CHAPTER I

N-BROMOSUCCINIMIDE (NBS) IN IONIC LIQUID:
A GREEN SYSTEM FOR RAPID OXIDATION OF 1,2-DIOLS,
α-HYDROXYKETONES AND ALCOHOLS

I.1: INTRODUCTION

I.1.1: Ionic Liquids

Ionic liquid is the name given to a liquid that consists only of ions and is different from a molten salt in a way that molten salt is generally referred to a high melting, highly viscous and corrosive medium whereas ionic liquids are already liquids at low temperatures (<100°C) and have relatively low viscosity. The first reported ionic liquid was ethyl ammonium nitrate which is a liquid at room temperature [m.p. 12°C].

The application of ionic liquids (ILs) as a new reaction media and catalyst for organic synthesis appeared at the end of 1980s. Acidic ionic liquids with chloroaluminate ions were used for the Friedel-Crafts catalysis and phosphonium halide melts were used successfully in nucleophilic aromatic substitution reactions. Their first application as the solvent for biphasic catalysis was reported by Chauvin et al. for the dimerization of propene by nickel complexes dissolved in acidic chloroaluminate melts. The concept of ionic liquids received a substantial boost when synthesis of a series of air and moisture stable imidazolium salts based on anions such as [BF_4]^- and [PF_6]^- was reported in 1992. Since then, there has been significant expansion in the variety of ionic liquids reported. The utility of ionic liquids has been exercised not only within the field of biphasic catalysis and organic synthesis, but also covers diverse applications such as separations, electrochemistry and photochemistry. A brief review on ionic liquids is presented below:

Composition of Ionic Liquids

The most commonly used cations in ionic liquids are alkylammonium, alkylphosphonium, N,N'-dialkylimidazolium, and N-alkylpyridinium cations. The most commonly utilized alkyl chains are methyl, ethyl, butyl, hexyl, octyl and decyl. The most commonly investigated IL cations and anions are shown in Figure I.1.
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Cations

<table>
<thead>
<tr>
<th>Imidazolium</th>
<th>Pyridinium</th>
<th>Pyrazolium</th>
<th>Ammonium</th>
<th>Phosphonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^1-N\equiv N\equiv R^2$</td>
<td>$N\equiv R^1$</td>
<td>$R^1-N\equiv R^2$</td>
<td>$R^1$</td>
<td>$R^1$</td>
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<tr>
<td>$R^1, R^2 = \text{alkyl}$</td>
<td>$R^1 = \text{alkyl}$</td>
<td>$R^1, R^2 = \text{alkyl}$</td>
<td>$R^1, R^2, R^3, R^4 = \text{alkyl}$</td>
<td>$R^1, R^2, R^3, R^4 = \text{alkyl}$</td>
</tr>
</tbody>
</table>

Anions

$\text{Cl}^-, \text{Br}^-, \Gamma, \text{Al}_2\text{Cl}_7^-, \text{NO}_3^-, \text{HSO}_4^-, \text{PO}_4^{3-}, \text{CB}_{11}\text{H}_{12}^-, (\text{MeO})_2\text{PO}_2^-, (\text{CF}_3\text{CF}_2)_3\text{PF}_3^-, \text{SO}_4^{2-}, \text{ClO}_4^-$

$\text{PF}_6^-, \text{BF}_4^-, \text{SbF}_6^-, \text{CF}_3\text{SO}_3^-, \text{CF}_3\text{COO}^-, \text{N(CN)}_2^-, (\text{CF}_3\text{SO}_2)_2\text{N}^-$

Figure I.1

Properties of Ionic Liquids

Melting Point and Vapour Pressure: The key criterion for the evaluation of an ionic liquid is, by definition its melting point. The melting points are influenced both by cations and anions. The interest for ILs has been centered on their possible use as "green" alternatives to volatile organic solvents, mainly because ILs are considered as non-volatile and consequently non-flammable at ambient and higher temperatures. ILs have no vapour pressure. This is a great advantage from a process engineering viewpoint, since separation by distillation of a reaction mixture becomes more effective as a method of product isolation. The well known problem of azeotrope formation between the solvent and the product does not arise.

Solubility in Water: The solubility of ILs in water is an important factor for the industrial application of these solvents. The solubility of ILs in water depends on the nature of anion, temperature and the length of alkyl chains. For the [bmim] cation, the anions like $[\text{BF}_4^-], [\text{CF}_3\text{COO}]^-, [\text{NO}_3^-], [\text{NMs}_2^-]$ and halide salts display complete miscibility with water at 25°C. However, upon cooling the [bmim]$\text{BF}_4$ aqueous solution to 4°C, a water rich phase separates out. Butylmethyl imidazolium [bmim] based ILs of other anions such as $[\text{PF}_6^-], [\text{SbF}_6^-]$ and $[\text{Tf}_2\text{N}]^-$ show low solubilities in water.\textsuperscript{9-12}

Density and Viscosity: The density of a material depends on how closely the ions can pack together and, hence on the size and shape of the ions and ion-ion interactions. A
considerable amount of data on the density of ILs is available in the literature.\textsuperscript{13} ILs are generally denser than either organic solvents or water, with typical density values ranging from 1.0 to 1.6 g cm\textsuperscript{-3}. The viscosity is dependent on the ion-ion interactions, such as Van der Waals interactions and hydrogen bonding, with greater interactions leading to higher viscosities. The viscosity of many ILs is generally one to three orders of magnitude higher compared to conventional solvents.

\textbf{Environmental Aspects:} Ionic liquids have often been discussed as promising solvents for “clean processes” and “green chemistry”\textsuperscript{14}. Ionic liquids have no measurable vapour pressure and so there is no loss of solvent through evaporation unlike the volatile organic solvents. With respect to the efforts to reduce catalyst consumption, two aspects of ionic liquids are important. Firstly, the special solubility characteristics of an ionic reaction medium enable a biphasic reaction procedure in many cases. Exploitation of the miscibility gap between the ionic catalyst phase and the products allows the catalyst to be isolated effectively from the product and be reused many times. Secondly, the non-volatile nature of ionic liquids enables more effective product isolation by distillation.

