

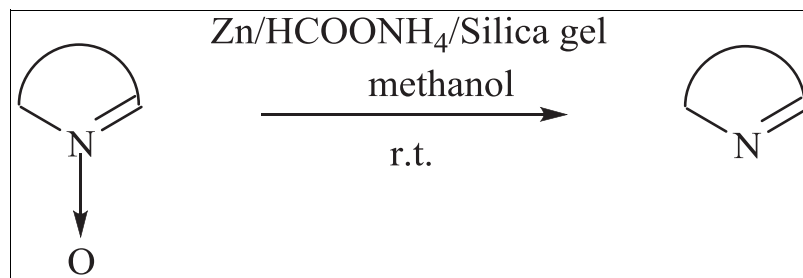
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An improved mild and selective method for the deoxygenation of a variety of amine *N*-oxides has been carried out in the presence of silica gel under mild conditions at room temperature to afford corresponding amines in relatively good yields without purification. The reaction is tolerant of a variety of functional groups such as hydroxyl, ester, acid, carbonyl, and cyano groups, as well as halogens. This method would be of great utility to synthesize various pyridines and amines easily.

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INTRODUCTION

Deoxygenation of amine *N*-oxides to corresponding amines in the presence of other reducible functional groups is a useful transformation in organic synthesis [1]. A wide variety of reagents and conditions for the deoxygenation of amine *N*-oxides have been reported, for example, $\text{POCl}_3/\text{K}_2\text{CO}_3$ [2], trifluoroacetic acid anhydride [3], aluminum iodide [4], $\text{Zn}/\text{Aq. NH}_4\text{Cl}$ [5], $\text{TiCl}_4/\text{SnCl}_2$ [6], catalytic hydrogenation [7], and $\text{Zn}/\text{ammonium formate}$ under reflux condition [8], silane/Mo catalyst [9], RuCl_3 [10], and boron reagents [11]. The aforementioned reports include complex metal catalysts, corrosive and expensive reagents, tedious work-ups and low yields, high reaction times, poor chemoselectivity, not readily available reagents, relatively severe reaction conditions, and impure products. In certain cases, the reagents employed for this transformation are expensive and toxic. Therefore, it is still desirable to develop easily accessible reaction conditions with operationally simple procedures for such reduction. Hence, we report here an improved

protocol for highly chemoselective reduction of substituted amine *N*-oxides to amines using zinc, ammonium formate, and silica gel. Various pyridines and amines were obtained in high yield and chemoselectivity by using cheap, nontoxic, widely available, and easily handled zinc as a catalyst and silica gel as a promoter.

RESULTS AND DISCUSSION

We report here silica gel as a heterogeneous promoter for the efficient conversion of amine *N*-oxides to their corresponding amines in the presence of $\text{Zn}/\text{ammonium formate}$ in MeOH at room temperature. Initially, a model reaction was examined using 4-methoxypyridine-*N*-oxide, zinc dust, and ammonium formate in the presence of silica gel (1 g) in methanol as solvent at room temperature (Scheme 1). After 10 min, 4-methoxypyridine (7) was isolated. An increase in the amount of silica gel did not affect the rate or yield of the reaction. Subsequently, we investigated the effect

Scheme 1. Deoxygenation of amine *N*-oxides.

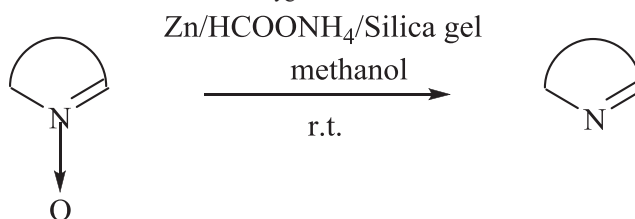
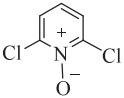
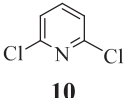
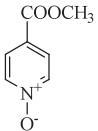
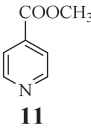
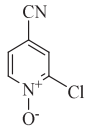
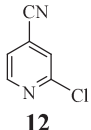
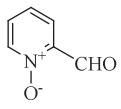
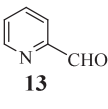
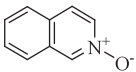
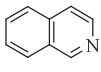
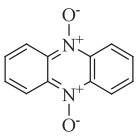
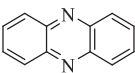
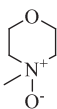
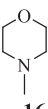


Table 1
Deoxygenation of various amine *N*-oxides at room temperature.

