



Various oxidative reactions with novel ion-supported (diacetoxyiodo)benzenes



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ABSTRACT

The oxidation of secondary alcohols and primary alcohols with two novel ion-supported (diacetoxyiodo) benzenes (IS-DIBs) **A** and **B** in the presence of a catalytic amount of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in dichloromethane at room temperature proceeded efficiently to provide the corresponding ketones and aldehydes, respectively, in good yields. The oxidative reaction of *N,N*-diisopropylbenzylamines with those IS-DIBs was also carried out to generate the corresponding aromatic aldehydes in good yields. In addition, the Hofmann rearrangement of primary amides in methanol under basic conditions and the oxidative 1,2-rearrangement of propiophenones in trimethyl orthoformate under acidic conditions with those IS-DIBs provided the corresponding methyl carbamates and methyl 2-arylpropanoates, respectively, in good yields. Moreover, treatment of acetophenones with those IS-DIBs in the presence of trifluoromethanesulfonic acid in acetonitrile generated the corresponding 5-aryl-2-methyloxazoles in good yields. In those five reactions, the desired products were obtained in good yields with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract. Moreover, ion-supported iodobenzenes, which were the co-products derived from IS-DIBs in the present oxidative reactions, were recovered in good yields and could be re-oxidized to IS-DIBs **A** and **B** for reuse in the same oxidative reactions.

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1. Introduction

Organic synthesis that features high efficiency and low toxicity and produces a minimal amount of reaction waste is very important for green chemistry. Efficient organic synthesis with less toxic reagents has been studied actively.¹ The oxidation of alcohols to ketones or aldehydes is one of the most fundamental, widely used, and important reactions in both research laboratories and production plants.² Among the various methods for the oxidation of alcohols to ketones or aldehydes, the Swern oxidation³ with dimethyl sulfoxide (DMSO) and oxalyl chloride or trifluoroacetic anhydride, and the Dess–Martin oxidation⁴ with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-2-one (Dess–Martin periodinane) are the most popular, efficient, and selective methods for the preparation of ketones or aldehydes from alcohols in organic synthesis, because both reactions do not require any toxic metals and proceed under mild and nearly neutral conditions. However, each reaction still has major drawbacks, i.e., dimethyl sulfide, a co-product of the Swern oxidation, is a highly malodorous volatile

compound that makes handling of the reaction extremely difficult, and Dess–Martin pentavalent periodinane is explosive. In 1997, the 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO)-mediated oxidation of alcohols to ketones or aldehydes with (diacetoxyiodo)benzene (DIB) in dichloromethane at room temperature was reported^{5a} and has become a very popular method for the efficient and selective oxidation of alcohols to ketones or aldehydes, due to simple experimental operation, the use of non-explosive trivalent iodine, and the lack of unpleasant odor.⁵ However, the reaction produces a stoichiometric amount of iodobenzene as a co-product, which must be removed by troublesome column chromatography on silica gel. To solve this problem and simplify the isolation of the desired product, the polymer-supported DIB, poly [4-(diacetoxyiodo)styrene], was developed.^{5b} However, there are still drawbacks, such as the low purity of carbonyl compounds after filtration of the reaction mixture because of containing low-molecular-weight polymer-supported iodobenzenes. Moreover, the elemental analysis of polymer-supported DIB must be carried out in each preparation of polymer-supported DIB to evaluate the loading rate of the (diacetoxy)iodo groups in the polymer-supported DIB. Recently, the oxidation of alcohols with a 1-(4'-diacetoxyiodobenzene)-3-methylimidazolium tetrafluoroborate/

