

# Synthesis and Characterisation of Bis[(methylthio)carbonyl]polysulphanes<sup>1</sup>

Andrew W. Mott and George Barany\*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

Bis[(methylthio)carbonyl]polysulphanes with a linear chain of 1—6 sulphurs have been prepared and characterised; in particular X-ray crystallographic analyses proved the structures of the tri- and tetra-sulphanes. The tri- to hexa-sulphanes were formed by reactions of *O,S*-dimethyl dithiocarbonate with the appropriate dichlorosulphane containing two less sulphurs. The disulphane was prepared by chlorination of *O*-*t*-butyl *S*-methyl dithiocarbonate or by controlled desulphurisation of the trisulphane using triphenylphosphine; further desulphurisation provided the monosulphide. (Methylthio)carbonyl-sulphenyl chloride is proposed as an intermediate in the above chlorination; it was synthesised by an indirect route and shown to rearrange to its isomer, (methylthio)carbonyl chloride.

Diethyl pyrocarbonate, the anhydride of ethyl carbonic acid, is a widely used reagent for the chemical modification of amino, imidazole, and sulphhydryl groups of proteins and nucleic acids.<sup>2,3</sup> We suggested earlier<sup>4</sup> that sulphur-containing analogues of diethyl pyrocarbonate may be of value both in biochemistry and in functional group protection for peptide and general organic synthesis. In contrast to the readily prepared<sup>4-6</sup> bis(alkoxycarbonyl) sulphide (7) and bis(alkoxythiocarbonyl) sulphide (8), the sole literature example<sup>7</sup> for an (alkylthio)carbonyl analogue was the formation of bis[(ethylthio)carbonyl] sulphide as an accidental by-product of the reaction between thioacetic acid and *S*-ethyl chlorothioformate.

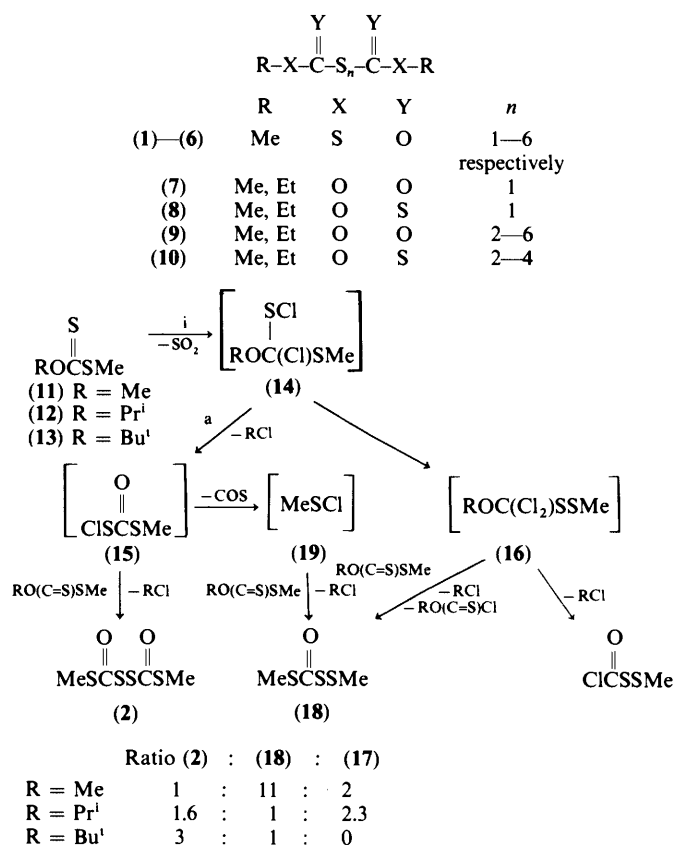
Recently,<sup>5,6</sup> we developed efficient routes for the synthesis of bis(alkoxycarbonyl)polysulphanes (9). The present report extends that work to the preparation and characterisation of bis[(methylthio)carbonyl]polysulphanes (1)—(6) with up to six linearly connected sulphurs. The novelty of these structures is in stark contrast with the extensive knowledge<sup>8</sup> about the isomeric bis(alkoxythiocarbonyl)polysulphanes (10). It is also significant that almost all of the approaches that are successful for the polysulphanes (7)—(10) fail when applied to the (alkylthio)carbonyl series.

## Results and Discussion

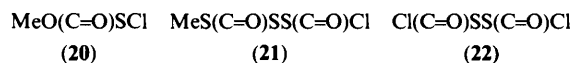
**Synthesis.**—The tri- and tetra-sulphanes (3) and (4) were both crystalline solids obtained from the reaction of *O,S*-dimethyl dithiocarbonate (11) with sulphur dichloride and sulphur monochloride respectively. The higher sulphanes (5) and (6) were made similarly, using dichloro-tri- or tetra-sulphane,<sup>9</sup> but were shown by h.p.l.c. analysis (see later) to have undergone considerable desulphurisation and disproportionation.

The disulphane (2) was first obtained<sup>10</sup> in 8% overall yield in the residue from the distillation of the mixture formed when *O,S*-dimethyl dithiocarbonate (11) was treated with sulphuryl chloride (0.5 equiv.); the same process provides *S*-methyl *S*-methylsulphenyl dithiocarbonate (18)<sup>5,10</sup> as the major product in 72% yield. We have now examined reactions which give compounds (2) and (18) in systems with secondary and tertiary alkoxy groups on the dithiocarbonate. Thus, the crude mixture from the chlorination of *O*-isopropyl *S*-methyl dithiocarbonate (12) contained (methylthio)carbonyl chloride (17),<sup>5</sup> and the disulphanes (18) and (2), in the molar ratio 2.3:1:1.6, whereas the product from a similar chlorination of *O*-*t*-butyl *S*-methyl dithiocarbonate (13) was principally the disulphane (2) (90% crude yield, 75% purity) which was obtained pure upon chromatography.

