

818. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part IV.* 1:1:3:3-Tetrakisalkylthio-propane and -propene, and their Oxidation Products.*

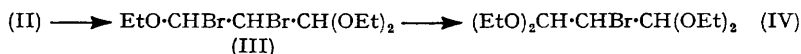
By EUGENE ROTHSTEIN and RONALD WHITELEY.

Methods for the preparation of 1:1:3:3-tetraethoxypropane (malonaldehyde diethyl acetal) and its 2-bromo-derivative have been developed and these substances have been converted into the corresponding 3:3-bis-alkylthio-1:1-diethoxy- and 1:1:3:3-tetrakisalkylthio-propanes. Elimination of hydrogen bromide from the bromo-derivatives yields the unsaturated compounds, the structure of which is discussed. Oxidation of 1:1:3:3-tetrakisalkylthio-propane and -propene affords the tetrasulphones which, in the latter series, are strong acids displacing carbonic acid from its salts.

PREVIOUS work on thioacetals (Rothstein, *J.*, 1940, 1550, 1553) has now been extended to the 1:3-bisthioacetals. 1:1:3:3-Tetrakisalkylsulphonylpropanes (I), the only related compounds hitherto prepared, were synthesised by condensation of the appropriate bisalkylsulphonylmethane with formaldehyde (Kötz, *Ber.*, 1900, **33**, 1123). The present starting materials were the acetals of malonaldehyde (*e.g.*, 1:1:3:3-tetra-alkoxypropane) and of bromomalonaldehyde (*e.g.*, IV). The former was prepared by addition of 0.5% ethanolic



hydrogen chloride to 1:3:3-triethoxyprop-1-ene (II). The compound (II) which is easily prepared on a large scale (Price and Moos, *J. Amer. Chem. Soc.*, 1945, **67**, 207) also reacts with bromine, yielding 1:2-dibromo-1:3:3-triethoxypropane (III) which in turn is converted by ethanol into the monobromo-derivative (IV); the structure of (IV) was con-



firmed by the preparation of derivatives and by hydrolysis to bromomalonaldehyde which was identical with that prepared from 3:3-diethoxyprop-1-yne (Grard, *Ann. Chim.*, 1930, **13**, 336).

* Part III, preceding paper.

4014 Rothstein and Whiteley: Reactions of Organic Derivatives of

The tetrakisalkylthiopropenes (X) did not contain "active" hydrogen. Boiling (X; R = Me) with potassium *tert.*-butoxide, however, led to the formation of an isomeric substance of a considerably lower boiling point* and oxidation of this yielded bismethylsulphonylmethane together with methanesulphonic acid. No tetrasulphone was isolated.

Elimination of hydrogen bromide from the bromo-derivative (XII) by means of potassium *tert.*-butoxide instead of piperidine gave a product isomeric with (XIII). Treatment with more ethanethiol yielded a tetrakisethylthio-derivative different from that obtained from (XIII); bisethylsulphonylmethane was obtained by oxidation.

Reaction of 2-bromo-1 : 1 : 3 : 3-tetrakisethylthiopropene (IX; R = Et) with sodium ethyl sulphide yielded the propene derivative which gave better analytical figures than that previously obtained by the action of piperidine and was converted into the tetrasulphone (XI) on oxidation. Finally, little difference in the shapes of the molecular extinction curves in the near ultra-violet was observed for hexane solutions of the different specimens of the tetrakisalkylthiopropenes. In all cases the characteristic shape of the thioacetal curve was somewhat smoothed out, but the optical densities measured for (X) were a good deal lower than for the other specimens.

