



Synthetic utility of iodic acid in the oxidation of benzylic alcohols to aromatic aldehydes and ketones



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ABSTRACT

Various primary and secondary benzylic alcohols were efficiently oxidized to aromatic aldehydes and aromatic ketones with iodic acid in DMF at 60 °C for 2 h and with iodic acid in the presence of TEMPO (5 mol %) in DMF at room temperature, respectively. The former method was effective for the oxidation of sterically hindered alcohols at 60 °C and the latter method was effective for the oxidation of less sterically hindered alcohols at room temperature.

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1. Introduction

The oxidation of alcohols is one of the most important organic transformation reactions, and therefore, studies for the mild oxidation methods of alcohols with less toxic reagents have been carried out extensively.¹ Among those methods, the oxidation of alcohols to aldehydes or ketones with trifluoroacetic anhydride or oxalyl chloride with dimethyl sulfoxide (DMSO) in the presence of Et₃N in CH₂Cl₂ (Swern oxidation),² with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-2-one (Dess–Martin periodinane oxidation) in CH₂Cl₂,³ with 2-iodoxybenzoic acid (IBX) in DMSO,⁴ with (diacetoxy)iodobenzene (DIB) in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO) in CH₂Cl₂,⁵ with DIB in the presence of 2-azaadamantane *N*-oxyl radical (AZADO) in CH₂Cl₂,⁶ and with NaClO in the presence of TEMPO and KBr in CH₂Cl₂–H₂O⁷ are the most popular and useful, because the reactions can be carried out under mild and transition-metal-free conditions. However, those methods have drawbacks, such as the formation of highly malodorous volatile dimethyl sulfide in the Swern oxidation, the use of explosive and expensive pentavalent iodine in the Dess–Martin periodinane and IBX oxidation, and the need to remove of iodobenzene, a co-product, from the reaction mixture by column chromatography in the DIB-TEMPO oxidation and the DIB-AZADO oxidation, etc. Among the many oxidants for the oxidation of alcohols, the use of iodic acid (HIO₃) as a less toxic reagent has been little studied, although iodic

acid is less expensive than (diacetoxy)iodobenzene (DIB), and is an inorganic reagent and not a transition-metal reagent. As synthetic uses of iodic acid, the oxidative dehydrogenation of ketones to α,β -unsaturated ketones with HIO₃ in DMSO at 50 °C,^{8a} the oxidation of alcohols to carbonyl compounds with iodic acid in the presence of KBr and wet SiO₂ in CHCl₃ at room temperature,^{8b} and the oxidation of alcohols to aldehydes and ketones with iodic acid in the presence of NaHSO₄ in wet acetonitrile at refluxing temperature^{8c} were reported. However, we would like to question the veracity of the third report.^{8c} Although we performed the oxidation of *p*-bromobenzyl alcohol, 1-phenylethanol, and (–)-menthol carefully on the basis of the reported reaction conditions, we obtained only a yield of 24% for *p*-bromobenzaldehyde, 5% for acetophenone, and 0% for (–)-menthone, together with the starting alcohols. Thus, we found that the reaction is not reproducible. Here, we would like to report a practical oxidation of primary and secondary benzylic alcohols to aromatic aldehydes and aromatic ketones, respectively, with iodic acid alone in DMF at 60 °C and with iodic acid in the presence of TEMPO in DMF at room temperature.

