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Boron-Iodine(III) Exchange Reaction: Direct Synthesis of Diaryliodonium Tetraarylborates from (Diacetoxyiodo)arenes by the Reaction with Alkali Metal Tetraarylborates in Acetic Acid

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Abstract: Reaction of (diacetoxyiodo)arenes with sodium or potassium tetraarylborates in acetic acid undergoes boron-iodine(III) exchange as well as ligand exchange reactions at room temperature, which provides a direct route to the regioselective synthesis of diaryliodonium tetraarylborates.
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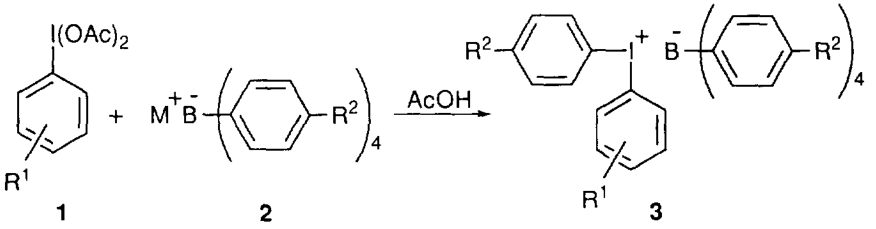
Photosensitive diaryliodonium salts possessing complex metal halide anions such as BF_4^-, AsF_6^-, PF_6^-, and SbF_6^- are very effective catalysts for the cationic and/or the free radical polymerizations of a wide range of monomers because of their ability to generate both strong acids and free radicals on photolysis as well as their insensitivity toward oxygen.[1] They have an important role in various industrial applications, especially in microelectronic lithography, the cure of various coatings, adhesives, printing inks, and printing plates.[1] The Brϕnsted acids generated upon photolysis of a diaryliodonium salt may cause deprotection of some phenolic polymers such as poly(4-*tert*-butoxystyrene)[2] and poly(4-(*tert*-butoxycarbonyloxy)styrene).[3]

Recently, diaryliodonium tetraarylborates **3** were developed as a selective free radical photoinitiator which does not liberate any Brϕnsted acids upon photolysis.[4] Diaryliodonium tetraarylborates **3** have been prepared from diaryliodonium halides by stepwise ligand exchange reactions, involving the initial conversion to the diaryliodonium hydroxide by treatment with basic silver oxide, followed by a ligand exchange with sodium tetraarylborates.[4,5] Transfer of a phenyl group of labile triphenyliodine to triphenylborane leads to the formation of diphenyliodonium tetraphenylborate **3aa**.[6] We report herein a direct synthesis of diaryliodonium tetraarylborates **3** from (diacetoxyiodo)arenes **1**, which involves, for the first time, the transfer of an aryl group of alkali metal tetraarylborates **2** to the hypervalent iodine(III) of **1**.



When (diacetoxyiodo)benzene **1a** was treated with 2 equivalent of sodium tetraphenylborate **2a** in dichloromethane at 0 °C under an atmosphere, a boron-iodine(III) exchange reaction occurred within 15 min to give diphenyliodonium tetraphenylborate **3aa** in 52% yield as colourless plates (mp, 194.5-196 °C).[7] Similarly,

Table 1 Synthesis of Diaryliodonium Salts **3** via Boron-Iodine(III) Exchange Reaction