Since 1 : 1 : 2-trisethylthiopropene (VIII) is oxidised to a mixture of 3 : 3- and 2 : 3-bisethylsulphonylprop-1-ene, it is arguable that the tetrasulphide (X) may contain a large proportion of 1 : 1 : 2 : 3 : 3-pentakisalkylthiopropene, $\text{EtS}\cdot\text{CH}[\text{CH}(\text{SEt})_2]_2$, which on oxidation yields the tetrasulphone. This would account for the low yields of the latter, as well as the poor analytical figures of the tetrathio-derivative, but the result of heating (IX) with sodium ethyl sulphide suggests that the pentathio-compound is not especially stable. Bearing in mind that oxidation of 3 : 3-bisethylthiopropene, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{SEt})_2$, yields 1 : 3-bisethylsulphonylpropene, $\text{Et}\cdot\text{SO}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{Et}$ (Rothstein, *J.*, 1940, 1560), it is not surprising that in the tetraethylthio-compounds this type of isomerisation should inhibit the formation of the sulphone.

The isomeric change encountered with potassium *tert.*-butoxide cannot be adequately explained. A tentative hypothesis is that a geometrical isomeride is formed. Molecular models show that steric hindrance between the alkylthio-groups may lead to restricted rotation of the C-C bond, affording two comparatively stable conformations. Of these two, one leads to ready migration of the alkylthio-group during oxidation, yielding 3 : 3 : 3 : 1-tetrakisalkylthiopropene. This on oxidation and fission would afford the bisalkylsulphonylmethane, as in the production of bismethylsulphonylmethane from trimethylthiomethane and hydrogen peroxide (Backer and Stedehouder, *Rec. Trav. chim.*, 1933, 52, 437).

The structures of the 1 : 1 : 3 : 3-tetrakisalkylsulphonylpropenes (XI; R = Me and Et) were confirmed by catalytic reduction to the saturated derivatives (I). The compounds (XI) are very stable, liberating carbon dioxide from sodium hydrogen carbonate. The sulphones are precipitated unchanged by the addition of mineral acid to the bicarbonate solutions and in this respect differ from the analogous 1 : 3-bisalkylsulphonylpropenes which polymerise when the anion is formed (Rothstein, *J.*, 1937, 309). The sulphone groups in the bisulphones are conjugated by means of the double bond and hence in their chemical properties resemble bismethylsulphonylmethane. Analogously the tetrasulphonyl derivatives resemble trimethylsulphonylmethane which is a strong acid, soluble in sodium carbonate (Bohme and Marx, *Ber.*, 1941, 74, 1667). In comparison with their disulphonyl analogues, the anions of the tetrakisalkylsulphonylpropenes are associated with a larger number of mesomeric structures, such as $\text{R}\cdot\text{O}_2\cdot\text{S}^-\cdot\text{C}(\text{SO}_2\text{R})\cdot\text{CH}:\text{C}(\text{SO}_2\cdot\text{R})_2$, and thus have extra stability. In contrast to the unsaturated compounds, 1 : 1 : 3 : 3-tetrakisalkylsulphonylpropenes (I) are insoluble in sodium carbonate but dissolve in sodium hydroxide. According to Kötzt (*loc. cit.*) acidification with mineral acids causes fission with the production of bisalkylsulphonylmethanes and formaldehyde. Carbon dioxide, however, has now been found to precipitate the tetrasulphone unchanged.

* Some methanethiol was eliminated in this reaction, suggesting the possible presence of pentakis-methylthiopropene.

EXPERIMENTAL

1 : 1 : 3 : 3-Tetraethoxypropane.—2-Bromo-1 : 1 : 3-triethoxypropane was prepared by a modification of Fischer and Giebe's method (*Ber.*, 1897, 30, 3056). 2 : 3-Dibromopropaldehyde (950 g., 4.39 moles) was boiled under reflux for 40 hr. with ethanolic 1% hydrogen chloride (1600 g., 34.8 moles) and then kept at room temperature for a further 2 days. The product was mixed with ice-water (3 l.), and the lower layer separated, washed with sodium hydrogen carbonate and dried (Na_2SO_4). The main product boiled at 108—114°/18 mm., but about 10% of the distillate boiled at 90—108°/18 mm. The latter portion was mixed with three times its weight of ethanolic 1% hydrogen chloride and, after 2 days, a further quantity of the triethoxy-compound was isolated. The total yield was 729 g. (65%). The bromotriethoxy-compound was converted into 1 : 3 : 3-triethoxyprop-1-ene by boiling it (729 g.) under reflux with potassium hydroxide (460 g.) and ethanol (1.5 l.) (Price and Moos, *J. Amer. Chem. Soc.*, 1945, 67, 207). The b. p. of the product was 89—91°/15 mm., and the yield 475 g. (78%).

