One-Pot Preparations of Diaryliodonium Bromides from Iodoarenes and Arenes, with Sodium Perborate as the Oxidant[†]

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Abstract: This paper reports a one-pot synthesis of the title bromides from both activated and deactivated iodoarenes which are first oxidized with *anhydrous* $NaBO_3 \cdot H_2O/Ac_2O/conc.H_2SO_4$ liquid mixtures, then coupled *in situ* with benzene and activated arenes and, finally, precipitated out with a KBr solution; this method is easy, cheap, safe and fairly effective.

Keywords: diaryliodonium bromides, iodoarenes, arenes, sodium perborate as oxidant

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Introduction

Symmetric and unsymmetric diaryliodonium salts, $Ar_2I^+X^-$ and $Ar(Ar')I^+X^-$, represent an important class of aromatic iodine(III) derivatives. They are used in organic synthesis mostly as *arylating reagents* for a large variety of organic and inorganic nucleophiles. Some of them display a biological activity or photochemical properties, hence they 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].

Indeed, there a multitude of different published methods for their preparation are available [1], and the relevant literature is still expanding nowadays with dislosures of some novel and possibly better methods [2]. In our opinion, some of these methods are rather costly and/or too complicated to be easily adopted in "ordinary" 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.

Results and Discussion
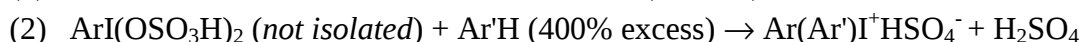
In 1995 we reported [3] a one-pot ("short-cut") synthesis of sparingly soluble *diaryliodonium bromides* (and iodides) from various iodoarenes, ArI, previously oxidized with *anhydrous* $CrO_3/AcOH/Ac_2O$/conc. H_2SO_4 systems to form soluble iodine(III) intermediates, $ArISO_4$ or $ArI(OSO_3H)_2$ (*not isolated*), then coupled *in situ* with benzene and *activated* arenes/heteroarenes (Ar'H) and, finally, precipitated out with excess aqueous KBr (or KI) solutions. The title bromides were obtained in 20-88% crude yields (for more information see Ref. [3]). This method was easier and shorter then many earlier methods [1], hence it was later often used in our laboratory [4-6], and elsewhere [7].

We also reported [3, 5] the very simple and effective *oxidative metatheses* in the **crude** iodonium bromides, iodides and chlorides into the corresponding **pure** tetrafluoroborates, tosylates, triflates, trifluoroacetates, etc.; such diaryliodonium salts with substantially *nonnucleophilic* counterions are the best arylating reagents [1]. However, there are some important, ***inherent limitations*** in the application of our short-cut method [3]. Only iodobenzene, haloiodobenzenes, and iodoarenes substituted with *electron-withdrawing* groups may effectively be applied to form the final iodonium bromides (or iodides). 4-Iodotoluene coupled oxidatively with benzene gave $4\text{-MeC}_6\text{H}_4(\text{Ph})\text{I}^+\text{Br}^-$ in only 20% crude yield, whereas iodoanisoles and iodoacetanilides were *oxidatively cleaved* by CrO_3 in acidic medium, hence their oxidative coupling with activated arenes was not possible. Thus, we have been looking for some novel and effective one-pot method, which would also be applicable for iodoarenes substituted with *electron-donating* groups. In fact, we have increasingly been interested in the mild and selective oxidative properties of **sodium perborate** (which is purchased either as "monohydrate" or "tetrahydrate" at a low price) widely used in chemical laboratories or in industry. It may be considered as a "dry carrier" of the hazardous and unstable hydrogen peroxide, is easy to handle, safe, and stable at room temperature [8]. Therefore, we have decided to use $NaBO_3 \cdot H_2O$ as the oxidant of choice, because it is more soluble in *acetic anhydride* than $NaBO_3 \cdot 4H_2O$. We know from our earlier work that **water**, due to its high hydration power, diminishes the oxidizing activity of inorganic (and organic) oxidants.

McKillop and Kemp [9] oxidized thirteen ArI (also those substituted with *electron-donating* groups!) to the corresponding $ArI(OAc)_2$ with $NaBO_3 \cdot 4H_2O$ (used in 900% excess) in a very large volume of glacial acetic acid within 4-8 hours, at 40-50°C. After recrystallizations, they obtained the

purified products in 66-80% yields. When we used *acetic anhydride* as the solvent of choice and $NaBO_3 \cdot H_2O$ as the oxidant, which allowed to lower considerably an excess of the oxidant applied to only 200% as well as the volume of the solvent applied, we obtained five $4\text{-}XC_6H_4I(OAc)_2$ (X = H, F, Br, Cl, MeO) as well as $2\text{-}MeOC_6H_4I(OAc)_2$ in 60-87% *crude* yields; after repeated recrystallizations, we obtained the purified products [10]. This preliminary work opened up a new way to develop the title one-pot method. We have also observed that a *preliminary period of stirring* $NaBO_3 \cdot H_2O$ with acetic anhydride at 30 ^{o}C (preferably within 90 min) enhances considerably the oxidizing activity of this solution. Recently, Indian chemists [11] have observed the generation of peracetic acid **on aging** of $NaBO_3 \cdot 4H_2O$ solutions in glacial acetic acid, confirmed by chemical tests.

