List of Publications/Patents

Paper’s published:

[1] Facile one-pot synthesis of $\alpha$-bromoketones from olefins using bromide/bromate couple as a nonhazardous brominating agent

Rajendra D. Patil, G. Joshi, Subbarayappa Adimurthy, B C. Ranu


[2] HBr-H$_2$O$_2$: A Facile protocol for regioselective synthesis of bromohydrins and $\alpha$-bromoketones and oxidation of benzylic/secondary alcohols to carbonyl compounds under mild aqueous conditions

Rajendra D. Patil, G. Joshi, S. Adimurthy


[3] KHSO$_4$ – A highly efficient and reusable heterogeneous catalyst for hydroarylation of styrenes

Rajendra D. Patil, G. Joshi, S. Adimurthy


[4] Green oxidation of methylarenes to benzoic acids with recyclable bromide/bromate in water

Rajendra D. Patil, S. Bhadra, S. Adimurthy, B. C. Ranu

*Synthetic Communications*, **2010**, 40, 2922-2999.

[5] Easy access to $\alpha$-bromoketones and epoxides from vic-dibromides under aqueous conditions

Rajendra D. Patil, S. Adimurthy, B. C. Ranu

[6] Copper-catalyzed aerobic oxidation of amines to imines under neat conditions with low catalyst loading

Rajendra D. Patil, Subbarayappa Adimurthy


[7] Direct and selective conversion of benzyl bromides to benzaldehydes with aqueous H₂O₂ without catalyst

Rajendra D. Patil, S. Adimurthy

Synthetic Communications, 2011, 41, 2712-2718.

[8] High atom efficient and environment-friendly preparation of herbicides bromoxynil and ioxynil

S. Adimurthy, G. Joshi, Rajendra D. Patil


Patents filed/applied


Manuscripts communicated

[1] Copper-powder catalyzed selective aerobic oxidation of amines to imines under solvent-free conditions

Rajendra D. Patil, Subbarayappa Adimurthy

[2] Oxidative rearrangement of vinyl bromides to $\alpha$-Bromoketones and direct synthesis of $\alpha,\alpha$-Dibromoketones from alkynes using HBr/H$_2$O$_2$ System

Ramachandra Reddy Donthiri, Rajendra D. Patil, Darapaneni Chandra Mohan, Subbarayappa Adimurthy

Manuscripts under preparation

[1] H-$\beta$–Zeolite-A highly efficient and reusable heterogeneous catalyst for hydroarylation and dimerization of Styrenes

Darapaneni Chandra Mohan, Rajendra D. Patil, S. Adimurthy
Papers presented in the Conferences/Symposium

[1] Green brominating reagent i.e. bromide/bromate couple is a versatile & ecofriendly reagent for an oxidation of olefins, methyl arenas to corresponding α-bromoketones, benzoic acid respectively

Rajendra.D. Patil, S. Adimurthy

“An International Conference on Emerging Trends in Chemistry” (ETIC-2010) held on January, 5\textsuperscript{th}-7\textsuperscript{th}, 2010 pp 41-42. Dept. of Chemistry, Pune University, Maharashtra (India). Young scientist award (Oral presentation).

[2] HBr-H\textsubscript{2}O\textsubscript{2}: A Facile protocol for regioselective synthesis of bromohydrins and α-bromoketones and oxidation of benzylic/secondary alcohols to carbonyl compounds under mild aqueous conditions

Rajendra.D. Patil, G. Joshi, S. Adimurthy

“The 3\textsuperscript{rd} International Symposium on Materials Chemistry, ISMC-2010” held on December, 7\textsuperscript{th}-11\textsuperscript{th}, 2010, pp 480-481. Chemistry Division, Bhabha Atomic Research Center (BARC) Trombay, Mumbai.

Best Paper award (Poster presentation).

[3] KHSO\textsubscript{4}-A highly efficient and reusable heterogeneous catalyst for hydroarylation of styrene

G. Joshi, Rajendra.D. Patil, S. Adimurthy

“The 3\textsuperscript{rd} International Symposium on Materials Chemistry, ISMC-2010” held on December, 7\textsuperscript{th}-11\textsuperscript{th}, 2010, pp 466-467. Chemistry Division, Bhabha Atomic Research Center (BARC) Trombay, Mumbai.

Best Paper award (Poster presentation).

