Organosulphur Compounds. Part VIII.[1] Reaction of Monothiocarboxylic Acids with Dicyclohexylcarbodi-imide and Other Reactions leading to Monothio-anhydrides

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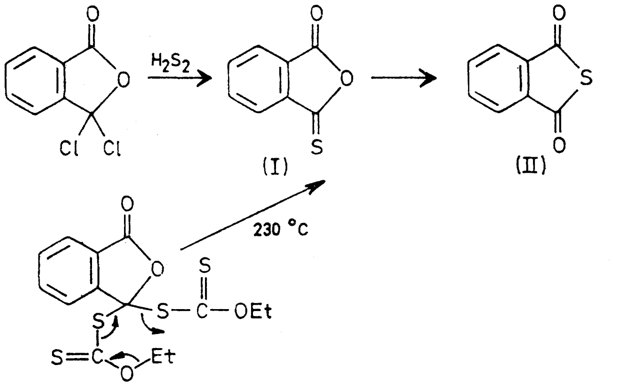
The reaction of monothiocarboxylic acids with dicyclohexylcarbodi-imide affords diacyl sulphides and dicyclohexylthiourea. In some cases the formation of *N*-acyl-*NN'*-dicyclohexylthioureas was observed. Diacyl sulphides were also obtained by treatment of *O*-trimethylsilyl thiocarboxylates with acyl chlorides. The mechanism of diacyl sulphide formation in both reactions is discussed. The reaction of thioacyl chlorides with salts and silyl esters of carboxylic acids gives the unstable unsymmetrical monothioanhydrides, which disproportionate to yield carboxylic anhydrides and unidentified sulphur-containing products. The mass spectral characteristics of diacyl sulphides and *O*-trimethylsilyl thiocarboxylates are reported.

ANHYDRIDES of mono- and di-thiocarboxylic acids can be classified according to the structural types (A)—(E).

$(RCO)_2S$ (A) $RCS\cdot O\cdot COR$ (B) $(RCS)_2O$ (C)

$RCS\cdot S\cdot COR$ (D) $(RCS)_2S$ (E)

Of these, only the symmetrical monothioanhydrides (A) (diacyl sulphides) are well known.[2] They are formed by acylation of free monothioacids or their anions,[3] and from the reaction of carboxylic acid anhydrides with phosphorus pentasulphide.[4] Recently mixed diacyl sulphides of type (A) have been synthesized.[5]



SCHEME 1

Only one example of a monothioanhydride of type (B) has been described: the phthalic thioanhydride (I) formed in the reaction of hydrogen disulphide with phthaloyl chloride.[6] This compound isomerises fairly readily to the symmetrical structure (II), which is thermodynamically more stable. For this reason the final product of thermal degradation of phthalide-3,3-diyl bis-(*O*-ethyl dithiocarbonate)[7] is phthaloyl sulphide (II) and not its isomer (I) which is undoubtedly formed in the first stage.

Published data regarding dithioanhydrides of types (C) and (D) and trithioanhydrides (E) are equally scarce. The majority occur in old literature and should be treated with caution. For example Lewis[8] treated the benzoyl chloride–pyridine complex with hydrogen sulphide and obtained a crystalline product which he identified as di(thiobenzoyl) oxide (PhCS·O·CSPh) on the basis of elemental analysis. So far confirmation of this structure has not been reported. The results of more recent studies[9-11] suggest that dithioanhydrides of types (D) and (E) probably exist in dimeric form, as substituted 1,3-dithietans or hexathia-adamantanes.

We now describe studies on the reaction of dicyclohexylcarbodi-imide (DCC) with monothiocarboxylic acids, and related studies devised to elucidate the mechanism of formation of diacyl sulphides in this reaction, and the mechanisms of formation and decomposition of non-cyclic monothioanhydrides of structure (B). We have previously shown that the reaction of DCC with phosphorus monothioacids[12] leads to monothiopyrophosphate systems having unsymmetrical structures.

Reaction of Monothiocarboxylic Acids with DCC.—The reactions of the acids (III) with DCC, carried out in diethyl ether at room temperature using two moles of thioacid for every mole of DCC, gave the correspond-

$$\underset{(III)}{2\,RCO\cdot SH} + C_6H_{11}\cdot N{=}C{=}N\cdot C_6H_{11} \longrightarrow \underset{(IV)}{(RCO)_2S} + \underset{(V)}{(C_6H_{11}NH)_2CS}$$

a; R=Me d; R=Ph
b; R=Et e; R=*o*-MeC$_6$H$_4$
c; R=Bu^t

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[1] Part VII, M. Mikołajczyk, S. Grzejszczak, W. Midura, and A. Zatorski, *Synthesis*, 1975, 278.

[2] E. E. Reid, 'Organic Chemistry of Bivalent Sulphur,' Chemical Publishing Co. Inc., New York, 1962.

[3] W. A. Bonner, *J. Amer. Chem. Soc.*, 1950, **72**, 4270.

[4] A. Kekule, *Annalen*, 1854, **90**, 309; E. O. Beckmann, *J. prakt. Chem.*, 1878, **17**, 439.

[5] H. Böhme and H. P. Stendel, *Annalen*, 1969, **730**, 121.

[6] C. M. Sharts and O. Wing Fong, *J. Org. Chem.*, 1967, **32**, 3709.

