J. Chem. Research (S), 1998, 266–267†

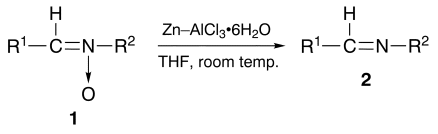
An Efficient Deoxygenation of Nitrones and Heteroarene N-Oxides†

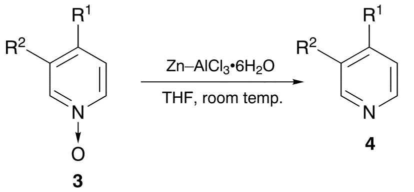
Dilip K. Dutta* **and Dilip Konwar**

Organic Chemistry Division, Regional Research Laboratory, Jorhat-785006, Assam, India

Selective deoxygenation of nitrones and heteroarene N-oxides with the Zn–$AlCl_3 \cdot 6H_2O$-THF system produces the corresponding imines and heteroarenes in high yield.

The selective deoxygenation of organic N-oxides is a subject of current interest in organic synthesis. Consequently a number of reagents, e.g. low-valent titanium,[1] phosphorus,[2] sulfur,[3] sodium hydrogen telluride,[4] tributyltin hydride,[4] Pd/C,[6] aluminium/nickel alloy,[7] tetrathiomolybdate,[8] *etc.* may be used to reduce the N–O bonds of nitrones[4] and heteroarene N-oxides.[1,5] However, there are various limitations to their general use: (i) expensive or not readily available reagents, (ii) low temperature and dry reaction conditions,[1(a,b)] (iii) side reactions and difficulties with the isolation of the product,[2(b)] (iv) drastic reaction conditions which effect the substituents,[9] (v) uncontrolled reaction of nitrones[4] and (vi) long reaction time.[8] Therefore, the development of efficient, cheap and readily available reagents requires great attention. We report here that nitrones and heteroarene N-oxides can be deoxygenated in excellent yields under mild conditions and with short reaction times by addition of Zn–$AlCl_3 \cdot 6H_2O$ to nitrones in THF.





The readily available nitrone **1a** (0.4 g, 2 mmol) was added to a well-stirred mixture of Zn (0.26 g, 4 mmol) and $AlCl_3 \cdot 6H_2O$ (1.0 g, 4 mmol) in THF (25 ml) at room temperature for 10 min. Aqueous work-up and evaporation of the organic solvent gave the corresponding imine **2a**. Yield 0.34 g (92%).

Interestingly, the carbon–carbon double bonds (entries 1g and 1h in Table 1) furan (entry 1d) and thiophene (entry 1f), which are susceptible to saturation, remain intact and only selective deoxygenation of the nitrone takes place. Moreover, aromatic methoxy (entry 1d) or chloro (entries 1b and 1c) substituted nitrones were selectively reduced. At the same time, when the reaction was extended to heteroarene N-oxides (entries 3a and 3b), the corresponding deoxygenated products were produced in good yields.

Although the mechanism of the reaction can not be assigned at this stage the single-electron transfer (SET) process cannot be ignored.[10] Accordingly, we believe that Al^0 generated from the reaction of zinc and aluminium chloride (formation of black slurry) is responsible for deoxygenation. Further work is in progress to explore the possible use of this reagent in other synthetic transformations.

In conclusion, we hope that the present method finds wide application in organic synthesis because of its short reaction time, high yields and use of a readily available reagent under mild conditions.

Experimental

Mps were determined on a Buchi apparatus and are uncorrected. Mass spectra were obtained using a Finnigan-MAT (1NCOS-50) spectrometer. IR spectra were recorded on a Perkin-Elmer 237B spectrophotometer and ^1H NMR spectra on a Varian T-60 spectrometer. Commercially available (BDH) $AlCl_3 \cdot 6H_2O$ and zinc dust were used directly. Tetrahydrofuran was used after distillation over KOH. Nitrones (**1a**–**h**) and heteroarene N-oxides (**3a**–**b**) were prepared as reported.[12]

Deoxygenation of Nitrones and Heteroarene N-oxides.—Nitrone **1a** (0.4 g, 2 mmol) was added to a vigorously stirred mixture of Zn (0.26 g, 4 mmol) and $AlCl_3 \cdot 6H_2O$ (1 g, 4 mmol) in THF (25 ml) at room temperature. An exothermic reaction occurred at the beginning of the reaction, which subsided after 10 min. The reaction mixture was then poured into a saturated NH_4Cl solution (50 ml) and extracted with diethyl ether (3 × 50 ml). The organic layer was washed with brine (2 × 50 ml) and dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure gave a solid mass