\textbf{Synthesis of Ionic Liquid}

Ionic liquids can be synthesized by quaternization of an amine or phosphane.\textsuperscript{15-16} In cases where quaternization to form the desired ion is not possible, it can be achieved by treatment with some Lewis acid M\textsubscript{X}\textsubscript{n} or by anion exchange. Synthesis of ILs using non conventional activation method (microwaves or ultrasounds) has also been described.\textsuperscript{17} However, ILs can decompose under sonochemical conditions.\textsuperscript{18}

\textbf{Ionic Liquids as Reaction Media}

\textbf{(A) Transition metal catalyzed reactions in ionic liquids}

Ionic liquids are able to dissolve organometallic compounds and therefore can be used as possible solvents for reactions involving homogeneous catalysts. The use of ionic liquids often allows a combination of solvent properties like water or common organic solvents. Some of the transition metal catalyzed reactions are discussed below:
(i) **Suzuki coupling:** Suzuki cross coupling of aryl halides with phenyl boronic acids in presence of palladium-bis(carbene)complex in [bmim]BF$_4$ has been reported under ultrasonic irradiation (eq. 1).\(^{19}\)

\[
\begin{align*}
&\text{Ph}^+ \text{X} \quad + \quad \text{Ph}^+ \text{B(OH)}_2 \\
&\text{Pd(PPh}_3)_4 \quad \text{[bmim]BF}_4, \text{Na}_2\text{CO}_3 \\
&\text{Ph}^+ \text{R}^1
\end{align*}
\]

(ii) **Stille Coupling:** Stille coupling is used for the preparation of polyarenes, diaryl and aromatic carbonyl compounds. Stille coupling reactions with Pd(0) and Pd(II) catalyst precursors have been reported in [bmim]BF$_4$ (eq. 2).\(^{20}\)

\[
\begin{align*}
&\text{O} \quad + \quad \text{RSn(Bu)}_3 \\
&\text{Pd(II)/CuI/Ph}_3\text{PAs} \quad \text{[bmim]BF}_4 \\
&\text{O} \quad \text{R}
\end{align*}
\]

(iii) **Hydrogenation:** de Souza *et al.* have reported rhodium catalyzed hydrogenation of cyclohexene in [bmim]BF$_4$.\(^{21}\) Hydrogenation of 1-pentene by “Osborn complex” [Rh(nbd)(PPh$_3$_2)]PF$_6$ (nbd = norbornadiene) as catalyst in ionic liquids has been reported (eq. 3).\(^{22}\)

\[
\begin{align*}
&\text{H}_2, \quad \text{[Rh(nbd)(PPh}_3)_2] \\
&\text{[bmim]A, A = BF}_4^-, \text{PF}_6^-, \text{SbF}_6^- \\
&\text{H}_2
\end{align*}
\]

Rhodium and cobalt catalyzed hydrogenation of butadiene and 1-hexene\(^{23}\) and Ru-catalyzed hydrogenation of aromatic compounds\(^{24}\) and acrylonitrile-butadiene copolymers\(^{25}\) have also been reported to be successful in ionic liquids.

(iv) **Hydroformylations:** The hydroformylation of 1-hexene to heptanal using Rh(OAc)$_4$ and PPh$_3$ as catalyst in phosphonium tosylate as ionic liquid has been described.\(^{26}\) The platinum catalyzed hydroformylation of 1-octene in [bmim]Cl/SnCl$_4$ has been reported to give high \textit{n-/iso-} selectivities (eq. 4).\(^{27}\)

\[
\begin{align*}
&\text{CHO} \\
&\text{CO/H}_2[\text{PtCl}_2(\text{PPh}_3)_2] \quad \text{[bmim]Cl/SnCl}_2 \\
&\text{CHO} \quad (>95\%) \\
&\text{CHO}
\end{align*}
\]
(v) Alkoxycarbonylation: Palladium catalyzed alkoxycarbonylation of aryl halides has been carried out in [bmim]BF₄ and [bmim]PF₆ (eq. 5).

\[
\text{Br} + \text{CO} + \text{ROH} + \text{NEt}_3 \xrightarrow{\text{Pd(II)/PPh_3}} \text{OR} + [\text{HNEt}_3]\text{Br} 
\]

(B) Other Organic Reactions in Ionic Liquids

Ionic liquids have been used in a number of other synthetic organic transformations, some of which are discussed below briefly.

Welton et al. and Seddon et al. reported that ionic liquids such as [bmim]BF₄, [bmim]ClO₄, [emim]CF₃SO₃ and [emim]PF₆ are effective solvents for Diels-Alder reaction between cyclopentadiene and methyl acrylate. Reactions in these ionic liquids showed significant strong endo selectivities (eq. 6).

\[
\text{C} + \text{CH}_2=\text{CHCOOMe} \xrightarrow{\text{Ionic Liquid}} \text{COOMe} + \text{COOMe} 
\]

The self-condensation of propanal to form 2-methylpent-2-enal has been carried out in non-coordinating imidazolium ionic liquids. The reaction proceeded through an aldol intermediate. The highest selectivity was observed in [bmim]PF₆. S-Proline catalyzed asymmetric direct aldol reaction of aromatic aldehydes with acetone and other ketones in ionic liquid [bmim]PF₆ gave good yields of aldol products with reasonable enantioselectivities even when 1-5 mol% of S-proline was used as a catalyst (eq. 7).

\[
\text{X-} + \text{H}+ \xrightarrow{\text{S-Proline, acetone}} \text{X-} + \text{COOMe} 
\]

Michael addition of acetylacetone to methyl vinyl ketone has been described by Nobile et al. in [bmim]BF₄ in presence of Ni(acac)₂ (eq. 8).
A number of other reactions like Friedel-Crafts reaction,\textsuperscript{34} Wittig reaction,\textsuperscript{35} Baylis-Hillman reaction\textsuperscript{36} and olefin metathesis\textsuperscript{37} have been successfully carried out in ionic liquids.

Epoxidation of olefins and allylic alcohols with UHP (urea hydrogen peroxide) in presence of methyltrioxorhenium (MTO) as catalyst has been reported in [bmim]PF\textsubscript{6}.\textsuperscript{38} Epoxidation of olefins with NaOCl using Jacobsen’s chiral Mn(III) salen complex immobilised on [bmim]PF\textsubscript{6} proved to be an efficient and recyclable method (eq. 9).\textsuperscript{39}

\[
\text{NC} \quad \text{Mn(salen), NaOCl} \quad \text{[bmim]PF}_6/\text{CH}_2\text{Cl}_2
\]

Yadav \textit{et al.} have reported the oxidation of alcohols to the corresponding carbonyl compounds (eq. 10) using hypervalent iodine reagents in ionic liquids.\textsuperscript{40} They have also reported conversion of olefins to halohydrins using $N$-halosuccinimides in [bmim]BF\textsubscript{4}-H\textsubscript{2}O (eq. 11),\textsuperscript{41} $\alpha$-halogenation of $\beta$-dicarbonyl compounds and cyclic ketones using $N$-halosuccinimides in ionic liquids (eq. 12)\textsuperscript{42} and synthesis of thiiranes from epoxides in [bmim]PF\textsubscript{6}-H\textsubscript{2}O (2:1, v/v) at room temperature (eq. 13).\textsuperscript{43}
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A large number of other reactions have been reported in ionic liquids.

