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OXIDATION OF PRIMARY ALIPHATIC AMINES WITH SODIUM PERBORATE

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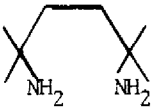
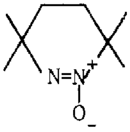
Summary: A biphasic system of ethyl acetate and water containing sodium perborate, sodium bicarbonate and N,N,N'N'-tetraacetylethylenediamine oxidizes primary aliphatic amines to aliphatic C-nitroso compounds in good to excellent yields.

Sodium perborate ($NaBO_3.nH_2O$, n = 1-4) is an inexpensive large scale industrial oxidant used in bleaching that is safe to handle.[1] An early report[2] in which benzil could be oxidatively cleaved to benzoic acid suggested that sodium perborate might be an effective oxidant that could be useful in organic functional group transformations, but it is only recently that sodium perborate has been used in organic synthesis.[4-12]

Our interest in developing methods for the oxidation of primary aliphatic amines to nitro compounds[13,14,15] prompted us to explore the use of sodium perborate in glacial acetic acid as a possible oxidizing medium for this transformation.[16] Under these conditions we were unable to oxidize 1-aminoadamantane. This result was similar to the unsuccessful attempts of McKillop[4] to oxidize t-butylamine and cyclohexylamine. However, by changing the reaction conditions, sodium perborate can be used to oxidize primary aliphatic amines. The conditions which were successful are based upon our previous observation that a biphasic system of ethyl acetate or dichloromethane containing sodium percarbonate, sodium bicarbonate and N,N,N'N'-tetraacetylethylenediamine (TAED) oxidized aliphatic primary amines to the corresponding C-nitroso compounds in good to excellent yields via the agency of the in situ generated peroxyacetic acid.[13] By substituting sodium perborate for sodium percarbonate in the conditions just described primary aliphatic amines are oxidized. In Table I are listed the primary amines that were oxidized and the yields of the products obtained.

Experimental Procedure: The amine (1.65 mmol), $NaHCO_3$(1.0g, 12 mmol), $NaBO_3\cdot 4H_2O$ (1.27g, 8.26 mmol) TAED (0.943g, 4.13 mmol) are added in sequence to a rapidly stirred biphasic mixture of EtOAc (25 mL) and water (25 mL). This mixture is stirred at room temperature for 2.5 hours. The organic layer is separated, and the aqueous layer is extracted with either EtOAc or CH_2Cl_2 (3 x 25 mL). The combined organic layer is washed sequentially with water (100 mL) and brine (100 mL). The organic layer is dried (Na_2SO_4 or $MgSO_4$), filtered, and the solvent removed by rotary evaporation with the bath temperature kept below 40°C. The resulting residue is then recrystallized or subjected to preparative layer chromatography.

TABLE I

$RNH_2 \xrightarrow[EtOAc/H_2O;\ R.T.\ 2.5hr.]{NaBO_3/NaHCO_3/TAED}$	% Yield	/Isolated Product				
R= dodecyl	65	$(RNO)_2$	27	RCH=NOH		
R= benzyl	100	RCH=NOH				
R= 2-phenethyl	44	$(RNO)_2$	30	RCH=NOH	26	RN=N(O)R
R= cyclohexyl	75	$(RNO)_2$				
R= 2-<u>endo</u>-norbornyl	78	$(RNO)_2$				
R= 1-adamantyl	78	$(RNO)_2$				
R= 2-adamantyl	80	$(RNO)_2$				
R= 3-noradamantyl	36	$(RNO)_2$				
	85					

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