A New Method for the Synthesis of Alkyl Aryl Sulfides

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Alkyl aryl sulfides are generally produced by the condensation of alkyl halides with thiophenolates.1,2) In previous papers,3,4) the authors have reported that methyl xanthates, $\mathrm{MeOCS_2R}$ (R=Me, Et, *n*-Pr), reacted with triethylamine to form the ammonium salts, $\mathrm{Et_3\overset{\oplus}{N}(Me)\overset{\ominus}{S}COSR}$, at room temperature and to form dithiolcarbonates at an elevated temperature. In a similar reaction of *S*-phenyl xanthates with triethylamine, alkyl aryl sulfides were obtained in a good yield, this reaction will be described in this communication.

Upon mixing *S*-phenyl methyl xanthate (I, b. p. 100—102°C/2 mmHg, n_D^{14} 1.6304. Found: S, 34.2%. Calcd. for $\mathrm{C_8H_8OS_2}$: S, 34.6%) and triethylamine at room temperature, immediate exotherms were observed with the evolution of carbonyl sulfide gas. After several minutes, methyl phenyl sulfide (b. p. 74.5—75°C/15 mmHg, n_D^{13} 1.5918) was produced in a 93% yield, while the amine remained almost unchanged. The equimolar mixture of I and triethylamine gave, at −20°C after 12 hr. in the form of pale yellow hygroscopic crystals needles (m. p. 57—59.5°C) in only a 3% yield by weight. These crystals were decomposed with aqueous hydrochloric acid to thiophenol, carbonyl sulfide and methyltriethylammonium chloride. Thus the structure of these crystals was concluded to be II (R=Et), similar to that of the salts3) produced from $\mathrm{MeOCS_2R}$ (R=Me, Et, *n*-Pr) and triethylamine. I and trimethylamine in benzene gave, at room temperature after 12 hr., white crystals (m. p. 130—134°C); these crystals showed reactions similar to those of II (R=Et) with aqueous hydrochloric acid. II (R=Me, Et) gave methyl or ethyl phenyl sulfide with methyl or ethyl iodide.

Methyl phenyl sulfide was also produced in a good yield by treating I with II (R=Et) at room temperature or with II (R=Me) at 70°C. These reactions may be summarized as follows:

$$\underset{\text{(I)}}{\mathrm{MeOCS_2Ph}} \xrightarrow[\text{(R=Me, Et)}]{\mathrm{R_3N}}$$

$$\mathrm{MeSPh} + \underset{\text{(II)}}{\mathrm{R_3\overset{\oplus}{N}(Me)\overset{\ominus}{S}COSPh}} + \mathrm{COS}$$

$$\mathrm{MeOCS_2Ph} \xrightarrow{\mathrm{II}} \mathrm{MeSPh} + \mathrm{COS}$$

$$\mathrm{R_3\overset{\oplus}{N}(Me)\overset{\ominus}{S}COSPh} \xrightarrow[\text{(R}'\text{=Me, Et)}]{\mathrm{R'I}}$$

$$\mathrm{R'SPh} + \mathrm{COS} + \mathrm{R_3\overset{\oplus}{N}(Me)\overset{\ominus}{I}}$$

Similarly, ethyl phenyl sulfide5) (b. p. 80—81°C/13.5 mmHg, n_D^{13} 1.5669) was obtained by the catalytic decomposition of *S*-phenyl ethyl xanthate1) (b. p. 95—97°C/1.5 mmHg, $n_D^{17.5}$ 1.6100) with triethylamine at 80°C with only a small amount of oily ammonium salt.

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