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REACTIONS OF THIOSULFONIC ACID ESTERS WITH AMINES

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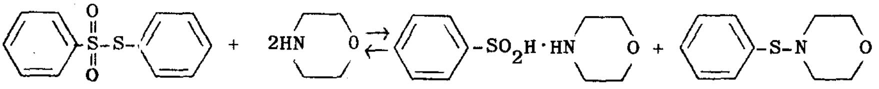
In a recent communication (1) Boldyrev and Kolesnikova reported the reaction of primary aliphatic amines, ammonia and hydrazine with esters of thiosulfonic acids (I) to form sulfenamides (II) and amine salts of sulfinic acids (III). They

$$\underset{\text{I}}{RSO_2SR'} + 2H_2NR'' \longrightarrow \underset{\text{II}}{R'\text{-}S\text{-}NHR''} + \underset{\text{III}}{RSO_2H\cdot H_2NR''}$$

reported that esters (I) of aliphatic R' react within minutes, whereas aryl esters require several days at room temperature, and that aromatic amines fail to react even at 100 to 110°. Studies of this reaction in our laboratory prior to their publication led to observations not entirely in accord with their results.

In addition we have found the reaction to be reversible. When methyl p-toluenethiolsulfonate was treated with a stoichiometric amount of morpholine in ether solution at room temperature, there was obtained 4-(methylthio)morpholine (b.p. 48-49°/5mm.; n^{25}_{D} 1.4977. Calcd. for $C_5H_{11}NOS$: C, 45.08; H, 8.33; N, 10.52. Found: C, 44.97; H, 8.22; N, 10.37) and morpholinium p-toluenesulfinate (m.p. 126-127.5°. Calcd. for $C_{11}H_{17}NO_3S$: C, 54.29; H, 7.04; N, 5.76. Found: C, 54.41; H, 7.22; N, 5.44). In each of several runs of varying lengths of time the same amount of unreacted thiosulfonate was isolated. The reversibility of the reaction was demonstrated by the treatment of 4-(methylthio)-morpholine with an equivalent of morphilinium p-toluenesulfinate in ethyl ether at room temperature for 20 hours to give methyl p-toluenethiolsulfonate (m.p. 56-59°) (2) isolated in 30% of the theoretical yield. Equilibrium constants of the reactions of a variety of thiolsulfonates with amines are being determined and will be reported in a later publication.

Contrary to the observations of the cited authors, we have found that unsubstituted aryl thiolsulfonates react with amines at approximately the same rate as do alkyl thiolsulfonates. Thus, when 0.05 mole of phenyl benzenethiolsulfonate (IV) is treated at room temperature with 0.20 mole of morpholine in ether, the salt (V) was observed to precipitate in about one minute, and after two hours the sulfenamide (VI) (m.p. 33-36°) (3) was isolated in 90% of the theoretical yield.



IV V VI

Finally, with regard to the reported unreactivity of aromatic amines, we have shown that o-nitrophenyl benzenethiolsulfonate reacts in ethanol at reflux temperature with p-anisidine, p-toluidine and aniline to give the N-(p-methoxyphenyl)-o-nitrobenzenesulfenamide (m.p. 138-140°; 51% yield) (4), N-(p-tolyl)-o-nitrobenzenesulfenamide (m.p. 136-138°; 89% yield) (5) and N-phenyl-o-nitrobenzenesulfenamide (m.p. 94-97°) (5), respectively. In the latter reaction the sulfenamide was isolated in very small yield, but the anilinium benzenesulfinate (m.p. 132°) (6) was obtained in 52%

yield. The driving force for the formation of the sulfenamide and the sulfinic acid salt is therefore enhanced not only by increased basicity of the amine, but also by decreased electron density about the divalent sulfur atom of the thiolsulfonate group.

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