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PYROLYSIS OF AROMATIC THIOLSULFONATES IN THE PRESENCE OF METALLIC COPPER

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Aryl arenethiolsulfonates were pyrolyzed in the presence of metallic copper to give the corresponding diaryl sulfides. A complex between thiolsulfonates and the copper was suggested as an intermediate, on the basis of ir spectra.

Although esters of substituted methanethiolsulfonic acid have been reported to undergo a thermal decomposition giving the corresponding monosulfides with the elimination of sulfur dioxide, arenethiolsulfonate esters are known to be thermally quite stable,$^{1)}$ with one exception of 2-arylazo-1-naphthyl 2-arylazonaphthalene-1-thiolsulfonates.$^{2)}$ We wish to report here that metallic copper promotes the thermolysis of arenethiolsulfonates to give sulfides.

Pyrolysis of phenyl benzenethiolsulfonate without a catalyst at 250°C in a vapor phase gave a 34% yield of diphenyl disulfide accompanied by only a small amount of diphenyl sulfide. However, the reaction course was drastically changed, when the pyrolysis was carried out using a reaction tube packed with metallic copper at the same temperature. The yield of diphenyl sulfide raised up to 68% without the formation of a trace of the disulfide.

$$C_6H_5SO_2SC_6H_5 \xrightarrow[\Delta]{Cu} C_6H_5SC_6H_5 \quad + \quad SO_2$$

Monosulfide preparation was also successful in a liquid phase. Heating of phenyl benzenethiolsulfonate (1 mmol) with copper powder (1 g) at 200°C for 24hr resulted in the formation of diphenyl sulfide in a 60% yield, with a liberation of sulfur dioxide. The thermolysis of p-tolyl p-toluenethiolsulfonate and 4-methoxyphenyl 4-methoxybenzenethiolsulfonate under the same conditions also gave the corresponding sulfides in yields of 59% and 58%, respectively. 4,4'-Dichlorodiphenyl sulfide, however, was formed only in a 19% yield from 4-chlorophenyl 4-chlorobenzenethiolsulfonate because of a simultaneous occurrence of the Ullmann-type side-reaction.

An adduct was obtained from the reaction of p-tolyl p-toluenethiolsulfonate and copper, when the reaction temperature was lowered to 150°C. The ir spectrum of this adduct indicated absorptions at lower wave number region, that is, at 1036 cm^{-1} and 930 cm^{-1}, while the stretching frequencies of sulfonyl group in p-tolyl p-toluenethiolsulfonate were observed at 1322 $cm^{-1}(\nu_{asym})$ and 1135 $cm^{-1}(\nu_{sym})$. These frequencies of the adduct closely resemble those of sulfinato complex $(CH_3C_6H_4SO_2)_2Cu(OH_2)_2$.[3] Thus the structure of the adduct between thiolsulfonate and copper is supposed to have a similar structure to the sulfinato complex. The adduct, when heated at 200°C, afforded di-p-tolyl sulfide, which shows that the adduct is the possible intermediate of the reaction.

When thiolsulfonate esters having different aromatic groups at each sulfur atom were used in the thermal reaction in the presence of copper, a mixture of sulfides was obtained where the main product was asymmetric sulfide. For example, p-tolyl benzenethiolsulfonate gave phenyl p-tolyl sulfide (40%), di-p-tolyl sulfide (23%) and diphenyl sulfide (7%). This result suggests that the main part of the reaction may involve desulfonylation of thiolsulfonate esters, although fission of SO_2-S bond may partly occur. In addition, when an equimolar mixture of phenyl benzenethiolsulfonate and p-tolyl p-toluenethiolsulfonate was subjected to the reaction in the presence of copper, diphenyl-, di-p-tolyl- and phenyl p-tolyl sulfides were obtained in a ratio of 1.3:1.2:2.0. If the reaction proceeds via a intramolecular pathway, the products should be diphenyl- and di-p-tolyl sulfides, and no formation of phenyl p-tolyl sulfide would be observed. Accordingly, the thermal reaction proceeds by an intermolecular pathway, which gives the calculated ratio of 1:1:2 for these three sulfides, after forming a complex between thiolsulfonates and copper.

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