[7] A. Shah, S. N. Singh, and M. V. George, *Tetrahedron Letters*, 1968, 3983.

[8] D. T. Lewis, *J. Chem. Soc.*, 1940, 831.

[9] A. Fredga, *Arkiv. Kemi Min. Geol.*, 1947, **25***B*, 5.

[10] K. Olsson, and H. Baeckstrom, and R. Engwall, *Arkiv. Kemi*, 1966, **26**, 219.

[11] M. Mikołajczyk and P. Kiełbasinski, unpublished results.

[12] M. Mikołajczyk, *Chem. Ber.*, 1966, **99**, 2083.

ing diacyl sulphides (IV) and dicyclohexylthiourea (V) in high yields. The symmetrical structure of the sulphides (IV) was confirmed by i.r. and n.m.r. spectra. T.l.c. of the crude products of the reactions with the thioacids (IIIa and d) showed that, in addition to the diacyl sulphides (IV) and thiourea (V), small amounts of the corresponding *N*-acyl-*NN'*-dicyclohexylthioureas (VI) are formed. These become the main products when the thioacids (III) contain strongly electron-attracting groups and if the thioacids and DCC are used in equimolar amounts. In the case of the acid (IIIf) the yield of the corresponding substituted thiourea (VIf) was almost quantitative, and chromatography did not show the presence of the corresponding bis-*p*-nitrobenzoyl sulphide. However, this sulphide was formed in small amounts when the molar ratio of the thioacid to DCC was 2 : 1. The product of the reaction of DCC with chlorothioacetic acid (IIIg), obtained in 74% yield, was analysed in the crude state, since it decomposed on attempted crystallisation. T.l.c. showed the presence of bischloroacetyl sulphide. An attempt to isolate the product of the reaction of trichlorothioacetic acid with DCC failed.

The foregoing results indicate that the reaction of DCC with monothiocarboxylic acids can proceed in either of two directions, and its course is analogous to that proposed by Khorana[13] for the reaction of DCC with carboxylic acids. However, in the case of monothiocarboxylic acids the mechanism shows interesting aspects connected with the ambident character of the monothioacid anion ($\mathrm{RCO{\cdot}S^- \longleftrightarrow RCS{\cdot}O^-}$). In the first stage the ambident anion attacks the protonated DCC molecule with sulphur as the nucleophilic centre.

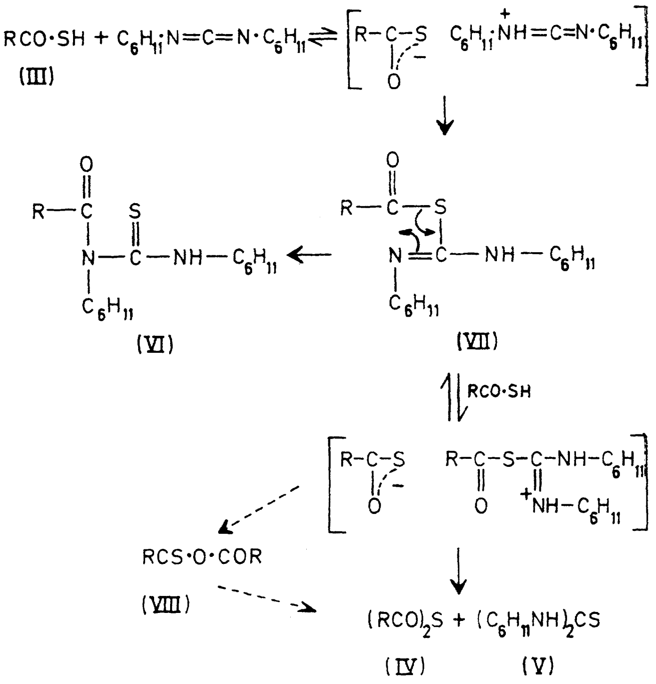
$$\mathrm{RCO{\cdot}SH + C_6H_{11}{\cdot}N{=}C{=}N{\cdot}C_6H_{11} \longrightarrow RCO{\cdot}N(C_6H_{11}){\cdot}CS{\cdot}NH{\cdot}C_6H_{11}}$$

(III) (VI)

f; R = p-$\mathrm{NO_2C_6H_4}$
g; R = $\mathrm{ClCH_2}$

This leads to an *S*-acylated isothiourea (VII), which can then react in either of two ways. Intramolecular *S*- ⟶ *N*-acyl migration leads to the *N*-acylthiourea (VI). Alternatively the protonated adduct (VII) can react with more monothiocarboxylate, which attacks the carbonyl carbon atom, giving the diacyl sulphide (IV) and dicyclohexylthiourea (V). However, at this stage two possible paths to the symmetrical sulphide (IV) can be considered. The first, direct path consists of attack of the sulphur atom of the ambident monothiocarboxylate on the carbonyl carbon atom. In the second path the thiocarboxylate attacks the protonated adduct (VII) with the oxygen atom. This leads to the unsymmetrical anhydride (VIII), which can isomerise to the symmetrical form. This possibility should be taken into account in the light of the already discussed studies on phthalic thioanhydrides (I) and (II), and calculations[14] on the basis of bond energies, which suggest that the symmetrical form (A) is thermodynamically more stable than the unsymmetrical form (B).