The essence of our novel method is given in the three equations below; for all preparative details see Experimental.

(1) $ArI + NaBO_3 \cdot H_2O + 2Ac_2O + 2H_2SO_4 \rightarrow ArI(OSO_3H)_2 + [NaBO_2] + 4AcOH$

(2) $ArI(OSO_3H)_2$ (*not isolated*) $+ Ar'H$ (400% excess) $\rightarrow Ar(Ar')I^+HSO_4^- + H_2SO_4$

(3) $Ar(Ar')I^+HSO_4^-$(*not isolated*) $+$ aq. KBr (in excess) $\rightarrow \downarrow Ar(Ar')I^+Br^- + KHSO_4$

Small samples of the crude bromides were *quickly* [3] recrystallized from MeOH to give the pure analytical samples. Their melting points agreed well with the literature data [3, 12], and their structures were confirmed by correct elemental analyses (Table 1) as well as ^{1}H-NMR spectra (not shown here); the spectra (in DMSO-d_6/DDS) displayed the sharp singlets located at ca. 2.20, 2.45, 2.75, and 4.20 ppm, characteristic of the $COC\mathbf{H}_3$, $4\text{-}C\mathbf{H}_3Ar$, 2- and $2,6\text{-}C\mathbf{H}_3Ar$, or $4\text{-}OC\mathbf{H}_3$ groups, respectively, as well as composite multiplets characteristic of the aromatic protons (the thoroughful integrations disclosed the total numbers of aromatic protons related to the aforesaid three-proton singlets); cf. our former papers [3, 5].

Conclusions

In this paper we present a novel one-pot method for easy and effective preparation of a number of diaryliodonium bromides (Table 1). They were produced from both activated and deactivated iodoarenes and 2-iodothiophene, which next were oxidatively coupled with activated arenes, in appropriate *anhydrous* $NaBO_3 \cdot H_2O/Ac_2O/conc.$ H_2SO_4 mixtures. Next, the iodonium bromides were precipitated out by the addition of excess KBr solution to the resulting final reaction mixtures. After their collection, washing, and air-drying, the final products were obtained in 23-98% *crude* yields; only small samples were purified and analysed. Sodium perborate monohydrate used as the oxidant is cheap, safe and effective; no *toxic* residues were left after the reactions - in a strong contrast to our former method [3].

Experimental

General

All iodoarenes, arenes, solvents as well as inorganic reagents were pure commercial products. The melting points of the purified diaryloiodonium bromides (Table 1) are uncorrected, and were measured

as follows. Since they depend on the duration of heating, after an approximate mp was taken in an open capillary tube, a new sample was introduced about 10 ^{o}C below this point, and the temperature was then raised at a rate of 4-5 ^{o}C per minute. ^{1}H-NMR solution spectra (not shown here) were recorded with a Tesla (100 MHz) spectrometer. Microanalyses were carried out at the Institute of Organic Chemistry, the Polish Academy of Sciences, Warsaw.

One-Pot Preparations of Diaryliodonium Bromides

NaBO$_3$·H$_2$O (37.5 mmol) was suspended in Ac$_2$O (17 mL), and this mixture was stirred at 30 ^{o}C for 90 min. An appropriate iodoarene (12.5 mmol) was then added, the mixture was stirred at 40 ^{o}C for 1.5 h, and at that point benzene or an appropriate activated arene (5 × 12.5 mmol) was added, and the mixture was cooled to 5-10 ^{o}C. Conc. (98%) H$_2$SO$_4$ (2.5 mL) was slowly added dropwise, with stirring, while keeping the temperature below 15 ^{o}C. Next, the mixtures were stirred, at appropriate temperature (10-30 ^{o}C) for a given time (4-6 h, but with benzene 48 h; see Table 1 for details). The final reaction mixtures were poured into cold water (150 mL) and stirred for 0.5-1 h. The unreacted organic substrates were extracted with Et$_2$O (2 × 20 mL), and the ethereal extracts were *discarded*. The aqueous layers, if dark-coloured, were decolourized with charcoal while boiling. To the cooled filtrates, excess aq. KBr (6 g KBr in 30 mL water) was added with stirring. After 1-2 h, the precipitates were collected, washed well with water, acetone, and Et$_2$O, air-dried, and weighed to give the iodonium bromides in 23-98% crude yields (Table 1). **Note**. When the iodoarenes and/or arenes used were solid compounds, which rendered the stirring more difficult, then an additional amount of Ac$_2$O (5-10 mL) was added to the reaction mixtures, prior to the addition of conc. H$_2$SO$_4$.