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KBr/[emim]BF₄ system,^{6a} a 1-(4'-diacetoxyiodobenzene)-3-methylimidazolium tetrafluoroborate/3-methylimidazolium-supported TEMPO/water system,^{6b} and a bifunctional catalyst bearing ionic-liquid-supported (2,2,6,6-tetramethylpiperidin-1-yl)oxyl and iodoarene moieties/peracetic acid system^{6c} was reported. However, there are still certain drawbacks, such as the addition to the carbon–carbon double bond of substrates by bromonium ion species, the solubility of substrates in water, and the reusability of reagents. Here, as part of our ongoing studies of trivalent iodines for organic synthesis,⁷ we would like to report the TEMPO-mediated oxidation of alcohols to ketones or aldehydes with ion-supported (diacetoxyiodo)benzenes (IS-DIBs),⁸ the oxidative reaction of *N,N*-diisopropylbenzylamines with IS-DIBs to generate aromatic aldehydes, the Hofmann rearrangement of primary amides with IS-DIBs in methanol to form methyl carbamates, the oxidative 1,2-rearrangement of propiophenones with IS-DIBs in trimethyl orthoformate to form methyl 2-arylpropanoates, and the formation of 5-aryl-2-methyloxazoles with acetophenones and IS-DIBs in acetonitrile. The experimental scheme is shown in Fig. 1.

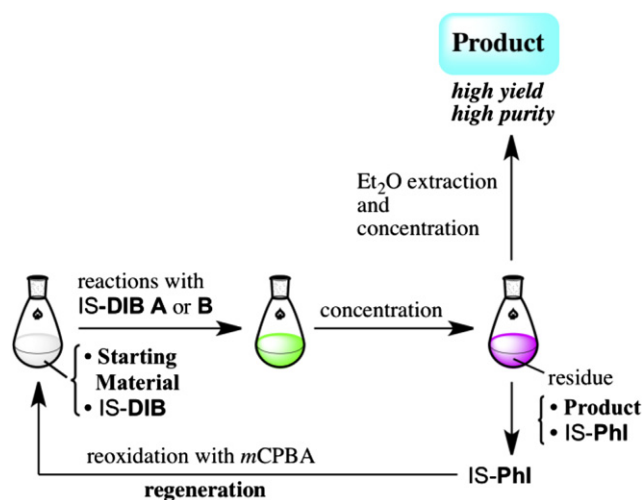
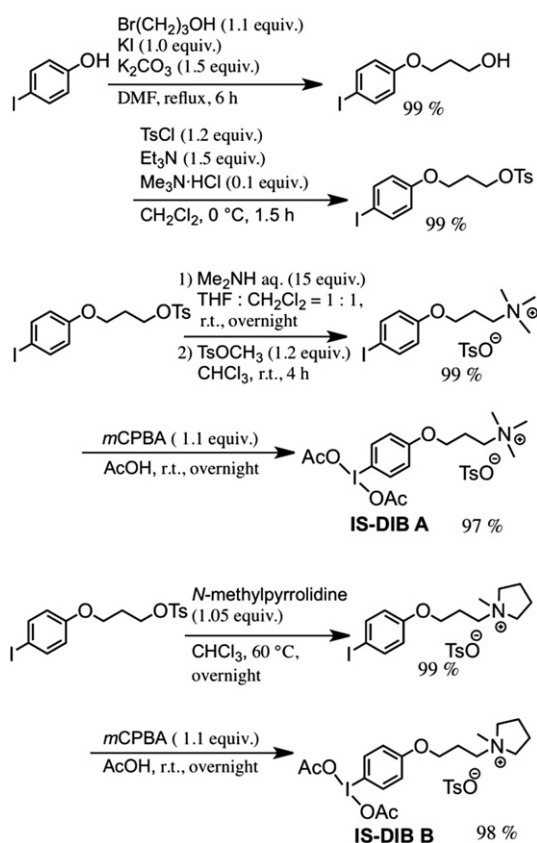


Fig. 1. Reaction, recovery, regeneration, and reuse of IS-DIB A and B.