I.1.2: Reactions of N-bromosuccinimide

N-Bromosuccinimide (NBS)\textsuperscript{44} is a versatile reagent in organic synthesis. A large number of organic transformations have been reported with this reagent. The reagent is a convenient source of bromine for both radical substitution and electrophilic addition reactions. The first application of this reagent for allylic bromination of alkenes was reported by Wohl (eq. 14).\textsuperscript{45a} It is a free radical substitution catalyzed by dibenzoyl peroxide or irradiation with visible light or both to effect initiation. The general mechanism of this Wohl-Ziegler reaction\textsuperscript{45} is given in Scheme I.1.

\[ \text{CH}_2\text{CH}=\text{CH}_2 + \text{Br}^- \rightarrow \text{CH}--\text{CH}--\text{CH}_2 + \text{HBr} \]

The formation of HBr is the result of a side reaction and the formation of Br\textsubscript{2} is the fast ionic reaction between NBS and HBr. High level of regioselectivity operates during the hydrogen-abstraction step of the chain mechanism, such that allylic methylene groups are attacked much more rapidly than allylic methyl groups (eqs. 15, 16).\textsuperscript{46}
Bromination of $\alpha,\beta$-unsaturated esters (eq. 17)\textsuperscript{47} and lactones (eqs. 18-20)\textsuperscript{48-50} using NBS, has been achieved in high yields.

Benzylic bromination is one of the most extensively studied reaction of NBS (eq. 21).\textsuperscript{51-53}

Hauser and Prasanna\textsuperscript{54} have reported the oxidative aromatization of polycyclic compounds including steroids and anthraquinone precursors (eq. 22). Phenols, anilines and other electron rich aromatic compounds can be mono-brominated with NBS in dimethylformamide in high yields and with high para selectivity (eq. 23).\textsuperscript{55} Bromination of quinoline, isoquinoline, quinazoline and quinoxaline could be achieved in presence of a strong acid (eq. 24).\textsuperscript{56}
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Carreno and co-workers\textsuperscript{57} have reported NBS as a mild and regiospecific nuclear brominating reagent for methoxybenzenes, naphthalenes, phenols, naphthols and activated pyridines in acetonitrile.

Oxidation of aldehydes and hydrazines to acid bromides and azo compounds respectively (eqs. 25, 26)\textsuperscript{58,59} has been reported with NBS. Regeneration of carbonyl compounds from tosyl hydrazones (eq. 27)\textsuperscript{60} has also been reported.

NBS has been used for oxidative cleavage and oxidation reactions in different media. Aliphatic $\alpha$-hydroxy acids undergo reaction with NBS in water to give aldehydes or ketones with loss of one carbon atom (eq. 28).\textsuperscript{61}

\[
\text{RR}^1\text{C(OH)COOH} + 2 \text{NBS} \xrightarrow{\text{H}_2\text{O}} \text{RR}^1\text{CO}
\]

$\text{R}^1 = \text{H, Alkyl}$
Oxidative degradation of phenyl acetic acid to benzaldehyde, polycarboxylic acids to aldehydes or ketones and citric acid to acetone with NBS have also been reported.\(^6\)

NBS is reported to bring about bond scission in tertiary amines with the formation of aldehydes and secondary amines in good yields (eq. 29).\(^6\) The results suggest that a methyl or methylene group attached to nitrogen is required and N-CH\(_2\) linkage is cleaved preferentially under these conditions. This carbon-nitrogen cleavage also occurs in \(\alpha\)-aminoacids to give aldehydes\(^6\) (eq. 30), while \(\beta\)-amino acids give acids with loss of two carbon atoms (eq. 31).\(^6\)

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{CH}_2)_3\text{N} & \xrightarrow{\text{NBS, Dioxane-H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} + (\text{C}_6\text{H}_5\text{CH}_2)_2\text{NH} \\
\text{NH}_2 & \xrightarrow{\text{NBS, H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} \\
\text{NH}_2 & \xrightarrow{\text{NBS, H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} \\
\text{NH}_2 & \xrightarrow{\text{i) KOH, ii) HCl}} \text{C}_6\text{H}_5\text{COOH}
\end{align*}
\]

Benzyl ethers react with NBS to give favorable yields of the corresponding benzaldehydes (eq. 32).\(^6\) Oxidation of sulfides to sulfoxides has also been reported with NBS in either aqueous medium or in methanol (eq. 33).\(^6\)

\[
\begin{align*}
\text{RC}_6\text{H}_4\text{CHCH}_2\text{COOH} & \xrightarrow{\text{NBS, H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} \\
\text{NH}_2 & \xrightarrow{\text{NBS, H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} \\
\text{NH}_2 & \xrightarrow{\text{NBS, H}_2\text{O}} \text{C}_6\text{H}_5\text{CHO} \\
\text{NH}_2 & \xrightarrow{\text{i) KOH, ii) HCl}} \text{C}_6\text{H}_5\text{COOH}
\end{align*}
\]

The conversion of olefins to \(\alpha\)-bromohydrins and subsequent dehydrohalogenation to epoxides is an excellent method for indirect epoxidation (eq. 34).\(^6\) Reactions with polyalkenic compounds have also been reported.\(^6\)

\[
\begin{align*}
\text{C} & \xrightarrow{\text{NBS, aq. DMF/THF}} \text{OH} \\
\text{I} & \xrightarrow{\text{Br}} \text{O} \\
\text{Ph} & \xrightarrow{\text{NBS, 5-10°C, MeOH}} \text{Ph}
\end{align*}
\]
Khurana et al.\textsuperscript{71a} have reported a simple procedure for the synthesis of benzils and aliphatic 1,2-diketones of cyclic and open chain compounds from the corresponding hydrobenzoins and 1,2-diols by refluxing with NBS in CCl\textsubscript{4} in the presence or absence of pyridine (eq. 35). They have also reported microwave accelerated oxidation of hydrobenzoins, benzoins and alcohols with NBS adsorbed on neutral alumina.\textsuperscript{71b}

\[
\begin{align*}
\text{R}^1\text{CHCHR}^2 & \xrightarrow{\text{NBS, CCl}_4, \text{Pyridine, Reflux}} \text{R}^1\text{C}==\text{C}R^2 \\
\text{R}^1, \text{R}^2 = \text{Aryl, Alkyl}
\end{align*}
\]

Ionic liquid promoted regioselective monobromination of aromatic substrates (eq. 36)\textsuperscript{72} and \(\alpha\)-monohalogenation of 1,3-diketones, \(\beta\)-ketoesters and cyclic ketones (eq. 37)\textsuperscript{73} with NBS has been reported in excellent yields in the absence of a catalyst. The ionic liquid could be recycled with consistent activity.

\[
\begin{align*}
\text{ArH} + \text{N-Br} & \xrightarrow{[\text{bimim}]\text{BF}_4, 28^\circ C} \text{H-N} + \text{ArBr} \\
\text{R}^1\text{C}==\text{C}R^2 + \text{N-Br} & \xrightarrow{[\text{bimim}]\text{PF}_6, \text{r.t.}} \text{R}^1\text{C}==\text{C}Br + \text{N-H} \\
\text{ArCHO} + \text{RNH}_2 + \text{HPO(OEt)}_2 & \xrightarrow{\text{NBS, Solvent-free}} \text{NHR} \circlearrowleft \text{OEt} \circlearrowleft \text{OEt}
\end{align*}
\]