A mixture of the triethoxypropene (120 g., 0.69 mole) and ethanol (300 g., 6.5 moles) containing 0.5% of hydrogen chloride was cooled in ice and kept for 48 hr., there being a slight darkening after 24 hr. The liquid was mixed with sodium hydrogen carbonate solution containing crushed ice, extracted with ether, and dried (K_2CO_3). The ethereal solution yielded 1 : 1 : 3 : 3-tetraethoxypropane, b. p. 106°/17 mm. (91 g., 60%) (Found: C, 59.6; H, 11.1. Calc. for $\text{C}_{11}\text{H}_{24}\text{O}_4$: C, 60.0; H, 10.9%).

Condensation of 1 : 1 : 3 : 3-Tetraethoxypropane with Methanethiol.—The tetraethoxypropane (60 g., 0.27 mol.) was cooled in ice and mixed with methanethiol (70 g., 1.45 moles) and glacial acetic acid (120 c.c.). Concentrated hydrochloric acid (120 c.c.) was slowly added to the well-stirred mixture, and stirring continued for a further 5 hr., the temperature being kept at 0°. The mixture was then added to water and extracted with ether and the extract washed free from acids with water. The dried (CaCl_2) solution was distilled under reduced pressure, glass wool being used instead of the conventional capillary air-leak owing to the oxidation which otherwise occurred. 1 : 1 : 3 : 3-Tetrakis-methylthio-propane had b. p. 110°/0.3 mm. (54 g., 87%) (Found: C, 36.8; H, 7.2; S, 56.1. $\text{C}_7\text{H}_{16}\text{S}_4$ requires C, 36.8; H, 7.0; S, 56.1%).

A slight excess of 2% potassium permanganate solution was slowly added to tetrakis-methylthio-propane (1 g.) in glacial acetic acid (20 c.c.). The manganese dioxide was dissolved by the passage of sulphur dioxide, and the 1 : 1 : 3 : 3-tetrakis-methylsulphonylpropane crystallised twice from glacial acetic acid. It (1.2 g., 77%) had m. p. 281—283° (Found: C, 23.6; H, 4.2; S, 35.9. $\text{C}_7\text{H}_{16}\text{O}_8\text{S}_4$ requires C, 23.6; H, 4.5; S, 35.9%). The compound was insoluble in cold ethanol, benzene, chloroform, and ethyl acetate.

Independent Synthesis of 1 : 1 : 3 : 3-Tetrakis-methylsulphonylpropane.—Bismethylthio-methane was prepared in 78% yield from methanethiol (24 g.) and formaldehyde (19 g. of 40% solution) in glacial acetic acid (60 c.c.). Concentrated hydrochloric acid was slowly added to the stirred mixture, the stirring being continued for a further 4 hr. (cf. Gibson, *J.*, 1941, 2637). The product was oxidised to bismethylsulphonylmethane, m. p. 148° (Backer, *Rec. Trav. chim.*, 1946, 65, 55), by aqueous potassium permanganate and sulphuric acid (Baumann and Kast, *Z. physiol. Chem.*, 1890, 14, 55, record m. p. 143°). Formaldehyde (0.7 g. of 40% solution) was added to bismethylsulphonylmethane (3 g.), dissolved in warm ethanol (60 c.c.). Piperidine (3 drops) was added, the mixture boiled under reflux for 30 min., and the insoluble tetra-sulphonylpropane filtered from the hot solution. Like the specimen previously prepared it separated from glacial acetic acid in microscopic cubes, m. p. 281—283°, and gave no depression of m. p. in admixture.