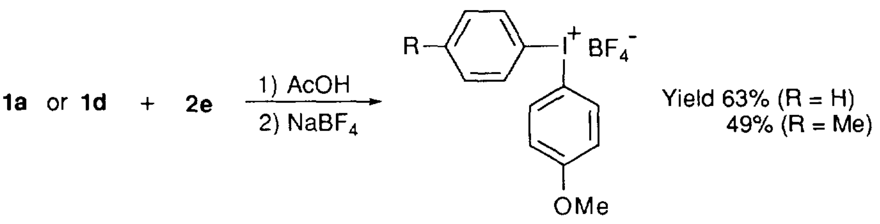
	Iodane		Borate			Product	
Entry	**1**	R^1	**2**	M	R^2	**3**	Yield (%)[a]
1	**1a**	H	**2a**	Na	H	**3aa**	91
2	**1a**	H	**2b**	Na	F	**3ab**	81
3	**1a**	H	**2c**	K	Cl	**3ac**	100
4	**1a**	H	**2d**	Na	Me	**3ad**	70
5	**1b**	*m*-NO_2	**2a**	Na	H	**3ba**	95
6	**1b**	*m*-NO_2	**2b**	Na	F	**3bb**	71
7	**1b**	*m*-NO_2	**2c**	K	Cl	**3bc**	83
8	**1b**	*m*-NO_2	**2d**	Na	Me	**3bd**	96
9	**1c**	*p*-Cl	**2a**	Na	H	**3ca**	82
10	**1c**	*p*-Cl	**2b**	Na	F	**3cb**	68
11	**1c**	*p*-Cl	**2c**	K	Cl	**3cc**	93
12	**1c**	*p*-Cl	**2d**	Na	Me	**3cd**	69
13	**1d**	*p*-Me	**2a**	Na	H	**3da**	100
14	**1d**	*p*-Me	**2b**	Na	F	**3db**	69
15	**1d**	*p*-Me	**2c**	K	Cl	**3dc**	92
16	**1d**	*p*-Me	**2d**	Na	Me	**3dd**	77
17	**1e**	*p*-MeO	**2a**	Na	H	**3ea**	89
18	**1e**	*p*-MeO	**2b**	Na	F	**3eb**	93
19	**1e**	*p*-MeO	**2c**	K	Cl	**3ec**	78
20	**1e**	*p*-MeO	**2d**	Na	Me	**3ed**	79
21	**1f**	*o*-MeO	**2a**	Na	H	**3fa**	83

[a] Isolated yields.

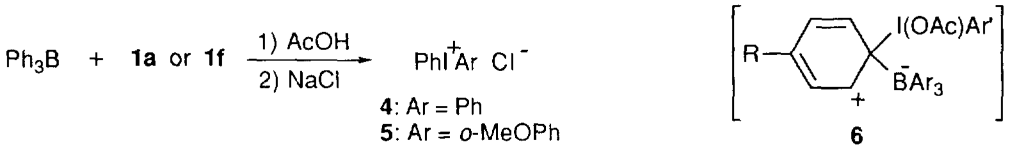
modest yields of **3aa** (44-52%) were obtained by the reaction in acetonitrile, methanol, or THF as a solvent. Use of an acid as an additive was found to be essential to the high yield synthesis of **3aa**. Thus, in the presence of BF_3-Et_2O (1 equiv.) as an additive, the yield of the reaction in dichloromethane was much improved up to 80%. Moreover, 91% yield of **3aa** was obtained in acetic acid at room temperature. Other phenyliodanes such as iodosylbenzene, (bis(trifluoroacetoxy)iodo)benzene, and (hydroxy(tosyloxy)iodo)benzene are also effective reagents for this boron-iodine(III) exchange reaction and their reaction with **2a** in acetic acid afforded **3aa** in 65%, 73% and 82% yields, respectively.

Examples of this boron-iodine(III) exchange reaction yielding diaryliodonium tetraarylborates **3** in acetic acid at room temperature have been collected in Table 1. (Diacetoxyiodo)arenes **1** with electron-withdrawing (NO_2 and Cl) as well as electron-donating substituents (Me and MeO) on the aromatic ring afforded **3** in good yields. The presence of highly electron-withdrawing CF_3 groups on the aromatic ring of tetraarylborates **2**, however, led to reduced reactivity towards aryliodanes **1**: for instance, sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate was recovered unchanged on prolonged treatment with **1a** in acetic acid (room temperature, 24 h).

