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Unexpected, Drastic Effect of Triflic Acid on Oxidative Diacetoxylation of Iodoarenes by Sodium Perborate. A Facile and Efficient One-Pot Synthesis of (Diacetoxyiodo)arenes

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$$\mathrm{ArI + AcOH \xrightarrow[\text{3-8 h, 40-45 °C, 86-99\%}]{NaBO_3{\cdot}4H_2O,\ \mathbf{CF_3SO_3H}} ArI(OAc)_2}$$

An easy, safe, and effective method for preparing (diacetoxyiodo)arenes from iodoarenes is presented. Addition of trifluoromethanesulfonic acid (triflic acid) as a promoter causes a drastic increase in the yield of (diacetoxyiodo)arenes in the reaction of iodoarenes with sodium perborate. The reaction of the iodoarenes with sodium perborate in acetic acid in the presence of triflic acid at 40−45 °C efficiently generates the corresponding (diacetoxyiodo)arenes in high yields within short time.

(Diacetoxyiodo)arenes, $ArI(OAc)_2$, and particularly the parent compound, (diacetoxyiodo)benzene [$PhI(OAc)_2$], have been known for a long time.[1−5] They have received a great deal of attention due to low toxicity, ready availability, easy handling, and reactivity similar to that of heavy metal reagents and anodic oxidation. They are potent, often chemoselective, oxidants widely used in modern organic synthesis. They are also used for the facile synthesis of, for example, iodosylarenes, [bis(trifluroacetoxy)iodo]arenes, [hydroxyl(tosyloxy)iodo]]arenes (*selective oxidants*), and aromatic iodonium salts (*arylating reagents*), etc.[2−6] Several methods are available for the preparation of (diacetoxyiodo)arenes. Historically, the first member, (diacetoxyiodo)benzene, was synthesized by Willgerodt in 1892 by dissolving iodosylbenzene in hot acetic acid.[7] The representative methods involve the reaction of iodosylarenes with acetic acid,[7] the direct oxidation of iodoarenes in acetic acid,[3−5,8−11] and the reaction of (dichloroiodo)arenes with metal acetates or acetic acid.[12,13]

The standard and most general method for the synthesis of $ArI(OAc)_2$ is the oxidative diacetoxylation of ArI by warm peracetic acid solution. However, it requires a very prolonged reaction (12−16 h) and the utmost care to maintain the exact temperature, 40 °C. Two-step conversion of various ArI to $ArI(OAc)_2$ in the anhydrous $CrO_3/AcOH/Ac_2O$/concentrated H_2SO_4 liquid system, followed by mixing with excess 20% aqueous ammonium acetate solution, is 8−16 times faster and ca. 5 times less expensive than the method of McKillop and Kemp.[8] However, this method is hardly applicable for iodotoluenes [$4\text{-}MeC_6H_4I(OAc)_2$ was obtained from $4\text{-}MeC_6H_4I$ in only 20% yield]. For ArI substituted with strong electron-withdrawing groups, the sodium periodate system is not applicable.[10] In the sodium percarbonate method,[11] 4-iodotoluene and 4-chloroiodobenzene were unexpectedly overoxidized to the corresponding iodylarenes. McKillop and Kemp[8] examined the reactions of a variety of iodoarenes with sodium perborate in acetic acid at 40 °C. This method is very simple and applicable for many iodoarenes. After crystallizations, they obtained the purified products in 71−80% yields; no attempt was made to optimize yields. However, electron-withdrawing substituents *ortho* or *para* to the iodine inhibit this reaction, and attempts to oxidize iodobenzene in either propionic or trifluoroacetic acid were unsuccessful. The starting material was also recovered from the attempted oxida-

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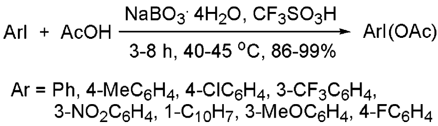
TABLE 1. Preparation of (Diacetoxyiodo)arenes from Iodoarenes[a]

entry	iodoarenes	time (h)	yield (%)
1	C_6H_5I	3	99
2	4-MeC_6H_4I	4	96
3	4-MeC_6H_4I	12	91[b]
4	4-ClC_6H_4I	6	95
5	3-$CF_3C_6H_4I$	4	95
6	3-$NO_2C_6H_4$ I	6	94
7	1-$IC_{10}H_7$	7	90
8	1,4-$I_2C_6H_4$[c]	8	97
9	3-$MeOC_6H_4I$	4	98
10	4-FC_6H_4I	8	86

[a] The reaction of an iodoarene (1 mmol) was carried out in AcOH (9 mL) with CF_3SO_3H (6 mmol) in the presence of $NaBO_3{\cdot}4H_2O$ (10 mmol) at 40−45 °C. [b] 4-Iodotoluene(10 mmol), $NaBO_3{\cdot}4H_2O$ (100 mmol), CF_3SO_3H (60 mmol), and AcOH (90 mL). [c] CH_2Cl_2 (3 mL) was added. The product was 1,4-bis(diacetoxyiodo)benzene.

SCHEME 1. Oxidative Diacetoxylation of Iodoarenes

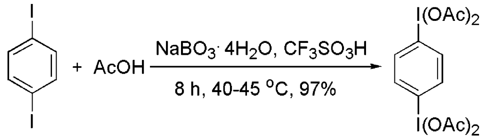


tions using nitric, sulfuric, or methanesulfonic acid as solvent. During the course of examination on the diacetoxylation of iodoarenes with an oxidant, we added triflic acid, CF_3SO_3H, to the reaction mixture of iodoarenes and sodium perborate in acetic acid. Surprisingly a drastic increase in the yield of (diacetoxyiodo)arenes was observed. It was found that this procedure provided a facile, effective method for preparation of (diacetoxyiodo)arenes from iodoarenes. Here we wish to report our finding of the new procedure.

