

## 2,2,6,6-TETRAMETHYLPIPERIDYL-1-THIYL

### A STABLE NEW RADICAL

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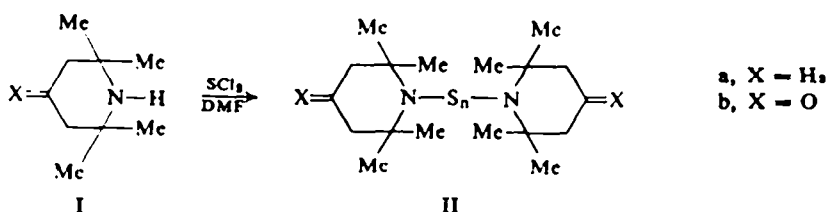
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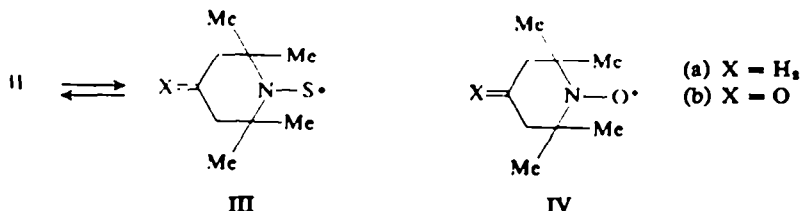
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**Abstract**—Bis[2,2,6,6-tetramethylpiperidyl-(1)]disulfide, and bis[4-oxo-2,2,6,6-tetramethylpiperidyl-(1)]disulfide have been prepared from the corresponding piperidines and sulfur dichloride ( $\text{SCl}_2$ ). They dissociate at 90–200° into radicals, the ESR-spectra of which are discussed.

THE disulfides IIa ( $n = 2$ ) and IIb ( $n = 2$ ) have been obtained from the reaction of the corresponding piperidines Ia and Ib with sulfur dichloride ( $\text{SCl}_2$ ) in dimethylformamide (DMF).



When sulfur chloride ( $\text{S}_2\text{Cl}_2$ ) was used in the same reaction with Ib, a mixture of the trisulfide IIb ( $n = 3$ ) and the disulfide IIb ( $n = 2$ ) was obtained, from which the trisulfide could be separated by chromatography. Similarly, when DMF was replaced by hexane or ether, a mixture of polysulfides IIa and IIb ( $n = 3-5$ ) was obtained from Ia and Ib, respectively, while piperidine with  $\text{S}_2\text{Cl}_2$  in ether gave only the corresponding disulfide.<sup>1</sup> The disulfides IIa and IIb are stable at room temperature.



However, when heated as a solid or in solution a three line electron spin resonance (ESR) spectrum was observed. This indicates that homolytic fission of the S—S-bond into the radicals 2,2,6,6-tetramethylpiperidyl-1-thiyl (IIIa) and 2,2,6,6-tetramethyl-4-oxo-piperidyl-1-thiyl (IIIb), respectively, takes place. The intensity of the ESR signal increased and decreased reversibly, as the temperature was raised or lowered

<sup>1</sup> A. Michaelis and K. Luxembourg, *Ber. Dtsch. Chem. Ges.* **28**, 165 (1895).

over a limited range. Above a certain temperature the compounds decomposed rapidly. The temperature ranges and ESR constants are given in Table 1. The data of the corresponding nitroxyl radicals IVa and IVb<sup>2,3</sup> are added for comparison.

TABLE 1

Radical	Reversible temp range	Decomposition temp	Hyperfine splitting oersted $\pm 0.2$	g-Factor $\pm 0.0005$
N—S IIIa	90–150°	170°	11.4	2.0173
IIIb	140–200°	220°	10.9	2.0171
N—O IVa	—	—	15.6	2.0061
IVb	—	—	14.5	2.0061

The ESR spectra of the N—S and N—O radicals are basically similar, all consisting of three hyperfine lines caused by interaction of the unpaired electron with the nitrogen-14 nucleus. The higher g-factor of the N—S radicals is in accordance with the spin-orbit coupling constant of sulfur (382 cm<sup>-1</sup>) which is larger than that of oxygen (151 cm<sup>-1</sup>). The smaller nitrogen hyperfine splitting in the N—S radicals shows that the unpaired spin density of the nitrogen atoms is smaller in these radicals than in the N—O radicals (strictly the isotropic hyperfine interaction is a measure of the spin density in the nitrogen s-orbital only). This corresponds to the fact that—because of the lower electronegativity of sulfur as compared to oxygen—the uncharged structure  $>\text{N—S}\cdot$  is more favoured than the dipolar structure  $>\text{N}^+\text{—S}^-$ , compared with the corresponding structures for the N—O radicals IVa and IVb. Molecular models show that steric hindrance contributes to the stability of IVa and IVb.<sup>3</sup> On replacement of oxygen by the larger sulfur atoms the bulk of the eight Me groups in IIa and IIb is too small for dissociation by steric repulsion. Similar conclusions have been reached for a series of substituted aromatic disulfides.<sup>4</sup>

The reversible formation of IIIa and IIIb from IIa and IIb therefore can be accounted for only by the energetically favourable accommodation<sup>5</sup> of the odd electron in the N—S-system of IIIa and IIIb. The formation of stable radical ions derived from tetrasulfur tetranitride or fragments thereof<sup>6</sup> support this view.