Reaction of O-*Trimethylsilyl Thiocarboxylates with Acyl Chlorides*.—In order to elucidate the mechanism of formation of diacyl sulphides (IV) in the reaction of DCC with thioacids (III) we have investigated the reaction of *O*-trimethylsilyl thiocarboxylates (IX) with acyl chlorides. The esters (IX) are formed during the silylation of salts of the thioacids (III) and exist exclusively in the thionic form.[15] For this reason we hoped that their reaction with acyl chlorides would lead to anhydrides of type (B). However, in the event, the diacyl sulphides (IV) were formed in almost quantitative yields, in addition to trimethylsilyl chloride. Investigation of the course of the reaction of the ester (IXa) with acetyl chloride by ^{1}H n.m.r. spectroscopy did not provide evidence for an intermediate unsymmetrical thioanhydride (VIIIa).



SCHEME 2

$$\mathrm{RCS{\cdot}O{\cdot}SiMe_3 + RCOCl \longrightarrow (RCO)_2S + Me_3SiCl}$$

(IX) (IV)

a; R = Me d; R = Ph
b; R = Et e; R = o-$\mathrm{MeC_6H_4}$
c; R = $\mathrm{Bu^t}$ f; R = p-$\mathrm{NO_2C_6H_4}$

This novel method of preparation of diacyl sulphides (IV) has many advantages, since the reaction can be carried out in the absence of solvent and the volatile trimethylsilyl chloride can easily be removed.

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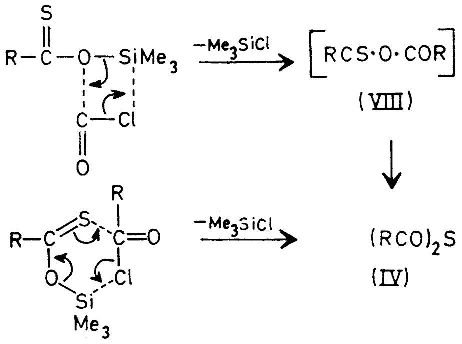
[13] H. G. Khorana, *Chem. Rev.*, 1953, **53**, 145.

[14] R. F. Hudson, 'Structure and Mechanism in Organo-phosphorus Chemistry,' Academic Press, New York, 1965, p. 123.

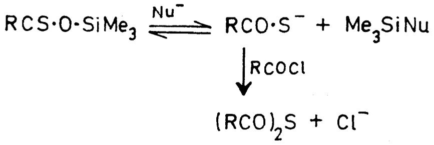
[15] B. Mertel and N. Duffaut, *Compt. rend.*, 1966, **263C**, 74.

In this simple condensation, as in the reaction of thioacids (III) with DCC, there are two possible pathways to the symmetrical sulphides (IV) (Scheme 3). If the cleavage of trimethylsilyl chloride takes place by



SCHEME 3

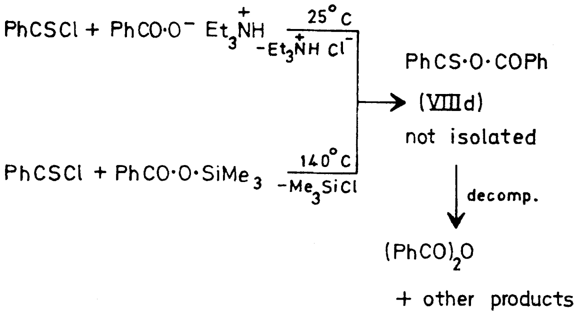
a cyclic four-centre mechanism, the initial product should be the unsymmetrical anhydride (VIII), which



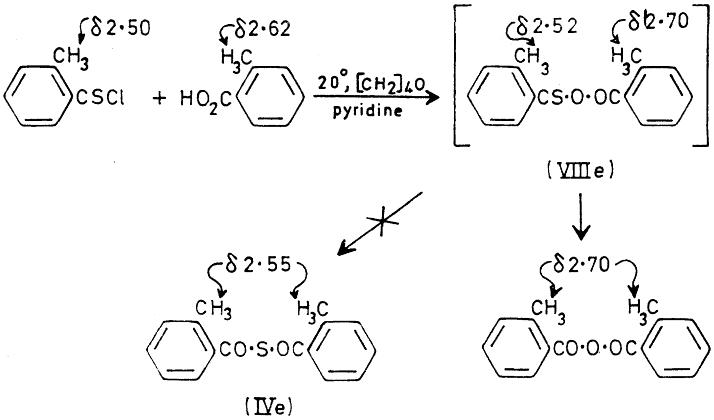
SCHEME 4

would rapidly isomerise to the sulphide (IV). On the other hand a cyclic six-centre transition state could yield the sulphide (IV) directly. Furthermore, the reaction could be catalysed by a trace of nucleophile (*e.g.* Cl$^-$) giving directly the sulphide (IV) (Scheme 4).†

Reaction of Thioacyl Chlorides with Salts and Silyl Esters of Carboxylic Acids.—In the search for other reactions leading to unsymmetrical thioanhydrides (VIII) we investigated the condensation of thioacyl chlorides with salts and silyl esters of carboxylic acids. In these cases the formation of compounds (VIII) as the primary products was obvious. Since aliphatic thioacyl halides are unknown, with the exception of derivatives containing trifluoromethyl groups,[16] we used thiobenzoyl chloride although it was expected to be less reactive. In fact the condensation of thiobenzoyl chloride with benzoic acid in the presence of triethylamine at room temperature was very slow, and the reaction with trimethylsilyl benzoate took place only on heating to 140 °C.