Three component reactions of aldehydes, amines and diethyl phosphite catalyzed by NBS leading to the corresponding \(\alpha\)-aminophosphonates under solvent-free conditions have been reported by Wu et al. (eq. 38).\textsuperscript{74}

A novel procedure for the synthesis of 14-aryl-14\(H\)-dibenzo[\(a,j\)]xanthenes through one pot condensation of 2-naphthol with aromatic aldehydes in presence of NBS as catalyst under solvent-free conditions (eq. 39)\textsuperscript{75} and synthesis of 2-substituted 1,4,5,6-
tetrahydropyrimidine derivatives catalyzed by NBS using ultrasonic irradiation in aqueous medium (eq. 40)\textsuperscript{76} have been reported.

\[
2 \text{ArCHO} + \begin{array}{c}
\text{OH} \\
\end{array} \rightarrow \begin{array}{c}
\text{NBS} \\
\text{Solvent-free, 110°C} \\
\end{array} \rightarrow \begin{array}{c}
\text{Ar} \\
\text{O} \\
\end{array} \tag{39}
\]

\[
\text{RCHO} + \begin{array}{c}
\text{H}_2\text{N} \\
\text{NH} \\
\text{NH}_2 \\
\end{array} \rightarrow \begin{array}{c}
\text{NBS} \\
\text{H}_2\text{O, 70°C} \\
\end{array} \rightarrow \begin{array}{c}
\text{HN} \\
\text{N} \\
\text{R} \\
\end{array} \tag{40}
\]

**I.1.3: Oxidation of Hydrobenzoins, Benzoins and Alcohols**

Carbonyl compounds including benzoins and benzils have received a great deal of attention because of their potential industrial applications. Benzils, in particular, have gained lot of importance because of their applications as photosensitive agents in photocurable coatings,\textsuperscript{77} as starting materials in organic and pharmaceutical synthesis,\textsuperscript{78} as precursors for heterocyclic moieties\textsuperscript{79} and also as biologically important compounds.\textsuperscript{80} Oxidation of hydrobenzoins to benzoins as well as benzils and oxidation of benzoins to benzils (eqs. 41, 42) has been reported by a wide variety of reagents.

\[
\text{R-CH-CH-R} \rightarrow \begin{array}{c}
\text{O} \\
\text{OH} \\
\end{array} \rightarrow \begin{array}{c}
\text{R-C-C-R} \\
\text{and/or} \\
\text{R-CH-C-R} \\
\text{OH} \\
\text{O} \\
\end{array} \tag{41}
\]

\[
\text{R-CH-C-R} \rightarrow \begin{array}{c}
\text{O} \\
\text{OH} \\
\end{array} \rightarrow \begin{array}{c}
\text{R-C-C-R} \\
\text{O} \\
\end{array} \tag{42}
\]

Some of the literature reported methods use CuSO\textsubscript{4}/Py,\textsuperscript{81} Bi\textsubscript{2}O\textsubscript{3}/H\textsuperscript{+},\textsuperscript{82} aq. HNO\textsubscript{3} solution,\textsuperscript{83} 4-MeO-Tempo,\textsuperscript{84} (4-AcNH-Tempo)-OTs-TsOH,\textsuperscript{85} 4-PhCO\textsubscript{2}-Tempo-electrolysis,\textsuperscript{86} n-Bu\textsubscript{4}[MoO(O\textsubscript{2})\textsubscript{2}C\textsubscript{5}H\textsubscript{4}N(O)CO\textsubscript{2}]\textsuperscript{87} and H\textsubscript{2}O\textsubscript{2}-[C\textsubscript{6}H\textsubscript{5}N-(CH\textsubscript{2})\textsubscript{15}CH\textsubscript{3}]\textsubscript{3}\{PO\textsubscript{4}[W(O)\textsubscript{2}]\textsubscript{2}\textsubscript{4}\}\textsuperscript{88} and bromamine-T using RuCl\textsubscript{3}.xH\textsubscript{2}O as catalyst in alkaline acetonitrile/ water (1:1) medium.\textsuperscript{89}

Oxidation of benzoins with zeolite A, without any oxidizing agent under solvent-free conditions and microwave irradiation,\textsuperscript{90} silica gel supported Bi(NO\textsubscript{3})\textsubscript{3}.5H\textsubscript{2}O under microwave irradiation in a solvent-free system\textsuperscript{91} and aerial oxidation in presence of aluminium oxide\textsuperscript{92} has been reported (eq. 42). Oxidation of benzoins to benzils with
catalytic amount of triarylstibanes under aerobic conditions has also been reported. This catalytic oxidation is heteroatom-specific for the antimony compound as no reaction takes place with other group 15 reagents such as triphenylphosphane, -arsane and -bismuthane.

Oxidation of alcohols to carbonyl compounds is one of the most fundamental functional group interconversion and has been achieved by an array of reagents. Oxidation of a variety of activated and non-activated secondary alcohols to their corresponding ketones has been reported with molecular oxygen using cobalt phthalocyanine as catalyst in the presence of powdered KOH (eq. 43).

\[
\begin{align*}
\text{R}^1\text{CH} & \quad \text{Cu(II) phthalocyanine,O}_2 \\
\text{OH} & \quad \text{Xylene, KOH, Heat} \\
\text{R}^1 & \quad \text{C} \quad \text{R}^2 \\
\text{O} & \quad \text{..(43)}
\end{align*}
\]

Oxidation of secondary alcohols with DMSO/N\textsubscript{2}H\textsubscript{4}H\textsubscript{2}O/I\textsubscript{2}/H\textsubscript{2}O/CH\textsubscript{3}CN gives ketones. This system selectively oxidizes secondary alcoholic groups in the presence of primary alcoholic groups. Oxidation of various electron rich alcohols has also been reported with I\textsubscript{2}O\textsubscript{5}/KBr. Secondary alcohols could be efficiently oxidized to ketones with H\textsubscript{2}O\textsubscript{2} using \(n\)-hexadecyltrimethyl ammonium heteropoly phosphatotungstate \([\{n-C\textsubscript{16}H\textsubscript{33}N(CH\textsubscript{3})\textsubscript{3}\}\textsubscript{3}\{PW\textsubscript{4}O\textsubscript{16}\}]\) as catalyst under solvent-free conditions.