Table 1. Preparative Details, Crude Yields, and Melting Points of the Purified
Diaryliodonium Bromides **1-24**   as well as their Elemental Analyses

Substrates ArI, Ar'H	Product Ar(Ar')I$^+$Br$^-$	Time [h]/ Temp. [^{o}C]^a	CrudeYield [%]	Mp [^{o}C]	Analyses [% I] Calcd/Found
PhI, PhH	Diphenyliodonium bromide (**1**)	48/30	51	246-247	35.15/35.3
PhI, PhMe	4-Methyldiphenyliodonium bromide (**2**)	5/15	65	199-200	33.83/33.6
PhI, Mesitylene	2,4,6-Trimethyldiphenyliodonium bromide (**3**)	5/15	82	166-167	31.48/31.6
PhI, PhOMe	4-Methoxydiphenyliodonium bromide (**4**)	5/15	91	211-212	32.45/32.4
PhI, PhNHAc	4-Acetylaminodiphenyliodonium bromide (**5**)	5/25	30	202-203	30.35/30.5
PhI, Thiophene	Phenyl(2-thienyl)iodonium bromide (**6**)	5/15	55	206-207	34.57/34.9

2-I-Thiophene, 3-MeC$_6$H$_4$OMe	4-Methoxy-2-methylphenyl(2-thienyl)iodonium bromide (**7**)	6/15	23	154-155	32.19/32.4
2-I-Thiophene, Thiophene	2,2'-Dithienyliodonium bromide (**8**)	6/15	30	183-184	34.01/34.4
2-MeC$_6$H$_4$I, PhOMe	4-Methoxy-2'-methyldiphenyl-iodonium bromide (**9**)	6/15	50	200-201	31.22/31.5
3-MeC$_6$H$_4$I, PhOMe	4-Methoxy-3'-methyldiphenyl-iodonium bromide (**10**)	6/15	55	171-172	31.22/31.5
4-MeC$_6$H$_4$I, PhOMe	4-Methoxy-4'-methyldiphenyl-iodonium bromide (**11**)	6/15	70	194-195	31.22/31.4
2-MeOC$_6$H$_4$I, PhOMe	2,4'-Dimethoxydiphenyliodonium bromide (**12**)	5/15	70	223-224	30.04/29.9
3-MeOC$_6$H$_4$I, PhOMe	3,4'-Dimethoxydiphenyliodonium bromide (**13**)	5/15	48	178-179	30.04/30.0
4-MeOC$_6$H$_4$I, PhOMe	4,4'-Dimethoxydiphenyliodonium bromide (**14**)	5/15	50	210-211	30.04/30.1
2-AcNHC$_6$H$_4$I, PhOMe	2-Acetylamino-4'-methoxydiphenyl-iodonium bromide (**15**)	5/15	50	193-194	28.32/27.9
3-AcNHC$_6$H$_4$I, PhOMe	3-Acetylamino-4'-methoxydiphenyl-iodonium bromide (**16**)	5/15	45	198-200	28.32/27.9
4-AcNHC$_6$H$_4$I, PhOMe	4-Acetylamino-4'-methoxydiphenyl-iodonium bromide (**17**)	5/10	40	206-207	28.32/28.6
4-ClC$_6$H$_4$I, 1,3-Xylene	4-Chloro-2',4'-dimethyldiphenyl-iodonium bromide (**18**)	5/15	55	185-186	29.96/30.1
4-ClC$_6$H$_4$I, Mesitylene	4-Chloro-2',4',6'-trimethyl-diphenyliodonium bromide (**19**)	5/15	25	201-202	29.00/29.4
4-ClC$_6$H$_4$I, PhOMe	4-Chloro-4'-methoxydiphenyl-iodonium bromide (**20**)	6/15	87	205-206	29.83/30.1
4-AcC$_6$H$_4$I, PhOMe	4-Acetyl-4'-methoxydiphenyl-iodonium bromide (**21**)	5/15	96	167-168	29.21/29.0
2-O$_2$NC$_6$H$_4$I, PhOMe	4-Methoxy-2'-nitrodiphenyliodonium bromide (**22**)	6/15	96	185-186	29.10/29.2
3-O$_2$NC$_6$H$_4$I, PhOMe	4-Methoxy-3'-nitrodiphenyliodonium bromide (**23**)	4/15	98	175-176	29.10/28.9
4-O$_2$NC$_6$H$_4$I, PhOMe	4-Methoxy-4'-nitrodiphenyliodonium bromide (**24**)	4/15	55	157-158	29.10/29.0

[a] Time and temperature of the acidic coupling reaction between a prior oxidized ArI and an appropriate Ar'H.

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Sample availability: Samples of crude compounds **1-24** are available from the authors. Samples of pure compounds **4**, **9-11**, **14-16** are available from MDPI.