In both cases we isolated in good yield the by-products of the reaction, *i.e.* triethylamine hydrochloride (92%) or chloro(trimethyl)silane (70%), but we were unable to isolate either the unsymmetrical thioanhydride (VIIId) or the expected product of its isomerisation, dibenzoyl sulphide (IVd). The only product isolated was benzoic anhydride. In view of the lack of the sulphide (IVd), and its stability under the reaction conditions, this result suggests that the anhydride (VIIId) does not isomerise to the sulphide (IVd), but disproportionates to benzoic anhydride and unidentified sulphur-containing products.



This is probable, since disproportionation is a characteristic of other mixed anhydrides.[17]

In order to obtain additional proof of the formation of the thioanhydrides (VIII) and their disproportionation, we monitored the course of the reaction of thio-*o*-toluoyl chloride with *o*-toluic acid in the presence of pyridine by ^{1}H n.m.r. spectroscopy (observation of the *o*-methyl signals). After mixing equimolar amounts of

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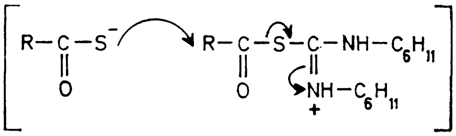
† We thank a referee for this suggestion.

[16] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 1965, **30**, 1375; M. S. Raasch, *ibid.*, 1972, **37**, 1347.

[17] D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, 1958, **23**, 1149 and references cited therein.

the reagents in tetrahydrofuran we observed two singlets at δ 2.62 and 2.50 corresponding to the acid and the chloride, respectively. After the addition of pyridine two new signals of almost equal intensity appeared at δ 2.70 and 2.52. These can be ascribed to non-equivalent methyl groups in the unsymmetrical anhydride (VIIIe). Then the spectrum was observed every hour. It showed gradual consumption of the substrates and an increase in the proportion of compound (VIIIe). At the same time we observed an increase in the intensity of the signal at δ 2.70 with respect to that at δ 2.52. The latter became smaller and broader. On completion, the spectrum of the crude product showed a high intensity singlet at δ 2.70 and a broad band instead of the signal at δ 2.52. By adding to the sample bis-(*o*-toluoyl) sulphide (IVe) and then *o*-toluic anhydride, we showed that the singlet at δ 2.70 corresponded to the methyl groups of the latter, and that the product did not contain the sulphide (IVe). Moreover, we were able to isolate *o*-toluic anhydride (identified by mixed m.p. and mass spectrum).

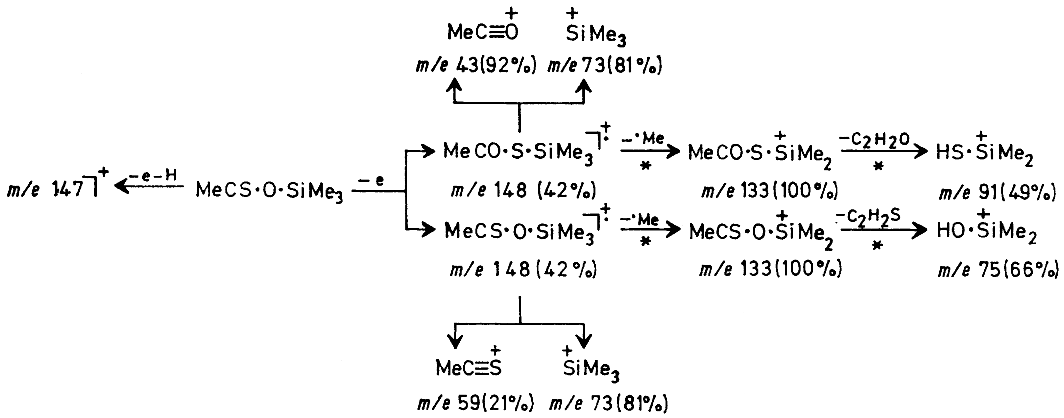
The above results prove that the intermediate is the thioanhydride (VIII), which is relatively unstable, and unlike the cyclic unsymmetrical thioanhydrides of type (I) decomposes to the corresponding anhydride.



Moreover, the fact that we obtained diacyl sulphides (IV) in the reactions of DCC with thioacids (III) and of acyl chlorides with silyl thio-esters (IX) proves that the thioanhydrides (VIII) are not formed in these reactions. This means that the anion of the thioacid (III) attacks protonated thiourea (VII) with the sulphur atom as the nucleophilic centre. For the same reasons, the reaction of the silyl thioesters (IX) with acyl chlorides gives directly the sulphides (IV).

Mass Spectra of Diacyl Sulphides (IV) *and* O-*Trimethylsilyl Thiocarboxylates* (IX).—Mass spectrometry was used as one of the methods of identification and characterisation of the foregoing products. The spectra of the diacyl sulphides (IV) show a weak molecular ion peak with intensity lower than 5% and with isotopic ratios characteristic of compounds containing one sulphur atom. The most important fragmentation process is the formation of $R-C\equiv O^+$, further fragmentation of which takes place in the usual way giving rise to the most intense peaks in the spectrum.

