An Efficient General Method for the Deoxygenation of *N*-Arylnitrones, Azoxybenzenes, and *N*-Heteroarene *N*-Oxides

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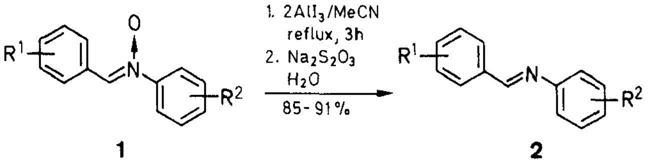
A new general method for the deoxygenation of *N*-oxides such as *N*-arylnitrones, azoxybenzenes, and *N*-heteroarene *N*-oxides uses aluminum iodide in acetonitrile. The deoxygenated products are obtained in high yields.

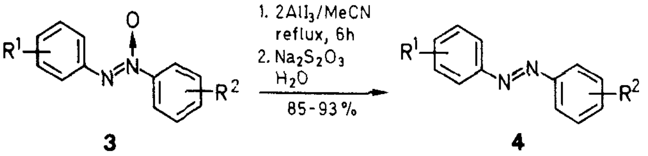
The selective deoxygenation of organic *N*-oxides is a subject of considerable interest in heterocyclic synthesis and a large number of reports are available on .the reduction of the N–O bond in different types of nitrones,[1] azoxybenzenes,[2,3] and *N*-heteroarene *N*-oxides.[4,5,6] Although many of deoxygenating reagents including sodium hydrogen telluride,[1] phosphorus,[2] aluminum-nickel alloy,[3] titanium(0) reagents,[4,5] tin derivatives,[6,7] silanes,[8,9] and alkalimetal hydrides[10] may be used for this purpose, there are various limitations to their general use, for example, difficult accessibility or high price, required drastic reaction conditions which affect substituents[11] and cause uncontrolled reduction of nitrones[1] or reductive cleavage of azoxy compounds[3] to amines rather than to expected imines or azo compounds, respectively. Thus, more efficient and easily available reagents are desired for the controlled and mild reduction of the N–O bond of organic *N*-oxides. The chemistry of aluminum(III) has acquired renewed interest in organic synthesis[12] and there are several reports on the use of aluminum iodide as a reagent for ether cleavage,[12,13] as catalyst in Friedel–Crafts alkylations,[14] and as reducing agent for sulfoxides.[15] We have recently found the versatile applicability of aluminum iodide as an economic and convenient reagent for the reductive cleavage of O–N bonds in heterocycles.[16] We now demonstrate the utility of aluminum iodide as a general and efficient deoxygenating reagent for *N*-oxides such as nitrones, azoxybenzenes, and *N*-heteroarene *N*-oxides.



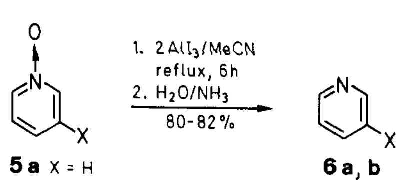
1, 2	R^1	R^2
a	H	H
b	H	4-Cl
c	4-Cl	H
d	3-Me	H

Aluminum iodide was freshly prepared by heating clean aluminum foil with iodine in dry acetonitrile (3 h) until the iodine color had disappeared. Reaction of this reagent with benzaldehyde *N*-arylnitrones **1** in refluxing acetonitrile afforded smooth deoxygenation of **1** to *N*-arylbenzaldimines **2** in high yields. There was no evidence for the formation of any secondary amine due to further reduction.

Extenson of the method to azoxybenzenes **3** (diaryldiazene *N*-oxides) gave the corresponding azobenzenes **4** as the sole products (Table). Similarly, reaction of aluminum iodide with pyridine and quinoline *N*-oxides **5** and **7**, respectively, afforded the deoxygenated products **6** and **8** in high yields, the chloro substituents in 3-chloropyridine 1-oxide (**5b**) and 4-chloroquinoline 1-oxide (**7b**) remaining unaffected although they are prone to dehalogenation reactions.[17]



3, 4	R^1	R^2
a	H	H
b	4-Cl	4-Cl
c	4-Me	4-Me



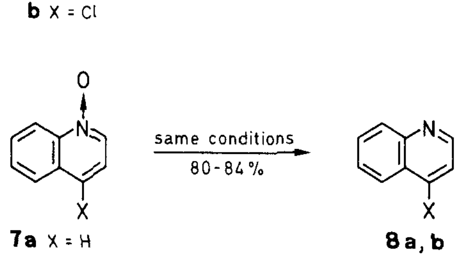


Table. Deoxygenation of *N*-Oxides **1**, **3**, **5**, **7** with Aluminium Iodide