Many of the reported procedures for the oxidation of hydrobenzoins, benzoins and alcohols have drawbacks in terms of expensive reagents, harsh reaction conditions, low yields and use of toxic solvents. The toxic and volatile nature of many organic solvents particularly the chlorinated hydrocarbons have posed a serious threat to environment. Consequently the methods that successfully minimize their use are the focus of much attention. In this respect, ionic liquids are attracting growing interest as alternative reaction media for various chemical and biochemical transformations. Their negligible vapour pressure, wide liquid range, tunable polarity and potential for recycling circumvent many of the problems associated with common organic solvents. In view of the importance of the aforesaid transformations, we decided to investigate the use of ionic liquid as a reaction medium for the oxidation of hydrobenzoins, benzoins and alcohols using NBS as an oxidant.
I.2: RESULTS AND DISCUSSION

Hydrobenzoin was chosen as the model substrate to optimize the reaction conditions for its quantitative oxidation. A reaction of hydrobenzoin (Ia) and NBS (1:1 molar ratio) was carried out in ionic liquid [bmim]BF₄ at 70°C (run 1). TLC analysis of the reaction mixture showed the appearance of two new spots on TLC besides the presence of starting material after 1 h. Both new compounds had R_f higher than the starting material. These two spots were found to correspond to benzil and benzoin by co-TLC with the authentic samples. The reaction was incomplete even after 10 h, and yielded only 60% of benzil after workup (run 1). Therefore, we decided to increase the molar ratio of Ia: NBS. Hence, a reaction of Ia was conducted using 1:2 molar ratio of Ia: NBS in [bmim]BF₄ under heating at 70°C. TLC of the reaction mixture showed the complete disappearance of the starting material after 1 h, and presence of two new spots corresponding to benzil and benzoin was confirmed by co-TLC with authentic samples. On continuing the reaction for another 1.5 h, complete oxidation of benzoin to benzil was observed. The reaction was worked up after 2.5 h and 92% of benzil (IIa) was isolated (run 2).

A reaction of hydrobenzoin (Ia) and NBS was then attempted in 1:3 molar ratio at 70°C but no significant improvement was observed in the time of completion of the reaction or yield of the product (run 3). The reaction of hydrobenzoin (Ia) and NBS (1:2) in [bmim]BF₄ was also performed at room temperature. The reaction was found to be incomplete even after 10 h. TLC analysis of the reaction mixture showed only a trace amount of benzil along with significant amount of benzoin and starting material (run 4). The oxidation of hydrobenzoin was then attempted in different ionic liquids using NBS as an oxidant. It was observed that the reactions using 1:2 molar ratio of Ia: NBS in [bmim]Br, [bmim]Cl and [bmim]PF₆ at 70°C showed complete disappearance of starting material after 3 h. However, TLC showed the formation of a mixture of benzoin and benzil. The reactions were continued for another 3 h, but low yield of benzil was obtained (runs 5-7). The potential of N-chlorosuccinimide (NCS) and N-iodosuccinimide (NIS) as oxidizing agents instead of NBS was also investigated under identical reaction conditions. Reactions of hydrobenzoin with NCS and NIS in [bmim]BF₄ at 70°C gave low yield of benzil (IIa) i.e. 80% and 79% respectively after 4 h (runs 8-9). All these results are listed in Table I.1.
Table I.1: Optimization of reaction conditions for the oxidation of hydrobenzoin (Ia) to benzil (IIa)

<table>
<thead>
<tr>
<th>Run</th>
<th>Oxidant</th>
<th>Ionic liquid</th>
<th>Molar ratio (Ia:Oxidant)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>% Yield (IIa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NBS</td>
<td>[bmim]BF₄</td>
<td>1:1</td>
<td>70</td>
<td>10</td>
<td>60⁺</td>
</tr>
<tr>
<td>2.</td>
<td>NBS</td>
<td>[bmim]BF₄</td>
<td>1:2</td>
<td>70</td>
<td>2.5</td>
<td>92</td>
</tr>
<tr>
<td>3.</td>
<td>NBS</td>
<td>[bmim]BF₄</td>
<td>1:3</td>
<td>70</td>
<td>2.5</td>
<td>92</td>
</tr>
<tr>
<td>4.</td>
<td>NBS</td>
<td>[bmim]BF₄</td>
<td>1:2</td>
<td>35</td>
<td>10</td>
<td>20⁺</td>
</tr>
<tr>
<td>5.</td>
<td>NBS</td>
<td>[bmim]Br</td>
<td>1:2</td>
<td>70</td>
<td>6</td>
<td>68</td>
</tr>
<tr>
<td>6.</td>
<td>NBS</td>
<td>[bmim]Cl</td>
<td>1:2</td>
<td>70</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td>7.</td>
<td>NBS</td>
<td>[bmim]PF₆</td>
<td>1:2</td>
<td>70</td>
<td>6</td>
<td>77</td>
</tr>
<tr>
<td>8.</td>
<td>NCS</td>
<td>[bmim]BF₄</td>
<td>1:2</td>
<td>70</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>9.</td>
<td>NIS</td>
<td>[bmim]BF₄</td>
<td>1:2</td>
<td>70</td>
<td>4</td>
<td>79</td>
</tr>
</tbody>
</table>

⁺ Reaction incomplete

It can be inferred from Table I.1 that the use of NBS as an oxidant and [bmim]BF₄ as the reaction medium was the optimum system for the oxidation of hydrobenzoin (Ia) to benzil (IIa) (eq. 44).

\[
\begin{align*}
\text{Ph} & \text{CH} \text{CH} \text{Ph} \\
\text{OH} & \text{OH} \\
\text{NBS, [bmim]BF}_4 & \text{70}°\text{C} \\
\rightarrow & \text{Ph} \text{C} \text{C} \text{Ph} \\
\text{Ia} & \text{IIa} \\
\end{align*}
\]

... (44)

Subsequently, oxidation of 4,4'-dichlorohydrobenzoin (Ib), 4,4'-dimethylhydrobenzoin (Ic), 4,4'-dibromohydrobenzoin (Id), 3,3'-dibromohydrobenzoin (Ie), 2,2'-dichloro hydrobenzoin (If), 4,4'-dimethoxyhydrobenzoin (Ig) and \(\alpha,\alpha^\prime\)-dihydronaphthoin (Ih) were carried out under similar reaction conditions and the corresponding 1,2-diketones \(i.e.,\) 4,4'-dichlorobenzil (IIb), 4,4'-dimethylbenzil (IIc), 4,4'-dibromobenzil (IID), 3,3'-dibromobenzil (IIe), 2,2'-dichlorobenzil (IIf), 4,4'-dimethoxybenzil (IIt) and \(\alpha,\alpha^\prime\)-naphthil (IIIb) were obtained in excellent yields (runs 10-16). All reactions were rapid, clean and no side product was either detected or isolated. Thereafter, we investigated the oxidation of aliphatic 1,2-diols under similar conditions. Aliphatic
1,2-diols namely, trans-cyclohexane-1,2-diol (Ii) and 9,10-dihydroxystearic acid (Ij) underwent successful oxidation to give the corresponding 1,2-diketones, *i.e.* cyclohexane-1,2-dione (IIIi) and 9,10-diketostearic acid (IIIj) respectively (eq. 45, runs 17-18). All these results are listed in Table I.2.