[4] A sustainable approach for important organic functional group transformations
Rajendra D. Patil, Girdhar Joshi, K. C. Chunavala, Subbarayappa Adimurthy

“Western India Research Scholars Meet (WIRSM-2011)” held on September, 17th, 2011. Dept. of Chemistry, MS University of Baroda, Vadodara. (Oral presentation).
Copper-Catalyzed Aerobic Oxidation of Amines to Imines under Neat Conditions with Low Catalyst Loading

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Abstract: The copper (I)-catalyzed direct synthesis of imines from amines under mild aerobic conditions is described. The method is applicable for the synthesis of various imines from corresponding amines such as benzylc, aliphatic, cyclic secondary, heteroaromatic species and the oxidative condensation of benzylamines with anilines extends the scope of the CuCl catalytic system. Noteworthy, solvent-free procedure, air as a benign oxidant, and the cheap and easy availability of the catalyst are the vital advantages of the method.

Keywords: copper; homogeneous catalysis; imines; oxidation; synthetic methods

Imines are important intermediates in the synthesis of various biologically active nitrogen-containing heterocyclic compounds and industrial synthetic processes. Significant progress has been made in recent years for the synthesis of imines, including the direct synthesis of imines from amines and alcohols in the presence of catalyst, self-condensation of primary amines with oxidant and oxidation of secondary amines. Most of these reactions were performed under solvent conditions. However, no attempts were made for the synthesis of imines by the direct oxidation of primary amines to the corresponding imines under neat conditions, probably due to the rapid dehydrogenation of imines to nitriles in solvent media.

Notably, most of the applications are based on complexes of precious metals such as palladium, ruthenium, gold and vanadium. The limited availability of these metals and their high price makes it highly desirable to search for more economical and environmentally-friendly alternatives. Thus, the selective, catalytic synthesis of benzylamines directly from primary benzyamines under relatively mild and neat conditions without producing waste is highly desirable economically and environmentally.

We recently reported a selective oxidation of various alcohols to the corresponding carbonyl compounds with a mild and selective oxidizing agent (BrOH) generated in-situ from the bromide/bromate couple in aqueous acidic medium [Eq. (1)].

\[ 2 \text{Br}^- + \text{BrO}_3^- + 3 \text{H}^+ \rightarrow 3 \text{BrOH} \] (1)

When the same species (BrOH) is used for the oxidation of benzylamine to the imine, lower yields were obtained under aqueous conditions. Based on these results we hypothesized that a related halogen species under non-aqueous conditions may possibly provide high selectivity for this transformation. To our delight, we found that copper catalysts function well in this context. Herein, we demonstrate a novel approach to the direct synthesis of imines from readily available benzyamines, under mild conditions using an inexpensive and commercially available copper catalyst and water as an oxidant [Eq. (2)]. To the best of our knowledge this is the first convenient catalytic process ever reported for efficient syntheses of imines from benzylamines using air as the oxidant under neat conditions with low catalyst loadings.

During our studies we examined the synthesis of imine (2a) using the copper-catalyzed aerobic oxidative imination of benzylamine under mild and solvent-free conditions (Table 1). Employment of
Facile one-pot synthesis of α-bromoketones from olefins using bromide/bromate couple as a nonhazardous brominating agent

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ABSTRACT

A new method for the preparation of α-bromoketones from olefins using bromide/bromate couple as a nonhazardous brominating agent has been developed. Several α-bromoketones were successfully prepared from a variety of olefins by this method. This procedure is an alternative to conventional molecular bromine.

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α-Bromoketones are versatile intermediates in organic synthesis. Numerous methods have been developed for the preparation of α-bromoketones from ketones with liquid bromine in the presence of protic and Lewis acids. Bromine is hazardous with associated risks in handling and transport. However, it is still being used by industry as well as academia due to its easy availability, low cost, and lack of a better alternative. A few other alternative procedures for α-bromination of carbonyl compounds avoid liquid bromine involve N-bromosuccinimide (NBS) and 4,4-dibromo-2,6-di-tert-butyl-cyclohexa-2,5-diene. Nevertheless, these brominating reagents have some limitations including their low atom efficiency and use of molecular bromine for their preparation.

