

number of representative thioesters (Table). It proved versatile and efficient, and also gave good yields from aromatic and hindered aliphatic acids, although these required longer reaction times. In each case the reaction was monitored by i.r. spectroscopy to determine the minimum conditions for essentially complete reaction, and these were the conditions used for the preparative procedure.



I.r. studies of the reaction between crotonic acid and tris(ethylthio)borane indicated that reaction proceeded normally. However, on work-up a mixture of the desired product and its ethanethiol adduct was obtained. Similar results are obtained in other preparations of thioesters of crotonic acid.⁸ In our reaction the addition of thiol probably occurs under sodium hydrogen carbonate catalysis⁸ during work-up.

The reactions of 4-nitrobenzoic and adipic acids were not very successful in the solvents tried (benzene, glyme, dioxan) because of insolubility of the acids or the intermediate acyloxyboranes. Nevertheless, i.r. spectroscopy indicated the formation of some thioester in each case.

Our main interest in this reaction has been in its development as a synthetic procedure, but we have made some observations that throw light on its course. The formation of carboxylic anhydrides (2) and oxybis(diacyloxy)boranes (3) is rapid at room temperature as indicated by the i.r. spectra of the reaction mixtures, which were identical in the carbonyl region with those of mixtures (1 : 1) of authentic (2) and (3) (R = n-C₅H₁₁, Ph, or Me) prepared separately.⁹ The later reactions leading from (2) and (3) to thioesters were slower with sterically hindered acids and for those acids with electron-donating substituents. Variation of solvent had little effect on the rate of reaction of (2) but that of (3) increased in the order CH₂Cl₂, CHCl₃ < C₆H₆ < (MeO-CH₂)₂, Et₂O. When the ratio of acid to B(SEt)₃ was 3 : 1, so that there was none of the borane left after the initial reaction but ethanethiol was still present, the rate of disappearance of (2) was little affected whereas (3) was not converted into thioester. This implies that (2) reacts with ethanethiol and possibly also the borane, but that (3) reacts almost exclusively with the borane. This conclusion accounts for the observation¹⁰ that oxybis(diacetoxy)borane was isolated after extended reflux of acetic acid with tris(isopropylthio)borane, since a deficiency of the borane was used in that instance. We cannot however confirm the claim¹⁰ that tris(acyloxy)boranes may be prepared by the action of carboxylic acids on tris(alkylthio)boranes.

In conclusion, reactions of tris(ethylthio)borane with carboxylic acids provide high yield syntheses of thio-

esters free from significant side products. The reactions are extremely simple to carry out, the borane reagents are easily prepared,¹¹ and may be stored in anhydrous conditions for several years without significant decomposition. Thus, although the reaction mechanism is complex, as a preparative method the reaction is highly convenient.

EXPERIMENTAL

Solvents other than ethers were dried by reflux over, and distillation from P₂O₅; ethers were refluxed over, and distilled from LiAlH₄. Liquid carboxylic acids other than acetic were purified by fractional distillation; solid acids were recrystallised from dry benzene and dried under vacuum (CaCl₂) for several days; acetic acid was distilled from 'boron acetate'. Thioester preparations were performed in a two-necked flask fitted with a serum-capped stopcock (side neck) and a reflux condenser topped by a CaCl₂-NaOH-CaCl₂ guard tube jointed at each end; the apparatus was assembled, flamed under vacuum, allowed to cool while still under vacuum, then refilled with dry air prior to admission of reagents. Liquids were transferred with dry syringes. Spectra were recorded on Unicam SP 200 (i.r.) and A.E.I. MS12 or MS9 (mass) spectrometers; for g.l.c. a Perkin-Elmer F11 instrument was used.

Tris(ethylthio)borane.—This was prepared by a modification of the method of Goubeau.¹¹ Ethanethiol (50 cm³, 41 g, 0.67 mol) in ethanol (95%; 150 cm³) and water (75 cm³) was added, dropwise and with stirring, to Pb(OAc)₂·3H₂O (132 g, 0.35 mol) in ethanol (95%; 250 cm³) and water (350 cm³), effluent thiol vapours being led through Cu(OAc)₂ solution. The mixture was stirred for 1 h at 45 °C, allowed to cool and settle, and filtered at the pump. The yellow solid was dried by refluxing with benzene in a Dean-Stark apparatus, and the solvent was then removed under reduced pressure to leave bis(ethylthio)lead (96 g, 89%).