Cleavage of the ester bond and loss of a silyl methyl group are the main fragmentation processes of the silyl esters (IX). Since in all spectra peaks corresponding to $R-C\equiv O^+$ are visible in addition to $R-C\equiv S^+$ fragments, it appears that in the mass spectrometer at least partial isomerisation of *O*-esters (IX) into their less stable *S*-ester isomers, resembling the Schönberg thione–thiol rearrangement,[18] takes place ($RCS\cdot O\cdot SiMe_3 \longrightarrow RCO\cdot S\cdot SiMe_3$). As illustrated in Scheme 5 for *O*-trimethylsilyl thioacetate (IXa) it is possible to formulate the ions $RC\overset{+}{S}\cdot O\cdot SiMe_2$ or $RCO\cdot S\cdot \overset{+}{S}iMe_2$, $HS\cdot\overset{+}{S}iMe_2$, $HO\cdot\overset{+}{S}iMe_2$, $\overset{+}{S}iMe_3$, $R-C\equiv\overset{+}{S}$, and $R-C\equiv\overset{+}{O}$ as key fragments. In the case of *O*-trimethylsilyl thiopivalate (IXc) cleavage of the t-butyl group is the preferred process and leads to the ions Me_3C^+ and $Me_3Si-\overset{+}{O}=C=S$ (*m/e* 57 and 133 respectively). In this case the fragments $R-C\equiv S^+$ and $R-C\equiv O^+$ have only low intensities.



SCHEME 5

EXPERIMENTAL

T.l.c. was performed by upward irrigation on plates coated with Merck silica gel G. ¹H N.m.r. spectra were measured with a JEOL-JNM-C-60 HL instrument, with chloroform, deuteriochloroform, and carbon tetrachloride as solvents and tetramethylsilane as internal standard. Mass spectra were recorded with a GCMS-LKB-9000S instrument. I.r. spectra were measured with a Spektromom-2000 spectrophotometer (KBr discs for solids and films for liquids). Solvents were dried over magnesium sulphate. Thiobenzoic acid (IIId), *p*-nitrothiobenzoic acid (IIIf), and thiopivalic acid (IIIc) were prepared from the corresponding acyl chlorides and hydrogen sulphide in

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[18] A. Schönberg and L. Y. Vargha, *Chem. Ber.*, 1930, **63**, 179.

pyridine.[19] Thiopropionic acid (IIIb) was obtained from propionic acid and phosphorus pentasulphide.[20] Chlorothioacetic acid (IIIg) and trichlorothioacetic acid were prepared from the corresponding acyl chlorides and hydrogen sulphide in the presence of aluminium trichloride.[21,22] Thio-*o*-toluic acid (IIIe) was synthesized by hydrolysis of trimethylsilyl thio-*o*-toluate (IXe); yield 54%, b.p. 110° at 18 mmHg, n_D^{21} 1.5768 (lit.,[23] b.p. 133° at 30 mmHg).

O-Trimethylsilyl Thioacetate (IXa).—To a solution of thioacetic acid (IIIa) (21.2 g, 0.28 mol) and chloro(trimethyl)silane (30.0 g, 0.28 mol) in ether (200 ml), triethylamine (28.4 g, 0.28 mol) was added dropwise with stirring. After 4 h triethylammonium chloride was filtered off and the filtrate was evaporated to give crude (IXa) which was purified by fractionation; yield 29.0 g (70.5%), b.p. 86—87° at 140 mmHg, n_D^{22} 1.4520 (lit.,[24] n_D^{25} 1.4513); *m/e* 148 (M^+, 42%), 147 (40), 133 (100), 91 (49), 75 (66), 73 (81), and 43 (92); $\delta(\mathrm{CCl_4})$ 0.38 (9 H, s) and 2.48 (3 H, s).

O-Trimethylsilyl Thiopropionate (IXb).—By the procedure described above, thiopropionic acid (IIIb) (12.0 g, 0.134 mol), chloro(trimethyl)silane (14.5 g, 0.134 mol), and triethylamine (13.5 g, 0.134 mol) gave a pure sample of (IXb) (13.4 g, 65%), b.p. 79—80° at 60 mmHg, n_D^{22} 1.4535. In an alternative procedure, to a solution of thioacid (IIIb) (7.6 g, 0.084 mol) in petroleum (40 ml) hexamethyldisilazane (4.6 g, 0.028 mol) was added, and the mixture was stirred under reflux for 2 h. The precipitated ammonium thiopropionate was filtered off and the filtrate was evaporated to afford crude (IXb). Distillation gave a pure *sample* (6.2 g, 82.5%), b.p. 59—60° at 28 mmHg, n_D^{19} 1.4530 (Found: C, 44.6; H, 8.5; S, 19.75. $C_6H_{14}OSSi$ requires C, 44.45; H, 8.65; S, 19.75%); *m/e* 162 (M^+, 13%), 147 (40), 91 (15), 75 (30), 73 (100), and 57 (39); $\delta(\mathrm{CCl_4})$ 0.38 (9 H, s), 1.20 (3 H, t), and 2.62 (2 H, q); $\nu_{\max}$ 2 960m, 1 450w, 1 340m, 1 240vs, 1 190s, 1 065m, 850vs, and 760m cm^{-1}.

