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ORIGINAL PAPER

Functional group transformation from amines to aldehydes via IBX oxidation

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Abstract IBX oxidation of secondary aryl amines has been applied towards their functional group transformation to aldehydes using a facile post-process with satisfactory yields. The oxidation of *N*-benzylmethylamine was used as a model substrate and suggested that the ratio of IBX oxidant to amine should be 2:1. Subsequently, several aryl amines were subjected to these standard conditions, which revealed that the oxidative activity depends on the electronic and steric structures of the substituent groups in the substrates. The oxidative selectivity to secondary amines was also discovered.

Keywords Functional group transformation · IBX · Oxidation · Amine · Aldehyde

Introduction

The introduction and interconversion of functional groups are all-important issues in organic chemistry for most of the chemical, physical, and biological properties of chemical compounds which are directly dependent on their functional groups (Girdhar et al. 2002; Paraschiv et al. 2002; Chen and Walsh 2004; Simmons et al. 2009; Crawford et al. 2012). Functional groups containing a heteroatom bonded to carbon, such as carbonyl, amino, imino, and haloalkanes, attract special attention, since they can be conveniently transferred between each other (Agami et al. 1996; Nakamura et al. 1994; Ishii et al. 2000; Mulvihill et al. 2001). Carbonyl groups as the proprietary moiety of aldehydes and ketones, which are important intermediates in the synthesis of carboxylic acids, imines, and alcohols, and can be used to realize the elongation of carbon chains (Janin et al. 2002; Yamago et al. 2003; Soloshonok and Kukhar 1996; Bordoloi 1993; Marshall and Schaaf 2001) which are usually prepared by the oxidation of alkenes (Yang and Zhang 2001), alkynes (Suzuki et al. 2001), halides (Das et al. 2003) and alcohols (Lahtinen et al. 2004), and the reduction of carboxylic acids (Goosen and Ghosh 2002). Aldehydes obtained from the oxidation of amines always serve as the intermediates towards the preparation of imines (Florea and Petride 2016; Naya et al. 2013). In this work, a novel way to prepare various benzaldehydes via IBX (*o*-iodoxybenzoic acid, Scheme 1) oxidation of amines has been discovered.

IBX is a precursor in the synthesis of Dess–Martin periodinane and has not been considered for synthetic purposes for very long time due to its noticeable insolubility in most organic solvents and water until its excellent oxidative activity under mild conditions in DMSO was exposed (Frigerio and Santagostino 1994). Over the last two decades, IBX has been developed as an effective oxidant to provide carbonyl groups including aldehydes and ketones from alcohols, epoxides, and acetals (Duschek and Kirsch 2011; Satam et al. 2010). At the reflux, IBX also demonstrates the ability to oxidize alcohols as a suspension in ethyl acetate, 1,2-dichloroethane, THF, or toluene in satisfactory yield (More and Finney 2002; Moorthy et al. 2004). IBX oxidation of amines provides the corresponding imine products and is considered to undergo

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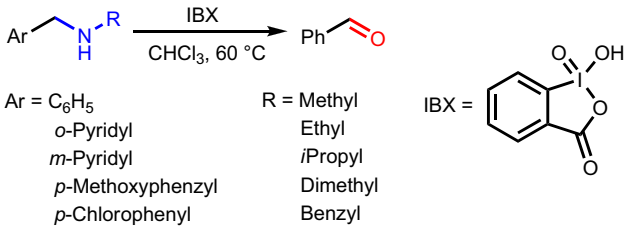


Scheme 1 IBX oxidation of amines to produce aldehydes

an ionic mechanism (Nicolaou et al. 2003, 2004) and affords a new way to synthesize *N*-substituted pyrroles (Murthy and Nageswar 2011; de Graaff et al. 2015) and bis-amides (Singh et al. 2017). We herein report the first successful IBX oxidization of amines to produce aldehydes (Scheme 1).

Experimental

Materials and apparatus

All the amines and aldehydes used in this study were obtained commercially (Tokyo Kasei Kogyo Co., Ltd.) and used without further purification. IBX was prepared from 2-iodobenzoic acid and oxone (Frigerio and Santagostino 1994). ^{1}H NMR (DMSO-d_6, δ): 7.20 (t, 1H), 7.44 (t, 1H), 7.66 (d, 1H), 7.94 (d, 1H). mp = 230–233 °C with explosive decomposition. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ at 25 °C on a JEOL JNM-ECZ400s spectrometer using $SiMe_4$ as an internal reference. ESI–MS spectra were recorded on an Agilent 1100 spectrometer.