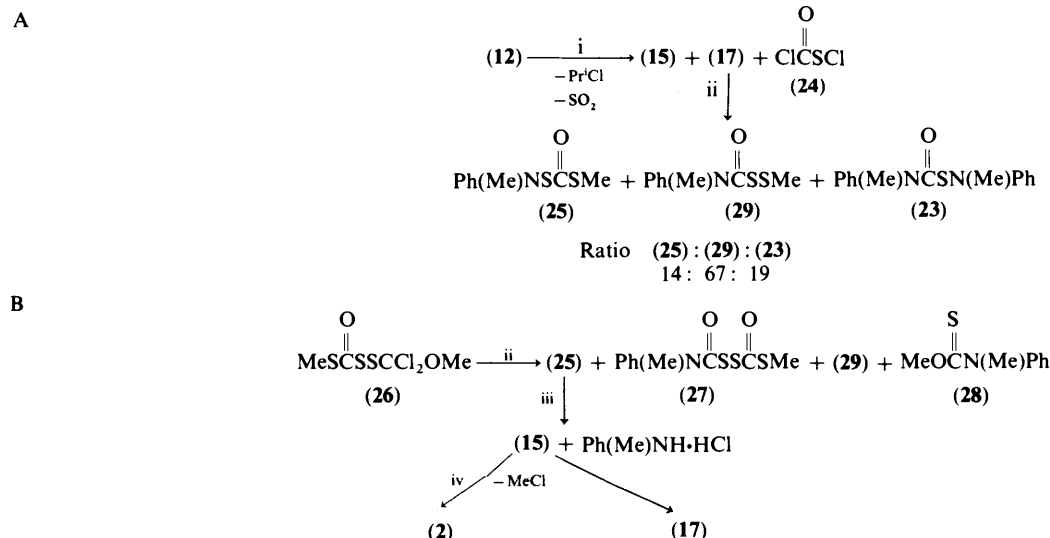
A possible explanation for the formation of compound (2) is outlined in Scheme 1. We have already shown<sup>10</sup> in primary



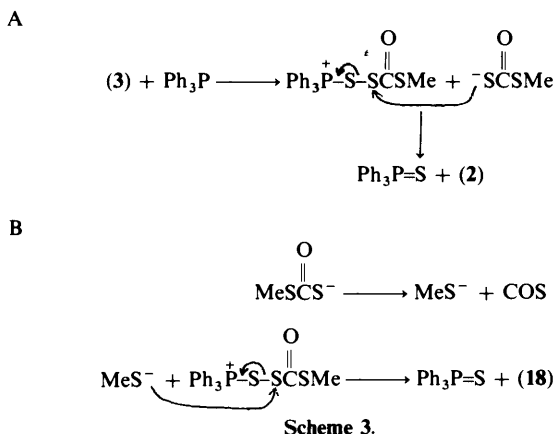
Scheme 1. Reagents: i, SO<sub>2</sub>Cl<sub>2</sub>



systems that the initial adducts (14; R = Me, Et) from the chlorination of the dithiocarbonates (11) rapidly rearrange to the alkoxydichloromethylmethyldisulphane intermediates (16; R = Me, Et) which are relatively stable but eventually lose alkyl chloride to form compound (17). Additionally, the intermediates (16) were shown<sup>10</sup> to react with additional dithiocarbonate (11) to provide compound (18). Now, when the alkoxy group (RO) is secondary or tertiary, the adducts (14) could lose alkyl chloride (route a), prior to their rearrangement



Scheme 2. Reagents: i, 2 SO<sub>2</sub>Cl<sub>2</sub> (see Scheme 1); ii, PhMeNH; iii, HCl; iv, MeO(C=S)SMe



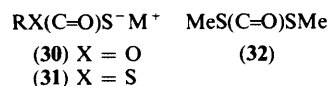
and further reactions, *via* (16; R = Pr<sup>i</sup>, Bu<sup>t</sup>) providing (17) and (18) (route b). This proposal postulates (methylthio)carbonyl-sulphenyl chloride (15) as an intermediate, which evidently reacts with a second equivalent of dithiocarbonate to give the disulphane (2) in an analogous manner to the reaction of the stable methoxycarbonylsulphenyl chloride (20) with compound (11) to give 1-methoxycarbonyl-2-(methylthio)carbonyldisulphane.<sup>5</sup> The sulphenyl chloride intermediate (15) may also account for some of (18), because loss of carbonyl sulphide would give methanesulphenyl chloride (19) which is known<sup>5</sup> to react with dithiocarbonates to yield this product.

The sulphenyl chloride (15) was not detected spectroscopically under any of the reaction conditions summarised in Scheme 1. Attempts to prepare it by chlorination of the disulphane (2) or (18) with sulphuryl chloride yielded methanesulphenyl chloride (19) together with the acid chloride (21) or (17), respectively. Thus, the C-SMe bond was cleaved rather than the central S-S bond. This stability of the S-S bond in a (C=O)SS(C=O) system to chlorination is consistent with our observation<sup>10</sup> that bis(methoxycarbonyl)disulphane (9; n = 2, R = Me) did not react with sulphuryl chloride, and a report<sup>11</sup> that chlorination of bis(acetyl)disulphane gives acetyl chloride and acetyldisulphanyl chloride.

When *O*-isopropyl *S*-methyl dithiocarbonate (12) was chlorinated with excess of sulphuryl chloride and quenched with *N*-methylaniline (Scheme 2A), the major products were

1-methyl-2-(*N*-methyl-*N*-phenylcarbamoyl)disulphane (29),<sup>5</sup> the *N*-methylanilide of (17), as well as *N,N'*-dimethyl-*N,N'*-diphenylcarbamoylsulphenamide (23)<sup>5</sup> derived from chlorocarbonylsulphenyl chloride (24), in turn formed by further chlorination<sup>12</sup> of the acid chloride (17). Another product of this reaction was the *N*-methylanilide of (15), *N*-methyl-*N*-phenyl-(methylthio)carbonylsulphenamide (25), which was identical with one of the products isolated when the reaction (Scheme 2B) of 1-(methylthio)carbonyl-2-methoxydichloromethyl-disulphane (26)<sup>5</sup> with excess of *N*-methylaniline was carried out in the same way<sup>10</sup> as that of 1-methoxycarbonyl-2-methoxydichloromethyl-disulphane with *N*-methylaniline. Other products from this reaction included the carbamoyldisulphane (29), 1-(methylthio)carbonyl-2-(*N*-methyl-*N*-phenylcarbamoyl)-disulphane (27),<sup>5</sup> and *O*-methyl-*N*-methyl-*N*-phenylthiocarbamate (28).<sup>5</sup> When the isolated sulphenamide (25) was treated with hydrogen chloride, the sulphenyl chloride (15) was obtained which reacted directly *in situ* with the dithiocarbonate (11) to give the disulphane (2). On standing in CDCl<sub>3</sub> at 25 °C, compound (15), prepared as above, rearranged cleanly to the acid chloride (17) with *t*<sub>½</sub> = 75 min; no methanesulphenyl chloride (19) was formed.

