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Chemoselective Deoxygenation of Nitrones and N-Oxides with Tetrathiomolybdate

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Abstract: Reaction of nitrones and N-oxides with benzyltriethylammonium tetrathiomolybdate 1 in acetonitrile (25°C) yielded the corresponding imines and amines in good yields. Sulfoxides and azoxy benzenes are unaffected.

Deoxygenation of nitrones and N-oxides is a valuable transformation in organic synthesis. This can be effected by various reagents like low valent titanium,[1] phosphorous,[2] sulfur[3] and tellurium[4] derivatives, tributyltinhydride[5] and Pd/C.[6] In general most of these reactions involve harsh reaction conditions, tedious work up and offer poor chemoselectivity.

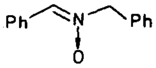
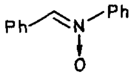
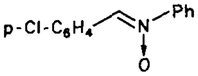
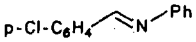
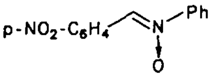
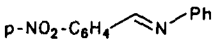
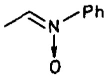
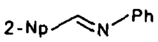
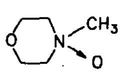
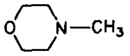
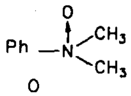
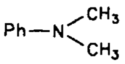
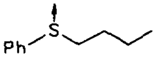
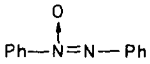
In continuation of our work on the use of benzyltriethylammonium tetrathiomolybdate $(PhCH_2NEt_3)_2MoS_4$, 1 as a reagent in organic synthesis,[7,8] it was decided to use the chemistry of induced internal redox reactions of 1 in the presence of electron acceptors.[9] In the course of this investigation we find that nitrones and N-oxides when treated with tetrathiomolybdate 1 in CH_3CN at 25°C underwent a smooth deoxygenation to afford the corresponding imines and amines in good yields. The results are summarized in Table 1.

As can be gauged from the table, the reagent can tolerate other reducible functional groups like chloro and nitro in the substrate (entries 3 and 4). Although N-oxides undergo deoxgenation with 1, sulfoxide (entry 8) and azoxy derivative (entry 9) remain unaffected under the reaction conditions. While the most commonly used reagents for deoxygenation do not discriminate between N-O and S-O bonds, the chemoselectivity obtainable with this reagent 1 is very unique. Thus, we have been able to demonstrate the utility of easily accessible tetrathiomolybdate 1 as a covenient reagent for effecting chemoselective deoxygenation of nitrones and N-oxides.

Typical Procedure: To a stirred solution of tetrathiomolybdate 1 (1.2 mmol) in CH_3CN (5ml) nitrone or N-oxide (1 mmol) in CH_3CN (2ml) was added at room temperature (25°C). After completion of the reaction, the solvent was evaporated and the residue was extracted with diethylether and filtered through a pad of Celite. Concentration of the ethereal solution gave the corresponding deoxygenated product. Products were purified by crystallisation or by bulb to bulb distillation.

Table 1

Deoxygenation of nirtones and N-oxides with tetrathiomolybdate **1**

Entry	Substrate	Product[a]	Time(h)	Yield(%)[b]
1			72	86
2			22	60
3			27	72
4			12	88
5			21	83
6			72	74
7			2	67
8		no reaction	72	-
9		- do -	72	-

[a] All the products gave satisfactory spectral data. [b] Yields refer to isolated products

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