2. Results and discussion

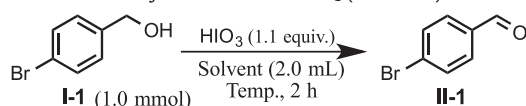
First, the oxidation of *p*-bromobenzyl alcohol **I-1** (1.0 mmol) with iodic acid (1.1 equiv) was carried out in acetonitrile (2.0 mL), *t*-butyl alcohol (2.0 mL), *N,N*-dimethylformamide (DMF, 2.0 mL), and dimethyl sulfoxide (DMSO, 2.0 mL) at 60 °C for 2 h to provide *p*-bromobenzaldehyde **II-1** in 22%, 36%, 95%, and 95% yields,

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respectively, as shown in Table 1. When the oxidation was carried out in DMF and DMSO at room temperature for 2 h, *p*-bromobenzaldehyde **II-1** was obtained in 12% and 25% yields, together with the starting material **I-1** in 81% and 72% yields, respectively. Thus, warming treatment at 60 °C is effective, and other less polar solvents, such as dichloromethane and chloroform, were not effective due to the insolubility of iodic acid in them. For example, the DMF solution of alcohol with iodic acid became a homogeneous solution at 60 °C, although the same reaction at room temperature did not produce a homogeneous solution.

Based on those results, various benzylic alcohols, such as *p*-methylbenzyl alcohol **I-2**, *p*-chlorobenzyl alcohol **I-3**, *m*-chlorobenzyl alcohol **I-4**, *o*-chlorobenzyl alcohol **I-5**, *p*-nitrobenzyl alcohol **I-6**, *p*-(trifluoromethyl)benzyl alcohol **I-7**, *p*-(methoxycarbonyl)benzyl alcohol **I-8**, *p*-(methylthio)benzyl alcohol **I-9**, *p*-methoxybenzyl alcohol **I-10**, *p*-(phenyl)benzyl alcohol **I-11**, and 1-naphthalenemethanol **I-12**, were treated with iodic acid (1.1 equiv) in DMF at 60 °C for 2 h to give the corresponding aromatic aldehydes **II-2~II-12** in good yields, as shown in Table 2 (Method A), although the treatment of *p*-(methylthio)benzyl alcohol **I-9** generated *p*-(methanesulfinyl)benzaldehyde **II-9'** in good yield. Thus, iodic acid oxidizes a sulfenyl group to a sulfinyl group. The same oxidation of *p*-(allyloxy)benzyl alcohol **I-13**, *p*-(1,3-dioxolan-2-yl)benzyl alcohol **I-14**, and cinnamyl alcohol **I-15** with iodic acid gave the corresponding aldehydes **II-13~II-15** in moderate yields. These results come from the partial oxidation of the carbon–carbon double bond and the partial hydrolysis of acetal by iodic acid under the present warming conditions. The same oxidation of benzylic alcohols bearing heteroaromatics, such as 2-thiophenemethanol **I-16** and 3-pyridinemethanol **I-17**, with iodic acid provided the corresponding aromatic aldehydes **II** in good yields, although the former compound gave a mixture of 2-thiophenecarboxaldehyde **II-16** (42%) and 5-iodo-2-thiophenecarboxaldehyde **II-16'** (41%). On the other hand, the oxidation of 2,4,6-trimethylbenzyl alcohol **I-18** and 2,4,6-triisopropylbenzyl alcohol **I-19** with iodic acid in DMF at 60 °C gave the corresponding aromatic aldehydes **II-18** and **II-19** in moderate yields, respectively. The oxidation of secondary benzylic alcohols, such as 1-phenylethanol **I-20**, 1-phenyl-1-propanol **I-21**, 1-phenyl-1-octanol **I-22**, 1-(4'-bromophenyl)ethanol **I-23**, 1-(4'-methylphenyl)ethanol **I-24**, diphenylmethanol **I-25**, phenyl-*p*-tolylmethanol **I-26**, and 1,2-diphenylethanol **I-27**, with iodic acid (2.0 equiv) in DMF at 60 °C for 2 h gave the corresponding aromatic ketones **II-20~II-27** in good yields, respectively. The yield of aromatic ketones with 2.0 equiv of iodic acid was better than that with 1.1 equiv of iodic acid for the oxidation of secondary benzylic alcohols, as shown in the oxidation of 1-phenylethanol **I-20** and 1-(4'-bromophenyl)ethanol **I-23**. Moreover, iodic acid (2.0 equiv) was used for the oxidation of α -(isopropyl)benzyl alcohol **I-28**, α -(cyclohexyl)benzyl alcohol **I-29**, α -(*t*-butyl)benzyl alcohol **I-30**, α -mesityl- α -ethylmethanol **I-31**, α -mesityl- α -cyclohexylmethanol **I-32**, and α -mesityl- α -*t*-butylmethanol **I-33**, which are sterically hindered benzylic alcohols, in DMF at 60 °C for 2 h to generate the