To bis(ethylthio)lead (60 g, 0.18 mol) suspended in dry pentane (200 cm³) under nitrogen and stirred, was added a solution of BCl₃ (12.5 g, 0.11 mol) in pentane (100 cm³), dropwise over 30 min. The mixture was stirred for 3 h at 20 °C, filtered under nitrogen through a sinter tube into a second two-necked flask, and evaporated under reduced pressure to remove the solvent. The residual liquid was transferred to a nitrogen-filled distillation apparatus, and fractionally distilled to give tris(ethylthio)borane (16.6 g, 80%); b.p. 78–81.5 °C at 1.3 mmHg, n_D²⁰ 1.5472 (lit.,¹² n_D²⁰ 1.5473).

S-Ethyl Hexanethioate.—To tris(ethylthio)borane (0.5 cm², 0.68 g, 3.5 mmol) in dry diethyl ether (5 cm³) was added hexanoic acid (0.35 g, 3 mmol). The reagents were thoroughly mixed and heated under reflux for 6 h, after which i.r. spectroscopy indicated that reaction was essentially complete. The mixture was cooled and extracted into pentane (50 cm³), and the extract was washed with ice-cold water (10 cm³), saturated NaHCO₃ solution (3 × 5 cm³), and water (2 × 5 cm³, 1 × 10 cm³), and dried (MgSO₄). The solvent was distilled off at atmospheric pressure and the residue was transferred with the aid of the

⁸ A. A. Schleppek and F. B. Zienty, *J. Org. Chem.*, 1964, **29**, 1910.

⁹ For a discussion of the dismutation of triacyloxyboranes see ref. 7 and A. Pelter, T. E. Levitt, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1970, 347.

¹⁰ J. M. Lalancette, F. Bessette, and J. M. Cliche, *Canad. J. Chem.*, 1966, **44**, 1577.

¹¹ J. Goubeau and H. W. Wittmeier, *Z. anorg. Chem.*, 1952, **270**, 16.

¹² B. M. Mikhailov and Yu. N. Bubnov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 368.

minimum quantity of dry diethyl ether to a small (*ca.* 2 cm³) one-piece distillation apparatus, and distilled to give *S*-ethyl hexanethioate (0.36 g, 79%); b.p. 80 °C at 14 mmHg; n_D^{25} 1.4555; ν_{CO} 1 680 cm⁻¹ (Found: C, 60.1; H, 10.2%; M^+ , 160.0923. C₈H₁₆OS requires C, 60.0; H, 10.0%; M , 160.0922).

The NaHCO₃ washings were acidified with concentrated hydrochloric acid, saturated with (NH₄)₂SO₄, and extracted with diethyl ether (2 × 25 cm³). The extract was dried (MgSO₄) and the solvent was removed under reduced pressure. The residual liquid was distilled onto a cold-finger under reduced pressure to yield hexanoic acid (0.029 g, 9%).

A similar reaction in benzene required 2 h reflux and produced *S*-ethyl hexanethioate (0.37 g, 81%). No attempt was made to recover hexanoic acid.