S. No.	Pyridine- <i>N</i> -oxide	Time (min)	Product	Yield (%) ^a
1		10	 1	92
2		10	 2	98
3		20	 3	94
4		10	 4	87
5		20	 5	80
6		10	 6	92
7		10	 7	96
8		10	 8	88
9		10	 9	91

(Continues)

Table 1
(Continued)

S. No.	Pyridine- <i>N</i> -oxide	Time (min)	Product	Yield (%) ^a
10		10	 10	88
11		10	 11	97
12		10	 12	89
13		10	 13	88
14		10	 14	92
15		20	 15	91
16		10	 16	82

^aIsolated yields.

of silica gel on the reaction. It was observed that there was no product formation without silica gel at room temperature.

Thus, methanolic solution of the amine *N*-oxides was admixed with anhydrous ammonium formate, silica gel (1 g), and freshly prepared Zn dust [12] at room temperature. Work up after 10–20 min involving filtration over celite, evaporation of MeOH, extraction with CHCl₃, and evaporation of the solvents afforded nearly pure amines in good yields (80–98%) without column chromatography. The ratio of the reagents used was 1:2:3 (substrate/zinc dust/ammonium formate) for mono *N*-oxides and 1:4:6 for bis *N*-oxides. In order to investigate the possibility of scope and limitations of this method, we have tested the selective deoxygenation of

amine *N*-oxides with other sensitive functional groups. A variety of functional groups (methoxy, cyano, chloro, hydroxy, acid, ester, and aldehyde) remain unchanged under the reaction conditions. But the nitro group was easily reduced under these reaction conditions to amino compound. It is interesting to note that the chloro substituent in 2,6-dichloropyridine-*N*-oxide (entry 10) remains unchanged, even though it is prone to dehalogenation reaction [13] and the position of the substituent in the heteroaromatic ring does not seem to have any effect on the deoxygenation. The method was also applied to aliphatic amine *N*-oxide resulting in the formation of corresponding amine in good yield. The results are presented in Table 1. The structural assignment for compounds is supported by IR, ¹H, ¹³C

NMR, and MS. Compounds **1** and **3** are known in the literature, and **6–16** are commercially available and were compared their IR, NMR, and MS spectra with those of authentic samples.

It was already reported that zinc dust acts as a catalyst and ammonium formate serves as a hydrogen source [14]. Although we have not established the mechanism experimentally, a possible explanation is proposed based on our earlier report that pyridine-*N*-oxide forms a strong pentacoordinated complex with silica [15]. Such activation of pyridine-*N*-oxide/amine *N*-oxide by silica favors the facile deoxygenation of *N*-oxide.

From Table 1, one can see that the reduction to compounds (**1–16**) has enhanced the utility of the procedure because these compounds with the ready availability of the additional nitrogen lone pair can participate in a range of reactions. In this context, compounds **3** and **5** are partially noteworthy in the formation of a variety of metal complexes and in the design of catalysts.

The advantages of the aforementioned method over the previous methods are (i) selective reduction of *N*-oxide in the presence of other reducible groups including ester, nitrile, carbonyl, and halogens, (ii) ready availability of reagents and easy to operate, (iii) rapid reaction, (iv) high yields, (v) avoidance of strong acidic media, (vi) no requirement of pressure apparatus, (vii) less expensive reagents and catalyst, (viii) no thermal heating, (ix) easy work-up as no chromatographic purification is required, and (x) the method was also applied to aliphatic amines *N*-oxides.

CONCLUSION

In conclusion, we have demonstrated an improved and alternate procedure for the deoxygenation of several amine *N*-oxides at room temperature in the presence of silica gel in good yields and shorter time periods. Although the literature reports a number of procedures for the deoxygenation of amine *N*-oxides, the excellent yields, simplicity, room temperature conditions, compatibility with various functionalities, and ease of isolation of the products make our procedure a practical alternative. This method would be of great utility to synthesize various pyridines and amines easily.