1 : 1 : 3 : 3-Tetrakis-methylthio-propane, b. p. 142°/0.4 mm. (yield, 9.9 g., 77%), was prepared from tetraethoxypropane (10 g.), ethanethiol (13 g.), glacial acetic acid (30 c.c.), and concentrated hydrochloric acid (30 c.c.) (Found: C, 46.4; H, 8.8; S, 44.6. $\text{C}_{11}\text{H}_{24}\text{S}_4$ requires C, 46.5; H, 8.5; S, 45.1%).

2-Bromo-1 : 1 : 3 : 3-tetraethoxypropane.—A solution of bromine (130 g., 0.81 mole) in carbon tetrachloride (50 c.c.) was slowly added to a stirred mixture of 1 : 3 : 3-triethoxyprop-1-ene (150 g., 0.86 mole), carbon tetrachloride (550 c.c.), and calcium carbonate (12 g.) cooled in ice. The liquid was then filtered, the solvent removed under reduced pressure, and ethanol (400 c.c.) added to the residue cooled in ice. After 4 days the solution was mixed with ice-water (1 l.) and the product extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate solution, dried (CaCl_2), and fractionated, affording 2-bromo-1 : 1 : 3 : 3-tetraethoxy-propane, b. p. 138—139°/18 mm. (192 g., 74%) (Found: C, 44.1; H, 7.7; Br, 26.9. $\text{C}_{11}\text{H}_{23}\text{O}_4\text{Br}$ requires C, 44.2; H, 7.7; Br, 26.7%).

4016 Rothstein and Whiteley: Reactions of Organic Derivatives of

Reactions of Bromotetraethoxypropane.—(a) *Hydrolysis.* The ethoxy-compound (12.4 g.) was warmed with concentrated hydrochloric acid (1 c.c.) until the mixture was homogeneous. After 48 hr. the bromomalonaldehyde (m. p. 148°) separated and was recrystallised from phenetole (Found: C, 24.2; H, 2.0; Br, 52.7. Calc. for $C_3H_3O_2Br$: C, 23.8; H, 2.0; Br, 53.0%). It was identical (mixed m. p.) with the product obtained from 3:3-diethoxyprop-1-yne and bromine (Gard, *Ann. Chim.*, 1930, 13, 336).

(b) *With aniline.* The tetraethoxy-derivative (1 g.) was added to aniline (1 g.) in concentrated hydrochloric acid (2 c.c.). The hydrochloride which separated overnight was decomposed by sodium hydrogen carbonate solution; the 2-bromo-1:1:3:3-tetrakisethoxythiopropene, recrystallised from ethanol, had m. p. 145° (Found: C, 59.5; H, 4.5; N, 9.0. $C_{15}H_{13}N_2Br$ requires C, 59.8; H, 4.3; N, 9.3%).

(c) *With methanethiol.* Concentrated hydrochloric acid (240 c.c.) was slowly added to a stirred mixture of the bisacetal (80 g., 0.27 mol.), glacial acetic acid (240 c.c.), and methanethiol (57 g., 1.2 moles) cooled in ice. Stirring was continued for 5 hr., and the mixture then poured into water (700 c.c.) and extracted with ether. The extract was washed with water until free from acid and dried ($CaCl_2$). The resulting 2-bromo-1:1:3:3-tetrakisethylthiopropene was extremely unstable, hydrogen bromide being spontaneously evolved at room temperature. Rapid darkening and complete decomposition occurred when the compound was distilled at 0.2 mm. It was therefore necessary to carry out the second stage of the synthesis without delay.