2. Results and discussion

Two IS-DIBs **A** and **B** (IS-DIBs), i.e., *N*-[3-(4'-diacetoxyiodo)phenoxy-1-propyl]-*N,N,N*-trimethylammonium 4''-methylbenzenesulfonate (IS-DIB **A**) and *N*-methyl-*N*-[3-(4'-diacetoxyiodo)phenoxy-1-propyl]pyrrolidinium 4''-methylbenzenesulfonate (IS-DIB **B**), were prepared by the oxidation of *N*-[3-(4'-iodophenoxy)-1-propyl]-*N,N,N*-trimethylammonium 4''-methylbenzenesulfonate and *N*-methyl-*N*-[3-(4'-iodophenoxy)-1-propyl]pyrrolidinium 4''-methylbenzenesulfonate, respectively, with *m*-chloroperoxybenzoic acid (*m*CPBA) in acetic acid at room temperature, as shown in Scheme 1.⁷⁰ *N*-[3-(4'-iodophenoxy)-1-propyl]-*N,N,N*-trimethylammonium 4''-methylbenzenesulfonate and *N*-methyl-*N*-[3-(4'-iodophenoxy)-1-propyl]pyrrolidinium 4''-methylbenzenesulfonate were easily prepared from commercially available *p*-iodophenol and 3-bromo-1-propanol in three steps, respectively, in good yields.

The oxidation of secondary and primary alcohols with IS-DIBs **A** and **B** (or DIB) in the presence of TEMPO in CH₂Cl₂ at room temperature was carried out by means of the same experimental procedure as that described in the literature.^{5a} Thus, to a solution of IS-DIB **A** or **B** (1.5 equiv) in CH₂Cl₂ were added alcohol (1.0 equiv) and TEMPO (10 mol %, 0.1 equiv). Then, the mixture was stirred at room temperature. After the disappearance of alcohol, the solvent was removed. Addition of water and extraction with diethyl ether provided ketone or aldehyde in good yield with high purity. Thus,



Scheme 1. Preparation of ion-supported (diacetoxyiodo)benzenes **A** and **B**.

when diphenylmethanol (**1a**) was used as the substrate in the oxidation with IS-DIBs **A** and **B**, benzophenone (**2a**) was obtained in 97% and 99% yields with 98% and 99% purity, respectively, by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract, as shown in Table 1. Here, use of an excess amount of IS-DIB suppressed the contamination of TEMPO into the diethyl ether extracts from the reaction mixture. On the other hand, when DIB was used as the oxidant for the oxidation of diphenylmethanol (**1a**) under the same conditions and procedure, benzophenone (**2a**) was obtained in 99% yield; however, its purity was 48% because of containing iodo-benzene. Therefore, the purification of benzophenone by column chromatography on silica gel was required. Here, when IS-DIBs **A** and **B** were used as the oxidant, the oxidation product was obtained in good yield with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract. The oxidation of 9-fluoreno (**1b**), 1-phenyl-1-propanol (**1c**), and 1-(5'-methylfuran-2'-yl)-1-pentanol (**1d**) with IS-DIBs **A** and **B** were carried out under the same conditions and procedure to give the corresponding ketones **2b**, **2c**, and **2d** in good yields with high purity, respectively, by simple extraction treatment of the reaction mixture. Moreover, the treatment of benzylic and allylic alcohols, such as *p*-chlorobenzyl alcohol (**1e**), *p*-methylbenzyl alcohol (**1f**), piperonyl alcohol (**1g**), 4-phenylbenzyl alcohol (**1h**), 2-thiophenemethanol (**1i**), geraniol (**1j**), and *trans*-cinnamyl alcohol (**1k**), with IS-DIBs **A** and **B** under the same conditions and procedure provided the corresponding aromatic aldehydes **2e–i** and α,β -unsaturated aldehydes **2j** and **2k** in good yields with high purity, respectively, by simple extraction treatment of the reaction mixture. The oxidation of primary alcohols, such as 1-adamantanemethanol (**1l**), β -citronellol (**1m**), and 8-(*p*-methylbenzenesulfonyloxy)-1-octanol (**1n**), with IS-DIBs **A** and **B** in the presence of TEMPO at room temperature provided the

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