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A NOVEL DEOXYGENATION OF THIOLSULFONATES AND SULFOXIDES WITH REDUCED IRON

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Reduced iron is a very effective reagent for deoxygenation of various thiolsulfonates 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 thiolsulfonates and sulfoxides by this reagent.

Reduction of thiolsulfonate esters using a metal, such as zinc dust or sodium amalgam, is described to be accompanied by a SO_2-S bond fission, resulting in the formation of thiolates and sulfinates.2) In the course of our recent investigation concerned with the desulfonylation of thiolsulfonates by a metal such as copper,3) the formation of disulfides was observed when thiolsulfonates were heated in the presence of metallic iron.

Thus, phenyl benzenethiolsulfonate (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

$$R^1SO_2SR^2 \xrightarrow[200^\circ C]{\text{Reduced Fe}} R^1SSR^2$$

indicate that a wide variety of thiolsulfonates are susceptible to this deoxygenation process. Representative examples of the deoxygenation reaction are shown in the Table. Phenyl p-toluenethiolsulfonate (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 temerature 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 thiolsulfonate. Copper forms initially a complex with thiolsulfonate analogous to the sulfinato complex, then it decomposes to give the

Table. Deoxygenation of Thiolsulfonates $R^1SO_2SR^2$

	Tiolsulfonate	Yield (%) of Disulfide
a	$R^1 = R^2 = C_6H_5$	91
b	$R^1 = R^2 = p\text{-}CH_3C_6H_4$	85
c	$R^1 = R^2 = p\text{-}CH_3OC_6H_4$	80
d	$R^1 = R^2 = p\text{-}ClC_6H_4$	71
e	$R^1 = p\text{-}CH_3C_6H_4$, $R^2 = C_6H_5$	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.

Sulfoxides[4] 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.

$$\underset{\text{III}}{\text{RSOR}} \xrightarrow[200^\circ\text{C}]{\text{Reduced Fe}} \underset{\text{IV}}{\text{RSR}}$$

$$\text{a; } R = C_6H_5, \quad \text{b; } R = C_2H_5$$

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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4) Concerning the deoxygenation of sulfoxides, see H. C. Brown and N. Ravindran, Synthesis, 42 (1973), and the references cited therein.

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