EXPERIMENTAL

Reagents and all solvents were analytically pure grade and were used without further purification. Melting points were recorded on a Fischer–Johns apparatus and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet Nexus 760 spectrometer (ThermoFisher Scientific,

Waltham, MA, USA) as KBr pellets and prominent peaks expressed in cm^{-1} . ^1H and ^{13}C NMR were recorded on a Bruker Avance 300 MHz NMR spectrometer (Bruker, Billerica, MA, USA) in CDCl_3 or $\text{DMSO}-d_6$ containing tetramethylsilane as an internal standard. Electron ionization (EI) and electrospray ionization (ESI) mass spectra were recorded on a VG 7070H and micromass Quattro LC instrument (Mc Kinley Scientific, Sparta Township, NJ, USA). Microanalyses were performed on an automated C, H, and N analyzer.

General procedure for the deoxygenation of mono amine *N*-oxides. To a stirred suspension of mono amine *N*-oxide (0.5 mmol) and freshly activated zinc dust (1 mmol) in MeOH (5 mL) was introduced anhydrous ammonium formate (1.5 mmol) and silica gel (1 g). The resulting mixture was left stirred at room temperature, filtered through celite and washed with MeOH (2 mL), and evaporated, and the resulting residue was triturated with CHCl_3 (15 mL). The CHCl_3 layer was washed with water (2×10 mL), dried over anhydrous Na_2SO_4 , and evaporated to afford the corresponding amines in good yield without purification.

General procedure for the deoxygenation of bis amine *N*-oxides. To a stirred suspension of bis amine *N*-oxide (0.5 mmol) and freshly activated zinc dust (2 mmol) in MeOH (5 mL) was introduced anhydrous ammonium formate (3 mmol) and silica gel (1 g). The resulting mixture was left stirred at room temperature, filtered through celite and washed with MeOH (2 mL), and evaporated, and the resulting residue was triturated with CHCl_3 (15 mL). The CHCl_3 layer was washed with water (2×10 mL), dried over anhydrous Na_2SO_4 , and evaporated to afford the corresponding amines in good yield without purification.

2-(Pyridin-2-ylamino)ethan-1-ol [16] (1). Colorless amorphous solid; Mp 63–65°C (Lit. 64–66°C); IR (KBr, ν cm^{-1}): 3350, 1660, 1606, 1345, 1062, 769; ^1H NMR (300 MHz, CDCl_3): δ 3.50 (m, 2H), δ 3.81 (m, 2H), δ 4.98 (br, 1H), δ 5.04 (br, 1H), δ 6.45 (d, 1H, $J = 8.30$ Hz), δ 6.59 (app t, 1H, $J = 5.47$ Hz), δ 7.41 (app t, 1H, $J = 8.49$ Hz), δ 8.04 (br, 1H); ^{13}C NMR (75.47 MHz, CDCl_3): δ 45.2, 62.6, 108.3, 112.8, 137.7, 146.8, 158.4; Ms (ESI) $m/z = 139$ (M+H) $^+$; Anal. Calcd for $\text{C}_7\text{H}_{10}\text{N}_2\text{O}$: C, 60.85; H, 7.30; N, 20.28%. Found: C, 60.75; H, 7.26; N, 20.25%.

2,2'-(Pyridin-2-ylazanediyl)bis(ethan-1-ol) (2). Pale brown liquid; IR (Neat, ν cm^{-1}): 3329, 2927, 1600, 1496, 1437, 1362, 1046, 770; ^1H NMR (300 MHz, CDCl_3): δ 3.68 (m, 4H, N- CH_2), δ 3.85 (m, 4H, O- CH_2), δ 6.61 (m, 2H, aromatic β' , β), δ 7.45 (app t, 1H, $J = 8.85$ Hz, γ), δ 8.05 (d, 1H, $J = 7.01$ Hz, α); ^{13}C NMR (75.47 MHz, CDCl_3): δ 53.4 (N-C), 61.8 (O-C), 107.1 (β'), 112.8 (β), 137.5 (γ), 147.3 (α), 158.8 (α'). Ms (ESI) $m/z = 183$ (M+H) $^+$; Anal. Calcd for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.29; H, 7.57; N, 15.20.