\[
\begin{array}{c}
R-\text{CH-CH-R'} \\
\text{OH- OH} \\
\text{I}
\end{array} \xrightarrow{\text{NBS, [bmim]BF}_4 \text{ 70°C}} \begin{array}{c}
\text{R-\text{C-C-R'}} \\
\text{IIi} \\
\end{array}
\ldots(45)
\]

(a) \( R = R' = \text{C}_6\text{H}_5 \)
(b) \( R = R' = 4\text{-ClC}_6\text{H}_4 \)
(c) \( R = R' = 4\text{-MeC}_6\text{H}_4 \)
(d) \( R = R' = 4\text{-BrC}_6\text{H}_4 \)
(e) \( R = R' = 3\text{-BrC}_6\text{H}_4 \)
(f) \( R = R' = 2\text{-ClC}_6\text{H}_4 \)
(g) \( R = R' = 4\text{-MeOC}_6\text{H}_4 \)
(h) \( R = R' = 1\text{-Naphthyl} \)
(i) \( R-R' = (\text{CH}_3)_2 \)
(j) \( R = \text{C}_8\text{H}_{17}, R' = \text{C}_7\text{H}_{14}\text{COOH} \)

In view of successful oxidation of 1,2-diols to 1,2-diketones, we investigated the application of NBS as an oxidant for the oxidation of \( \alpha \)-hydroxyketones in [bmim]BF_4. Reaction using 1: 1 molar ratio of benzoin to NBS, under otherwise identical conditions resulted in an incomplete reaction with an inferior yield (51%) of IIa. However, \( \alpha \)-hydroxyketones namely benzoin (IIIa), 4,4'-dichlorobenzoin (IIIb), 4,4'-dimethylbenzoin (IIIc) and butyroin (IIId) underwent complete oxidation to corresponding 1,2-diketones *i.e.* benzil (IIa), 4,4'-dichlorobenzil (IIb), 4,4'-dimethylbenzil (IIc) and octane-4,5-dione (IIk) respectively, by using 1: 2 molar ratio of substrate: NBS in [bmim]BF_4 at 70°C (eq. 46, runs 19-22).

\[
\begin{array}{c}
R-\text{CH-C-R} \\
\text{OH O} \\
\text{III}
\end{array} \xrightarrow{\text{NBS, [bmim]BF}_4 \text{ 70°C}} \begin{array}{c}
\text{R-\text{C-C-R'}} \\
\text{II} \\
\end{array}
\ldots(46)
\]

(a) \( R = \text{C}_6\text{H}_5 \)
(b) \( R = 4\text{-ClC}_6\text{H}_4 \)
(c) \( R = 4\text{-MeC}_6\text{H}_4 \)
(d) \( R = n- \text{C}_3\text{H}_7 \)
Table I.2: Oxidation of hydrobenzoins and α-hydroxyketones using NBS in [bmim]BF_4 at 70°C

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>% Yield (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.</td>
<td>4,4'-Dichlorohydrobenzoin (Ib)</td>
<td>IIb</td>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>11.</td>
<td>4,4'-Dimethylhydrobenzoin (Ic)</td>
<td>IIc</td>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>12.</td>
<td>4,4'-Dibromohydrobenzoin (Id)</td>
<td>IIId</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>13.</td>
<td>3,3'-Dibromohydrobenzoin (Ie)</td>
<td>IIe</td>
<td>2</td>
<td>81</td>
</tr>
<tr>
<td>14.</td>
<td>2,2'-Dichlorohydrobenzoin (If)</td>
<td>IIIf</td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>15.</td>
<td>4,4'-Dimethoxyhydrobenzoin (Ig)</td>
<td>IIg</td>
<td>2</td>
<td>87</td>
</tr>
<tr>
<td>16.</td>
<td>α,α'-Dihydronaphthoin (Ih)</td>
<td>IIh</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>17.</td>
<td>Cyclohexane-1,2-diol (Ii)</td>
<td>IIi</td>
<td>2.5</td>
<td>85</td>
</tr>
<tr>
<td>18.</td>
<td>9,10-Dihydroxystearic acid (Ij)</td>
<td>IIj</td>
<td>2.5</td>
<td>70</td>
</tr>
<tr>
<td>19.</td>
<td>Benzoin (IIIa)</td>
<td>IIa</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>20.</td>
<td>4,4'-Dichlorobenzoin (IIIb)</td>
<td>IIb</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>21.</td>
<td>4,4'-Dimethylbenzoin (IIIc)</td>
<td>IIc</td>
<td>1.5</td>
<td>85</td>
</tr>
<tr>
<td>22.</td>
<td>Butyroin (IIId)</td>
<td>IIk</td>
<td>2.5</td>
<td>80</td>
</tr>
</tbody>
</table>

*General reaction conditions: hydrobenzoin or α-hydroxyketones (1.0 mmol), NBS (2.0 mmol), [bmim]BF_4 (5.0 mmol)

The recyclability of the ionic liquid was also investigated. Reactions using hydrobenzoin (Ia) as substrate, showed that the recovered ionic liquid could be used for oxidation upto two runs without any appreciable loss of efficiency by adding 2 equiv. of NBS for each run and afforded 91% and 89% of IIa after 1\textsuperscript{st} cycle and 2\textsuperscript{nd} cycle. However, the yield decreased gradually in third cycle as depicted in Figure I.2.
The successful oxidations of 1,2-diols and α-hydroxyketones led us to believe that alcohols could also be oxidized under these conditions. Therefore, we attempted the oxidation of different alcohols using NBS in [bmim]BF$_4$. Variously substituted secondary aromatic alcohols i.e., 9-fluorenol (IVa), diphenylmethanol (IVb), (4-chlorophenyl)phenylmethanol (IVc), (4-bromophenyl)phenylmethanol (IVd), bis(4-chlorophenyl)methanol (IVe), 1-phenylethanol (IVf), 1-(4-bromophenyl)ethanol (IVg), 1-(4-chlorophenyl)ethanol (IVh), 1-(4-nitrophenyl)ethanol (IVi), 1-(4-methylphenyl)ethanol (IVj) and 1-(4-methoxyphenyl)ethanol (IVk) underwent smooth oxidation with NBS using 1:2 molar ratio of substrate: NBS in [bmim]BF$_4$ at 70°C and afforded the corresponding carbonyl compounds i.e. 9-fluorenone (Va), benzophenone (Vb), 4-chlorobenzophenone (Vc), 4-bromobenzophenone (Vd), 4,4'-dichlorobenzophenone (Ve), acetophenone (Vf), 4-bromoacetophenone (Vg), 4-chloroacetophenone (Vh), 4-nitroacetophenone (Vi), 4-methylacetophenone (Vj) and 4-methoxyacetophenone (Vk), respectively (runs 23-33).

