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A NEW METHOD FOR DEOXYGENATION OF HETEROAROMATIC N-OXIDES WITH CHLOROTRIMETHYLSILANE/SODIUM IODIDE/ZINC

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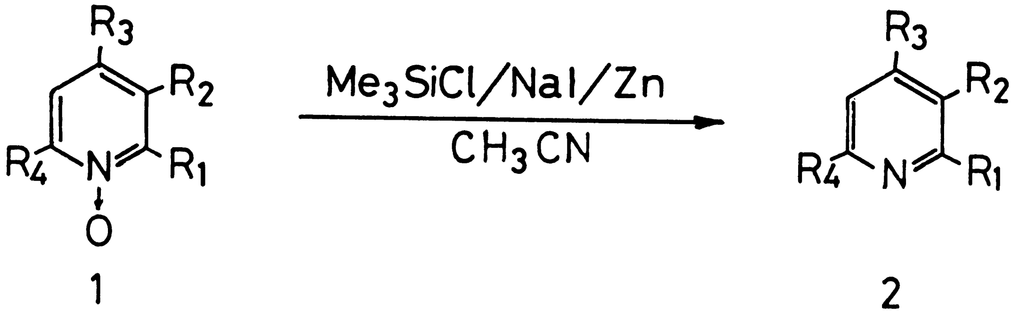
Heteroaromatic N-oxides are easily deoxygenated with chlorotrimethylsilane/sodium iodide/zinc in acetonitrile to give the corresponding parent bases in good yields.

Deoxygenation of heteroaromatic N-oxides is an important transformation frequently encountered in the synthesis of heteroaromatic compounds.1) The reduction was usually accomplished using trivalent phosphorus compounds, sulfur compounds, metal hydrides, dissolving metals etc.1) Recent several methods contain the photochemical deoxygenation of N-oxides in the presence of Lewis acid or triphenylphosphine,2) in situ generation of sulfur monooxide from sulforanes,3) a combination of sulfur dioxide and trialkylamine,4) and the use of phosphorus tetraiodide prepared from phosphorus and iodine.5) Chlorotrimethylsilane/sodium iodide in acetonitrile is a versatile reagent for carbon-oxygen bond cleavage in various organic compounds such as esters, ethers, acetals, and alcohols.6) Olah et al. reported that sulfoxides are easily deoxygenated with chlorotrimethylsilane/sodium iodide to the corresponding sulfides.7) There have been few reports on carbon-nitrogen bond cleavage in N-oxides by means of other silicon compounds.8) In connection with our studies on synthetic manipulations of oxygen-containing compounds,6) we wish to report here a new method for deoxygenating heteroaromatic N-oxides under mild and aprotic conditions. The reaction of an N-oxide with chlorotrimethylsilane/sodium iodide without zinc gave a only small amount of deoxygenated product (2 - 3%).

The reaction with dichlorodimethylsilane/sodium iodide gave the product in 17 - 20% yield. However, the N-oxide (1) reacted with chlorotrimethylsilane/sodium iodide in the presence of zinc to afford the corresponding parent base (2) in high yields.



To a mixture of sodium iodide (90 mmol) and zinc dust (60 mmol) in acetonitrile (30 ml), a solution of N-oxide 1 (30 mmol) and chlorotrimethylsilane (90 mmol) in acetonitrile (30 ml) was added dropwise with stirring over 1 h. During the addition, the reaction temperature was kept at 35 - 40 °C. Then the reaction mixture was heated to 55 - 60 °C with stirring for 1 h. After cooling to room temperature, the white precipitate was filtered off and washed with diethyl ether (3 X 30 ml). The combined filtrate was poured into a 5% aqueous sodium hydroxide solution (100 ml). White solide precipitated was filtered off, and washed with diethyl ether (4 X 30 ml). The organic layer was separated and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure (below 30 °C), the residue was distilled under reduced pressure to yield the pure heteroaromatic amine 2. The purity was examined by G.L.C. (OV-17 on Chromosorb W, 100 °C). The results are summarized in Table 1. When two equivalent of chlorotrimethylsilane and sodium iodide were used in the case of 2-methylpyridine N-oxide, the yield of the product was reduced to 60%. The reduction of 4-nitropyridine N-oxide with the reagent was unsuccessful. The reaction proceeds exthothermically, accompanied by the formation of hexamethyldisiloxane, sodium chloride, and zinc halide.

The deoxygenation of alicyclic ketones with chlorotrimethylsilane/zinc has been reported to yield the olefins in moderate yields.[9)] But N-oxides were not deoxygenated with the reagent without sodium iodide.

Table 1 Deoxygenation of N-oxides 1 with $Me_3SiCl/NaI/Zn^{a)}$

R^1	R^2	R^3	R^4	Yield (%)[b)]
Me	H	H	H	88
H	Me	H	H	92
H	H	Me	H	80
Me	H	H	Me	95
Cl	H	H	H	85
MeO	H	H	H	81
CN	H	H	H	45
H	H	CN	H	47
-CH=CH-CH=CH-		H	H	91

a) Molar ratio of Sub. /Me_3SiCl/NaI/Zn is 1/3/3/2.
b) Based upon the amounts of isolated.

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