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A USEFUL SYNTHESIS OF SULFIDES FROM THIOL ESTERS

G. Edwin Wilson, Jr. and Joseph G. Riley
Department of Chemistry, Polytechnic Institute of Brooklyn
333 Jay Street, Brooklyn, New York 11201

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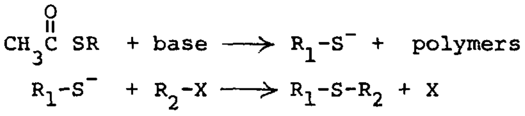
In the course of a program aimed at delineating the synthetic capabilities of thiol ester α-anions we have uncovered a general one-step synthesis of sulfides from thiol esters under non-aqueous conditions. Except for special cases where a presumed transesterification of thiol esters was effected using methoxide ion in methanol[1] to form the mercaptide ion necessary for displacement, all generally used syntheses of sulfides from other than commercially available mercaptans involve hydrolysis of thiol esters[2], isothiouronium salts[3] or xanthates[4] to obtain a mercaptide intermediate.

Mercaptide ion is released rapidly and quantitatively when a thiol ester with at least one α-hydrogen atom is treated with a strong non-nucleophilic base. When the heterogeneous reaction mixture is then allowed to react with an alkylating agent, high yields of sulfides and innocuous polymeric products are obtained(Table 1). Because these reactions may be carried out in aprotic media this method offers the opportunity to effect sulfide synthesis in the presence of hydrolytically unstable functions.



$$CH_3\overset{O}{\overset{\|}{C}}SR + \text{base} \longrightarrow R_1\text{-}S^- + \text{polymers}$$
$$R_1\text{-}S^- + R_2\text{-}X \longrightarrow R_1\text{-}S\text{-}R_2 + X$$

The reactions proceed equally well in alcohols, whereupon the acyl portion is isolated as an ester.

Preliminary evidence indicates that the sequence of events in the formation of mercaptide ion involves initial removal of an α-proton from the thiol ester followed by decomposition of this intermediate into mercaptide ion and a ketene. Under the basic conditions involved, ketene polymerization occurs readily.[5] Thus, when a thiol ester of diphenylacetic acid was employed, a gum having characteristics of a diphenylketene polymer was obtained. Ketene polymers are thermally very stable, and consequently most liquid sulfides may be isolated by simple distillation from the reaction mixture.

TABLE I

Formation of Sulfides from Thiolesters

$$CH_3COSR_1 + R_2X \xrightarrow{Base} R_1SR_2$$

R_1	R_2	X	BASE	SOLVENT	YIELD[a]
ethyl	benzyl	Br	KO-t-Bu	ether	91
ethyl	benzyl	Cl	$LiC(Ph)_3$	ether	59
ethyl	benzyl	Br	$LiC(Ph)_3$	ether	93
ethyl	ethyl	$\overset{+}{O}(C_2H_5)_2BF_4^-$	LiH	DMF	65
ethyl	ethyl	I	$LiC(Ph)_3$	ether	77
ethyl	ethyl	p-tosyl	$LiC(Ph)_3$	ether	68
ethyl	ethyl	$\overset{+}{O}(C_2H_5)_2BF_4^-$	$LiC(Ph)_3$	sulfolane	89
ethyl	ethyl	$\overset{+}{O}(C_2H_5)_2BF_4^-$	$LiN[Si(CH_3)_3]_2$	ether	78
ethyl	ethyl	$\overset{+}{O}(C_2H_5)_2BF_4^-$	$LiN[Si(CH_3)_3]_2$	ether	70
phenyl	methyl	I	KO-t-Bu	ether	79
phenyl	methyl	I	$LiC(Ph)_3$	ether	91
phenyl	allyl	Br	$LiC(Ph)_3$	ether	74
t-butyl	methyl	I	KO-t-Bu	glyme	89

a Yields represent percent conversion based on thiolester.

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