N,N'-Bis(pyridin-2-yl)ethane-1,2-diamine [17] (3). Dark brown solid; Mp: 134–136°C; IR (KBr, ν cm^{-1}): 3229, 2905, 2867, 1605, 1572, 1527, 1437, 1331, 1148, 767; ^1H NMR (300 MHz, CDCl_3): δ 3.57 (s, 4H), δ 6.39 (d, 2H, $J = 8.49$ Hz), δ 6.56 (app t, 2H, $J = 6.6$ Hz), δ 7.38 (app t, 2H, $J = 8.68$ Hz), δ 8.07 (d, 2H, $J = 4.15$ Hz); ^{13}C NMR (75.47 MHz, CDCl_3): δ 42.2, 107.7, 113.2, 137.6, 148.0, 158.7; Ms (EI) m/z : 214 (M^+).

N,N'-Dimethyl-*N,N'*-bis(pyridin-2-yl)ethane-1,2-diamine (4). Pale brown liquid; IR (Neat, ν cm^{-1}): 3413, 2926, 1599, 1500, 1426, 772; ^1H NMR (300 MHz, CDCl_3): δ 2.73 (s, 3H), δ 3.05 (s, 3H), δ 3.23 (m, 2H), δ 3.82 (m, 2H), δ 6.60 (d, 1H, $J = 8.79$ Hz), δ 6.69 (app t, 1H, $J = 6.83$ Hz), δ 7.55 (app t, 1H, $J = 8.79$ Hz), δ 8.13 (d, 1H, $J = 3.90$ Hz); ^{13}C NMR (75.47 MHz, CDCl_3): δ 33.1, 37.4, 47.5, 47.9, 106.3, 112.6, 137.7, 147.2, 158.2. Ms (ESI) m/z : 166 ($\text{M}+\text{H}^+$); Anal. Calcd for $\text{C}_9\text{H}_{15}\text{N}_3$: C, 65.42; H, 9.15; N, 25.43. Found: C, 65.29; H, 9.11, N, 25.25.

N,N'-Dimethyl-*N,N'*-bis(pyridin-2-yl)ethane-1,2-diamine (5). Pale brown solid; Mp: 128–132°C; IR (KBr, ν cm^{-1}): 3427, 2923, 1602, 1501, 1425, 1323, 985, 770; ^1H NMR (300 MHz, CDCl_3): δ 3.03 (s, 6H), δ 3.76 (s, 4H), δ 6.48–6.54 (m, 4H), δ 7.40 (app t, 2H, $J = 8.87$ Hz), δ 8.16 (d, 2H, $J = 5.85$ Hz); ^{13}C NMR (75.47 MHz, CDCl_3): δ 37.2, 48.1, 105.9, 111.6, 137.5, 147.9, 158.2; Ms (EI) m/z : 242 (M^+); Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_4$: C, 69.39; H, 7.49; N, 23.12. Found: C, 69.31; H, 7.42, N, 23.03.

4-(Piperidin-1-yl)pyridine [18] (6). Pale yellow solid; Mp: 78–80°C; IR (KBr, ν cm^{-1}): 3340, 2962, 2805, 1605, 1520, 1430, 815; ^1H NMR (300 MHz, CDCl_3): δ 1.69 (m, 6H), δ 3.50 (m, 4H), δ 6.74 (d, 2H, $J = 5.80$ Hz), δ 8.25 (br, 2H); ^{13}C NMR (75.47 MHz, CDCl_3): δ 24.0, 25.2, 47.3, 107.5, 146.2, 155.6; Ms (EI) $m/z = 162$ (M^+).

4-Methoxyppyridine [19] (7). Colorless liquid; IR (Neat, ν cm^{-1}): 3345, 1606, 1453, 1328, 1064, 758; ^1H NMR (300 MHz, CDCl_3): δ 3.88 (s, 3H), δ 6.89 (br, 2H), δ 8.54 (br, 2H); ^{13}C NMR (75.47 MHz, CDCl_3): δ 55.3, 110.5, 149.9, 166.7; Ms (EI) $m/z = 109$ (M^+).

2-Picolinic acid [20] (8). White solid; Mp: 138–140°C; IR (KBr, ν cm^{-1}): 2915, 1718, 1587, 1450, 1351, 1295, 1087, 752; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 7.66 (d, 1H, $J = 6.20$ Hz), δ 8.03–8.10 (m, 2H), δ 8.75 (d, 1H, $J = 6.20$ Hz), δ 10.08 (s, 1H); Ms (EI) m/z : 123 (M^+).