In analogy to methods used to prepare the bis(alkoxy-carbonyl)disulphanes (9; n = 2), sodium methanethiolate was treated with bis(chlorocarbonyl)disulphane (22)<sup>5</sup> or 1-chlorocarbonyl-2-(methylthio)carbonyldisulphane (21);<sup>5</sup> the desired product (2) was formed together with substantial amounts of dimethylsulphane and sulphenyl dithiocarbonate (18). Whereas compound (9; n = 2) can be formed by oxidation of Bender's salt (30), an attempt at the iodine oxidation of the analogue (31)<sup>13</sup> was unsuccessful. Finally, although iodomethane<sup>5</sup> and Lewis acids<sup>14</sup> isomerise *O,S*-dimethyl dithiocarbonate (11) to *S,S'*-dimethyl dithiocarbonate (32), attempts to isomerise bis(methoxythiocarbonyl)disulphane (10; R = Me, n = 2) in the same way also gave compound (32).



Desulphurisation of the trisulphane (3), using<sup>15</sup> triphenyl-phosphine, provided another approach to the disulphane (2). The suggested mechanism for this transformation is shown in Scheme 3A, and rationalisation for the observed formation of

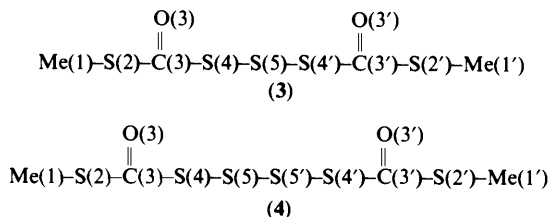


Figure 1. Crystallographic numbering schemes for compounds (3) and (4)

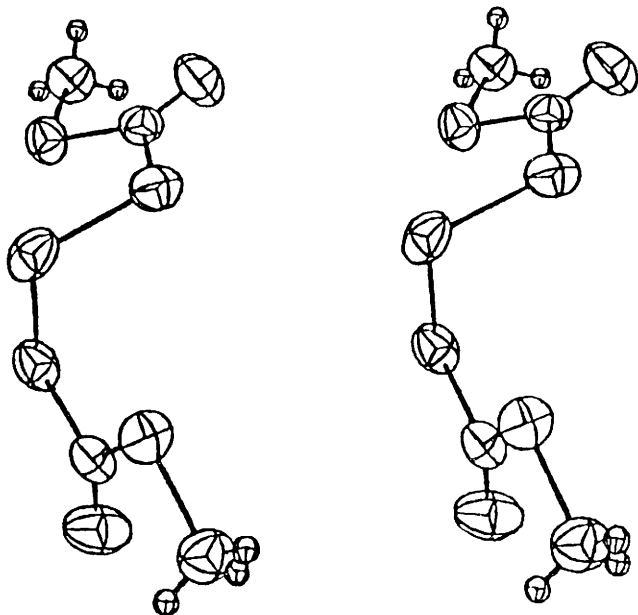


Figure 2. Stereoview of compound (3)

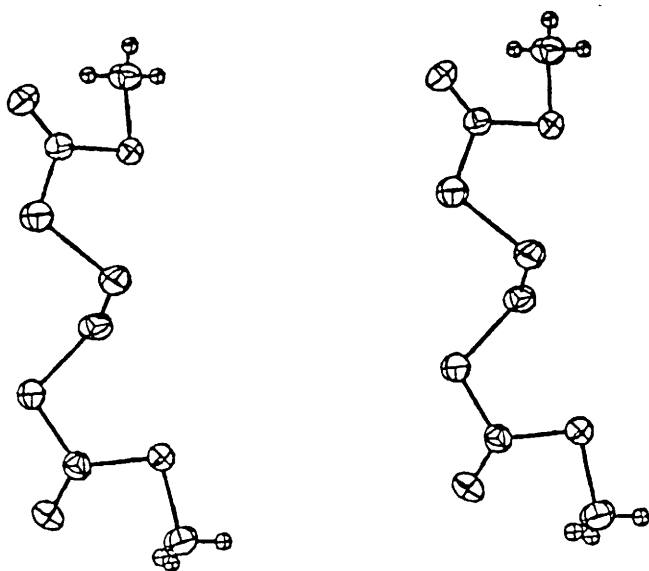


Figure 3. Stereoview of compound (4)

sulphenyl dithiocarbonate (18) as the principal by-product (10–15%) is shown in Scheme 3B.

The thioanhydride (1) was obtained in good yield by

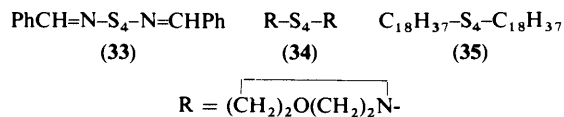


Table 1. Final positional parameters with e.s.d.s in parentheses

Bis[(methylthio)carbonyl]trisulphane (3)

Atom	x	y	z
C(1)	-0.132 7(2)	0.229 4(7)	0.445 7(1)
C(3)	0.051 5(2)	0.164 6(6)	0.372 0(1)
O(3)	0.112 1(2)	0.314 2(6)	0.412 27(8)
S(2)	-0.102 01(5)	0.048 5(2)	0.372 89(3)
S(4)	0.124 51(5)	0.060 1(2)	0.303 38(3)
S(5)	0.000 00(0)	-0.218 0(2)	0.250 00(0)
H(1A)	-0.205(3)	0.222(8)	0.445(2)
H(1B)	-0.087(3)	0.160(9)	0.476(1)
H(1C)	-0.111(4)	0.425(12)	0.448(3)

Bis[(methylthio)carbonyl]tetrasulphane (4)

C(1)	0.198 43(8)	0.034 2(4)	0.254 4(3)
C(3)	0.137 19(7)	0.358 8(4)	0.358 7(2)
O(3)	0.176 96(6)	0.485 4(3)	0.379 8(2)
S(2)	0.131 31(2)	0.062 84(9)	0.283 79(7)
S(4)	0.078 60(2)	0.488 38(10)	0.408 93(7)
S(5)	0.022 92(2)	0.217 40(10)	0.380 14(7)
H(1A)	0.224 0(8)	0.043(4)	0.353(3)
H(1B)	0.202 3(8)	0.150(5)	0.169(3)
H(1C)	0.199 4(9)	-0.115(5)	0.214(3)

desulphurisation of compound (3) directly with triphenylphosphine (2 equiv.). The reaction of *S*-methyl chlorothioformate with sodium sulphide<sup>5,6</sup> or lithium sulphide,<sup>16</sup> however, gave compound (32) rather than (1).

The polysulphanes (1)–(6) were observed to decompose slowly in the presence of alcohols forming dimethylpolysulphane mixtures; for example, a solution of the sulphide (1) in [<sup>2</sup>H<sub>4</sub>]methanol, followed by <sup>1</sup>H n.m.r. spectroscopy, contained 20% dimethylsulphane after 90 min. Also, attempts to distil the trisulphane (3) (bulb-to-bulb oven 134 °C, 0.08 mmHg) resulted in considerable decomposition with the formation of the sulphenyl dithiocarbonate (18), together with dimethyl-trisulphane and -tetrasulphane.