The above bromo-compound was freed from the last traces of ether and methanethiol, and the residue mixed with an ethereal solution of piperidine (30 g., 0.35 mol.). The liquid was kept for 4 days, during which piperidine hydrobromide was slowly deposited, and then the salt was filtered off, the filtrate being washed free from excess of base with water. The dried ($CaCl_2$) solution was fractionally distilled and the main product collected at 125—145°/0.2 mm. (glass wool). A further distillation, through a short, jacketed, Vigreux column, afforded 1:1:3:3-tetrakisethylthiopropene, b. p. 138—140°/0.3 mm. (63%), as a straw-coloured oil. Repeated fractionation failed to yield an analytically pure compound (Found: C, 35.8; H, 7.1; S, 56.5. Calc. for $C_7H_{14}S_4$: C, 37.2; H, 6.2; S, 56.6%).

(d) *With ethanethiol.* 2-Bromo-1:1:3:3-tetrakisethylthiopropene was prepared in the same way as the methyl compound, from the bromoacetal (60 g., 0.2 mole), ethanethiol (56 g., 0.9 mole), glacial acetic acid (180 c.c.), and concentrated hydrochloric acid (180 c.c.). Reaction with piperidine (24 g., 0.28 mole) was complete in 14 days, the product distilling at 150—158°/0.35 mm. Fractionation yielded 1:1:3:3-tetrakisethylthiopropene, b. p. 156—158°/0.35 mm. (35.4%). Here again, complete purification could not be accomplished (Found: C, 45.8; H, 8.4; S, 45.5. Calc. for $C_{11}H_{22}S_4$: C, 46.8; H, 7.8; S, 45.4%).

Reaction between 2-Bromo-1:1:3:3-tetrakisethylthiopropene and Sodium Ethyl Sulphide.—An ethereal solution of the product from the bromomalonaldehyde diacetal (9 g.), ethanethiol (15 g.), acetic acid (27 c.c.), and concentrated hydrochloric acid (27 c.c.) was washed with water, dried (K_2CO_3), and added to an ethanolic solution of sodium ethyl sulphide (from 2 g. of ethanethiol). The reaction was completed by 1 hr.' boiling and the product isolated as usual. Distillation, with purified nitrogen for the "air"-leak, was accompanied by considerable decomposition. The main fraction (3.1 g., 37%) was 1:1:3:3-tetrakisethylthiopropene, b. p. 130—131°/0.01 mm. (Found: C, 46.1; H, 8.3; S, 45.3%). Oxidation afforded the tetrakisethylsulphonyl derivative described below.

Reactions of Tetrakisalkylthiopropenes.—(a) *With hydrogen peroxide.* 1:1:3:3-Tetrakisethylthiopropene (4 g., 0.02 mole) reacted vigorously (boiling) with 30% hydrogen peroxide (20 g., 0.18 mole) and glacial acetic acid (50 c.c.). After a final heating under reflux for 30 min., and evaporation on the steam-bath, the residue was dried (P_2O_5) and converted into the acid chloride (b. p. 60—70°/18 mm.; 1.5 g.) by treatment with small portions of phosphorus pentachloride with ice-cooling until no further reaction occurred, and finally the amide was prepared in ethereal solution. Extraction of the solid so formed with hot chloroform afforded methanesulphonamide which separated from ethanol-benzene (1:1) in plates, m. p. 91° (1.2 g.) (Found: C, 12.9; H, 5.3. Calc. for CH_5O_2NS : C, 12.6; H, 5.3%).

In a second experiment, with the same methylthiopropene (4.2 g.), hydrogen peroxide (26 g.), and acetic acid (26 c.c.), the temperature was not allowed to rise above 20°, the mixture becoming homogeneous in 24 hr. After 7 days, it was concentrated on the steam-bath, and water (10 c.c.) was added to the residual oil. This precipitated colourless crystals which were purified by dissolution in warm sodium hydrogen carbonate solution and, after filtration, reprecipitation with concentrated hydrochloric acid. Crystallisation from ethyl acetate

[1953] *Elements Capable of Valency-shell Expansion. Part IV.* 4017

furnished 1 : 1 : 3 : 3-tetrakisethylsulphonylpropene as cubes, m. p. 196—197° (0.5 g., 7.6%) (Found: C, 23.6; H, 4.2; S, 36.0. $C_7H_{14}O_8S_4$ requires C, 23.7; H, 4.0; S, 36.2%). The filtrate from the sulphone afforded methanesulphonic acid, identified as the amide as before. A solution of the tetrasulphone in sodium hydrogen carbonate decolorised potassium permanganate immediately.

