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## Efficient Synthesis of Aromatic Carboxylic Acids from Aryl Ketones in Ionic Liquid

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Abstract: Conversion of aryl ketones to the corresponding aromatic carboxylic acids has been achieved using sequential treatment of HDNIB and urea-hydrogen peroxide in [bmim] $BF_4$  ionic liquid.

Keywords: Carboxylic acids, ionic liquid, ketones, peroxide

The oxidative carbon–carbon cleavage reaction of aryl ketones to aromatic carboxylic acids is a fundamental reaction in organic synthesis. In general, oxidative degradation reactions of aryl ketones are generally conducted in strong acidic or basic conditions. A number of oxidative reagents have been developed for the carbon–carbon cleavage reaction of aryl ketones in acidic systems such as Mn(NO<sub>3</sub>)<sub>2</sub>/Co(NO<sub>3</sub>)<sub>2</sub>,<sup>[11]</sup> Re<sub>2</sub>O<sub>7</sub>/*tert*-butyl hydroperoxide,<sup>[2]</sup> and sodium nitrite/pyridinium poly(hydrogen fluoride).<sup>[3]</sup> The reported reagent systems utilizing basic conditions for the oxidative degradation of aryl ketones include KOH/DMF,<sup>[4]</sup> NaClO/ $\beta$ -cyclodextrin,<sup>[5]</sup> *tert*-BuOK/ 1,3-dinitrobenzene,<sup>[6]</sup> and *tert*-BuOK/sodium percarbonate.<sup>[7]</sup> There are only a few literature methods that are conducted in neutral reaction conditions for the conversion of ketones to the corresponding carboxylic acids. Examples of these methods utilize pentafluoroiodobenzene bis(trifluoroacetate)<sup>[8]</sup> and *N*-bromophthalimide/mercuric(II) acetate.<sup>[9]</sup>

Recently, we have found an efficient route, occurring under neutral conditions, for the oxidation of aryl ketones into the carboxylic acids using initial reaction of aryl ketones with [hydroxy(2,4-dinitrobenzenesulfonyloxy) iodo]benzene (HDNIB) in acetonitrile, followed by the reaction with

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$$Ar \xrightarrow{O} R \xrightarrow{1} HDNIB, [bmim]BF_4, 1 h \xrightarrow{O} Ar \xrightarrow{O} OH$$

$$2) UHP, 2 - 6 h$$

$$HDNIB = Ph \xrightarrow{O} - O-S \xrightarrow{O} - NO_2$$



tetrabutylammonium (meta)periodate in refluxing 1,4-dioxane.<sup>[10]</sup> However, the necessary switching of the reaction solvents during the reaction procedure makes this protocol rather inconvenient for practical applications. Therefore, it would be very desirable to develop the oxidative degradation reactions of aryl ketones occurring under a single solvent in one-pot conditions. We envisioned that a HDNIB/urea-hydrogen peroxide addition compound (UHP) combination in ionic liquid<sup>[11]</sup> could behave in a way similar to the HDNIB/tetrabutylammonium (meta)periodate system. After examination of the usefulness of HDNIB/UHP oxidation system, we have newly found that the sequential treatment of aryl ketones with HDNIB and UHP in 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF<sub>4</sub>, successfully afforded the corresponding aromatic carboxylic acids (Scheme 1). Treatment of  $\alpha$ -[(2,4-dinitrobenzene)sulfonyloxy] ketone intermediates, preformed via the reaction of ketones with HDNIB for 1h at 60°C in [bmim]BF<sub>4</sub> with UHP, afforded the corresponding carboxylic acids in high yields. The results are summarized in Table 1. As shown in Table 1, both aryl methyl ketones and aryl methylene ketones were oxidized equally well

Table 1. Oxidative conversion of aryl ketones to carboxylic acids

Entry	Substrate	Product	Yield $(\%)^a$
1	Acetophenone	Benzoic acid	85
2	4-Methylacetophenone	4-Methylbenzoic acid	78
3	4-Bromoacetophenone	4-Bromobenzoic acid	78
4	4-Chloroacetophenone	4-Chorobenzoic acid	80
5	4-Fluoroacetophenone	4-Fluorobenzoic acid	76
6	4-Nitroacetophenone	4-Nitrobenzoic acid	66
7	Propiophenone	Benzoic acid	80
8	4-Methylpropiophenone	4-Methylbenzoic acid	76
9	4-Bromopropiophenone	4-Bromobenzoic acid	78
10	4-Chloropropiophenone	4-Chlorobenzoic acid	75
11	4-Fluoropropiophenone	4-Fluorobenzoic acid	78
12	Butyrophenone	Benzoic acid	67

<sup>a</sup>Isolated yield.

in high yields. The yields of the carboxylic acids obtained in this study are always superior to the previous results obtained using HDNIB/Bu<sub>4</sub>NIO<sub>4</sub>.<sup>[10]</sup> Replacement of UHP by the Bu<sub>4</sub>NIO<sub>4</sub> at the present reaction conditions gave much lower yields of the carboxylic acids. The use of conventional organic solvents (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN) instead of the [bmim]BF<sub>4</sub> gave the negligible formation of the carboxylic acid at the present reaction conditions. Presumably, the oxidative cleavage reactions occurred via well-known  $\alpha$ -hydoxyperoxo ketones formed by the reaction of  $\alpha$ -[(2,4-dinitrobenzene)sulfonyloxy] ketone intermediates with UHP.<sup>[1]</sup>

In summary, we have developed a new and efficient method for the oxidative degradation reaction of aryl ketones to the corresponding aromatic carboxylic acids by the treatment with HDNIB and UHP in  $[bmim]BF_4$  ionic liquid.

#### **EXPERIMENTAL**

The 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF<sub>4</sub>) was obtained from Fluka. The HDNIB was prepared by following the method presented in the literature.<sup>[10]</sup>

# General Procedure for Oxidative Cleavage Reaction of Aryl Ketones

HDNIB (0.562 g, 1.2 mmol) was added to a solution of ketones (1.0 mmol) in [bmim]BF<sub>4</sub> (1 mL). The mixture was stirred for 1 h at 60°C. UHP (0.141 g, 1.5 mmol) was added to the solution, and the reaction continued for an additional 2–6 h. After completion of the reaction, the product was extracted with diethyl ether (30 mL) and washed with aqueous 10% sodium carbonate solution (2 × 20 mL). The aqueous layer was neutralized with dilute hydrogen chloride, and the product was extracted with diethyl ether (2 × 25 mL). The organic layer was dried over sodium sulfate and evaporated to give the desired carboxylic acid.

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