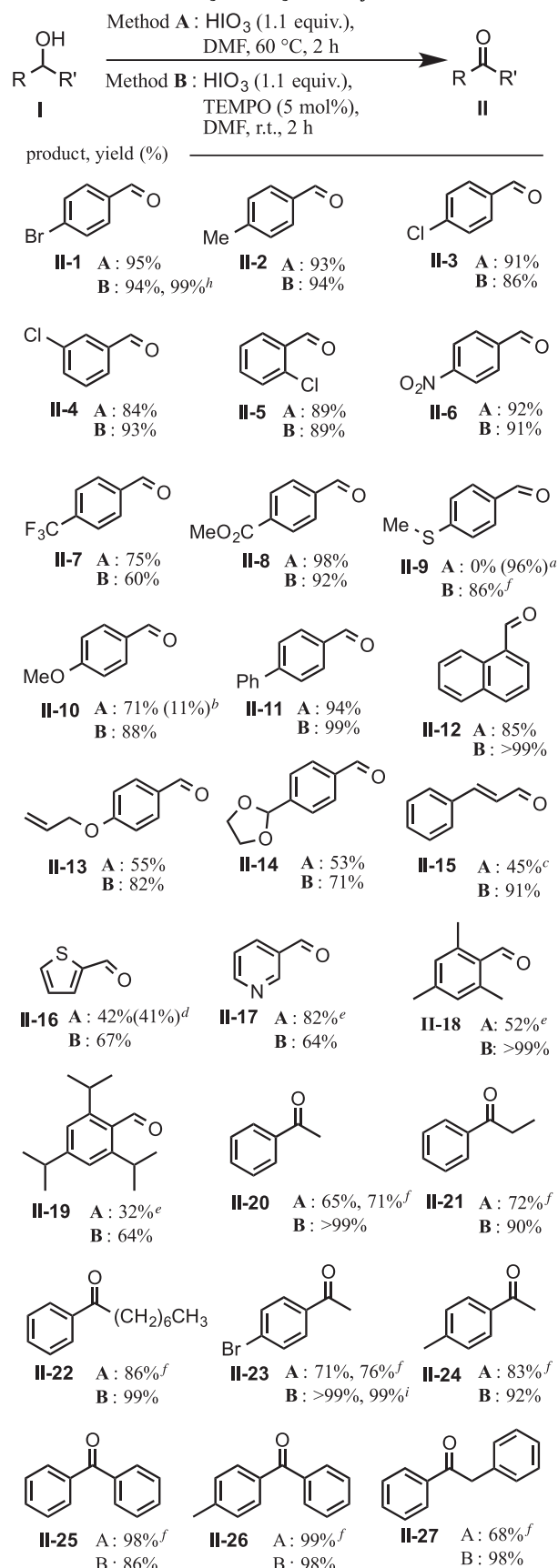
Table 1
Oxidation of 4-bromobenzyl alcohol **I-1** with HIO₃ (Method A)



Entry	Solvent	Temp (°C)	Yield (%)
1	CH ₃ CN	60	22 (70) ^a
2	<i>t</i> -BuOH	60	36 (64) ^a
3	DMF	60	95
4	DMSO	60	95
5	DMF	rt.	12 (81) ^a
6	DMSO	rt.	25 (72) ^a

^a Yield of recovered **I-1**.

Table 2
Oxidation of Alcohols with HIO₃ and HIO₃-TEMPO systems



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