*High Performance Liquid Chromatography (H.P.L.C.).*—Reversed phase h.p.l.c. was used to examine mixtures of the polysulphanes (1)–(6); in particular, it provided additional evidence for the identities of the penta- (5) and hexa-sulphane (6). A plot of log (retention time corrected for void volume) against the number of sulphur atoms in the polysulphane chain was linear for each concentration of the methanol–water eluant, a criterion previously reported for other polysulphanes with alkyl<sup>17</sup> or alkoxy-carbonyl<sup>6</sup> groups. For methanol–water (68:32), log [retention time (min) – void retention time (2.7 min)] = 0.51 + 0.28 (no. of S atoms), and with methanol–water (85:15), log (retention time – 2.7) = 0.18 + 0.17 (no. of S atoms).

*Crystal Structures.*—To further our understanding of the novel compounds (3) and (4), X-ray crystal structure analyses were carried out (Figures 1–3; Tables 1 and 2). Bis(methoxythiocarbonyl)trisulphane (10; R = Me, *n* = 3), the isomer of (3), was solved earlier by Husebye and co-workers.<sup>18</sup> Compound (4) is the first bis(acyl)tetrasulphane structure to be solved, and, in fact, only three other organic tetrasulphanes have been reported earlier. These are 1,4-bis(benzylideneamino)tetrasulphane (33),<sup>19</sup> 1,4-dimorpholino-

**Table 2.** Interatomic distances (Å) with e.s.d.s in parentheses

	(3)	(4)
C(1)–S(2)	1.795(6)	1.794(4)
C(3)–S(2)	1.740(4)	1.742(4)
C(3)–O(3)	1.198(6)	1.201(4)
C(3)–S(4)	1.795(4)	1.801(4)
S(4)–S(5)	2.040(2)	2.032(2)
S(5)–S(5')		2.055(2)

Interatomic angles (°) with e.s.d.s in parentheses

	(3)	(4)
C(1)–S(2)–C(3)	99.4(2)	98.1(2)
S(2)–C(3)–O(3)	126.0(3)	125.8(3)
S(2)–C(3)–S(4)	117.1(3)	117.5(2)
O(3)–C(3)–S(4)	116.9(3)	116.7(2)
C(3)–S(4)–S(5)	105.5(2)	105.7(2)
S(4)–S(5)–S(4')	107.8(1)	
S(4)–S(5)–S(5')		106.2(1)

Selected dihedral angles (°)

	(3)	(4)
C(3)–S(4)–S(5)–S(5')		–87.3
C(3)–S(4)–S(5)–S(4')	83.1	
S(2)–C(3)–S(4)–S(5)	–6.2	5.2
C(1)–S(2)–C(3)–S(4)	–175.9	179.3
S(5)–S(4)–C(3)–O(3)	175.5	–174.9
C(1)–S(2)–C(3)–O(3)	2.2	–0.5
S(4)–S(5)–S(5')–S(4')		–78.8

tetrasulphane (34),<sup>20</sup> and 1,4-bis(octadecyl)tetrasulphane (35).<sup>21</sup>

A comparison of the isomeric trisulphanes indicates a similar central S(4)–S(5) bond length and S–S–S angle. In the trisulphane (3), the C(3)–S(4) bond length is 1.795 Å, nearer to that<sup>22</sup> of a single C–S bond (1.81 ± 0.01 Å) than the 1.74 Å reported for bis(methoxythiocarbonyl)trisulphane, where conjugation with the thiocarbonyl bond shortens this bond.

In the tetrasulphanes (4) and (33)–(35), the central S(5)–S(5') bond length is close to the 2.07 ± 0.02 Å reported<sup>22</sup> for the S–S bond in S<sub>8</sub>. The side S(4)–S(5) bond length is always shorter and depends on the terminal groups. The central S–S–S torsional angle in compound (4) is 78.8°, which comes closer to the optimal 90° postulated by Pauling<sup>23</sup> than the corresponding value for the other three tetrasulphanes. Finally, the crystal structure of compound (4) is *trans,trans*, as in (34) and (35), whereas compound (33) is reported to have a *cis,cis* structure about the two S(4)–S(5) bonds.

## Experimental

**General.**—M.p.s were determined on a Fisher-Johns apparatus, and are uncorrected. I.r. spectra were obtained on a Perkin-Elmer spectrophotometer on ca. 0.1M-solutions in CDCl<sub>3</sub>. N.m.r. spectra were observed on a Varian HFT 80/CFT 20 spectrometer at 80 MHz (<sup>1</sup>H) and 20 MHz (<sup>13</sup>C). Samples were dissolved in CDCl<sub>3</sub> and resonances are expressed in p.p.m. downfield from tetramethylsilane (accuracy ±0.01 p.p.m. for <sup>1</sup>H n.m.r. and ±0.1 p.p.m. for <sup>13</sup>C n.m.r.). U.v. absorption spectra were measured on a Beckman 35 spectrophotometer, in 95% ethanol. H.p.l.c. was carried out on a Beckman-Altex system comprising two 112 pumps, a 165 variable wavelength detector, a 421 controller, and an Ultrasphere-ODS column (4.6 mm × 250 mm). Electron-ionization mass spectra were obtained on a Kratos/AEI-MS30 instrument, at 70 eV and a source temperature of 200 °C. Ether refers to diethyl ether.

**Materials.**—Unless indicated otherwise, solvents and chemicals were reagent grade and used without further purification. *O*-Isopropyl *S*-methyl dithiocarbonate (12) was prepared from potassium isopropyl xanthate and iodomethane [70% yield, b.p. 34 °C (1.5 mmHg); lit.,<sup>8</sup> b.p. 65–68 °C (5 mmHg)]. Other starting materials are described in our previous publication.<sup>5</sup>

**Bis[(methylthio)carbonyl] Sulphide (1).**—Triphenylphosphine (12.8 g, 48.8 mmol) was added slowly at 0 °C to a stirred solution of compound (3) (6 g, 24.4 mmol) in ether (150 ml). Stirring was continued for 30 min at 25 °C, then the mixture was filtered and evaporated. The residue was taken up in ether (25 ml), filtered to remove further triphenylphosphine sulphide, and evaporated to give a yellow oil (5.15 g, 116%) containing compound (1) (70%), triphenylphosphine sulphide (12%), compound (18) (15%), and compound (2) (3%). A bulb-to-bulb distillation (oven temperature 25–90 °C, 0.3 mmHg) yielded compound (1) (3.45 g, 78%) essentially free of the phosphine and compound (2), but still containing some (18). An additional bulb-to-bulb distillation (oven temperature 80–85 °C, 0.2 mmHg) gave bis[(methylthio)carbonyl] sulphide (2.16 g, 49%), ρ 1.35, 97% pure by h.p.l.c. (Found: C, 26.4; H, 3.5; S, 52.8. C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>S<sub>3</sub> requires C, 26.36; H, 3.32; S, 52.77%). δ<sub>H</sub> 2.46; δ<sub>C</sub> 13.4, 181.4 p.p.m.; ν<sub>max</sub>. 1 710s, 1 645s, 840s, and 800vs cm<sup>-1</sup>; λ<sub>max</sub>. 260 nm (log ε 4.00); *m/z* 182 (*M*<sup>+</sup>, 2%), 122 (*M* – COS, 7), 94 (MeSSMe<sup>+</sup>, 14), 75 (MeSCO<sup>+</sup>, 100), 60 (COS<sup>+</sup>, 24), and 47 (MeS<sup>+</sup>, 39).