A survey of the existing literature revealed that α-bromoketones have been synthesized mainly from ketones. Surprisingly, we have found limited reports for the preparation of α-bromoketones from olefins. The direct conversion of alkenes to α-chloroketones is reported with chlorom chloride. However, the same strategy for α-bromoketones is not explored in the literature.

Despite the fact that the reactions of olefins with NBS is well documented in the literature to obtain bromohydrins, it is seldom extended to get α-bromoketones. As olefins substituted with a variety of functionalities are easily accessible we assumed that a convenient procedure from olefins using an alternative mild brominating agent will be appreciated.

Our continuous efforts to achieve maximum bromide atom efficiency and minimize waste generation, as well as elimination of the use of hazardous liquid bromine led us to develop a versatile brominating reagent, a bromide–bromate couple, and we have already demonstrated a few useful applications.

Herein, we report further results using this brominating reagent for the direct synthesis of α-bromoketones from olefins

Table 1: Optimization of reaction conditions for α-bromoketone synthesis

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Product ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dioxane</td>
<td>8</td>
<td>71/17/12</td>
</tr>
<tr>
<td>2</td>
<td>Acetonitrile</td>
<td>8</td>
<td>40/47/8</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>8</td>
<td>3/39/24</td>
</tr>
<tr>
<td>4</td>
<td>CH2Cl2</td>
<td>8</td>
<td>13/19/77</td>
</tr>
<tr>
<td>5</td>
<td>EtO</td>
<td>8</td>
<td>13/3/76</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>8</td>
<td>1/5/8</td>
</tr>
<tr>
<td>7</td>
<td>Dioxane</td>
<td>7.5</td>
<td>60/11/1</td>
</tr>
<tr>
<td>8</td>
<td>Dioxane</td>
<td>7.5</td>
<td>61/10/2</td>
</tr>
<tr>
<td>9</td>
<td>Dioxane</td>
<td>8</td>
<td>56/32/2</td>
</tr>
</tbody>
</table>

a * Yields unless otherwise stated.
b Isolated yield with 2.5 equiv of BrOH.
c Isolated yield with 3.0 equiv of BrOH.
d Reaction with NBS.
HBr—H₂O₂: A Facile Protocol for Regioselective Synthesis of Bromohydrins and α-Bromoketones and Oxidation of Benzylic/Secondary Alcohols to Carbonyl Compounds under Mild Aqueous Conditions

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HBr—H₂O₂ is efficiently activated in water under mild conditions, allowing the bromohydroxylation of various styrenes. HBr—H₂O₂ is more economic and easy to handle and offers sufficiently high regioselectivity (100%) for bromohydrin synthesis. Further activation of bromohydrin with a catalytic amount of HBr (50 mol %) and H₂O₂ in water affords α-bromoketones in moderate to good yields in a single step. Oxidation of benzylic/secondary alcohols to the corresponding carbonyl compounds has been achieved with the HBr (10 mol %) and H₂O₂ efficiently in aqueous dioxane under ambient conditions.

1. Introduction

Bromohydrins and α-bromoketones are compounds of high practical utility. These bromo intermediates are useful in the synthesis of numerous functionalized compounds such as antitumor and antibacterial agents and antioxidants as well as specialty chemicals, agrochemicals, and pharmaceuticals. There are many known methods for the synthesis of bromohydrins either by the reaction of olefins with NBS (N-bromosuccinimide) or by the ring-opening of an epoxide with the addition of halo acids. The direct use of HBr for the selective synthesis of bromohydrins from olefins has not been explored. However, the HBr—H₂O₂ system has been reported for a number of elegant bromination reactions by J. Iskra and co-workers including the α-bromination of ketones. Our study on various vicinal functionalizations of olefins and the one-pot synthesis of α-bromoketones from olefins revealed that limited literature reports are available for the access to α-bromoketones from olefins. On the other hand, the development of sustainable, efficient, and selective catalysts for the oxidation of alcohols to aldehydes is a fundamental goal in chemistry. During recent decades, manifold transition metal-catalyzed reactions have been discovered which have significantly improved organic transformations. Notably, most of the applications are based on complexes of precious metals such as palladium, platinum, gold, ruthenium, and other metal catalysts. TEMPO-imidazolium salts are efficient metal-free oxidants reported recently for the oxidation of various alcohols. The limited availability of these metals and their high price make it highly desirable to search for more economical and environmentally friendly alternatives. On the basis of our previous study, selective oxidation of various organic substrates with bromate in combination with a catalytic amount of bromide could be achieved under ambient conditions. Our present study shows that HBr—H₂O₂ can regioselectively provide bromohydrins and α-bromoketones from olefins (Scheme 1) and is effective for the selective oxidation of benzylic/secondary alcohols to the corresponding carbonyl compounds under mild conditions (Scheme 2).