IBX oxidation of amines

N-Benzylmethylamine

A solution of amine (55 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 12 h. The resulting suspension was filtered and the filtrate washed in sequence with 10% NaOH (5 mL × 3), 1 M HCl (5 mL × 3) and water. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to afford the desired product (43 mg, 91% yield). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 10.08 (s, 1H), 7.93 (d, 2H, J = 8.0 Hz), 7.68 (d, 1H, J = 4.0 Hz), 7.59 (t, 2H, J = 4.0 Hz) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 192.47, 136.37, 134.49, 129.76, 129.01, 121.72 ppm. ESI–MS: M + H^+, found 107.1 (calc. 107.12).

N-Ethylbenzylamine

A solution of amine (61 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 16 h. The resulting suspension was filtered and the filtrate was washed in sequence with 10% NaOH (5 mL × 3), 1 M HCl (5 mL × 3) and water. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to afford the desired product (34 mg, 71% yield).

N-Benzylisopropylamine

A solution of amine (67 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 24 h. The resulting suspension was filtered and the filtrate was washed in sequence with 10% NaOH (5 mL × 3), 1 M HCl (5 mL × 3) and water. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to afford the desired product (12 mg, 27% yield).

Dibenzylamine

A solution of amine (89 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 24 h. The resulting suspension was filtered and the filtrate was washed in sequence with 10% NaOH (5 mL × 3), 1 M HCl (5 mL × 3) and water. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to afford the desired product (37 mg, 81% yield).

o-Pyridylmethylamine

A solution of amine (55 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 24 h. The resulting suspension was filtered and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel and ethyl acetate) to afford the desired product (41 mg, 89% yield). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 10.08 (s, 1H), 7.93 (d, 2H, J = 8.0 Hz), 7.68 (d, 1H, J = 4.0 Hz), 7.59 (t, 2H, J = 4.0 Hz) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ = 193.44, 152.75, 150.21, 137.10, 127.90, 121.72 ppm. ESI–MS: M + Na^+, found 130.1 (calc. 130.11).

m-Pyridylmethylamine

A solution of amine (55 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 24 h. The resulting

suspension was filtered and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, ethyl acetate) to afford the desired product (43 mg, 93% yield). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 10.18$ (s, 1H), 9.14 (s, 1H), 8.90 (d, 1H, $J = 4.0$ Hz), 8.23 (d, 1H, $J = 4.0$ Hz), 7.55 (t, 1H, $J = 4.0$ Hz) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): $\delta = 190.78$, 154.73, 152.07, 135.83, 131.4, 124.11 ppm. ESI–MS: M + Na^+, found 130.1 (calc. 130.11).

N-(p-Methoxybenzyl)-N-methylamine

A solution of amine (68 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 6 h. The suspension was filtered and the filtrate was washed in sequence with 10% NaOH (5 mL × 3), 1 M HCl (5 mL × 3), and water. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to afford the desired product (57 mg, 91% yield). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 9.89$ (s, 1H), 7.85 (d, 2H, $J = 8.0$ Hz), 7.01 (d, 2H, $J = 8.0$ Hz), 3.90 (s, 3H) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): $\delta = 190.89$, 164.60, 132.01, 129.91, 114.31, 55.60 ppm. ESI–MS: M + Na^+, found 159.1(calc. 159.15).

N-(4-Chlorophenyl)-N-methylamine

A solution of amine (70 mg, 0.45 mmol) and IBX (252 mg, 0.90 mmol) in 10 mL of $CHCl_3$ was heated at reflux with vigorous stirring for 4 h. The resulting suspension was filtered and the filtrate was washed in sequence with 10% NaOH (5 mL × 3), 1 M HCl (5 mL × 3), and water. The organic layer was dried with $MgSO_4$ and removed in vacuo to afford the desired product (60 mg, 94% yield). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 9.98$ (s, 1H), 7.82 (d, 2H, $J = 8.0$ Hz), 7.51 (d, 2H, $J = 8.0$ Hz) ppm. ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): $\delta = 186.22$, 136.29, 130.01, 126.24, 124.79 ppm. ESI–MS: M + H^+, found 141.7 (calc. 141.57).

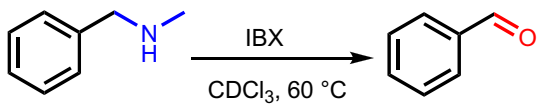
Screening for solvents

N-Benzylmethylamine (7 mg) and IBX (25 mg) in different solvents including ethyl acetate, THF, *n*-hexane, acetone, acetonitrile, and DMSO was heated at 60 °C with vigorous stirring for 4 h. The resulting suspension was filtered and the solvent removed in vacuo. The resulting residue was dissolved into 0.6 mL of $CDCl_3$ and the yield evaluated using ^{1}H NMR spectroscopy.

