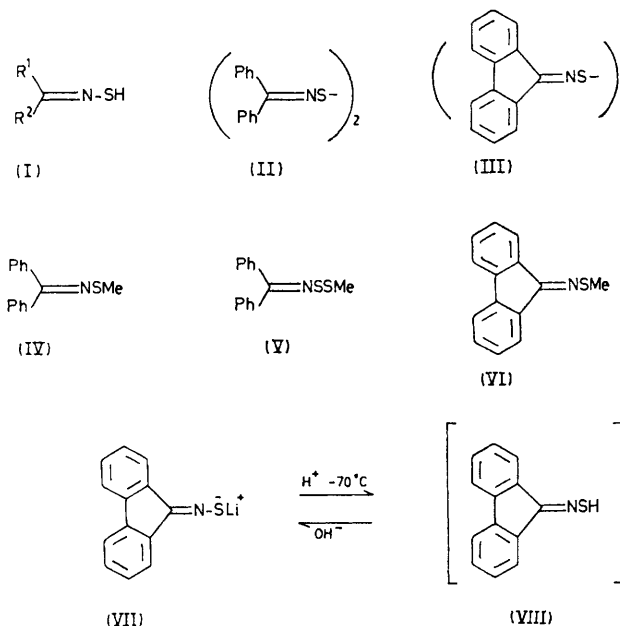


## Evidence for the Existence of a Thio-oxime

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**Summary** The synthesis of a thio-oxime is described which is stable at  $-70^{\circ}\text{C}$ ; the corresponding anion is stable at room temperature in the absence of oxygen.

DESPITE the fact that oximes are one of the most well known of carbonyl derivatives, the sulphur analogues, thio-oximes (I) are unknown. Our recent interest in the N-S bond<sup>1</sup> prompted a search for possible methods of preparing thio-oximes. The disulphide<sup>2</sup> (III) was reduced with chromium(II) acetate-dimethylformamide-thiol; the only products isolated were thiobenzhydrol, the corresponding disulphide, and benzophenone. Similarly the fluorenone derivative (III) gave fluorene-9-thiol and fluorenimine. Reduction of the disulphide (II) with lithium (3 equiv.)-ethylamine<sup>3</sup> (at  $-50^{\circ}\text{C}$ ) followed by treatment of the mixture with MeI gave (IV) and (V). Similar treatment of the disulphide (III) gave only (VI) (53%). The disulphide (III) did not react with MeI under these conditions. Reduction (Li-NH<sub>3</sub>) of the disulphide (III) at  $-70^{\circ}\text{C}$  followed by evaporation gave a red solid, presumed to be the lithium salt (VII). The salt (VII) is stable under argon at room temperature but rapidly deteriorates in the presence of oxygen. In dry tetrahydrofuran the salt (VII) gives a violet solution,  $\lambda_{\text{max}}$  251 ( $\epsilon$  23,800), 270 (3000), and 575 (6200) nm, that slowly decomposed to at least eight compounds (t.l.c.). Sulphur, fluorene-9-thiol, bisfluorene-9-yl disulphide, bifluorenylidene, fluorenone, and fluorene-9-ylidenamine were detected. Careful addition of acetic acid (at  $-20^{\circ}\text{C}$ ) to the salt (VII) gave H<sub>2</sub>S and several other compounds (t.l.c.). If the addition was carried out at  $-70^{\circ}\text{C}$  a pale yellow solution



was produced that turned dark violet [regeneration of (VII)] when aqueous KOH was added. Treatment of the pale yellow solution at  $-70^{\circ}\text{C}$  with diazomethane gave (VI) (13%). These data support the existence of a thio-oxime (VIII) which decomposes above  $-70^{\circ}\text{C}$ .

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