2. Experimental Section

General Procedure for the Synthesis of Bromohydrins from Olefins. Representative procedure for 2-bromo-1-phenylethan-1-ol (Table 1, entry 1): To a reaction mixture containing styrene (0.52 g, 5.0 mmol), water (15 ml), and 46% aqueous HBr (6.0 mmol, 1.2 equiv) was added 30% aqueous H₂O₂ (7.5 mmol, 1.5 equiv) during a period of 1 h at room temperature. The above reaction mixture was then refluxed for 5 h (TLC). After completion of the reaction, a sample was withdrawn and analyzed by GC-MS, which showed 100% formation of the desired bromohydrin (2-bromo-1-phenylethan-1-ol) based on GC area %. To isolate the product, it was extracted with ethyl acetate (15 ml × 3). The combined organic layers were washed with dilute solutions of Na₂S₂O₃. Finally it was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (hexane—ethyl acetate 95:5) to afford the pure 2-bromo-1-phenylethan-1-ol (1.81 g, 9.02 mmol) in 94% yield. The spectroscopic data (¹H and ¹³C NMR) was in good agreement with the reported data. A similar procedure was followed for the syntheses of bromohydrins listed in Table 1.

General Procedure for the Synthesis of α-Bromoketones from Olefins. Representative procedure for 2-bromo-1-phenylethan-1-one (Table 3, entry 1): The first stage of obtaining bromohydrin was followed as mentioned above (general procedure for the synthesis of bromohydrins). The above reaction
**KHSO₄: a highly efficient and reusable heterogeneous catalyst for hydroarylation of styrenes**

Rajendra D. Patil · Girdhar Joshi · Subbarayappa Adinurthy

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**Abstract** Hydroarylation of styrenes with arenes/heteroarenes using KHSO₄ (10 mol%) as an efficient heterogeneous catalyst is described. High conversion and selectivity (>99%) were observed for hydroarylation of styrenes with 2-naphthol at reflux temperature of 1,2-dichloroethane. Yields were quantitative with all styrenes. Moderate to good conversions and selectivities were achieved with other aromatics and heteroaromatics under the same conditions. Regeneration and reusability of KHSO₄ were demonstrated. Addition of a trace amount of water could help to reactivate the KHSO₄ through dispersion and to facilitate the hydroarylation reaction.

**Keywords** KHSO₄ · Heterogeneous catalysis · Hydroarylation · Styrenes · Aromatics

**Introduction**

Functionalization of arenes and heteroarenes is of great importance in synthesis of pharmaceuticals, and agro- and fine chemicals; therefore, various procedures for their acylation and alkylation have been reported. Transition-metal-catalyzed hydroarylation of alkenes is of particular importance due to its high selectivity, synthetic efficiency, and environmental friendliness. Traditionally, these transformations are performed by Friedel–Crafts reactions with acyl or alkyl halides in combination with at least equimolar quantities of a Lewis acid. Recently, promising transition-metal- and acid-catalyzed C–H transformations of arenes and heteroarenes have been reported [1–6]. A number of catalytic systems, including ruthenium [7–10], palladium [11–17], platinum [18–20], nickel [21], and indium [22], have been employed for functionalization of heterocycles through carbon–carbon bond formation. Prominent systems, Bi(OTf)₃ [23], BiCl₃ [24], and FeCl₃ [25] catalyzed hydroarylation of styrenes were also reported for synthesis of a variety of 1,1-diarylkylalkanes in good yields. Boronic esters/acids with palladium complex [26], iodoxy [27], and an ion-exchange resin [28] are recent developments in the hydroarylation of alkenes. However, these methods require use of stoichiometric or excess amounts of strong acids/bases and air/moisture-sensitive organometallic reagents. In most studies, the halide salts obtained as byproducts are drawbacks of these reactions.