In our laboratory, we found a quick and efficient method for preparing $ArI(OAc)_2$ in high yield within short time from the corresponding iodoarenes in AcOH, using commercial sodium perborate, $NaBO_3$, as an oxidant and triflic acid, CF_3SO_3H, as an additive. The results are given in Table 1. The oxidizing ability of $NaBO_3$ is much improved by addition of CF_3SO_3H, which is 30 times stronger than concentrated H_2SO_4.[14] Thermal stability of CF_3SO_3H is far superior to that of other acids.[15] $NaBO_3$ is used as a strong oxidizing agent in many applications. It is a very cheap, safe, nontoxic, and easily handled oxidant (stable, colorless, crystalline solid).[16] The oxidation of iodoarenes to (diacetoxyiodo)arenes can be easily scaled up and provides the advantages of CF_3SO_3H and $NaBO_3$ outlined above, together with the complete absence of effluent or byproduct problems. The essence of our novel method is described in Scheme 1.

The oxidative diacetoxylation reactions shown in Schemes 1 and 2 were carried out at 40−45 °C, in AcOH using $NaBO_3$. The presence of CF_3SO_3H (in stoichiometric quantities) in the reaction mixture enhances considerably the oxidizing activity ,and we obtained the purified products in 86−99% yields. When CF_3SO_3H was replaced for concentrated H_2SO_4, the final yields of $ArI(OAc)_2$ were not improved. Table 1 shows that the reaction proceeds satisfactorily both with iodoarenes containing electron-donating substituents and with iodoarenes with electron-withdrawing substituents. This method was unaffected for trisubstituted iodoarenes due to the steric effect.

SCHEME 2. Double Oxidative Diacetoxylation of 1,4-Diiodobenzene



The effect of CF_3SO_3H is not clear now, but there are two possible explanations for the effect of CF_3SO_3H on the oxidative diacetoxylation of iodoarenes. One is the increase in solubility of $NaBO_3$ by adding CF_3SO_3H. On adding CF_3SO_3H, $NaBO_3$ is suspended, miscible in AcOH, and it becomes easy to oxidize iodoarenes. Another is that an in situ generated (diacetoxyiodo)arene participates the oxidation of iodoarenes. The (diacetoxyiodo)benzene undergoes the ligand exchange with CF_3SO_3H to probably form an $ArI(OTf)_2$, which is highly reactive[17] and can oxidize iodoarenes. Such oxidation using a reactive hypervalent iodine compound, [hydroxy(tosyloxy)iodo]-benzene, has been observed to proceed under mild conditions.[18]

In summary, we have developed a considerably improved preparative procedure that is easy, quick, cheap, and possibly environmentally benign. The new method gives (diacetoxyiodo)arenes in high yields by the reaction of iodoarenes with $NaBO_3$ in AcOH in the presence of CF_3SO_3H at 40−45 °C. Because of its simplicity and high yields, we believe that the present method will be widely used.

Experimental Section

Optimized Procedure for Preparing (Diacetoxyiodo)-benzene from Iodobenzene. Sodium perborate tetrahydrate (10 mmol) was slowly added portionwise during 10 min to a stirred solution of iodobenzene (1 mmol) in glacial acetic acid (9 mL) with CF_3SO_3H (6 mmol) at 40−45 °C, and the mixture was stirred at this temperature until TLC analysis indicated completion of reaction. Reaction time needed 3 h. The solution was then concentrated to half its volume by evaporation of acetic acid under reduced pressure, and water (10 mL) was added. The solid separated was collected by filtration, washed with water, and dried in air. A second crop of product was obtained by extraction of the filtrate with dichloromethane (3 × 10 mL) followed by drying of the combined extracts (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation under reduced pressure. The combined crude products were purified by recrystallization from acetic acid/hexane.

(Diacetoxyiodo)benzene: white solid (0.321 g, 99%); mp 162−163 °C (lit.[19] mp 161.1−162.2 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 1.91 (s, 6 H, $MeCO_2$), 7.37−7.43 (m, 2 H, ArH), 7.48−

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7.54 (m, 1 H, ArH), 7.97−8.02 (m, 2 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 134.9, 131.7, 131.0, 121.5, 20.4.

Large-Scale Preparation of 1-(Diacetoxyiodo)-4-methylbenzene from 4-Iodotoluene. Sodium perborate tetrahydrate (100 mmol) was slowly added portionwise during 20 min to a stirred solution of 4-iodotoluene (2.188 g, 10 mmol) in glacial acetic acid (90 mL) with CF_3SO_3H (60 mmol) at 40−45 °C, and the mixture was stirred at this temperature until TLC analysis indicated completion of reaction. Reaction time needed 12 h. The solution was then concentrated to half its volume by evaporation of acetic acid under reduced pressure, and water (100 mL) was added. The solid separated was collected by filtration, washed with water, and dried in air. A second crop of product was obtained by extraction of the filtrate with dichloromethane (3 × 100 mL) followed by drying of the combined extracts (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation under reduced pressure. The combined crude products were purified by recrystallization from acetic acid/hexane to give 3.055 g (91%) of 1-(diacetoxyiodo)-4-methylbenzene.

1-(Diacetoxyiodo)-4-methylbenzene: mp 106−108 °C (lit.[19] mp 106−110 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 6 H, $MeCO_2$), 2.44 (s, 3 H, Me), 7.29 (d, $J = 8.6$ Hz, 2 H, ArH), 7.97 (d, $J = 8.6$ Hz, 2 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 142.5, 134.8, 131.6, 118.1, 21.4, 20.2.

Supporting Information Available: General procedure and characterization data for the compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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