A General Procedure for the Conversion of a Carbonyl Group into a Thione Group with Tetraphosphorus Decasulfide

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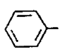
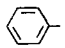
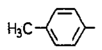
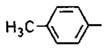
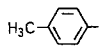
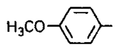
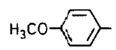
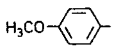
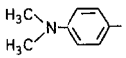
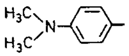
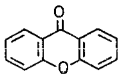
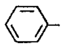
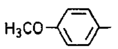
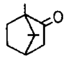
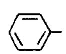
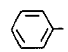
Although tetraphosphorus decasulfide (P_4S_{10}) has been long known[1] as a reagent for the sulfurization of carbonyl groups, it has never achieved general importance for the synthesis of thiono compounds[2,3,4]. Useful results have only been reported with carboxamides[4,5] and some cyclic ketones[2,3]. In these synthetic investigations, the carbonyl compound, dissolved in a non-polar solvent such as toluene, was generally refluxed with suspended P_4S_{10}. The isolation of the sulfur derivative is simple, since residual phosphorus compounds are insoluble in the solvent. Reactions of carbonyl compounds with silicon disulfide or boron sulfide[6], recently proposed as alternatives for sulfurizations with P_4S_{10}, have been carried out in the same solvent.

It is remarkable that the use of more polar solvents in these reactions seems to have never been attempted, although a very polar intermediate has been suggested[7] for the (incompletely understood) sulfurization of amides with P_4S_{10}, and the catalytic influence of salts on this reaction has long been recognized[8].

In our investigations on reactions of orthoesters, ketals, and several kinds of carbonyl compounds with P_4S_{10}, we found that the conversions were much faster in polar solvents than in toluene. Addition of two molar equivalents of sodium sulfide, carbonate, or hydrogen-carbonate to the reaction mixture further accelerated the transformation and clear solutions were obtained with evolution of heat. Under these conditions, several types of carbonyl compounds (**1**; see Table) could be converted into the corresponding thiono compounds (**3**), often in higher yields than by known methods.

Little is known about the interaction of P_4S_{10} with inorganic salts in organic solvents, but it may be assumed that such solutions contain the anion $X_2PS_2^{\ominus}$ ($X^{\ominus}$ is the monovalent anion in the salt used) in monomeric or polymeric form[9,10]. In solutions prepared from P_4S_{10} and sodium carbonate or hydrogen-carbonate, which evolve carbon dioxide, $OPS_2^{\ominus}$ and $SPS_2^{\ominus}$ (**2**) should thus be present. For sulfurization reactions, such solutions have to be used when freshly prepared, because they become syrupy on standing or heating, probably due to polymerization.

Table. Conversion of Carbonyl Compounds (**1**) into Thiono Compounds (**3**)

R^1	R^2	Reaction Conditions[c]	Molar Equivalents of P_4S_{10}	Molar Equivalents of $NaHCO_3$	Solvent	Concentration of **1** (%)	Isolation Procedure	Yield (%)	m.p. or b.p. (Lit. value)
		30°, 3 hr	1.5	6	acetonitrile	10	B	65	m.p. 51–53°[a] (m.p. 52–54°; b.p. 129–133°/0.06 torr)[12]
		30°, 3 hr	1.5	6	acetonitrile	10	A	80	m.p. 74–75° (m.p. 76°)[13]
		30°, 3 hr	1.5	6	acetonitrile	10	A	85	m.p. 105°
		30°, 3 hr	1.5	6	acetonitrile	10	A	85	m.p. 116–118° (m.p. 116°)[13]
		30°, 3 hr	1.5	6	acetonitrile	10	A	85	m.p. 200–202° (dec) (m.p. 198–205°)[6]
		30°, 3 hr	1.5	6	THF	10	A	75	m.p. 156–158° (m.p. 157–158°)[6]
CH_3		30°, 4 hr	1.0	4	diglyme	20	B	35	b.p. 78–82°/1 torr (b.p. 97–100°/12 torr)[14]
t-C_4H_9		30°, 4 hr	1.0	4	diglyme	20	B	55	b.p. 102°/0.6 torr
		120°, 5 hr	1.5	6	diglyme	20	A	70	m.p. 143–145° (m.p. 145°)[2]
H	C_2H_5O-	30°, 5 hr	0.15	0.6	diglyme	50	D	(18)[b]	b.p. 86–87° (b.p. 86.5–87.5°)[15]
CH_3	C_2H_5O-	reflux, 24 hr	0.1	0.01	none		C	(14)[b]	b.p. 105° (b.p. 108–110°)[16]
	H_3CO-	80°, 24 hr	0.15	0.01	none		C	(25)[b]	b.p. 107–108°/15 torr (b.p. 112–115°/26 torr)[17]
CH_3	C_2H_5S-	reflux, 6 hr	1.0	4	diethyl ether	(20)	C	50	b.p. 44°/16 torr (b.p. 61°/24 torr)[18]
	C_2H_5S-	reflux, 6 hr	1.0	4	diethyl ether	(20)	C	60	b.p. 154°/14 torr (b.p. 155–160°/15 torr)[12]
H	$(H_3C)_2N-$	reflux, 5 hr	0.6	2	diethyl ether	(20)	C	85	b.p. 108°/14 torr (b.p. 111–113°/10 torr)[19]