**Results and discussion**

In view of our ongoing quest for green and sustainable processes for functionalization of alkenes [29–33] and alkynes [34] for diverse applications, we envisioned a metal-free catalyst system for hydroarylation of styrenes with aromatic compounds in the presence of KHSO₄ (10 mol%) as an efficient catalyst under mild conditions (Scheme 1).

These reactions are particularly interesting from the viewpoint of green chemistry because hydroarylation exhibits perfect atom efficiency and relies on the use of simple arene reactants and safe catalysts, no production of toxic waste material, applicability of various substrates, and heterogeneous catalysis, allowing facile catalyst/product separation. Careful choice of inorganic acid, solvent, and reaction conditions enabled us to develop a
GREEN OXIDATION OF METHYLALENES TO BENZOIC ACIDS WITH BROMIDE/BROMATE IN WATER

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An efficient and convenient procedure has been developed for the oxidation of methylarenes to the corresponding benzoic acids using a bromide/bromate-based reagent system in water. Regeneration and reusability of the bromide/bromate reagent is demonstrated.

Keywords: Benzoic acids; bromide/bromate; methylarenes; oxidation

INTRODUCTION

The oxidation of methyl aromatics into the corresponding benzoic acids is an important transformation in organic synthesis as these carbonyl derivatives constitute versatile building blocks in pharmaceutical and polymer industries.[1] A variety of oxidizing agents such as KMnO₄, CrO₃, Na₂Cr₂O₇, TiO₂, NaIO₄, and HNO₃ are available to effect this key reaction.[2-6] However, these metallic reagents are often required in stoichiometric amounts, and these procedures are associated with environmental pollution because of the large amounts of hazardous metallic wastes. Moreover, purification of the reaction products is often very tedious because of the difficulty in separation of the metal residues from the product. Despite the industrial importance of this process and ever-growing environmental concerns, efficient catalytic systems have been rarely described.[7] Recently, WO₃/70% tert-butyl hydroperoxide (TBHP)/aqueous NaOH has been reported.[8] Although several methods are known for the synthesis of aromatic carboxylic acids, preparation under mild conditions without use of heavy-metal catalysts and generation of waste is an ultimate goal in view of technical, economical, and industrial aspects. As a part of our continuing activities to develop green procedures that avoid hazardous reagents,[9] we report herein a novel, heavy-metal-free, and recyclable reagent system for the oxidation of methylarenes to
EASY ACCESS TO α-BROMOKETONES AND EPOXIDES FROM vic-DIBROMIDES UNDER AQUEOUS CONDITIONS

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The conversion of vic-1,2 dibromides to α-bromoketones and epoxides using H2O/dioxane and NaOH/water respectively under mild conditions has been described.

Keywords: α-Bromoketones; bromohydrins; epoxides; vic-dibromides

INTRODUCTION

Organic reactions in water have received increased attention primarily because of their environmental acceptability, abundance, and low cost.[1] Water as the reaction medium is certainly the best choice in the constant search for cheaper, cleaner, and more efficient technologies for the transformations of organic molecules.[2] Moreover, water also exhibits unique reactivity and selectivity that cannot be attained in conventional organic solvents.[3]

Vicinal halohydrins, α-bromoketones, and epoxides are versatile intermediates for the synthesis of a variety of biologically important natural products, fine chemicals, and pharmaceuticals.[4] Thus, a number of procedures have been developed for preparation of bromohydrins, which involve either ring opening of epoxides by hydrogen bromide or metal bromides[5] or addition of BrOH to an olefin.[6] The procedures reported for the preparation of α-bromoketones are primarily based on the reaction of carbonyl compounds with elemental bromine,[7] N-bromosuccinimide (NBS),[8] and 4,4-dibromo-2,6-di-tert-butyl-cyclohexa-2,5-dienone.[9] Although a number of methods have been reported for these transformations, development of an efficient procedure in water without any catalyst will be highly appreciated.

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DIRECT AND SELECTIVE CONVERSION OF BENZYL BROMIDES TO BENZALDEHYDES WITH AQUEOUS H₂O₂ WITHOUT CATALYST

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GRAPHICAL ABSTRACT

R = H, NO₂, Cl, Br, CH₃, etc.

Abstract The facile and selective conversion of benzylic bromides to benzaldehydes using H₂O₂ as a benign oxidizing agent in an aqueous medium is described. Under these conditions, good yields of benzaldehydes were obtained.