## EXPERIMENTAL

M.p.s were determined on a Kofler hot stage and are uncorrected. TLC (Merck Silica Gel, CS<sub>2</sub>, EtOH = 100/2 and spraying with AgNO<sub>3</sub> soln) was used for analysis of IIa and IIb.

**ESR measurements.** Solid samples of the disulfides IIa and IIb were degassed and sealed under pure N in silica tubes. Concentrated solns of the disulfides in iodobenzene were prepared in a similar

<sup>2</sup> E. G. Rozantzev and M. B. Neiman, *Tetrahedron* **20**, 131 (1964).

<sup>3</sup> A. Rassat and H. Lemaire, *J. Chim. Phys.* **61**, 1576, 1580 (1964). O. Hayes Griffiths, D. W. Cornell and H. M. McConnell, *J. Chem. Phys.* **43**, 2909 (1965).

<sup>4</sup> For an excellent review on sulfur radicals see: U. Schmid, *Angew. Chem.* **76**, 629 (1964) and Refs. 10, 11 and 12 cited.

<sup>5</sup> J. W. Linnett, *J. Am. Chem. Soc.* **83**, 2651 (1961).

<sup>6</sup> D. Chapman, R. M. Golding, A. G. Massey, J. T. Moelwyn-Hughes, *Proc. chem. Soc.* 377 (1961)

manner. The samples were heated *in situ* in a Varian V 4502-05 ESR spectrometer, using a standard variable temp accessory. A proton resonance magnetometer was used to calibrate the magnetic field and the *g*-factors were obtained by comparison with that of  $\alpha,\alpha'$ -diphenylpicrylhydrazyl ( $g = 2.0036$ ).

*Bis*[2,2,6,6-tetramethylpiperidyl-(1)] disulfide (IIa,  $n = 2$ ). 33.8 g (0.24 mole) 2,2,6,6-tetramethylpiperidine were dissolved in 100 ml dry DMF, cooled to  $-40^\circ$  and 6.2 g (0.06 mole)  $\text{SCl}_2$  added dropwise. Stirring was continued for 10 min, then the reaction mixture was poured into water, the solid material filtered off and recrystallized from aqueous EtOH, yield 6.8 g (66%), m.p.  $84-85^\circ$ . (Found: N, 8.10; S, 18.42. Calc. for  $\text{C}_{18}\text{H}_{34}\text{N}_2\text{S}_2$  (344): N, 8.15; S, 18.62%.)

*Bis*[4-oxo-2,2,6,6-tetramethylpiperidyl-(1)] disulfide (IIb,  $n = 2$ ). 37.2 g (0.24 mole) 2,2,6,6-tetramethylpiperidone-4 were dissolved in 100 ml dry DMF cooled to  $-40^\circ$  and 6.2 g (0.06 mole)  $\text{SCl}_2$  were added dropwise during a period of 30 min. Stirring was continued for a further 10 min and then the reaction mixture was poured into water. The solid material was filtered off, dried and recrystallized twice from hexane, yield 9.1 g (81%), m.p.  $145-147^\circ$ . (Found: N, 7.60; S, 17.36. Calc. for  $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$  (372): N, 7.51; S, 17.23%.)

*Bis*[4-oxo-2,2,6,6-tetramethylpiperidyl] trisulfide (IIb  $n = 3$ ). 15.5 g (0.1 mole) 2,2,6,6-tetramethylpiperidone-4 and 10.1 g (0.1 mole)  $\cdot \text{NEt}_3$  were dissolved in 80 ml dry DMF, cooled to  $-40^\circ$  and 6.8 g (0.05 mole)  $\text{S}_2\text{Cl}_2$  added dropwise and stirring was continued for 10 min. The reaction mixture was poured into water and the solid material (14.4 g, m.p.  $92-120^\circ$ ) was chromatographed on 500 g of silica gel with  $\text{CCl}_4$ . A small amount of S was eluted, followed by 1.5 g of IIb ( $n = 3$ ) and a mixture of the disulfide and the trisulfide (7.6 g). The trisulfide was recrystallized from EtOH, m.p.  $133-135^\circ$ . (Found: N, 6.83; S, 24.61. Calc. for  $\text{C}_{18}\text{H}_{28}\text{O}_2\text{N}_2\text{S}_3$  (404): N, 6.90; S, 23.81%.)