Results and discussion

N-Benzylmethylamine was employed as a model compound in the oxidation reaction using IBX and $CDCl_3$ was employed as the solvent for in situ investigation of the oxidation. Although the reaction afforded interesting imine products including *N*-benzylidenemethanamine and 1*H*-isoindole in a 1:1 ratio upon IBX oxidation in DMSO (Nicolaou et al. 2003, 2004), the present oxidation reaction surprisingly only yielded benzaldehyde without any oxidation by-products (Scheme 2). The amount of IBX used in the oxidation reaction was optimized using the ^{1}H NMR spectra recorded in $CDCl_3$ (Fig. 1). The presence of 1 equiv. of oxidant produced about 60% conversion of the amine compound in 12 h and prolonging the reaction time did not afford any more aldehyde product. The yield was improved upon the addition of more IBX. The product yield increased by about 12% with the addition of 1.2 equiv. of IBX and kept on increasing to 83% upon adding more oxidant (1.5 equiv. of IBX). Finally, complete transformation from the amine to aldehyde was accomplished in the presence of 2 equiv. of IBX. The solvent effect on the oxidation was investigated using various solvents including ethyl acetate, THF, *n*-hexane, acetone, and acetonitrile (Table 1). It was interesting to note that the oxidation activity of IBX significantly depends on the polarity of the solvent used. The benzaldehyde product was provided with acceptable yields of 71 and 59% in ethyl acetate and THF, respectively. However, there was only a 34% yield obtained in *n*-hexane and just trace aldehyde was observed in the solvents, acetone, and acetonitrile. The oxidation of *N*-benzylmethylamine in DMSO provided 55% conversion to the aldehyde, which could be attributed to the good solubility of IBX in DMSO. The results indicated that the IBX oxidation of *N*-benzylmethylamine could benefit in solvents with moderate polarity ($CHCl_3$, ethyl acetate and THF), while the reactivity decreases in highly polar solvents (acetone and acetonitrile) and non-polar solvents (*n*-hexane).

Nicolaou proposed that IBX oxidation of secondary amines to yield the corresponding imine products goes through an ionic mechanism on the basis of the formation of an IBX-amine complex (Scheme 3, Step 1), which was identified using ESI–MS and ^{1}H NMR spectroscopy, and the by-product aldehydes were attributed to hydrolysis of the imine (Nicolaou et al. 2003, 2004). Although no imine intermediate was observed in the present case, even when



Scheme 2 IBX oxidation of *N*-benzylmethylamine

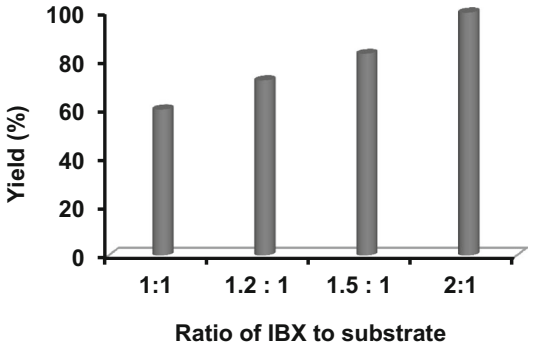
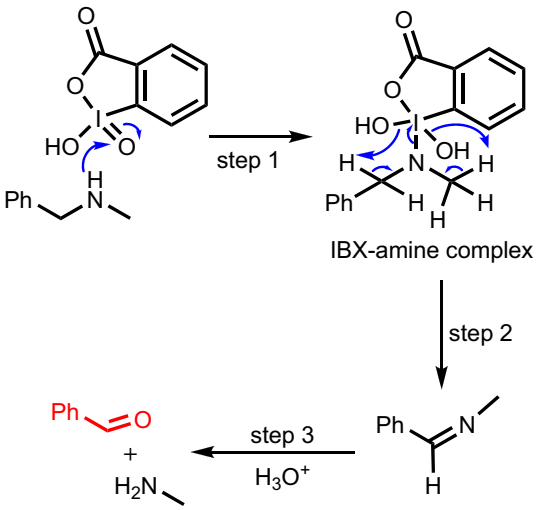


Fig. 1 Oxidation of *N*-benzylmethylamine with different amounts of IBX in 12 h in $CDCl_3$. The yields were determined using ^1H NMR spectroscopy

Table 1 Oxidation of *N*-benzylmethylamine with 2 equiv. of IBX in different solvents at 60 °C for 12 h

Entry	Solvent	Yield (%)
1	Chloroform	91
2	Ethyl acetate	71
3	THF	59
4	*n*-Hexane	34
5	Acetone	<5
6	Acetonitrile	<5
7	DMSO	55

The yields were calculated using ^1H NMR spectroscopy



Scheme 3 Possible mechanism for IBX oxidation of *N*-benzylmethylamine to give benzaldehyde

