Asian Journal of Chemistry Vol. 21, No. 2 (2009), 949-952

Simple Oxidation of Benzylic Halides with 1-Butyl-3-methyl Imidazolium Periodate

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Radical halogenation at the benzylic position, followed by the oxidation of the resulting halide is one of the most practical methods leading to the formation of desired carbonyl compounds. Thus, an efficient method for this oxidation conversion with the help of ionic liquid. A variety of benzyl halides with different substituent were converted to the corresponding aldehydes by 1-butyl-3-methyl imidazolium periodate at room temperature in high yields.

Key Words: Oxidation, 1-Butyl-3-methyl imidazolium periodate, Benzylic halides.

INTRODUCTION

Selective oxidation of the benzylic and allylic positions of arenes and alkenes to the corresponding carbonyl compounds is an important task especially in the synthesis of bioactive and medicinally significant compounds[1-3]. Radical halogenation at the benzylic and allylic positions, followed by the oxidation of the resulting halides is one of the most practical methods leading to the desired carbonyl compounds. The oldest method for such a conversion constitutes the Hass-Bender reaction, which involves O-alkylation of the nitronate anion followed by decomposition of the resulting intermediate[4]. The Sommelet reaction is another well-known reaction to effect this transformation and involves the use of hexamethylenetetramine to afford the formaldehyde imine derivative of the primary amine, which tautomerizes to the methyl imine of the desired carbonyl compound. While the former method requires a strong base, the latter has limited substrate scope[5].

Several methods have been developed to carry out this conversion such as the Krohnke reaction (pyridine followed by *p*-nitrosodimethylaniline)[6], the Kornblum reaction (DMSO/$NaHCO_3$)[7] and a number of its variants[8], the use of N-alkoxypyridinium salts[9], potassium chromate[10], $NaIO_4$–DMF[11], oxodiperoxovanadate[12], *etc*[13-15]. All of these procedures, however, are invariably associated with certain limitations in terms of acid/base conditions, long reaction times, poor yields, substrate scope, high temperature, *etc*.

In continuation of our recent studies with the help of ionic liquids, we explored the possibility of conversion of halides to the corresponding carbonyl compounds in a simple fashion. Herein, we report that 1-butyl-3-methyl imidazolium periodate can be conveniently utilized to accomplish the conversion of benzylic halides to the corresponding aldehydes/ketones in better yields under mild reaction conditions.

EXPERIMENTAL

The isolated products were identified by comparison of their physical and spectral data with those of authentic samples. IR spectra were recorded on a BOMEM FT-IR spectrometer and ^{1}H NMR spectra were obtained with a 400 MHz Bruker spectrometer. Melting points were uncorrected. The purity of products and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica gel PolyGram SILG/UV 254 plates. All the reagents and solvents used were of AR grade.

Preparation of 1-butyl 3-methyl imidazolium periodate: In a typical reaction, 1-bromobutane (0.23 mol) and 1-methylimidazole (0.25 mol) was placed in a beaker, mixed thoroughly and the mixture was heated intermittently in an unmodified household microwave oven (butane-1500 W) at 30 % power (30 s irradiation with 30 s mixing) until a clear single phase was obtained. The bulk temperature was *ca.* 100 °C. The resulting ionic liquid was then cooled, washed with ether (3 × 2 mL) to remove unreacted starting materials and the product was dried under vacuum at 80 °C to afford 1-butyl-3-methyl imidazolium periodate.

Equimolar sodium periodate was added to 1-butyl-3-methylimidazolium bromide and heated in an unmodified microwave (butane-1500 W) at 30 % power (15 s irradiation with 30 s mixing for max. 2 min). The yellow solid precipitate (NaBr and excess sodium periodate) was filtered off. The resultant orange 1-butyl-3-methyl imidazolium periodate was dissolved in dichloromethane to precipitate a small quantity of impurities, which was filtered off and the filtrate evaporated to dryness.