In addition, no formation of *p*-methoxyphenyl(phenyl)iodonium tetrakis(*p*-methoxyphenyl)borate **3ae** was detected in the reaction of sodium tetrakis(*p*-methoxyphenyl)borate **2e** with **1a**. However, when the reaction mixture was treated with an aqueous $NaBF_4$ solution to undergo a ligand exchange on iodine(III), *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate was isolated in 63% yield. Similar results were obtained in the reaction of **2e** with **1d**. These results clearly indicate that, in these cases, the boron-iodine(III) exchange reactions do occur. However, the reduced stability of the electron-rich counter anion, tetrakis(*p*-methoxyphenyl)borate, in acidic media as compared to the other tetraarylborates probably renders **3ae** unstable under the reaction conditions.[8] General procedure for synthesis of diaryliodonium tetraarylborates **3** is as follows: To a solution of sodium or potassium tetraarylborate **2** (2 equiv.) in dry acetic acid (10 mL $mmol^{-1}$) was added (diacetoxyiodo)arene **1** (1 equiv.) at room temperature under an atmosphere and the mixture was stirred for 30 min. After evaporation *in vacuo*, the residue was dissolved in dichloromethane. Filtration and evaporation gave a solid, which was washed several times with hexane and/or diethyl ether. Recrystallization gave pure **3**.



The exclusive electrophilic attack at the *ipso* position of tetraarylborates **2** by aryliodanes **1** activated by the protonation with acetic acid is noteworthy, since the electrophilic aromatic alkylation and acylation of arylborates have been shown to occur at either the *ipso*, *ortho*, or *para* positions.[9,10] The observed exclusive *ipso* substitution yielding **3** probably involves the intermediacy of a zwitterion **6**, as proposed in the protodeboronation of tetraphenylborate with HCl.[11] Both ionic and single electron transfer mechanisms for generation of **6** seem to be possible.[10,12]



Although there is no firm evidence, it has been suggested that the reaction of sodium tetraphenylborate **2a** with acetic acid at room temperature produces triphenylborane via protodeboronation;[13] therefore, it is conceivable that triarylboranes generated *in situ* are the real arylating reagents for the reaction with aryliodanes **1**. Exposure of triphenylborane to **1a** in acetic acid at room temperature for 30 min afforded, after ligand exchange with an aqueous NaCl solution, diphenyliodonium chloride **4** in 90% yield. Similarly, with **1f** phenyl(*o*-methoxyphenyl)iodonium salt **5** was obtained in 97% yield. Therefore, a reaction mechanism involving the initial formation of triarylborane from **2** via protodeboronation, which in turn reacts with **1** to give

3, cannot be ruled out. It is to be noted that the reaction of triphenylborane with a threefold excess of **1a** afforded 165 mol % of diphenyliodonium chloride.

Whatever the mechanism, the method is attractive from the practical standpoint because of its mildness, cleanliness, regioselectivity, and the ease with which the diaryliodonium tetraarylborates may be isolated. The preliminary data presented suggest that the boron-iodine(III) exchange reaction takes place under mild conditions.

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7. **3aa:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 8 H), 7.58 (br t, *J* = 7.9 Hz, 2 H), 7.41 (br d, *J* = 7.9 Hz, 4 H), 7.35 (br t, *J* = 7.9 Hz, 4 H), 7.02 (t, *J* = 7.2 Hz, 8 H), 6.82 (t, *J* = 7.2 Hz, 4 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 165.1, 136.43, 134.95, 133.21, 132.77, 127.05, 122.99, 114.37. ^{11}B NMR (128 MHz, DMSO-d_6) δ -25.27 (relative to $B(OMe)_3$ external standard). MS FAB (positive ions): *m/z* 281 (Ph_2I^+). MS FAB (negative ions): *m/z* 319 (Ph_4B^-). Anal. Calcd for $C_{36}H_{30}BI$: C, 72.02; H, 5.04. Found: C, 71.83; H, 5.17.
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