The oxidation reactions of aromatic primary alcohols e.g. cinnamyl alcohol (IVl), (anthracen-9-yl)-methanol (IVm), (naphthalen-1-yl)-methanol (IVn) and phenylmethanol (IVo) gave corresponding aldehydes viz. 3-(phenyl)propenal (VI), 9-anthraldehyde (Vm), 1-naphthaldehyde (Vn) and benzaldehyde (Vo) respectively in good yields (runs 34-37).

All these results are tabulated in Table I.3 and are summarized in eq. 47.
### Table I.3: Oxidation of alcohols using NBS in [bmim]BF₄ at 70°C

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate (IV)</th>
<th>Product</th>
<th>Time (h)</th>
<th>% Yield (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.</td>
<td>9-Fluorenol (IVa)</td>
<td>Va</td>
<td>1</td>
<td>93</td>
</tr>
<tr>
<td>24.</td>
<td>Diphenylmethanol (IVb)</td>
<td>Vb</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>25.</td>
<td>(4-Chlorophenyl)phenylmethanol (IVc)</td>
<td>Vc</td>
<td>1</td>
<td>84</td>
</tr>
<tr>
<td>26.</td>
<td>(4-Bromophenyl)phenylmethanol (IVd)</td>
<td>Vd</td>
<td>1</td>
<td>87</td>
</tr>
<tr>
<td>27.</td>
<td>Bis(4-chlorophenyl)methanol (IVe)</td>
<td>Ve</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>28.</td>
<td>1-Phenylethanol (IVf)</td>
<td>Vf</td>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>29.</td>
<td>1-(4-Bromophenyl)ethanol (IVg)</td>
<td>Vg</td>
<td>1</td>
<td>82</td>
</tr>
<tr>
<td>30.</td>
<td>1-(4-Chlorophenyl)ethanol (IVh)</td>
<td>Vh</td>
<td>1</td>
<td>82</td>
</tr>
<tr>
<td>31.</td>
<td>1-(4-Nitrophenyl)ethanol (IVi)</td>
<td>Vi</td>
<td>2</td>
<td>86</td>
</tr>
<tr>
<td>32.</td>
<td>1-(4-Methylphenyl)ethanol (IVj)</td>
<td>Vj</td>
<td>1.5</td>
<td>78</td>
</tr>
<tr>
<td>33.</td>
<td>1-(4-Methoxyphenyl)ethanol (IVk)</td>
<td>Vk</td>
<td>1.5</td>
<td>85</td>
</tr>
<tr>
<td>34.</td>
<td>Cinnamyl alcohol (IVl)</td>
<td>Vl</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>35.</td>
<td>(Anthracen-9-yl)-methanol (IVm)</td>
<td>Vm</td>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td>36.</td>
<td>(Naphthalen-1-yl)-methanol (IVn)</td>
<td>Vn</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>37.</td>
<td>Phenylmethanol (IVo)</td>
<td>Vo</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>38.</td>
<td>Heptan-1-ol (IVp)</td>
<td>Vp</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>39.</td>
<td>Octan-1-ol (IVq)</td>
<td>Vq</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>40.</td>
<td>Cyclohexanol (Vla)</td>
<td>VIIa</td>
<td>2</td>
<td>85ᵇ</td>
</tr>
<tr>
<td>41.</td>
<td>Octan-2-ol (Vlb)</td>
<td>VIIb</td>
<td>2</td>
<td>82ᵇ</td>
</tr>
<tr>
<td>42.</td>
<td>Heptan-4-ol (Vlc)</td>
<td>VIIc</td>
<td>2</td>
<td>77ᵇ</td>
</tr>
<tr>
<td>43.</td>
<td>Pentan-3-ol (Vld)</td>
<td>VIIId</td>
<td>2</td>
<td>75ᵇ</td>
</tr>
</tbody>
</table>

*a* General reaction conditions: alcohols (1.0 mmol), NBS (2.0 mmol), [bmim]BF₄ (5.0 mmol)  
*b* In case of secondary aliphatic alcohols, corresponding bromides were obtained, rather than ketones

In view of the successful oxidation of benzylic and allylic alcohols, we investigated the reaction of aliphatic alcohols with NBS in ionic liquids. Reactions of primary aliphatic alcohols like heptan-1-ol (IVp) and octan-1-ol (IVq) with NBS in [bmim]BF₄ resulted in the formation of corresponding oxidized product *i.e.* 1-heptanal (Vp) and 1-octanal (Vq), respectively (Table I.3, runs 38, 39) (eq. 47). There was no further oxidation of these aldehydes to corresponding carboxylic acids.
(a) \( R-R' = 9\text{-Fluorenyl} \)
(b) \( R = R' = C_6H_5 \)
(c) \( R = C_6H_5, R' = 4\text{-ClC}_6H_4 \)
(d) \( R = C_6H_5, R' = 4\text{-BrC}_6H_4 \)
(e) \( R = R' = 4\text{-ClC}_6H_4 \)
(f) \( R = C_6H_5, R' = \text{CH}_3 \)
(g) \( R = 4\text{-BrC}_6H_4, R' = \text{CH}_3 \)
(h) \( R = 4\text{-ClC}_6H_4, R' = \text{CH}_3 \)
(i) \( R = 4\text{-O}_2\text{NC}_6H_4, R' = \text{CH}_3 \)
(j) \( R = 4\text{-MeC}_6H_4, R' = \text{CH}_3 \)
(k) \( R = 4\text{-MeOC}_6H_4, R' = \text{CH}_3 \)
(l) \( R = \text{Cinnamyl}, R' = \text{H} \)
(m) \( R = 9\text{-Anthryl}, R' = \text{H} \)
(n) \( R = 1\text{-Naphthyl}, R' = \text{H} \)
(o) \( R = C_6H_5, R' = \text{H} \)
(p) \( R = n\text{-C}_6H_{13}, R' = \text{H} \)
(q) \( R = n\text{-C}_7H_{15}, R' = \text{H} \)

However, reactions of secondary aliphatic alcohols namely, cyclohexanol (VIa), octan-2-ol (VIb), heptan-4-ol (VIc) and pentan-3-ol (VIId) with NBS in [bmim]BF\(_4\) at 70°C, resulted in the formation of bromocyclohexane (VIIa), 2-bromooctane (VIIb), 4-bromoheptane (VIIc) and 3-bromopentane (VIId) respectively (Table I.3, runs 40-43) (eq. 48). Cholesterol and triphenyl methanol remained unreacted under our optimized reaction condition, even after continuing the reaction for 24 h.