Table 1 Deoxygenation of nitrones and heteroarene N-oxides

					Mp/Bp (°C)		
Entry	R^1	R^2	Reaction time (*t* min.)	Yield[a] (%)	Found	Reported	Ref.
1a	Ph	Ph	10	92	52	52	11
1b	p-ClC_6H_4	Ph	10	90	64–65	64–65	12
1c	Ph	p-ClC_6H_4	15	88	62	63	12
1d	p-$CH_3OC_6H_4$	Ph	15	81	63–64	64	12
1h	Ph	p-$MeOC_6H_4$	15	82	70	70–71	12
1f	Thiophenyl	Ph	15	80	122–124[b]	122–125[b]	13
1g	Furyl	Ph	15	82	57–58	58	14
1h	Ph-CH=CH	Ph	10	84	108–109	109	15
3a	H	H	20	76	164–163[c]	165–166[c]	16*a*
3b	CH_3	CH_3	25	80	162–163[c]	163[c]	16*b*

[a]IR, ^1H NMR and mass spectra were in accord with those of authentic samples. [b]At 2 mmHg. [c]Mp of the picrate derivative.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

which on recrystallization from ethanol gave **1a**. Yield: 0.34 g (92%); mp 52 °C.

Similarly, the compounds **1b**–**h** and heteroarene N-oxides **3a**,**b** were deoxygenated to the corresponding imines and heteroarenes, which were purified by recrystallization or column chromatography.

We thank the Director, Regional Research Laboratory, Jorhat for providing necessary facilities for this work.

Received, 24th November 1997; Accepted, 20th January 1998
Paper E/7/08471D

References

1 (*a*) M. Malinoswaki, *Synthesis*, 1987, 732; (*b*) R. Balicki, *Chem. Ber*., 1990, 647.
2 (*a*) T. R. Emerson and C. W. Rees, *J. Chem. Soc*., 1962, 17, 1917; (*b*) E. Howard and W. F. Olszewski, *J. Am. Chem. Soc*., 1959, **81**, 1483.
3 H. Kagami and S. Motoki, *J. Org. Chem*., 1978, **43**, 1267.
4 D. H. R. Barton, A. Fekih and Z. Lusinchi, *Tetrahedron Lett*., 1985, **26**, 4603.
5 (*a*) S. Kozuka, T. Akasaka, S. Furumai and S. Dae, *Chem. Ind.* (*London*), 1974, 452; (*b*) B. Jousseaume and E. Chanson, *Synthesis*, 1987, 55.
6 R. Balick, *Synthesis*, 1989, 645.
7 G. Lunn, E. B. Sansone and L. K. Keefer, *Synthesis*, 1985, 1104.
8 P. Ilankumaran and S. Chandrasekaran, *Tetrahedron Lett*., 1995, **36**, 4881.
9 A. R. Katritzky and J. M. Lagowski, *Chemistry of Heterocylic N-Oxides*, Academic Press, London, 1971.
10 Z. Yang and D. J. Barton, *J. Chem. Soc., Chem. Commun*., 1992, 233.
11 L. A. Bigelow and H. Eatough, *Org. Synth*., 1941, Coll. Vol. I, 80.
12 A. Roe and J. A. Montgomery, *J. Am. Chem. Soc*., 1953, **75**, 910.
13 R. W. Drisko and H. Makennis Jr, *J. Am. Chem. Soc*., 1952, **74**, 2626.
14 J. S. Sandhu, P. S. Sethi and S. Mohan, *Chem. Ind*. (*London*), 1970, 1595.
15 R. E. Miller, *J. Org. Chem*., 1961, **26**, 2327.
16 (*a*) *Dictionary of Organic Compounds*, 4th edn., ed. J. R. A. Pollock and R. Stevens, Eyre Spottiswoode, London, 1965, vol. 5, 2815; (*b*) *Dictionary of Organic Compounds*, 4th edn., ed. J. R. A. Pollock and R. Stevens, Eyre Spottiswoode, London, 1965, vol. 2, 1216.