**Bis[(methylthio)carbonyl]disulphane (2).**—A. Analogous to the preparation of compound (1), triphenylphosphine (8.5 g, 32.6 mmol) was added to a solution of compound (3) (8 g, 32.6 mmol) in ether (120 ml). The crude product (6.83 g, 98%), containing some compounds (1) and (18) and triphenylphosphine sulphide, was distilled bulb-to-bulb (oven temperature 130 °C, 0.1 mmHg) to give bis[(methylthio)carbonyl]disulphane (3.60 g, 52%), ρ 1.38, 90% pure by h.p.l.c.; δ<sub>H</sub> 2.48; δ<sub>C</sub> 14.0, 186.8 p.p.m.; ν<sub>max</sub>. 1 715s, 1 645vs, 830vs; λ<sub>max</sub>. 241 (log ε 4.19).

B. Sulphuryl chloride (3.9 ml, 48.3 mmol) was added dropwise with stirring to compound (13) (15.9 g, 96.7 mmol) at –30 °C. After being slowly warmed to room temperature, the mixture was evaporated to yield a yellow oil (9.34 g, 90%) consisting of compounds (2) and (18) (3:1 by <sup>1</sup>H n.m.r.). Chromatography on silica gel with light petroleum (b.p. 30–60 °C) as eluant provided compound (18) (0.33 g) followed by pale yellow compound (2) (6.62 g, 64%), >90% pure by h.p.l.c., ρ 1.40 (Found: C, 22.3; H, 3.0; S, 59.7. C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>S<sub>4</sub> requires C, 22.42; H, 2.82; S, 59.83%); *m/z* 214 (*M*<sup>+</sup>, 1%), 186 [MeS(CO)SSMe<sup>+</sup>, 6], 158 (MeSSSSMe<sup>+</sup>, 7), 126 (MeSSSSMe<sup>+</sup>, 4), 94 (23), 79 (MeSS<sup>+</sup>, 23), 75 (100), 60 (56), and 47 (38). When this same procedure was carried out with compound (12) (2 g, 13.3 mmol) and sulphuryl chloride (0.54 ml, 6.7 mmol), a mixture of compounds (2), (17), and (18) in the ratio of 1.6:2.3:1 (<sup>1</sup>H n.m.r.) was obtained. The above procedure should be compared with that used to prepare (18), see later.

**Bis[(methylthio)carbonyl]trisulphane (3).**—*O,S*-Dimethyl dithiocarbonate (11) (7.7 g, 63.2 mmol) was added to freshly purified sulphur dichloride (2 ml, 31.6 mmol) at 0 °C. A vigorous evolution of gas occurred and the colour turned from red to yellow. After warming to 25 °C any residual methyl chloride was removed by rotary evaporation to give a yellow oil (8.18 g, 105%) shown by h.p.l.c. to comprise compounds (2) (5%), (3) (78%), (4) (5%), and (11) (10%). The product solidified upon standing for several days; crystals were collected by filtration, washed with light petroleum (b.p. 30–60 °C), and dried over paraffin-wax to yield bis[(methylthio)carbonyl]trisulphane (5.29 g, 68%), white needles, m.p. 45–46 °C, 95%

pure by h.p.l.c. (Found: C, 19.65; H, 2.6; S, 65.25.  $C_4H_6O_2S_5$  requires C, 19.50; H, 2.45; S, 65.06%);  $\delta_H$  2.50;  $\delta_C$  14.1, 187.8 p.p.m.;  $\nu_{max}$ . 1 715s, 1 645vs, 870s, and 830vs,  $cm^{-1}$ ;  $\lambda_{max}$ . 246 nm ( $\log \epsilon$  4.06);  $m/z$  246 ( $M^{+}$ , 0.1%), 186 (1), 158 (7), 126 (17), 94 (31), 79 (44), 75 (66), 60 (100), and 47 (30).

*Bis[(methylthio)carbonyl]tetrasulphane (4)*.—As in the preparation of compound (3), *O,S*-dimethyl dithiocarbonate (11) (22.5 g, 0.18 mol) was added to sulphur monochloride (12.5 g, 90 mmol) at 0 °C. Crude yield 27.1 g (107%). After a few days at -20 °C under light petroleum (b.p. 30–60 °C), the product solidified. A portion (4.0 g) of this oily solid was recrystallised from dichloromethane–light petroleum to give *bis[(methylthio)carbonyl]tetrasulphane* (2.83 g, 76%), pale yellow plates, m.p. 48–50 °C, >90% pure by h.p.l.c. (Found: C, 17.0; H, 2.3; S, 68.9.  $C_4H_6O_2S_6$  requires C, 17.25; H, 2.17; S, 69.08%);  $\delta_H$  2.50;  $\delta_C$  14.2, 187.8 p.p.m.;  $\nu_{max}$ . 1 715s, 1 645vs, 870s, and 830 vs  $cm^{-1}$ ;  $\lambda$  237infl. nm ( $\log \epsilon$  4.06);  $m/z$  278 ( $M^{+}$ , 0.4%), 250 ( $M - CO$ , 1), 190 ( $M - CO - COS$ , 2), 186 (1), 158 (7), 126 (16), 94 (13), 79 (44), 75 (100), 60 (58), and 47 (33).

*Bis[(methylthio)carbonyl]-pentasulphane (5) and -hexasulphane (6)*.—*O,S*-Dimethyl dithiocarbonate (11) (1 g, 8.2 mmol) was added to a solution of dichlorotrisulphane<sup>9</sup> or dichlorotetrasulphane<sup>9</sup> in  $CCl_4$  at 0 °C (0.9M; 5 ml, 4.5 mmol). After the mixture had been warmed to 25 °C, the  $CCl_4$  was removed by rotary evaporation. The reaction was allowed to continue for 1 h at 25 °C after which methyl chloride was removed by rotary evaporation. The crude products [(1.15 g, 93%) or (1.16 g, 83%)] were analysed by h.p.l.c. and shown to contain products (3) (13%), (4) (20%), (5) (34%), and (6) (33%), or (3) (30%), (4) (21%), (5) (19%), and (6) (30%), respectively. For compound (5),  $\delta_H$  2.51;  $\lambda$  240infl. nm ( $\log \epsilon$  4.14); for (6),  $\delta_H$  2.51;  $\lambda_{max}$ . 221 nm ( $\log \epsilon$  4.25).