Two different pathways have been proposed for the oxidation of alcohols with NBS.\(^99\)

In the first approach, oxidation proceeds through \(\alpha\)-halogenation of the alcohols followed by rapid loss of hydrogen halide (Path A, Scheme I.2). In this mechanism, the rate determining step is the cleavage of the alpha C-H bond to form the halo intermediate. In the second approach, it has been proposed that the alcohols form a hypobromite which readily loses HBr to form the corresponding carbonyl product (Path B, Scheme I.2).
We believe that oxidations are taking place by path B in our reactions by initial formation of hypobromite intermediate followed by loss of HBr to give the carbonyl compound. In order to confirm the reaction pathway, reaction of 2-benzyloxy-naphthalene was carried out with NBS under identical conditions. It was observed that no reaction takes place even after 24 h and 2-benzyloxy-naphthalene was recovered unchanged (eq. 49). This is obviously due to non availability of hydroxyl hydrogen to form hypobromite. Further no evidence was found for the α-halogenation of starting material as reported in case of ethers, thereby supporting the fact that reaction proceeds through initial hypobromite intermediate.

Formation of secondary alkyl bromides in case of secondary alcohols must be proceeding by a different pathway. The work is underway to extend the scope of the reaction and to understand its reaction pathway.

In conclusion, the present catalyst free protocol for oxidation of hydrobenzoins, benzoins and alcohols is facile, clean and environmentally friendly. Meanwhile, the method has several advantages such as higher yields, shorter reaction times, easy setup, easy work up, reusable ionic liquid and wide applicability.

I.3: EXPERIMENTAL

All melting points were recorded on a Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer FT-IR SPECTRUM-2000.
NMR spectra were recorded on FT-NMR model R-600 Hitachi (60 MHz) with TMS as internal standard. The products were identified by co-TLC, m.p., IR and NMR spectra. Hydrobenzoins were prepared by reductive coupling of aldehydes by Al-KOH.100 Aliphatic alcohols were prepared by hydroxylation of corresponding olefins. The preparation of acyloins was carried out by acyloan condensation.

**General procedure for the preparation of hydrobenzoins**100

In a 100 mL round-bottomed flask, fitted with a water condenser and mounted over a magnetic stirrer, was placed the aldehyde (n mmol), aluminium powder (2n mmol) and methanol (10 mL/g of aluminium). KOH (6n mmol) was added and the reaction mixture was stirred at room temperature. A vigorous reaction ensued immediately. The progress of the reaction was monitored for complete disappearance of carbonyl compound by TLC. The reaction mixture was filtered to remove unreacted aluminium powder and water was added to the filtrate. A solid precipitated out which was filtered at reduced pressure. The solid product was recrystallized from aqueous ethanol to obtain pure hydrobenzoins.

**Preparation of [bmim]Cl**101

In a typical reaction, 1-methylimidazole (1.0 mmol) and n-butyl chloride (1.10 mmol) were added to a round-bottomed flask fitted with a reflux condenser and mounted on a magnetic stirrer. The mixture was stirred vigorously at 70-80ºC for 72 h under nitrogen. The viscous liquid so obtained was washed well with diethyl ether (3×60 mL) and dried on rotary evaporator to yield [bmim]Cl.

**Preparation of [bmim]Br**102

In a typical reaction, 1-methylimidazole (1.0 mmol) and n-butyl bromide (1.0 mmol) were added to a round-bottomed flask fitted with a reflux condenser and mounted on a magnetic stirrer. The mixture was stirred vigorously at 70-80ºC for 72 h under nitrogen. The viscous liquid so obtained was washed well with diethyl ether (3×60 mL) and dried on rotary evaporator to yield [bmim]Br.
Preparation of \([\text{bmim}]\text{BF}_4\) and \([\text{bmim}]\text{PF}_6\)^{103}

In a typical reaction, NaBF\(_4\) (1.0 mmol) was added to a solution of (1.0 mmol) of \([\text{bmim}]\text{Br}\) in 100 mL of dry acetone. After 48 h of stirring at room temperature, the reaction mixture was filtered through a sintered funnel. The filtrate was concentrated on a rotary evaporator to yield a viscous liquid. Dichloromethane (75 mL) was added to the residue to cause precipitation of any remaining NaBr. The precipitate was filtered through a sintered funnel and the filtrate concentrated again on rotary evaporator to obtain \([\text{bmim}]\text{BF}_4\). For the preparation of \([\text{bmim}]\text{PF}_6\), same procedure was followed as above by replacing NaBF\(_4\) with KPF\(_6\).

General Procedure for the Oxidation of 1,2-diols, \(\alpha\)-hydroxyketones and alcohols with NBS-[\text{bmim}]BF\(_4\) using hydrobenzoin (Ia) as representative example

In a typical experiment, a mixture of hydrobenzoin (1.0 mmol), \(N\)-bromosuccinimide (2.0 mmol) and \([\text{bmim}]\text{BF}_4\) (5.0 mmol) along with a stir bar was placed in a 50 mL RB flask fitted with a calcium chloride guard tube and mounted over a magnetic stirrer. The reaction mixture was stirred magnetically in an oil-bath maintained at 70°C for the appropriate time (Tables I.2). After completion of reaction as monitored by TLC using petroleum ether: ethyl acetate (80:20, v/v), the reaction mixture was cooled to room temperature. The mixture was extracted with diethyl ether (3×10 mL). The combined ether layer was washed with water (3×10 mL) and dried over anhyd. Na\(_2\)SO\(_4\). The solution was concentrated on a rotary evaporator to give a yellow solid, which was identified as benzil (0.19 g, 92%) by m.p., mix. m.p., IR and \(^1\)H NMR spectra.

The recyclability of the ionic liquid, was examined by repeating the above reaction. On completion of reaction, as monitored by TLC, the reaction mixture was cooled to room temperature. The product obtained was extracted in diethyl ether, leaving behind ionic liquid and the by product of NBS \(i.e\). succinimide as residue. The residue was diluted with ethyl acetate and the insoluble succinimide, was removed by filtration. The ethyl acetate was evaporated under reduce pressure to give ionic liquid which was dried before use at 80°C under vacuum for 30 min. The recovered ionic liquid could be used for oxidation up to two runs without any appreciable loss of efficiency by adding 2 equiv. of NBS for each run and afforded 91% and 89% of benzil after 1\(^{st}\) and 2\(^{nd}\) cycles. However, the yield of benzil decreased in the third cycle.
Representative Example

4,4'-Dibromobenzil (II\text{d}): Yellow solid; Yield: 82%; M.p.: 225-226°C (Lit. 224-226°C);\textsuperscript{104} IR ($v_{\text{max}}$ cm$^{-1}$) (KBr): 2980, 1664, 1586; $^1$H NMR (60 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J=8.4$ Hz, 4H, Ar), 7.67 (d, $J=8.0$ Hz, 4H, Ar).

Product-Profile

<table>
<thead>
<tr>
<th>Run</th>
<th>Product</th>
<th>Physical State</th>
<th>Melting Point (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td>Obs.</td>
<td>Lit.</td>
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<tr>
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<td>100-105</td>
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<td>1-Naphthaldehyde (Vn)</td>
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<td>Benzaldehyde (Vo)</td>
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</table>
I.4: REFERENCES


Chapter I