O-Trimethylsilyl Thiopivalate (IXc).—Thiopivalic acid (IIIc) (9.2 g, 0.078 mol), chloro(trimethyl)silane (8.6 g, 0.079 mol), and triethylamine (8.0 g, 0.079 mol) treated as described for (IXa), gave the ester (IXc) (8.5 g, 57.5%), b.p. 72° at 30 mmHg, n_D^{21} 1.4433 (lit.,[25] n_D^{20} 1.4440); *m/e* 190 (M^+, 11%), 175 (10), 147 (24), 133 (16), 85 (3), 75 (20), 73 (100), and 57 (9); $\delta(\mathrm{CCl_4})$ 0.38 (9 H, s) and 1.25 (9 H, s).

O-Trimethylsilyl Thiobenzoate (IXd).—Silylation of thiobenzoic acid (IIId) (14.7 g, 0.106 mol) with chloro(trimethyl)silane (12.0 g, 0.11 mol) in the presence of triethylamine (11.0 g, 0.109 mol) in ether (200 ml) gave, after the usual work-up, the pure ester (IXd) (16.0 g, 71.5%), b.p. 75—77° at 0.75 mmHg, n_D^{19} 1.5565 (lit.,[25] n_D^{20} 1.5565); *m/e* 210 (M^+, 75%), 195 (100), 121 (37), 105 (95), 91 (2), 77 (83), 75 (18), 73 (57), 51 (51), and 45 (44); $\delta(\mathrm{CCl_4})$ 0.47 (9 H, s) and 7.1—7.45 and 8—8.25 (5 H, m).

O-Trimethylsilyl Thio-o-toluate (IXe).—The *ester* was prepared by the method of Kricheldorf and Leppert [25] and purified by distillation; yield 15.1%, b.p. 85—88° at 0.8 mmHg, n_D^{19} 1.5460 (Found: C, 59.85; H, 7.4; S, 14.6. $C_{11}H_{16}OSSi$ requires C, 58.95; H, 7.15; S, 14.3%); $\delta(\mathrm{CCl_4})$ 0.48 (9 H, s), 2.48 (3 H, s), and 7.2—7.9 (4 H, m); $\nu_{\max}$ 3 090w, 2 950m, 1 680s, 1 600w, 1 500m, 1 460m, 1 300s, 1 240s,br, 850s, and 760s.

O-Trimethylsilyl p-Nitrothiobenzoate (IXf).—A solution of *p*-nitrothiobenzoic acid (IIIf) (3.0 g, 0.0164 mol) and hexamethyldisilazane (0.9 g, 0.0056 mol) in ether (15 ml) was stirred for 3 h. The precipitated ammonium *p*-nitrothiobenzoate was filtered off and the filtrate was evaporated to give crude (IXf) as an orange solid (2.4 g, 86.0%), m.p. 66—71° (sealed tube) (Found: C, 45.8; H, 4.75; N, 6.35. Calc. for $C_{10}H_{13}NO_3SSi$: C, 47.05; H, 5.1; N, 5.5%), contaminated with a small amount of ammonium *p*-nitrothiobenzoate. Further purification was difficult owing to its sensitivity to moisture.

Reaction between Monothiocarboxylic Acids (III) *and Dicyclohexylcarbodi-imide* (DCC).—(i) *Thioacetic acid* (IIIa) *and* DCC (2 : 1). To a cooled (ice–salt bath), stirred solution of DCC (10.3 g, 0.05 mol) in ether (50 ml), a solution of (IIIa) (7.6 g, 0.1 mol) in ether (50 ml) was added slowly, and the mixture was left overnight. The precipitated dicyclohexylthiourea (V) was filtered off, washed with ether, and recrystallized from ethanol; yield 7.8 g (65%), m.p. 179—181° (lit.,[26] 181—182°). T.l.c. analysis [petroleum–benzene–chloroform–acetone (3 : 4 : 4 : 3)] showed that before recrystallization (V) contained a small proportion of the *N*-acetylthiourea (VIa) [R_F 0.57 for (V) and 0.26 for (VIIa)].

The ethereal solution was evaporated and the residue distilled to give diacetyl sulphide (IVa) (4.8 g, 82%), b.p. 69—78° at 38 mmHg, n_D^{20} 1.4800. G.l.c. indicated the presence of up to 5% of thioacetic acid, acetic acid, and acetic anhydride. Further distillation afforded analytically pure sulphide (IVa) (3.2 g, 54.7%), b.p. 76—77° at 42 mmHg, n_D^{21} 1.4805 (lit.,[27] n_D^{21} 1.4810; lit.,[28] n_D^{21} 1.4826) (Found: C, 40.5; H, 5.2; S, 27.0. $C_4H_6O_2S$ requires C, 40.7; H, 5.2; S, 27.1%); *m/e* 118 (M^+, <2%) and 43 (100); $\delta(\mathrm{CCl_4})$ 2.5 (6 H, s).

(ii) *Thiopropionic acid* (IIIb) *and* DCC (2 : 1). Similar treatment of DCC (5 g, 0.0243 mol) with (IIIb) (4.35 g, 0.0485 mol) in ether (80 ml) afforded the thiourea (V) (4.9 g, 84%), m.p. 181—182° (from ethanol) and *dipropionyl sulphide* (IVb) (2.2 g, 62%), b.p. 94—95° at 30 mmHg, n_D^{20} 1.4800 (Found: C, 49.55; H, 6.9; S, 21.9. $C_6H_{10}O_2S$ requires C, 49.3; H, 6.85; S, 21.9%); *m/e* 146 (M^+, 5%) and 57 (100%); $\delta(\mathrm{CCl_4})$ 1.15 (6 H, t) and 2.84 (4 H, q); $\nu_{\max}$ 2 980m, 2 910m, 1 760s, 1 710vs, 1 460m, 1 405w, 1 390w, 1 080s, 1 000s, 940s, 920vs, 895s, and 700s cm^{-1}.