*Chlorination of O-Isopropyl S-Methyl Dithiocarbonate (12)*. (Scheme 2A).—Sulphuryl chloride (0.24 ml, 2.9 mmol) was added dropwise to a solution of *O*-isopropyl *S*-methyl dithiocarbonate (12) (0.22 g, 1.5 mmol) in [ $^2H$ ]chloroform (2 ml) at 0 °C. After 10 min at 25 °C, the solution was shown by the  $^1H$  n.m.r. spectrum to contain 2-chloropropane;  $\delta_H$  1.52 (6 H, d,  $J$  6.5 Hz), 4.22 (1 H, m); compound (17),  $\delta_H$  2.58 (s); compound (19)  $\delta_H$  2.90 (s); and compound (15) in the molar ratio 1 : 0.73 : 0.16 : 0.11. This solution was then added slowly at 0 °C to a solution of *N*-methylaniline in chloroform (2M; 2 ml, 4 mmol). After 5 min at 25 °C, the solution was washed with HCl (1M; 30 ml) and water (30 ml), dried ( $MgSO_4$ ), and evaporated to yield a yellow oil (0.3 g) comprising compounds (25) (14%), (29) (67%), and (23) (19%) by n.m.r. and h.p.l.c.

*Iodine Oxidation of Potassium S-Methyl Dithiocarbonate (31)*.—Carbonyl sulphide was bubbled for 5 min at 0 °C into a solution of sodium methanethiolate (5 g, 71 mmol) in acetonitrile–water (12 : 1; 130 ml). The uptake of COS was 4.46 g (74 mmol). The solvents were evaporated and the gummy residue dissolved in water (25 ml). A portion (5 ml) of this solution was taken and a saturated solution of iodine in chloroform was added dropwise until a brown colour remained. The excess of iodine was removed by washing with sodium thiosulphate solution, and the organic layer was separated, dried ( $MgSO_4$ ), and evaporated to yield a yellow oil (0.31 g, 32% recovery of methyl groups) containing *S*-methyl *S*-methylsulphenyl dithiocarbonate (18) (53%), dimethyldisulphane (19%), dimethyltrisulphane (17%), and dimethyltetrasulphane (11%), but no disulphane (2) by n.m.r. and h.p.l.c.

*Reaction of 1-Chlorocarbonyl-2-(methylthio)carbonyl-disulphane (21) with Sodium Methanethiolate*.—The acid

chloride (21)<sup>5</sup> [2.9 g, 13.4 mmol; containing 1.5 mmol of (17)] was added to a suspension of sodium methanethiolate (1 g, 14.3 mmol) in ether (10 ml) at 0 °C. After warming to 25 °C, the mixture was stirred for 45 min, filtered, and evaporated to yield a yellow oil (1.83 g, 76% by changed starting material) comprising compounds (2) (21%) and (18) (38%), and methyl disulphide (31% by h.p.l.c.). Assuming that all of compound (17) gave (18), then the acid chloride (21) is calculated to have given products (2) (27%) and (18) (33%), and dimethyldisulphane (40%).

*Reaction of Bis(chlorocarbonyl)disulphane (22) with Sodium Methanethiolate*.—Bis(chlorocarbonyl)disulphane (22)<sup>5</sup> (2.73 g, 14.3 mmol) was added to a suspension of sodium methanethiolate (2.2 g, 31.5 mmol) in ether at 0 °C. After warming to 25 °C, the mixture was stirred for 15 min, filtered, and evaporated to yield a yellow oil (1.06 g, 30%) comprising compounds (2) (19%) and (18) (41%), and dimethyldisulphane (40%).

*Reaction of S-Methyl Chlorothioformate with Sodium Sulphide*.—*S*-Methyl chlorothioformate (1.26 g, 11.4 mmol) in chloroform (7 ml) was shaken with a solution of sodium sulphide nonahydrate (1.64 g, 6.84 mmol) in water (7 ml). After 3 h, the organic layer was separated, dried ( $MgSO_4$ ), and evaporated to yield a colourless liquid (0.21 g, 30%), identified as *S,S'*-dimethyl dithiocarbonate (32) by n.m.r. and by the h.p.l.c. retention time.

*Reaction of S-Methyl Chlorothioformate with Lithium Sulphide*.<sup>16</sup>—A solution of lithium triethylborohydride (Super Hydride) in tetrahydrofuran (1M; 10 ml, 10 mmol) was added to sulphur (0.16 g, 5 mg atom) under nitrogen. After 15 min, *S*-methyl chlorothioformate (1.1 g, 10 mmol) was added dropwise to the yellow solution. The yellow colour faded and a white precipitate formed. After 2 h, ether (20 ml) was added and the solution was filtered and evaporated to give a colourless oil (0.46 g, 67%), *S,S'*-dimethyl dithiocarbonate (32).

*S-Methyl O-t-Butyl Dithiocarbonate (13)*.—The preparation of the title compound has been inadequately described previously.<sup>2,4</sup> Carbon disulphide (33 ml, 0.55 mol) was added over 15 min to a solution of potassium *t*-butoxide (60.0 g, 0.53 mol) in *p*-xylene (1.2 l) at 75 °C. The resulting yellow solid was collected by filtration, washed extensively with benzene, and dried over paraffin wax. A portion of this stable solid (23.8 g, 0.13 mol) was suspended in ether (200 ml), and iodomethane (11.8 ml, 0.19 mol) was added slowly. After being stirred for 2 days, the mixture was filtered and evaporated to yield a yellow oil (14.6 g, 71%), used for subsequent reactions without further purification. Upon storage at 25 °C, compound (13) decomposed to 2-methylpropene, carbonyl sulphide, and methanethiol via a Chugaev reaction, but a sample stored for 4 months at -20 °C was unchanged;  $\delta_H$  1.70 (9 H, s, Bu<sup>1</sup>), 2.46 (3 H, s, Me).

