

A New Method for the Synthesis of Alkyl Aryl Sulfides

By Hiroshi YOSHIDA, Saburo INOKAWA and Tsuyoshi OGATA

Department of Synthetic Chemistry, Faculty of Technology, Shizuoka University, Oiwake, Hamamatsu

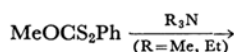
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Alkyl aryl sulfides are generally produced by the condensation of alkyl halides with thiophenolates.^{1,2)} In previous papers,^{3,4)} the authors have reported that methyl xanthates, MeOCS_2R ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}$), reacted with triethylamine to form the ammonium salts, $\text{Et}_3\text{N}^+(\text{Me})\text{SCOSR}^-$, 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.

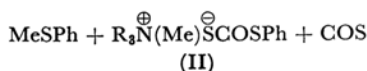
Upon mixing *S*-phenyl methyl xanthate (I, b. p. $100\text{--}102^\circ\text{C}/2\text{ mmHg}$, n_D^{20} 1.6304. Found: S, 34.2%. Calcd. for $\text{C}_8\text{H}_8\text{OS}_2$: S, 34.6%) and triethylamine at room temperature, immediate exotherms were observed with the evolution of carbonyl sulfide gas. After several minutes, methyl phenyl sulfide (b. p. $74.5\text{--}75^\circ\text{C}/15\text{ mmHg}$, n_D^{20} 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. $57\text{--}59.5^\circ\text{C}$) 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 ($\text{R} = \text{Et}$), similar to that of the salts⁵⁾ produced from MeOCS_2R ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}$) and triethylamine. I and trimethylamine in benzene gave, at room temperature after 12 hr., white crystals (m. p. $130\text{--}134^\circ\text{C}$); these crystals showed reactions similar to those of II ($\text{R} = \text{Et}$) with aqueous hydrochloric acid. II ($\text{R} = \text{Me}, \text{Et}$) gave methyl or ethyl phenyl sulfide with methyl or ethyl iodide.

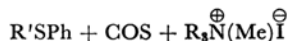
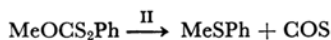
Methyl phenyl sulfide was also produced in a good yield by treating I with II ($\text{R} = \text{Et}$) at room temperature or with II ($\text{R} = \text{Me}$) at 70°C . These reactions may be summarized as follows:



(I)



(II)



Similarly, ethyl phenyl sulfide⁵⁾ (b. p. $80\text{--}81^\circ\text{C}/13.5\text{ mmHg}$, n_D^{20} 1.5669) was obtained by the catalytic decomposition of *S*-phenyl ethyl xanthate¹⁾ (b. p. $95\text{--}97^\circ\text{C}/1.5\text{ mmHg}$, n_D^{20} 1.6100) with triethylamine at 80°C with only a small amount of oily ammonium salt.

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4) H. Yoshida, S. Inokawa and T. Ogata, *ibid.*, **86**, 1179 (1965).

5) A. I. Vogel, *J. Chem. Soc.*, **1948**, 1820.