Oxidation of benzylic halides with 1-butyl 3-methyl imidazolium periodate: In a typical experiment, 1-2 mmol of the benzyl halide and 1.5-2.0 equiv of 1-butyl-3-methyl imidazolium periodate were stirred at room temperature. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the product was decanted and purified by TLC (10 % ethyl acetate in petroleum ether). The resulting aldehyde was identified by its boiling point, IR and ^{1}H NMR spectroscopic properties.

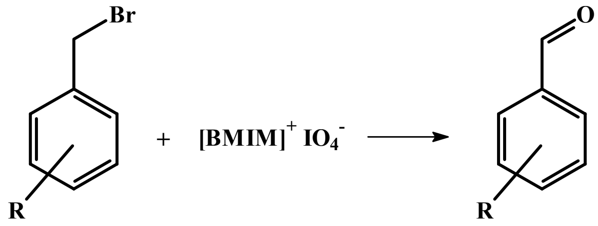
RESULTS AND DISCUSSION

The oxidation of organic halides to the corresponding aldehydes or ketones is a useful synthetic transformation which, in many cases, affords more convenient access to the carbonyl compound than the oxidation of the corresponding alcohol.

It was found that as compared to those observed in conventional oxidation, incorporating the oxidant ionic liquid would enhance reactivity and can oxidize even the aryl chloride in the absence of any catalyst and thereby lead to a methodology under mild conditions. It was reported before that benzyl chloride react only sluggishly leading to low yields products and in the case of oxidation by H_2O_2/ethanol no desired product was obtained.

Moreover, the high polarity of the ionic liquids permit to be used as the reaction medium for oxidation of a wide range of substrates, especially those highly polar ones, which are sparingly soluble in common organic solvents. The other advantage was related to fast, facile and observable preparation of the product phase that could be easily decantable.

According to the reaction (**Scheme-I**) only 1 equiv of oxidant is sufficient for the oxidation of benzyl halides under the reaction conditions. Further oxidation of benzaldehyde derivatives were not observed.



Scheme-I: Oxidation of benzylic halides with 1-butyl 3-methyl imidazolium periodate

To maximize the yields, the reaction conditions were optimized with *p*-chloro benzyl chloride as a representative case. The same reaction conditions, however, works satisfactorily for a broad range of benzyl halides. In summary, we have shown that 1-butyl-3-methyl imidazolium periodate can be conveniently employed as an oxidant/solvent for the conversion of benzyl halides to the corresponding carbonyl compounds even in the case of aryl chloride without the need of KBr or other catalyst in corresponding isolated yields (Table-1). Enhanced reaction rates, high conversions and simple product separation are the notable features observed in ionic liquids. On the other hand the use of an easily accessible and recyclable ionic liquids makes this procedure quite simple, more convenient and environmentally benign.

TABLE-1
YIELDS AND CONDITIONS FOR THE OXIDATION OF THE BENZYLIC HALIDES TO THE CORRESPONDING ALDEHYDES BY 1-BUTYL-3-METHYL IMIDAZOLIUM PERIODATE

Substrate	Time (min)	Yield (%)
2-Chlorobenzylchloride	6.0	95
2-Chlorobenzylbromide	3.0	96
2-Hydroxybenzylchloride	4.0	95
2-Hydroxybenzylbromide	2.0	96
4-Nitrobenzylchloride	0.5	94
2-Methoxybenzylchloride	3.0	96
4-Methoxybenzylchloride	2.0	94
4-Chlorobenzylchloride	5.0	95
4-Chlorobenzylbromide	3.0	96

ACKNOWLEDGEMENTS

The authors appreciate Prof. Nahid Pourreza for reviewing the paper and also gratefully acknowledge financial support of this research by Shahid Chamran (Ahvaz) University, Iran.

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(*Received*: 20 October 2007; *Accepted*: 13 September 2008) AJC-6858