*(Methylthio)carbonylsulphenyl Chloride (15)*.—Hydrogen chloride was slowly bubbled through a solution of *N*-methyl-*N*-phenyl(methylthio)carbonylsulphenamide (25) (20 mg) in [ $^2H$ ]chloroform (1 ml) for 2 min during which time the colour turned from pale to dark yellow. A portion of the resulting solution of (methylthio)carbonylsulphenyl chloride (15),  $\delta_H$  2.53 (s), was taken, and *O,S*-dimethyl dithiocarbonate (11) (10 mg) was added. After being washed with 1M-HCl and dried, the resulting solution was shown by n.m.r. and h.p.l.c. to contain compound (2), unchanged (11), and methyl chloride. The remainder of the solution of (15) was maintained at 25 °C and rearrangement to the isomeric (methylthio)carbonyl chloride (17) was observed with  $t_{\frac{1}{2}}$  = 75 min.

1-Methoxy- and 1-Ethoxy-dichloromethyl-2-methylthio-*disulphanes* (**16**).—A. Sulphuryl chloride (1 equiv.) was quickly added at 0 °C to a solution of *O*-methyl or *O*-ethyl *S*-methyl dithiocarbonate (**1M**) in light petroleum (b.p. 30–60 °C). After being stirred for 30 min at 25 °C, the mixture was evaporated to provide the yellow liquids (**16**) in nominal yields of 95% [ $>95\%$  pure by n.m.r.; small amounts of (**18**) in the product]. Short-path distillation [ $R = \text{Me}$ ; b.p. 46–50 °C (0.06 mmHg);  $R = \text{Et}$ ; b.p. 45–57 °C (0.05 mmHg)] gave, with 85% recovery, distillates containing (**16**), and the lower boiling alkoxythiocarbonyl chloride,  $\text{RO}(\text{C}=\text{S})\text{Cl}$ , and methanesulphenyl chloride (**19**) present in equal amounts. These recombined completely within 1 day at –20 °C to yield pure compound (**16**).

B. An equimolar amount of alkoxythiocarbonyl chloride and freshly prepared methanesulphenyl chloride (**19**)<sup>5</sup> were combined at –78 °C and rapidly equilibrated to give compound (**16**). There appears to be a reversible equilibrium between these starting materials and (**16**) [from 80–95% (**16**) at 25 °C to 95% (**16**) at –20 °C]. Within several days at 25 °C, compound (**16**) lost alkyl chloride to give (**17**)<sup>5</sup> in quantitative yield, as shown by its conversion with *N*-methylaniline into carbamoyldisulphane (**29**).

C. An equal volume of a 1M solution of methanethiol in  $\text{CH}_2\text{Cl}_2$  was added at –78 °C to a 1M-solution of alkoxydichloromethanesulphenyl chloride,<sup>5</sup>  $\text{ROCCl}_2\text{SCl}$ , in dichloromethane; compound (**16**) was shown to form rapidly by <sup>1</sup>H n.m.r. (**16**;  $R = \text{Me}$ ),  $\delta_{\text{H}}$  3.76 (3 H, s, MeO), 2.64 (3 H, s, MeS);  $\delta_{\text{C}}$  24.1, 56.6, and 119.3 p.p.m.;  $\nu_{\text{max}}$ . 1 270s, 1 115vs, 830s, and 800s  $\text{cm}^{-1}$ ; (**16**;  $R = \text{Et}$ ),  $\delta_{\text{H}}$  1.36 (3 H, t,  $J$  7.1 Hz), 2.64 (3 H, s), and 4.11 (2 H, q,  $J$  7.1 Hz);  $\nu_{\text{max}}$ . 1 270s, 1 115vs, 830s, and 800s  $\text{cm}^{-1}$ .

*S*-Methyl *S*-Methylsulphenyl Dithiocarbonate (**18**), with Bis[(methylthio)carbonyl]disulphane (**2**) as a By-product.—Sulphuryl chloride (5.8 ml, 62 mmol) was added slowly to a solution of the dithiocarbonate (**11**) (17.5 g, 144 mmol) in light petroleum (b.p. 30–60 °C) (70 ml). The mixture warmed by the exothermic reaction, and was refluxed for 3 h. The solvent was then evaporated to yield a yellow oil (21.5 g) which was shown by n.m.r. to comprise unchanged (**11**) (37%), (**16**) (31%), (**18**) (13%),  $\text{MeO}(\text{C}=\text{S})\text{Cl}$  (7%), (**17**) (8%), and (**2**) (4%) (molar percentages in parentheses). Distillation of this crude chlorination mixture at an aspirator vacuum yielded pure compound (**18**) (6.9 g, 72%); b.p. 93 °C (9.5 mmHg) [lit.,<sup>5</sup> b.p. 37–39 °C (0.1 mmHg)]. The residue (2.2 g) contained a mixture of compounds (**18**) and (**2**) in approximately equimolar amounts. Bulb-to-bulb distillation of this residue [oven temperature 105–107 °C (0.1 mmHg)] gave pure compound (**2**) (1.1 g, 8%), as a colourless oil (Found: C, 22.3; H, 3.0; S, 59.9.  $\text{C}_4\text{H}_6\text{O}_2\text{S}_4$  requires C, 22.42; H, 2.82; S, 59.83%).

*N*-Methyl-*N*-phenyl(methylthio)carbonylsulphenamide(**25**).—*N*-Methylaniline (4.28 g, 40 mmol) was added slowly to a solution of (methylthio)carbonyl methoxydichloromethyl disulphane (**26**)<sup>5</sup> (1 g, 4 mmol) in dichloromethane (20 ml) at 0 °C. After 1 h at 25 °C, the solution was washed twice each with HCl (1M; 250 ml) and water (250 ml), dried ( $\text{MgSO}_4$ ), and evaporated to yield a mixture (1.16 g) of compounds (**2**) (9%), (**29**) (18%), (**25**) (31%), (**27**) (21%), and (**28**) (21%); the relative proportions were established<sup>5</sup> by n.m.r. and h.p.l.c. [ $R_f$  for (**25**) (flow 0.9 ml/min,  $\text{MeOH}-\text{H}_2\text{O}$ , 68:32) 20.6 min]. Pure *N*-methyl-*N*-phenyl(methylthio)carbonylsulphenamide (**25**) [43 mg, 10% overall yield from (**26**)] was obtained by liquid chromatography of the crude mixture (540 mg) on a Lobar Size B (310–25) Si-60

column eluting with dichloromethane–light petroleum (b.p. 30–60 °C) (40:60);  $\delta_{\text{H}}$  2.34 (3 H, s,  $\text{CH}_3\text{S}$ ), 3.48 (3 H, s,  $\text{CH}_3\text{N}$ ), and 6.9–7.5 (5 H, m, Ph);  $m/z$  213 ( $M^{+}$ , 17%), 185 ( $M - \text{CO}$ , 21), 106 ( $\text{PhNMe}^+$ , 100), 77 (75), 75 ( $\text{MeSCO}^+$ , 25), and 60 (69); the spectrum differed from that of the isomer (**29**).