(iii) *Thiopivalic acid* (IIIc) *and* DCC (2 : 1). DCC (3.5 g, 0.017 mol) and (IIIc) (4.0 g, 0.034 mol) in ether (40 ml) gave in the same way the thiourea (V) (4.0 g, 97%), m.p. 179—182°, and *dipivaloyl sulphide* (IVc) as a solid (2.9 g, 84.5%), b.p. 65—66° at 0.8 mmHg, m.p. 26° (Found: C, 59.4; H, 8.8; S, 15.8. $C_{10}H_{18}O_2S$ requires C, 59.4; H, 8.9; S, 15.85%); *m/e* 202 (M^+, <2%), 85 (61), 57 (100), and 41 (40); $\delta(\mathrm{CCl_4})$ 1.22 (18 H, s); $\nu_{\max}$ 2 990s, 1 790s, 1 750vs, 1 700vs, 1 480s, 1 465s, 1 400m, 1 375m, 1 030m, 940m, 890vs, and 795vs cm^{-1}.

(iv) *Thiobenzoic acid* (IIId) *and* DCC (2 : 1). To a solution of DCC (5.6 g, 0.0271 mol) in ether (40 ml), thiobenzoic acid (IIId) (7.5 g, 0.0542 mol) in ether (40 ml) was added. The mixture was stored overnight at room tem-

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perature. The precipitated thiourea (V) was filtered off and the ethereal solution was evaporated. The residue was treated with carbon tetrachloride (20 ml) and a second crop of (V) was isolated [total yield after recrystallisation from ethanol 4.8 g (73.5%), m.p. 179—181°]. T.l.c. [petroleum–benzene–chloroform–acetone (4 : 5 : 4 : 1)] showed that the crude (V) was contaminated with *N*-benzoyl-*NN'*-dicyclohexylthiourea (VId) [R_F 0.3 for (V) and 0.25 for (VId)]. Evaporation of the carbon tetrachloride solution afforded the sulphide (IVd) (4.7 g, 71%), m.p. 47—48° (from ether–petroleum) (lit.,[29] 48°); *m/e* 242 (M^+, <2%), 105 (100), 77 (35), and 51 (13).

(v) *Thio-*o*-toluic acid* (IIIe) *and DCC* (2 : 1). Similar treatment of (IIIe) (1.6 g, 0.0105 mol) with DCC (1.08 g, 0.005 25 mol) in ether (20 ml) afforded thiourea (V) (1.1 g, 87.2%), m.p. 173—176°, and *di-*o*-toluoyl sulphide* (IVe) (0.7 g, 49.6%), m.p. 52—53° (from benzene) (Found: C, 71.35; H, 5.4; S, 11.75. $C_{14}H_{14}O_2S$ requires C, 71.1; H, 5.2; S, 11.85%); *m/e* 270 (M^+, <2%), 119 (100), 91 (25), and 65 (9); $\delta(CCl_4)$ 2.55 (3 H, s) and 7.1—7.55 and 7.85—8.1 (4 H, m).

(vi) p-*Nitrothiobenzoic acid* (IIIf) *and DCC* (1 : 1). A mixture of the thio-acid (IIIf) (1.5 g, 0.0082 mol) and DCC (1.7 g, 0.0082 mol) in ether (20 ml) was kept overnight. Removal of ether left NN'*-dicyclohexyl-*N-p-*nitrobenzoylthiourea* (VIf) (2.6 g, 82%), m.p. 155—157° (from benzene) (from n-pentane, m.p. 159—161°) (Found: C, 61.5; H, 6.9; N, 10.8; S, 7.95. $C_{20}H_{27}N_3O_3S$ requires C, 61.7; H, 6.95; N, 10.8; S, 8.25%); *m/e* 389 (M^+, <2%), 248 (<2), 239 (4), 163 (17), 150 (48), 141 (3), 120 (8), 104 (38), 98 (23), and 55 (100); $\nu_{max.}$ 3 400s, 3 200m, 2 900s, 2 810m, 1 620vs, 595m, 1 520vs, 1 450m, 1 410s, and 1 340vs cm^{-1}.

(vii) *Chlorothioacetic acid* (IIIg) *and DCC* (1 : 1). A solution of DCC (2.1 g, 0.0102 mol) and (IIIg) (1.13 g, 0.0102 mol) in ether (30 ml) was stored at room temperature overnight. The precipitated *N*-chloroacetyl-*NN'*-dicyclohexylthiourea (VIg) was filtered off (2.4 g, 74%); m.p. 185—205°. Since attempted recrystallisation caused decomposition, spectral measurements and elemental analysis were carried out on the crude sample (Found: C, 56.95; H, 7.8; N, 9.25; S, 10.0. Calc. for $C_{15}H_{25}ClN_2OS$: C, 56.85; H, 7.9; N, 9.85; S, 10.1%); $\delta(CDCl_3)$ 1—2.5br (22 H, m), 3.45br (1 H, s), and 4.3 (2 H, s); $\nu_{max.}$ 3 400m, 2 900s, 2 820s, 1 760s, 1 600vs, 1 450m, 1 380s, and 1 340 cm^{-1}. T.l.c. [benzene–acetone–chloroform (5 : 2 : 1)] showed that the product contained traces of bischloroacetyl sulphide (IVg) [R_F 0.05 for (IVg) and 0.75 for (VIg)].