Keywords Benzyl bromides; hydrogen peroxide; oxidation benzaldehydes

INTRODUCTION

Organic reactions in water have received increased attention primarily because of their environmental acceptability, abundance, and low cost. Water as the reaction medium is certainly the best choice in the constant search for cheaper, cleaner, and more efficient technologies for the transformations of organic molecules. Moreover, water also exhibits unique reactivity and selectivity that cannot be attained in conventional organic solvents.

The development of sustainable, efficient, and selective catalysts and reagents for the oxidation of alcohols to aldehydes is an important and fundamental reaction in academia and industry. During the past decade, many transition-metal-catalyzed reactions have been uncovered for direct oxidation of benzylic alcohols to aldehydes. The scarcity of these precious metals and their high price limits their applications. The conversion of benzyl halides to benzaldehydes is the best alternate as benzyl halides are easily accessible from methyl arenes. Many methods have been

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High atom efficient and environment-friendly preparation of herbicides bromoxynil and ioxynil

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Received 16 July 2009; accepted (revised) 5 October 2010

High atom efficient and environment-friendly preparation of herbicides bromoxynil and ioxynil using bromide/bromate and iodide/iodate couple as halogenating reagent in water at room temperature is described.

Keywords: Bromide/bromate, atom efficient, herbicide, bromoxynil, ioxynil

The use of 3,5-dibromo-4-hydroxybenzonitrile (bromoxynil) I and 3,5-diiodo-4-hydroxybenzonitrile (ioxynil) II are well established as herbicides1. Certain esters of bromoxynil, especially the octanoate, have been used extensively as herbicides in the control of broad-leaved weeds, particularly in crop growing areas2. Although the esters have been shown to be highly effective, they have been produced only by incurring productivity penalties, which are aggravated by the expensive and cumbersome purifications that have till now been required.

Bromoxynil and ioxynil were first synthesized by Auwers and Reis3 in 1896 by a complex four step procedure starting with 4-hydroxybenzaldehyde, an uneconomical method involving bromination, formation of the aldoxime, dehydration with concomitant acetate formation and hydrolytic removal of the acetate. Muller et al.4 has described a procedure for bromination of 4-hydroxybenzonitrile with elemental bromine in methanolic acetic acid. The product produced by the Muller process was recovered by contacting the resulting bromination mixture with aqueous methanolic sodium hydrogen sulfite. Luckenbaugh et al.5 describes the production of bromoxynil or its sodium salt by carrying out bromination with elemental bromine in an aqueous suspension, especially aqueous caustic, followed by a chlorine sparge. Most of the reported methods for bromoxynil preparation involves the use of elemental bromine in their process67. Despite the industrial importance of bromination process and the ever growing environmental concerns, the use of liquid bromine for bromination reaction is still very common in industry as well as in academia is probably due to its easy availability, low cost and lack of a better alternative. Moreover, purification of the reaction products is often demanding and laborious.

Results and Discussion

Recently we introduced a green brominating reagent utilizing the precursor of liquid bromine manufacture8. This precursor comprises a 5:1 mole ratio of NaBr-NaBrO3 (designated as BR-A) which releases bromine on demand (in-situ) upon acidification (Eq. 1).

\[ 5 \text{NaBr} + \text{NaBrO}_3 + 6\text{HCl} \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} + 6\text{NaCl} \]  

(1)

Alternatively, this reagent (BR-A) when treated with NaOCl furnished another reagent with a composition of 2:1 mole ratio of NaBr-NaBrO3 (Eq. 2) (designated as BR-S) and used as such. This reagent (BR-S) releases BrOH on acidification (Eq. 3) and provides quantitative atom efficiency in aromatic

\[ 5\text{NaBr} + \text{NaBrO}_3 + 3\text{NaOCl} \rightarrow 4\text{NaBr} + 2\text{NaBrO}_3 + 3\text{NaCl} \]  

(2)

\[ 2 \text{Br}^- + \text{BrO}_3^- + 3 \text{H}^+ \rightarrow 3 \text{BrOH} \]  

(3)

substitution and olefinic addition reactions which have been reported by us for few useful applications9. Our continuous efforts to achieve maximum bromide atom efficiency and minimize waste generation, as well as elimination of the use of hazardous liquid bromine and volatile organics led us to extend the utility of these reagents towards the preparation of extremely valuable herbicide bromoxynil (Eq 4)10.