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Methyltrioxorhenium and Sodium Bromide-Catalyzed Oxidation of Alcohols to Carbonyl Compounds with H_2O_2 Using 1-Butyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid as a Novel Recyclable Green Solvent

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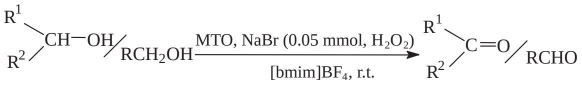
A variety of primary and secondary alcohols have been oxidized to the corresponding aldehydes and ketones in excellent yields with aqueous 30% hydrogen peroxide by using methyltrioxorhenium and sodium bromide as a catalyst system and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[bmim]BF_4$) as a recyclable green solvent.

The development of new synthetic methodologies using room temperature ionic liquids as environment friendly recyclable solvents has received considerable interest in recent years due to their unique properties like non-volatile nature, good solvating capability, high stability in air/moisture, negligible vapor pressure and ability to dissolve a wide range of organic and inorganic compounds.[1] Furthermore, their hydrophobicity/hydrophilicity can be easily altered by the modification of the cation and anion. Room temperature ionic liquids have been widely used as solvents in various organic reactions such as hydrogenation,[2] hydroformylation,[3] carbon–carbon bond forming,[4] Diels–Alder,[5] Heck,[6] Friedel–Crafts reactions,[7] and oligomerization.[8] However, there are only a few reports on the use of ionic liquids as solvents in the catalytic oxidation reactions of organic compounds.[9]

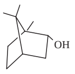
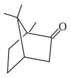
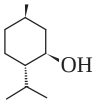
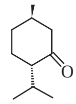
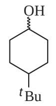
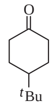
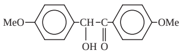
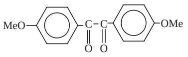
The oxidation of alcohols to carbonyl compounds is an important synthetic transformation both from fundamental and academic points of view.[10] Apart from the use of various conventional oxidants like $KMnO_4$, MnO_2, CrO_3, SeO_2, which produce copious amounts of undesirable wastes, a variety of effective catalytic methods using molecular oxygen/hydrogen peroxide as enviro-economic oxidants with transition-metal-based catalysts have been reported in the literature for this transformation.[11] The reported catalytic oxidation methods for the oxidation of alcohols to carbonyl compounds employ volatile organic compounds (VOCs) like aromatic and halogenated hydrocarbons as solvents, which are not only toxic and/or hazardous but also contribute to serious environmental problems. Ionic liquids due to their inherent properties, such as non-volatile nature, high thermal stability, high solvating ability towards a range of organic and inorganic compounds, ease of recovery and recyclability, have proven to be excellent reaction media in organic synthesis.[12] In this context various oxidation reactions, such as epoxidation of alkenes,[13] oxidation of aromatic aldehydes,[14] and Baeyer–Villiger oxidation,[15] have been reported in the literature using MTO–H_2O_2 system in ionic liquids. We, herein, report for the first time the use of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[bmim]BF_4$) as an efficient, recyclable green solvent for the oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones with aqueous 30% hydrogen peroxide using a methyltrioxorhenium (MTO) and NaBr catalytic system (Scheme 1).

A variety of primary and secondary alcohols were selectively oxidized to the corresponding aldehydes and ketones using the MTO and NaBr catalytic system with aq 30% hydrogen peroxide in $[bmim]BF_4$ at room temperature. The results are summarized in Table 1. Among the various alcohols studied, benzoins were found to be most reactive and required shorter reaction times for oxidation. Furthermore, aromatic substituted secondary alcohols were found to be more reactive as compared to the aliphatic/alicyclic alcohols. In the case of primary alcohols, aliphatic alcohols were found to be less reactive than benzylic alcohols and gave poor yields of the corresponding



Scheme 1.

Table 1. Oxidation of Alcohols to Aldehydes and Ketones[a)]

Entry	Substrate	Product	Reaction time/h	Yield /%[b)]
1	Ph_2CHOH	Ph_2CO	3.5	95
2	PhCH(OH)Me	PhCOMe	4.0	92
3	Cyclohexanol	Cyclohexanone	3.0	80
4			5.0	72
5			5.5	70
6			3.0	85
7	Cyclopentanone	Cyclopentanone	6.0	70
8	$PhCH_2OH$	PhCHO	3.5	65
9	p-$Me(C_6H_4)CH_2OH$	p-$Me(C_6H_4)CHO$	3.5	75
10	PhCH(OH)COPh	PhCOCOPh	1.5	96
11			1.5	95
12	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CHO$	6.0	55[c)]

a) Reaction conditions: alcohol (1 mmol), 30% H_2O_2 (2 mmol), MTO (0.01 mmol), NaBr (0.05 mmol) in $[bmim]BF_4$ (1 mL) at room temperature under atmospheric pressure. b) Isolated yields. c) The conversion of n-butanol to n-butanal was estimated by GC.

