

SYNTHESIS OF ANHYDRIDES BY DESULPHURIZATION OF THIOESTERS

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Desulphurization reactions have been used recently to effect ring closures¹ and for the synthesis of ethers by desulphurization of sulphenate esters.² We wish to report that the desulphurization of thioesters by mercury(II) carboxylate salts affords anhydrides in high yield. Recent syntheses of anhydrides from carboxylic acids include the photolysis of a mixture of diphenylmercury, tri-n-butylphosphine, and carboxylic acid³ and the reaction of a mixture of carboxylic acid, diphenylmercury, and benzophenone diphenylmercaptole.⁴

The desulphurization of thioesters proceeds rapidly at room temperature, and yields a mixture of mercuric sulphide, ester, and anhydride. The mercuric sulphide and ester are easily removed by filtration and distillation respectively. Thioesters are readily accessible from nitriles⁵ or by direct thioacylation of an alcohol.⁶

The rapid reaction of mercuric acetate with a number of thioamides, compared with the much slower reaction of other mercury salts, has been noted previously.⁷ Mercuric chloride forms fairly stable complexes with thioacetamide,⁸ which are hydrolysed slowly with precipitation of mercuric sulphide, whereas mercuric sulphide is precipitated very rapidly when mercuric acetate is treated with thioacetamide in aqueous solution. Taylor and Smith⁷ found the rate of the latter reaction to be first order in mercury(II) and independent of ionic strength, which was consistent with the thioacetamide reacting as an uncharged species. The rapid desulphurization of a number of other thiocarbonyl compounds by mercuric acetate has been noted,⁹⁻¹¹ but the use of hydroxylic solvents left in doubt the origin of the oxygen which replaces the sulphur of the thiocarbonyl group.

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¹ Corey, E. J., and Block, E., *J. org. Chem.*, 1969, **34**, 1233.

² Barton, D. H. R., Page, G., and Widdowson, D. A., *Chem. Commun.*, 1970, 1466.

³ Mukaiyama, T., Kuwajima, I., and Suzuki, Z., *J. org. Chem.*, 1963, **28**, 2024.

⁴ Mukaiyama, T., and Katsuyama, H., *Bull. chem. Soc. Japan*, 1968, **41**, 2703.

⁵ Schmidt, U., Heyman, E., and Kabitzke, K., *Chem. Ber.*, 1963, **96**, 1478.

⁶ Hedgley, E. J., and Leon, N. H., *J. chem. Soc. (C)*, 1970, 467.

⁷ Taylor, D. C., and Smith, D. M., *Analyt. Chem.*, 1964, **36**, 1924.

⁸ Petrie, S., and Lipiec, T., *Roczn. Chem.*, 1965, **39**, 1725.

⁹ Jones, F. N., and Andreades, S., *J. org. Chem.*, 1969, **34**, 3011.

¹⁰ Bottecher, B., *Chem. Ber.*, 1948, **81**, 376.

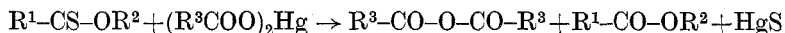
¹¹ Landquist, J. K., *J. chem. Soc. (C)*, 1970, 63.

In the present work, a number of thioesters were desulphurized using solutions of mercury(II) carboxylate salts in chloroform, methylene chloride, or pyridine. An immediate precipitate of mercuric sulphide was produced in each case, thus showing

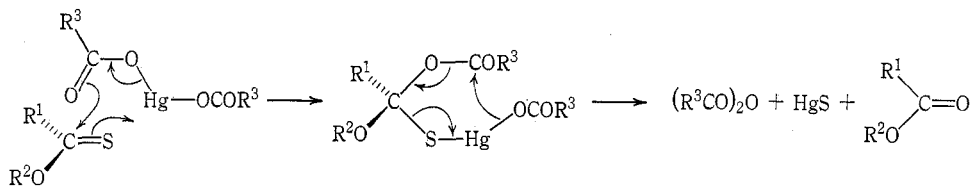
TABLE 1
DESULPHURIZATIONS OF THIOESTERS

Thioester	Mercuric Salt	Solvent	Yields (%)	
			Anhydride	Ester
Cholestanyl thioacetate	acetate	pyridine	—	90
Cyclohexyl thioacetate	acetate	γ -picoline	75	82
	butyrate	chloroform	84	95
	valerate	dichloromethane	89	100
	pivalate	chloroform	87	100
	laurate	pyridine	96	95
Ethyl thiobenzoate	propionate	dichloromethane	86	98
	valerate	dichloromethane	84	100
	laurate	pyridine	82	89

that the mercury salt serves as a source of oxygen as well as a sulphur acceptor. The reaction appears to be general (Table 1) and obeys the stoichiometry:



