

A NOVEL DEOXYGENATION OF THIOLSULFONATES AND SULFOXIDES
WITH REDUCED IRON

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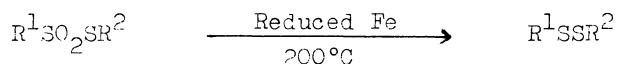
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Reduced iron is a very effective reagent for deoxygenation of various thiol-sulfonates and sulfoxides to give the corresponding disulfides and sulfides, respectively.

Reduced iron is known to be a good reagent to reduce a nitro group to an amino group.¹⁾ We wish to report here the deoxygenation of thiol-sulfonates and sulfoxides by this reagent.

Reduction of thiol-sulfonate esters using a metal, such as zinc dust or sodium amalgam, is described to be accompanied by a SO₂-S bond fission, resulting in the formation of thiolates and sulfinates.²⁾ In the course of our recent investigation concerned with the desulfonylation of thiol-sulfonates by a metal such as copper,³⁾ the formation of disulfides was observed when thiol-sulfonates were heated in the presence of metallic iron.

Thus, phenyl benzenethiol-sulfonate (Ia, 1 mmol) was deoxygenated by reduced iron (2.0 g) on heating at 200°C for 10 hr under reduced pressure (1 mmHg) to give diphenyl disulfide (IIa) as the sole product (91% yield). Preliminary results



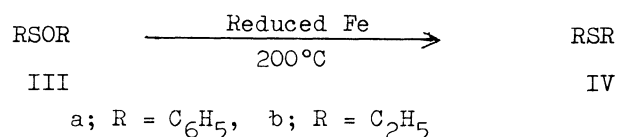
indicate that a wide variety of thiol-sulfonates are susceptible to this deoxygenation process. Representative examples of the deoxygenation reaction are shown in the Table. Phenyl p-toluenethiol-sulfonate (Ie) gave a mixture of disulfides, i. e. phenyl p-tolyl, diphenyl and di-p-tolyl disulfides. When the deoxygenation reaction was conducted at higher temperature or under atmospheric pressure, further desulfurized product, i. e. monosulfide was formed as a by-product.

It is of interest to note that metallic copper and iron show different reactivities toward thiol-sulfonate. Copper forms initially a complex with thiol-sulfonate analogous to the sulfinato complex, then it decomposes to give the

Thiolsulfonate	Yield (%) of Disulfide
a $R^1 = R^2 = C_6H_5$	91
b $R^1 = R^2 = p-CH_3C_6H_4$	85
c $R^1 = R^2 = p-CH_3OC_6H_4$	80
d $R^1 = R^2 = p-ClC_6H_4$	71
e $R^1 = p-CH_3C_6H_4, R^2 = C_6H_5$	78
f $R^1 = R^2 = C_2H_5$	59

desulfonylated product, i. e. monosulfide.³⁾ On the other hand, no complex formation as an intermediate could be observed in the reaction with iron metal. But in this case, since there is a difference between the conversion amount of the thiolsulfonate and the yield of the product when the reaction temperature was lower than 200°C, it may proceed through a complex analogous to the reaction with copper, and then resulted in the formation of deoxygenated product, i. e. disulfide, along with an elimination of an oxidized iron.

Sulfoxides⁴⁾ were easily deoxygenated in the same manner. When diphenyl sulfoxide (IIIa) was heated with reduced iron at 200°C for 2 hr under reduced pressure, diphenyl sulfide (IVa) was obtained in a quantitative yield. The reaction was slower



for dialkyl sulfoxide. In order to achieve 65% yield of diethyl sulfide (IVb), it was necessary to heat diethyl sulfoxide (IIIb) with reduced iron at 200°C for 4 hr.

The deoxygenation with reduced iron thus appears to be rather general utility, while the process is not applicable to the removal of oxygens from sulfone compounds.

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