Other Thioesters.—The following thioesters were prepared like *S*-ethyl hexanethioate (solvents and conditions as recorded in the Table): (i) *S*-ethyl 2-methylpropanethioate, from 2-methylpropanoic (isobutyric) acid (0.25 g) and tris(ethylthio)borane (0.64 g); yield 0.28 g (79%); b.p. 140 °C at 760 mmHg; n_D^{25} 1.4385; ν_{CO} 1 680 cm⁻¹ (Found: C, 54.6; H, 9.6%; M^+ , 132.0608. C₈H₁₂OS requires C, 54.5; H, 9.1%; M , 132.0608); also recovered was 2-methylpropanoic acid (0.012 g, 5%); (ii) *S*-ethyl 2,2-dimethylpropanethioate, from 2,2-dimethylpropanoic (pivalic) acid (0.29 g) and tris(ethylthio)borane (0.65 g); yield 0.31 g (75%) in diethyl ether, but only 53% in benzene, because of difficulty of separation from solvent in a quantitative manner; b.p. 82 °C at 60 mmHg; n_D^{25} 1.4425; ν_{CO} 1 680 cm⁻¹ (Found: C, 57.8; H, 10.0%; M^+ , 146.0768. C₇H₁₄OS requires C, 57.5; H, 9.6%; M , 146.0765); also recovered was pivalic acid (0.017 g, 5%); (iii) *S*-ethyl thiobenzoate, from benzoic acid (0.34 g) and tris(ethylthio)borane (0.64 g); yield 0.36 g (78%) in glyme, 0.33 g (72%) in benzene; n_D^{22} 1.5704 (lit.,^{13a,b} n_D^{25} 1.5703; n_D^{21} 1.5715); ν_{CO} 1 665 cm⁻¹ (Found: M^+ , 166.0449. Calc. for C₉H₁₀OS: M , 166.0452) [the recovered acid, in this case a solid, was simply washed with the minimum quantity of cold Et₂O and evaporated to dryness; 0.031 g (9%) for reaction in glyme; 0.041 g (12%) in benzene]; (iv) *S*-ethyl 4-methoxy-

thiobenzoate, from 4-methoxybenzoic acid (0.40 g) and tris(ethylthio)borane (0.62 g); yield 0.41 g (78%); b.p. 112 °C at 7 mmHg; (lit.,^{13b} 109–110 °C at 0.5 mmHg); n_D^{22} 1.5790; ν_{CO} 1 660 cm⁻¹ (Found: C, 61.8; H, 6.4%; M^+ , 196.0561. Calc. for C₁₀H₁₂O₂S: C, 61.2; H, 6.2%; M , 196.0558); 4-methoxybenzoic acid (0.059 g, 15%) was recovered as described for benzoic acid.

Reaction of Acetic Acid with Tris(ethylthio)borane.—Acetic acid (0.27 g) was refluxed with tris(ethylthio)borane (1.12 g) in benzene (5 cm³) for 1 h, and the product was worked up as for the hexanoic acid reaction to give a solution of *S*-ethyl methanethioate in ether–benzene. Ether was removed on a spinning-band distillation column, and the pure thioester was then obtained from the benzene solution by preparative g.l.c. on Apiezon M; yield 0.17 g (39%); ν_{CO} 1 684 cm⁻¹ (Found: M^+ 104.0289. Calc. for C₄H₈OS: M , 104.0296).

To the crude thioester solution obtained from an identical reaction was added octane (0.213 g) as standard, and the quantity of thioester was estimated by g.l.c. (2 m 10% Apiezon L; 65 °C); yield 0.34 g (77%).

Reaction of Crotonic Acid with Tris(ethylthio)borane.—Crotonic acid (0.24 g) was refluxed with tris(ethylthio)borane (0.66 g) in benzene (10 cm³) for 6 h. The i.r. spectrum then showed bands at 1 640 cm⁻¹ (C=C) and 1 670 cm⁻¹ (C=O). However, during the standard work-up the relative intensity of the 1 640⁻¹ band diminished, consistent with base-catalysed addition of ethanethiol to the unsaturated thioester.⁸ Mass spectrometry confirmed the presence of some *S*-ethyl 3-ethylthiobutanethioate (Found: M^+ , 192.0643. Calc. for C₈H₁₆OS₂: M , 192.0643), although g.l.c. (2 m 10% Apiezon L; 65 °C) indicated a predominance of one component. The reaction was not studied further.

We thank the S.R.C. for studentships (to T. E. L. and K. S.).

[6/2342 Received, 29th December, 1976]

¹³ (a) J. I. G. Cadogan and H. N. Moulden, *J. Chem. Soc.*, 1961, 5524; (b) D. P. N. Satchell and I. I. Secemski, *J. Chem. Soc. (B)*, 1970, 1306.