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Table 2. Effect of Various Solvents on the Oxidation of Benzhydrol

Entry	Solvent	Reaction time/h	Yield/%[a)]
1	Acetonitrile	6.5	80
2	1,2-Dichloroethane	10	50
3	Dichloromethane	10	40
4	[bmim]BF_4	3.5	95
5	Neat	5.0	55

a) Isolated yields.

aldehydes. The effect of bromide was also explored for this reaction using benzhydrol as the substrate. The oxidation of benzhydrol (1 mmol) when carried out with aq 30% hydrogen peroxide (2 mmol) in presence of catalytic amount of methyltrioxorhenium (MTO, 0.01 mmol) in [bmim]BF_4 at room temperature gave only 20% yield of the benzophenone after 10 h. However, the same amount of benzophenone was produced within 3.5 h in the presence of a catalytic amount of bromide. The use of chloride (NaCl) as a co-catalyst in place of the bromide afforded a poor yield of the benzophenone and required longer reaction time for the oxidation. The oxidized product was separated from the reaction mixture by simple extraction with diethyl ether, and the ionic liquid was used as such for subsequent experiments after adding fresh substrate and oxidant (aqueous 30% H_2O_2) under similar reaction conditions. The benzophenone was isolated in the same yield without further addition of either CH_3ReO_3 or sodium bromide. The catalysis could be repeated up to three times, indicating the reusability and recyclability of both the catalyst and ionic liquid.

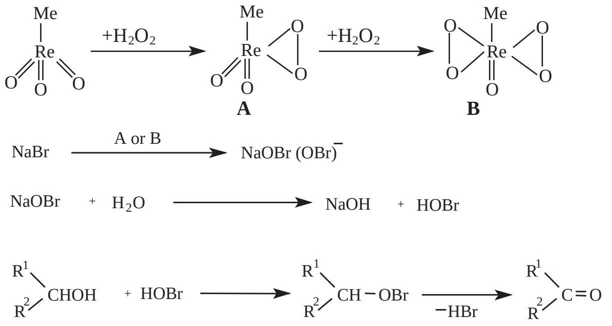
The oxidation of benzhydrol using acetonitrile, dichloroethane, dichloromethane, and the ionic liquid as solvent was studied to evaluate their relative efficiencies, and the results are summarized in Table 2. Among the different solvents studied, [bmim]BF_4 was found to be the best both in terms of shorter reaction time and better yield of the product. The effect of temperature was also examined for the oxidation of benzhydrol by carrying out the oxidation at 80 °C under similar reaction conditions. The temperature showed only marginal effects upon the rate of reaction.

The exact mechanism of this reaction is not clear at this stage; however, it probably involves the formation of the peroxorhenium species A and B by the reaction of MTO with hydrogen peroxide, which in turn converts the bromide in to hypobromite.[16] The reaction of sodium hypobromite with water gives hypobromous acid,[17] which then subsequently reacts with alcohol to afford a hypobromite species[18] followed by abstraction of hydrogen to afford the corresponding ketone (Scheme 2).

Experimental

All of the alcohols were commercially available and used without further purification. Methyltrioxorhenium and the ionic liquid [bmim]BF_4 was purchased from Aldrich and use as purchased.

Typical Experimental Procedure. To a stirred mixture of benzhydrol (1.0 mmol, 0.18 g), aq 30% hydrogen peroxide (2.0 mmol, 0.22 mL) and sodium bromide (5.0 mol %, 0.050 mmol, 5.2 mg) in [bmim]BF_4 (1 mL) was added MTO (1.0 mol %, 0.010 mmol, 0.025 g) at room temperature. The progress of the reaction was monitored by TLC (SiO_2). After completion, the reaction mixture was extracted with diethyl ether. The ether layer was washed with water (two times) and dried over anhydrous $MgSO_4$. Evaporation of the ether gave a crude mixture, which was purified by column chromatography (hexane:ethyl acetate = 9:1). The solvent was evaporated under reduced pressure to afford pure benzophenone (95%, 0.17 g). Other alcohols were similarly oxidized and their reaction times and yields are summarized in Table 1.



Scheme 2.

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