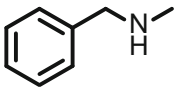
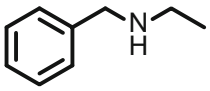
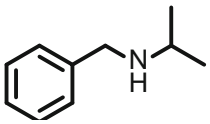
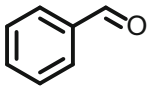
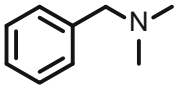
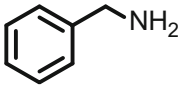
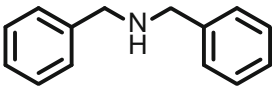
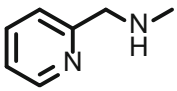
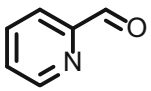
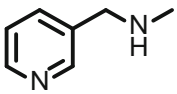
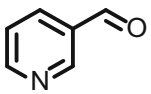
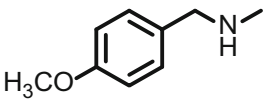
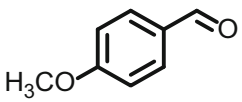
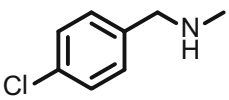
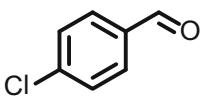
the reaction time was shortened or the oxidation process was directly traced using ^1H NMR spectroscopy in $CDCl_3$. We believe that benzaldehyde was the product of the hydrolysis of the imine formed as the primary product (Scheme 3) and the higher acidity using an excess amount of IBX under the reaction conditions in refluxing chloroform and longer reaction times could well accelerate hydrolysis of the imine intermediate.

To probe this IBX oxidation in more detail, several amines were subjected to these standard conditions. The results show that the oxidations provide aryl aldehydes as the desired product and alkyl amines as the leaving moieties (Table 2), which indicates that the benzyl moiety between the aryl rings and amino groups is more active due to the activation of the conjugated structures. On the other hand, the activity was clearly affected by the species on both the aryl and amino groups. *N*-benzylmethylamine, as the simplest structure among the substrates studied, was oxidized using IBX with quantitative conversion (Entry 1) in 12 h. The oxidation was decreased with more complicated alkyl substituents on the amino N atom even when the reaction times were prolonged to 24 h. The oxidation conversion was 78% for *N*-ethylbenzylamine (Entry 2) and only 35% for *N*-benzylisopropylamine (Entry 3), which revealed a steric hindrance effect on the oxidation activity. The tertiary amine, *N*,*N*-dimethylbenzylamine (Entry 4), was not oxidized using IBX due to lacking the necessary N–H bond. Dibenzylamine was subjected to this oxidation reaction to give an 81% conversion (Entry 6) despite the fact that it contains a bulky benzyl group, which is very close to the conversion observed for *N*-ethylbenzylamine and, hence, suggests that the steric effect depends on the first substitute only. The primary amine, benzylamine, was also subject to the IBX oxidation reaction, but very little of the corresponding aldehyde product was observed in the ^1H NMR spectrum (Entry 5), which was possibly due to its relatively weak activity to form the IBX-amine complex. Other secondary amines, including the *N*-heterocyclic aryl amines *o*- and *m*-pyridylmethylamine, were also used as substrates in the IBX oxidation reaction. As expected, *o*-pyridylmethylamine produces *o*-pyridinecarboxaldehyde in a very good yield in spite of applying a longer reaction time (24 h) (Entry 7) and *m*-pyridylmethylamine exhibits similar activity to *N*-benzylmethylamine (Entry 8). It was surprisingly that *N*-(*p*-methoxybenzyl)-*N*-methylamine and *N*-(4-chlorophenyl)-*N*-methylamine behave the most effectively in all the above mentioned cases with 100% conversion in 6 h (Entry 9 and 10), which could be attributed to the electronic effect of the substituent groups on the phenyl ring.

Conclusions

In summary, the functional group transformation directly from a secondary amino group to an aldehyde group upon oxidation using the hypervalent iodine reagent, IBX, has

Table 2 Oxidation of arylamine with 2 equiv. of IBX in $CHCl_3$

1			12	100 (91)
2			16	78 (71)
3			24	35 (27)
4			24	trace
5			24	trace
6			24	81 (72)
7			24	100 (89)
8			12	100 (93)
9			6	100 (91)
10			6	100 (94)

[a]The yields were directly determined using ^{1}H NMR spectroscopy with the isolated yields included in the parentheses

[b]No other by-products species are observed

been achieved in $CDCl_3$, which is a successful attempt to broaden the application of IBX in organic chemistry and develop a novel pathway to synthesize aldehydes from secondary aryl amines. A mechanism of the in situ hydrolysis of an IBX–amine complex has been proposed to explain the oxidation process. The oxidative activity

depends on the structures of the substrates; in more specific terms, their effect on the transformation is related to the electronic and steric structures of both the aryl and alkyl moieties in the substrates. Furthermore, the restricted oxidation of primary and tertiary amines reveals the selectivity of this approach to this functional group transformation.

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