The Stability of *NN*-Dialkylthiohydroxylamines

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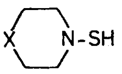
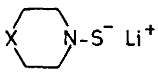
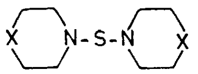
Summary The thiohydroxylamines (Ia) and (Ib) have been prepared *in situ* by protonation at −70 °C of the corresponding stable thiohydroxylamate anions (IIa) and (IIb).

Although thiohydroxylamines (>N-SH) have been postulated as reaction intermediates,[1] and in mass spectral fragmentations,[2] their specific preparation and properties have not been previously described. We were encouraged by the recent synthesis of thio-oximes[3] (=N-SH) to see if an analogous method could be used for thiohydroxylamines.

The disulphide (IIIa) was reduced with lithium (4 g atom equiv.) in liquid ammonia at −50 °C. After evaporation of the ammonia the resulting white solid was quenched with methyl iodide (at room temp.) and on work up gave (Va)[4,6] (67%) and (Vc)[5,6] (1—5%). (Va) arises by reaction of the thiohydroxylamate anion (IIa) with methyl iodide, (Vc) being derived from some N–S bond reduction. In a blank experiment without addition of lithium (IIIa) was recovered unchanged. Similarly the disulphide (IIIb) after reduction with lithium and quenching with methyl iodide (4 h in boiling ether) yielded (Vb)[4,6] and (Vd)[5,6] in the ratio 2·5 : 1. In order to obtain pure (Va) [or (Vb)] directly without (Vc) [or (Vd)] as a contaminant the monosulphides (IVa) and (IVb) were reduced with lithium and treated with methyl iodide to yield (Va), (48%) and (Vb), (55%) respectively. The white thiohydroxylamate anion (IIa), derived from either (IIIa) or (IVa), was stable at room temperature under dry nitrogen but decomposed rapidly (< 1 h) in boiling tetrahydrofuran giving sulphur and morpholine on work up. If the thio anion (IIa) from (IIIa) was treated with acrylonitrile at room temperature, the isolated products were (Ve) (33%) and (VI) (41%). When the thio anion (IIa) was protonated with 1 equiv. of acetic acid, at −70 °C, a pale yellow solution was obtained. The solution darkened on warming to ambient temperature with the evolution of some hydrogen sulphide (detected by lead acetate papers); work up gave sulphur (34%) and morpholine (isolated as the benzoylamide, 64%). The anion can be protonated at −70 °C, warmed to −40 °C for 1 h, cooled to −70 °C and regenerated by the addition of 1 equiv. of butyl-lithium after which quenching with methyl iodide gave a 25% yield of (Va). If however the mixture was warmed to −20 °C, in a similar process, only a 2·4% yield of (Va) was produced. Warming to −10 °C gave no (Va) on work up. If the thioanion (IIa) was treated with an excess of acetic acid (5 equiv.) at −70 °C for 2 min followed by treatment with butyl-lithium then methyl iodide, hydrogen sulphide was detected and only a trace amount of (Va) could be isolated. This indicates that the thiohydroxylamate anion (IIa) can be protonated at −70 °C to give


(I)


(II)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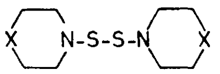
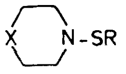
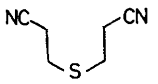

(III)

a; X = O
b; X = CH$_2$

(V) (a) X = O, R = Me
(b) X = CH$_2$, R = Me
(c) X = O, R = -SMe
(d) X = CH$_2$, R = -SMe
(e) X = O, R = S·CH$_2$CH$_2$CN

(VI)

the thiohydroxylamine (Ia) which decomposes at temperatures greater than −40 °C. The anion (IIb) can be similarly treated with acetic acid but the protonated form (Ib) appears to be unstable even at −70 °C.

The results are consistent with the following argument. A negative charge is more stable on sulphur than on nitrogen. Therefore, in the absence of protonation, there is little reason for (IIa) or (IIb) to lose sulphur. On the other hand protonation on nitrogen of (Ia) or (Ib) provides an easy loss of a proton and sulphur to give the parent base. In keeping with this argument, thio-*N*-oxides have never been observed.

All stable new compounds gave satisfactory spectroscopic data and correct analyses.

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