Reaction[a]	Yield (%)	mp (°C) or bp (°C) found	mp (°C) or bp (°C) reported
1a → **2a**	91	52	52[18]
1b → **2b**	89	62	62[19]
1c → **2c**	88	66	66[20]
1d → **2d**	85	314	313-314[20]
3a → **4a**	93	68	68[21]
3b → **4b**	91	188	188[21]
3c → **4c**	85	144	144[21]
5a → **6a**	80	115 (164-165[b])	115.5 (164-165[b])
5b → **6b**	80	237 (203-204[b])	238 (203-204[b])
7a → **8a**	82	148 (134[b])	148 (135[b])
7b → **8b**	84	31 (211-212[b])	32 (212-213[b])

[a] All products were identified by TLC, mp, bp, MS, IR spectrometry, and/or ^{1}H-NMR data.

[b] Mp of picrate.

Attempts to affect deoxygenation of *N*-oxides **1**, **3**, **5**, and **7** using aluminum chloride or bromide under identical condition only led to isolation of starting material. Further, the reaction of iodine with the same *N*-oxides in refluxing acetonitriles did not lead to deoxygenation.

Acetonitrile was dried with P_2O_5 and freshly distilled prior to use. Melting points were determined on a Büchi apparatus and are uncorrected. Mass spectra were obtained using a AEIMS 30 spectrometer. IR spectra were recorded on a Perkin-Elmer 237 & 580B spectrophotometer, ^{1}H-NMR spectra on a Varian T-60 spectrometer.

Aluminum Iodide Solution in Acetonitrile:

Clean pieces of aluminum foil (0.54 g, 0.02 mol) are placed in dry MeCN (50 mL) and N_2. To this is added I_2 (7.61 g, 0.03 mol) and the mixture is heated at reflux temperature for 3 h. Formation of AlI_3 is accompanied by disappearance of the iodine color. The solution thus obtained (containing 0.02 mol of AlI_3) can be directly used in the deoxygenation reactions.

***N*-Phenylbenzaldimine (*N*-Benzylideneaniline, 2a); Typical Procedure for the Deoxygenation of Nitrones:**

To the freshly prepared solution of AlI_3 (8.16 g, 20 mol) in MeCN (50 mL) is added benzaldehyde *N*-phenylnitrone (**1a**; 1.97 g, 10 mol) and the mixture is refluxed under anhydrous conditions for 5 h. The solvent is evaporated on a rotary evaporator and the residue is treated with H_2O (100 mL). The resultant mixture is extracted with $CHCl_3$ (4 x 25 mL). The extract is washed with 10 % $Na_2S_2O_3$ solution (2 x 20 mL), dried (Na_2SO_4), and evaporated to give **2a**; yield: 1.65 g (91 %); mp 52 °C (EtOH) (Lit.[18] mp 52 °C).

Azobenzene (4a); Typical Procedure for the Deoxygenation of Azoxybenzenes:

To the freshly prepared solution of AlI_3 (8.16 g, 20 mol) in MeCN (50 mL) is added azoxybenzene (**3a**; 1.98 g, 10 mol) and the mixture is refluxed under anhydrous conditions for 6 h. Work up as above gives **4a**; yield: 1.62 g (89 %); mp 62 °C (EtOH/H_2O) (Lit.[21] mp 62 °C).

Pyridine (6a); Typical Procedure for the Deoxygenation of *N*-Heteroarene *N*-Oxides:

To the freshly prepared solution of AlI_3 (8.16 g, 20 mol) in MeCN (50 mL) is added pyridine *N*-oxide (**5a**; 0.95 g, 10 mol) and the mixture is refluxed under anhydrous conditions for 6 h. The solvent is then removed and the residue is poured into H_2O (100 mL). The resultant mixture is made basic (pH 8) with 25 % aqueous NH_3 and extracted with Et_2O (4 x 100 mL). The organic layer is washed with H_2O (200 mL), dried (Na_2CO_3), and evaporated to give **6**; yield: 0.63 g (80 %); bp 115 °C; picrate, mp 164-165 °C (benzene) (Lit.[19] mp 165-166 °C).

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