Pyridin-2-ol [21] (9). Pale yellow solid; Mp: 103–105°C; IR (KBr, ν cm^{-1}): 3260, 3096, 2933, 1639, 1608, 1418, 1242, 1099, 981, 781; ^1H NMR (300 MHz, CDCl_3): δ 6.31 (app t, 1H, $J = 6.42$ Hz), δ 6.63 (d, 1H, $J = 9.14$ Hz), δ 7.42 (d, 1H, $J = 5.43$ Hz), δ 7.48 (app t, 1H, $J = 8.65$ Hz); Ms (EI) $m/z = 95$ (M^+).

2,6-Dichloro pyridine [22] (10). Colorless solid; Mp: 82–84°C; IR (KBr, ν cm^{-1}): 2941, 1563, 1481, 1408, 1362, 1163, 1136, 993, 791; ^1H NMR (300 MHz,

CDCl_3): δ 7.26 (d, 2H, $J = 7.20$ Hz), δ 7.63 (dd, 1H, $J = 7.5, 7.5$ Hz); Ms (EI) $m/z = 148$ (M^+).

Methyl isonicotinate [23] (11). Colorless liquid; IR (Neat, ν cm^{-1}): 3054, 2888, 1738, 1296, 1109, 758; ^1H NMR (300 MHz, CDCl_3): δ 3.92 (s, 3H), δ 7.86 (d, 2H, $J = 6.45$ Hz), δ 8.78 (d, 2H, $J = 6.32$ Hz); Ms (EI) $m/z = 137$ (M^+).

2-Chloroisonicotinonitrile [24] (12). White solid; Mp: 70–72°C; IR (KBr, ν cm^{-1}): 3086, 2468, 2240, 1547, 1381, 1217, 886, 847; ^1H NMR (300 MHz, CDCl_3): δ 7.48 (dd, 1H, $J = 2.10, 7.50$ Hz), δ 7.64 (d, 1H, $J = 2.10$ Hz), δ 8.56 (d, 1H, $J = 7.50$ Hz); Ms (EI) $m/z = 138$ (M^+).

2-Pyridine carboxaldehyde [25] (13). Yellow liquid; IR (Neat, ν cm^{-1}): 3092, 2876, 1725, 1582, 1281, 1006, 758; ^1H NMR (300 MHz, CDCl_3): δ 7.71–7.48 (m, 1H), δ 7.94 (dd, 2H, $J = 18.3, 7.1$ Hz), δ 8.82 (s, 1H), δ 10.09 (s, 1H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 121.23, 127.50, 136.75, 149.82, 152.40, 192.94; Ms (EI) $m/z = 107$ (M^+).

Isoquinoline [26] (14). Pale yellow liquid; IR (Neat, ν cm^{-1}): 3065, 1628, 1586, 1500, 1381, 1260, 940, 864; ^1H NMR (300 MHz, CDCl_3): δ 7.73–7.52 (m, 3H), δ 7.81 (d, $J = 8.2$ Hz, 1H), δ 7.96 (d, $J = 8.2$ Hz, 1H), δ 8.52 (d, $J = 5.8$ Hz, 1H), δ 9.25 (s, 1H); ^{13}C NMR (75.47 MHz, CDCl_3): δ 120.48, 126.47, 127.26, 127.64, 127.68, 130.37, 135.79, 142.96, 152.51.

Phenazine [27] (15). Pale brown solid; ^1H NMR (CDCl_3 , 300 MHz): δ 7.77–7.79 (m, 4H), δ 8.18–8.21 (m, 4H); ^{13}C NMR (CDCl_3 , 75.47 MHz): δ 129.6, 130.4, 143.4.

4-Methyl morpholine [28] (16). Pale yellow liquid; IR (Neat, ν cm^{-1}): 2962, 2893, 1454, 1338, 1202, 1071, 906, 864; ^1H NMR (300 MHz, CDCl_3): δ 2.28 (s, 3H), δ 2.39 (s, 4H), δ 3.90–3.59 (m, 4H); ^{13}C NMR (75.47 MHz, CDCl_3): δ 46.47, 55.46, 66.45.

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