
| $C_6H_6$<br>**$(C_6H_5)_2I^+Br^-$** | 70 | 6 | 229 |
| $C_6H_5F$<br>**$(4\text{-}FC_6H_4)_2I^+Br^-$** | 64 | 3 | 238 |
| $C_6H_5Cl$<br>**$(4\text{-}ClC_6H_4)_2I^+Br^-$** | 66 | 3 | 199-200 |
| $C_6H_5Br$<br>**$(4\text{-}BrC_6H_4)_2I^+Br^-$** | 25 | 3 | 198-199 |
| $C_6H_5I$<br>**$(4\text{-}IC_6H_4)_2I^+Br^-$** | 30 | 3 | 197 |
| $C_6H_5CH_3$<br>**$(4\text{-}CH_3C_6H_4)_2I^+Br^-$** | 45 | 6 | 178 |
| $C_6H_5NO_2$<br>**$(3\text{-}O_2NC_6H_4)_2I^+Br^-$** | 44 | 0 | 178-179 |

a) The same as the footnote a in Table 1.


**Table 3.** Oxidative anion metatheses in crude symmetrical diaryliodonium bromides, $Ar_2I^+Br^-$, to form the respective pure symmetrical diaryiodonium tetrafluoroborates, $Ar_2I^+BF_4^-$.

| Initial diaryiodonium bromide<br>$Ar_2I^+Br^-$ | Yield (%) for pure<br>$Ar_2I^+BF_4^-$ | Mp ($^o$C)[a]<br>for pure product | Solvent used for<br>purification[b] |
|---|---|---|---|
| $(C_6H_5)_2I^+Br^-$ | 82 | 135-136 | $CH_2Cl_2/CCl_4$ |
| $(4\text{-}BrC_6H_4)_2I^+Br^-$ | 64 | 158-160 | $CH_2Cl_2/CCl_4$ |
| $(4\text{-}ClC_6H_4)_2I^+Br^-$ | 65 | 159-160 | $CH_2Cl_2/CCl_4$ |
| $(3\text{-}HOOCC_6H_4)_2I^+Br^-$ | 71 | 197-199 | $EtOH/CCl_4$ |
| $(3\text{-}HOOC\text{-}6\text{-}CH_3C_6H_3)_2I^+Br^-$ | 66 | 237-239 | $EtOH/CCl_4$ |
| $(3\text{-}HOOC\text{-}6\text{-}CH_3OC_6H_3)_2I^+Br^-$ | 85 | 273-274 | $EtOH/CCl_4$ |

a) The same as the footnote a in Table 1.
b) Boiling solvent used for dissolving/solvent used for precipitation.