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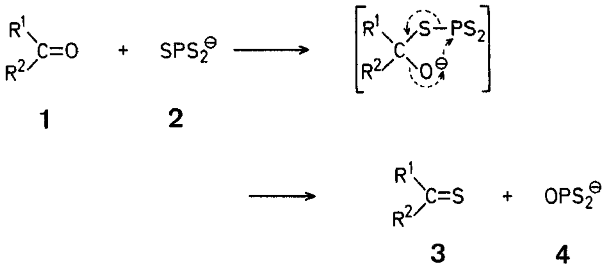
[a] After recrystallization from methanol.

[b] Conversion of starting compound (which was used in large excess).

[c] The amounts of carbonyl compounds used were 0.02 mol for benzophenones and xanthone and 0.1 mol for other compounds.

Sulfurization may be due to nucleophilic attack of these anions on the carbonyl C-atom followed by elimination of $O_2PS^\ominus$ or $OPS_2^\ominus$ (**4**), respectively, e.g.



If R^1 or R^2 is a good leaving group (as in acid chlorides), no thiono compound (**3**) is obtained[11], probably as a consequence of substitution of the leaving group. For aromatic ketones, the reaction rate is lower when R^1 or R^2 is electronegative, suggesting that nucleophilic attack of the negative oxygen on phosphorus in the addition product is rate-determining.

In general, the reaction rates are higher in acetonitrile than in the other solvents used (see Table), but the nitrile is not completely inert towards P_4S_{10}. During work-up under hydrolyzing conditions, thioacetamide is formed as a side product. With more reactive compounds such as carboxamides, even diethyl ether can be used as a solvent, although it does not give clear solutions with the sulfurizing agent. With esters, except formates, the best yields of thione derivatives are obtained when no solvent and only a catalytic amount of sodium sulfide or hydrogen-carbonate is used. We have no explanation for these observations.

Conversion of Carbonyl Compounds into Thiono Compounds; General Procedure:

All sulfurization reactions were performed by dissolving the carbonyl compound in a suitable solvent, adding the solution of P_4S_{10} in the same solvent, and adding solid sodium-hydrogen carbonate to the mixture under stirring and at such a rate as allowed by the evolution of carbon dioxide. Stirring was then continued for several hours. Experimental details are given in the Table. Isolation of the products was performed using several, slightly different procedures:

Isolation Procedure A: The reaction mixture was poured into water. The solid product which separated was isolated by filtration, washed several times with water, and dried at low pressure (0.5 torr) and ~50°.

Isolation Procedure B: Ether was added to the reaction mixture. The ethereal solution was washed several times with aqueous sodium-hydrogen carbonate (5%) and water, dried, and distilled at low pressure.

Isolation Procedure C: The reaction mixture was diluted with ether, filtered, and the filtrate distilled at low pressure.

Isolation Procedure D: Low-boiling reaction products were distilled from residual phosphorus compounds in the reaction mixture at low pressure and collected in a dry-ice trap. They were purified by redistillation.

Using these procedures, the products contained in some cases small amounts (up to 10%) of the starting compound. Pure samples (> 95%), however, could be obtained by redistillation or recrystallization. O-Ethyl thioacetate contained some S-ethyl thioacetate, which could not be separated by distillation. To obtain a pure sample, the S-ethyl thioacetate was converted into ethyl dithioacetate via the sulfurization described. Separation of O-ethyl thioacetate and ethyl dithioacetate was possible by distillation.

All products were identified and checked for purity by ^{1}H-N.M.R. and in the case of aromatic ketones also by I.R. spectrometry. A comparison of the melting and boiling points found with values from the literature is given in the Table.

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