*Structure Determination*.—Compound (**3**).  $\text{C}_4\text{H}_6\text{O}_2\text{S}_5$ ,  $M$ , 246.41, flat plates,  $a = 10.841(3)$ ,  $b = 4.323(2)$ ,  $c = 21.145(5)$  Å,  $\beta = 97.18(2)^\circ$ ,  $U = 983$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.665$  g  $\text{cm}^{-3}$ , space group  $C2/C$  (No. 15), Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å.

Compound (**4**).  $\text{C}_4\text{H}_6\text{O}_2\text{S}_6$ ,  $M$ , 278.48, hexagonal plates,  $a = 25.372(6)$ ,  $b = 5.563(5)$ ,  $c = 7.974(2)$  Å,  $\beta = 107.30(2)^\circ$ ,  $U = 1075$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.721$  g  $\text{cm}^{-3}$ , space group  $C2/C$  (No. 15), Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å.

Crystals of approximate size 0.45 × 0.40 × 0.18 mm were mounted in an Enraf-Nonius CAD4 diffractometer, with the sample cooled to  $-10 \pm 2$  °C. At ambient temperature, crystals decomposed upon extended exposure to the X-ray beam. Intensity data for 1 597 [for (**3**)] and 1 714 [for (**4**)] independent reflections ( $0 < 2\theta < 60^\circ$ ) were collected by the  $\omega$  scan technique.

*Solution and refinement*. These were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP Program library.<sup>25</sup> The structures were solved by direct methods (MULTAN) and refined by full-matrix least-squares methods using 891 [for (**3**)] and 1 239 [for (**4**)] reflections with  $F_o^2 > 2\sigma(F_o^2)$ , converging to  $R = 0.034$ ,  $R_w = 0.041$  for (**3**) and  $R = 0.033$ ,  $R_w = 0.041$  for (**4**). The largest peak in the final difference Fourier maps had a magnitude less than  $0.2 \text{ e} \text{ \AA}^{-3}$ .

Final positional parameters are given in Table 1, and interatomic distances and angles are listed in Table 2, together with selected dihedral angles. Final observed and calculated structure factors and thermal parameters are available as a Supplementary Publication (SUP No. 56063, 12 pp.).\*

### Acknowledgements

We thank Professor Doyle Britton for insights and invaluable contributions on the X-ray structure determinations, Dr. Edmund A. Larka for obtaining mass spectra, and Ms. Lori J. Enloe for her enthusiastic experimental assistance. Purchase of the X-ray diffractometer and structure-solving equipment was aided by a grant from NSF (CHE-77-28505) and this research was funded by grants from the National Institutes of Health (GM 28934 and AM 01099), Research Corporation (Leo H. Baekeland Grant), and Chicago Community Trust (Searle Scholars Programme).

### References

- A. W. Mott and G. Barany, presented in part at the 17th Great Lakes Regional Meeting of the American Chemical Society, St. Paul, MN, June 1–3, 1983.
- E. W. Miles, *Methods Enzymol.*, 1977, **47**, 431.
- L. Ehrenberg, I. Fedorcsak, and F. Solymosy, *Prog. Nucleic Acid Res. Mol. Biol.*, 1976, **16**, 189.
- G. Barany, B. W. Fulpius, and T. P. King, *J. Org. Chem.*, 1978, **43**, 2930.
- G. Barany, A. L. Schroll, A. W. Mott, and D. A. Halsrud, *J. Org. Chem.*, 1983, **48**, 4750 and references cited therein.
- G. Barany and A. W. Mott, *J. Org. Chem.*, 1984, **49**, 1043.
- S. Motoki and H. Satsumabayashi, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2930.
- E. E. Reid, 'Organic Chemistry of Bivalent Sulfur,' Chemical Publishing, New York, 1962, vol. 4.
- F. Fehér, in 'Handbook of Preparative Inorganic Chemistry,' ed. G. Brauer, Academic Press, New York, 1963, vol. 1, pp. 373–376.
- G. Barany, *Tetrahedron Lett.*, 1983, **24**, 5683.
- H. Böhme and M. Clement, *Liebigs Ann. Chem.*, 1952, **576**, 61.

\* For details of the Supplementary Publications Scheme see Instructions for Authors (1984) in *J. Chem. Soc., Perkin Trans. I*, 1984, Issue 1.

- 12 A. W. Mott, S. J. Eastep, U. Słomczyńska, and G. Barany, *J. Labelled Comp. Radiopharm.*, 1984, **21**, 329.
- 13 K. N. Tantry and M. L. Shankaranarayana, *Proc. Indian Acad. Sci. Sect. A*, 1979, **88**, 457 (*Chem. Abstr.*, 1980, **92**, 118832a).
- 14 T. Kawata, K. Harano, and T. Taguchi, *Chem. Pharm. Bull.*, 1973, **21**, 604; M. W. Fichtner and N. F. Haley, *J. Org. Chem.*, 1981, **46**, 3141.
- 15 T. Mukaiyama and H. Takei in 'Topics in Phosphorus Chemistry,' eds. E. J. Griffith and M. Grayson, John Wiley, New York, 1976, vol. 8, pp. 587—645; C. G. Moore and B. R. Trego, *Tetrahedron*, 1963, **19**, 1251.
- 16 J. A. Gladysz, V. K. Wong, and B. S. Jick, *Tetrahedron*, 1979, **35**, 2329.
- 17 K. O. Miller, B. Masloch, and H. J. Mockel, *Z. Anal. Chem.*, 1976, **280**, 293.
- 18 N. J. Brøndmo, S. Esperos, and S. Husebye, *Acta Chem. Scand., Ser. A*, 1975, **29**, 93.
- 19 J. C. Barrick, C. Calvo, and F. P. Olsen, *Can. J. Chem.*, 1973, **51**, 3691.
- 20 O. Foss and V. Janickis, *J. Chem. Soc., Dalton Trans.*, 1979, 632.
- 21 A. W. Schwab, R. D. Gilardi, and J. L. Flippen-Anderson, *Phosphorus Sulfur*, 1981, **10**, 123.
- 22 'CRC Handbook of Chemistry and Physics,' ed. R. C. Weast, CRC Press, Florida, 1979, vol. 60.
- 23 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960.
- 24 L. A. Carpino, P. H. Terry, and P. J. Crowley, *J. Org. Chem.*, 1961, **26**, 4336; K. A. Jensen, U. Anthoni, and A. Holm, *Acta Chem. Scand.*, 1969, **23**, 1916.
- 25 B. A. Frenz in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Delft University Press, Delft, 1978.

Received 13th December 1983; Paper 3/2198