Reaction between O-*Trimethylsilyl Thiocarboxylates* (IX) *and Acyl Chlorides*.—(i) *Diacetyl sulphide* (IVa) *from* (IXa) *and acetyl chloride*. Acetyl chloride (46.8 g, 0.6 mol) was added to (IXa) (73.2 g, 0.495 mol) and the mixture was stored overnight. Chloro(trimethyl)silane and the excess of acetyl chloride were removed and the residue was distilled to give pure diacetyl sulphide (IVa) (56 g, 96%), n_D^{21} 1.4810.

(ii) *Dipropionyl sulphide* (IVb) *from* (IXb) *and propionyl chloride*. Similar treatment of (IXb) (4 g, 0.0246 mol) with propionyl chloride (2.8 g, 0.03 mol) gave (IVb) (2.7 g, 75%), b.p. 88—90° at 20 mmHg, n_D^{21} 1.4795.

(iii) *Dipivaloyl sulphide* (IVc) *from* (IXc) *and pivaloyl chloride*. From (IXc) (2.3 g, 0.012 mol) and pivaloyl chloride (1.45 g, 0.0121 mol) (IVc) was obtained (2.1 g, 86%) [1.5 g (61.2%), b.p. 65° at 0.8 mmHg after redistillation].

(iv) *Dibenzoyl sulphide* (IVd) *from* (IXd) *and benzoyl chloride*. To a solution of (IXd) (2.1 g, 0.01 mol) in petroleum (10 ml), benzoyl chloride (1.4 g, 0.01 mol) was added, and the mixture was stored for 2 days. The precipitated (IVd) was filtered off; yield 2.1 g (86.7%), m.p. 47—48°.

(v) *Di-*o*-toluoyl sulphide* (IVe) *from* (IXe) *and* o*-toluoyl chloride*. A mixture of (IXe) (1.9 g, 0.0085 mol) and *o*-toluoyl chloride (1.35 g, 0.0085 mol) in petroleum (20 ml) was left overnight; evaporation gave (IVe) in quantitative yield. Recrystallisation from benzene afforded pure material (1.5 g, 66%), m.p. 52—53°.

(vi) *Bis-*p*-nitrobenzoyl sulphide* (IVf) *from* (IXf) *and* p*-nitrobenzoyl chloride*. A solution of (IXf) (0.45 g, 0.001 76 mol) and *p*-nitrobenzoyl chloride (0.3 g, 0.0016 mol) in ether was stored overnight. Filtration then gave pure *sulphide* (IVf) (0.4 g, 74%), m.p. 166—168° (lit.,[30] 148°) (Found: C, 50.75; H, 2.5; N, 8.55; S, 9.65. $C_{14}H_8N_2O_6S$ requires C, 50.6; H, 2.4; N, 8.45; S, 9.65%); *m/e* 332 (M^+, <0.1%), 150 (100), 120 (10), 104 (56), 92 (30), 76 (53), and 50 (34); $\nu_{max.}$ 1 735vs, 1 665m, 1 600s, 1 520vs, 1 405w, 1 350vs, 1 310s, 1 180vs, 1 160vs, 1 105m, 1 005w, 880vs, 860s, 840vs, 760m, 710s, and 695s.

Reaction of Thiobenzoyl Chloride with Trimethylsilyl Benzoate.—Thiobenzoyl chloride (2 g, 0.0126 mol) and trimethylsilyl benzoate (2.5 g, 0.0126 mol) were heated at 140 °C for 7 h and trimethylsilyl chloride was separated (0.98 g, 70%). After several days a solid crystallised from the residue (m.p. 36—40°; mixed m.p. with benzoic anhydride 37—41°; lit.,[31] m.p. 41° for benzoic anhydride).

Reaction of Thiobenzoyl Chloride with Benzoic Acid.—To a solution of benzoic acid (1.22 g, 0.01 mol) and thiobenzoyl chloride (1.56 g, 0.01 mol) in ether (30 ml), triethylamine was added dropwise with stirring. After 8 h the precipitated triethylammonium chloride was filtered off (1.2 g, 92%). From the residue crystalline benzoic anhydride (m.p. 35—40°) was separated (mixed m.p. 36—40°).

*Reaction of Thio-*o*-toluoyl Chloride with* o*-Toluic Acid*.—A mixture of the chloride (1.3 g, 0.007 65 mol) and *o*-toluic acid (1.05 g, 0.007 65 mol) in tetrahydrofuran (10 ml) was treated with triethylamine (0.815 g, 0.008 mol). The mixture was left overnight and then triethylammonium chloride was filtered off (0.9 g, 85.5%). Evaporation left a residue from which *o*-toluic anhydride was separated; m.p. 34—37°; mixed m.p. 35—38° (lit.,[32] 38—39° for *o*-toluic anhydride); M^+ 270.

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