The rapid precipitation of mercuric sulphide during desulphurization by mercuric acetate in pyridine (but not by mercuric chloride in acetic acid) suggests the formation of a 1:1 complex which could rearrange via a cyclic transition state (Scheme 1) to give an ester and anhydride as the principal organic products. In contrast, when



Scheme 1

cholestanyl thioacetate was heated with excess mercuric chloride in pyridine in a sealed ampoule, the reaction was incomplete after 20 hr and a mixture of cholest-2-ene, 3 β -acetoxycholestane, and starting material was obtained. It was found that the mercury salts did not react with the thiocarbonyl group of carbon disulphide, carbonyl sulphide, or thiophosgene.

Experimental

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points are uncorrected. N.m.r. spectra were recorded on a Varian A-60 spectrometer, using solutions in deuteriochloroform with tetramethylsilane as internal standard. Ultraviolet spectra were recorded on a Perkin-Elmer 137 spectrophotometer.

Cholestanyl Thioacetate

To cholestanol (5 g) in chloroform (30 ml) was added acetonitrile (30 ml), and the solution was saturated with dry hydrogen chloride. After 4 hr the chloroform was removed by distillation under reduced pressure and the residue was dissolved in pyridine. The solution was saturated with dry hydrogen sulphide and the product isolated by extraction with chloroform. The crude thioester was chromatographed on silica gel (400 g). Elution with light petroleum-benzene (6:1) gave *cholestanyl thioacetate* which crystallized from methanol as colourless flakes, m.p. 91.5–93°, $[\alpha]_D^{20}$ 0° (c, 1.00 in CHCl_3); λ_{max} 245 and 368 nm (ϵ 12400 and 27); n.m.r. δ 5.30 (m, C3-H), 2.50 (s, OCSMe) (Found: C, 77.8; H, 11.0; S, 7.2. $\text{C}_{29}\text{H}_{50}\text{OS}$ requires C, 78.0; H, 11.3; S, 7.2%).

Cyclohexyl Thioacetate

The thioester was prepared from cyclohexanol and acetonitrile by the method of Schmidt.⁵ Fractional distillation gave *cyclohexyl thioacetate*, b.p. 121–123°/15 mm (Found: C, 61.0; H, 8.9; S, 20.1. $\text{C}_8\text{H}_{14}\text{OS}$ requires C, 60.7; H, 8.9; S, 20.2%).

Ethyl Thiobenzoate

Ethyl thiobenzoate was prepared as described in the literature and had b.p. 72–76°/1 mm (lit.⁵ 111–114°/10 mm) (Found: C, 65.3; H, 6.2; S, 19.0. Calc. for $\text{C}_9\text{H}_{10}\text{OS}$: C, 65.1; H, 6.1; S, 19.3%).

Mercuric Salts

A commercial sample (B.D.H.) of mercuric acetate was purified by crystallization from acetic acid. The other mercury salts were prepared by warming mercuric oxide with c. 1.5 mol. propn. of the appropriate carboxylic acid. The salt was collected by filtration, washed with ether, and purified by crystallization from chloroform to give: mercuric propionate, m.p. 111–112°; mercuric butyrate, m.p. 102–103°; mercuric valerate, m.p. 87–88°; mercuric pivalate, m.p. 230–232° (lit.¹² 235°); mercuric laurate, m.p. 121–122° (lit.¹³ 100°).

Desulphurization Reaction

A solution of the mercury salt (0.5 mmol) was treated with a solution of the thioester (0.5 mmol) and the mixture stirred for 10 min. Any unchanged mercury salt was destroyed by passing dry hydrogen sulphide through the solution. The solution was filtered through silica gel, and excess solvent removed by distillation through a short fractionating column. The residue was examined by g.l.c. using a 6-ft column with silicone SF96 stationary phase and flame ionization detector. Products were identified by peak enhancement with authentic specimens and yields (Table 1) were determined by the addition of a known mass of dimethylaniline as an internal standard.

¹² Kharasch, M. S., and Stavely, F. W., *J. Am. chem. Soc.*, 1923, **45**, 2961.

¹³ Whitmore, W. F., and Lauro, M., *Ind. Engng Chem.*, 1930, **22**, 646.