A similar oxidation of 1 : 1 : 3 : 3-tetrakisethylthiopropene yielded 1 : 1 : 3 : 3-tetrakisethylsulphonylpropene which separated from ethanol in cubes, m. p. 154° (9.6%) (Found: C, 32.0; H, 5.5; S, 30.8. $C_{11}H_{22}O_8S_4$ requires C, 32.2; H, 5.4; S, 31.2%). The filtrate from the tetrasulphone contained ethanesulphonic acid which was converted into the amide as above. Recrystallisation of the ethanesulphonamide from ether yielded a product, m. p. 58° (31%) in agreement with the recorded m. p.

(b) *Reduction.* 1 : 1 : 3 : 3-Tetrakisethylsulphonylpropene (0.2 g.) was shaken in glacial acetic acid (10 c.c.) for 8 hr. with hydrogen at atmospheric pressure in the presence of Adams catalyst (0.1 g.). No heat was required and, after filtration, 1 : 1 : 3 : 3-tetrakisethylsulphonylpropane was extracted from the residue with warm sodium hydroxide solution. Passage of carbon dioxide through the alkaline solution precipitated the saturated sulphone (0.1 g.), which was identified by comparison (mixed m. p.) with an authentic specimen. The filtrate was acidified with concentrated hydrochloric acid, affording unchanged starting material (0.07 g.).

(c) *Attempted ethylation.* A solution of potassium (0.37 g., 0.0095 mole) in *tert.*-butanol (15 c.c.), tetrakisethylthiopropene (2 g., 0.0088 mole), and ethyl bromide (2 g., 0.18 mole) was boiled for 2.5 hr. under reflux. The solvent was distilled, the residue dissolved in ether, and the solution washed free from potassium bromide with water. The dried ($CaCl_2$) solution yielded two fractions when distilled: (i) b. p. 118—130°/0.25 mm. (0.7 g.), almost certainly identical with the substance described in the next experiment (Found: C, 37.8; H, 6.9%); and (ii) b. p. 130—140°/0.25 mm., mainly unchanged starting material (afforded tetrakisethylsulphonylpropene when oxidised).

(d) *Reaction with potassium tert.-butoxide.* The tetrakisethylthio-compound (2 g., 0.0088 mole) was boiled under reflux for 5 hr. with *n*-potassium *tert.*-butoxide (25 c.c., 0.025 mole). The solvent was distilled off under reduced pressure, the residue dissolved in ether, and the solution washed with water. Acidification of the aqueous layer yielded methanethiol, identified as its mercuric compound (m. p. 174°). The dried ($CaCl_2$) ethereal solution yielded a *tetrakis-methylthiopropene* (1.4 g.), b. p. 122—125°/0.3 mm., isomeric with the original sulphide (Found: C, 37.5; H, 6.5; S, 56.0. $C_7H_{14}S_4$ requires C, 37.2; H, 6.2; S, 56.6%).

The above product was dissolved in glacial acetic acid (8 c.c.), and 30% hydrogen peroxide (8 g.) added, the temperature being kept at $>20^\circ$. After 5 days, the liquid was reduced to 2 c.c. on the steam-bath, the residue depositing bismethylsulphonylmethane which separated from water in colourless plates, m. p. 148° (0.25 g.) (Found: C, 21.3; H, 5.0; S, 37.0. Calc. for $C_3H_8O_4S_2$: C, 20.9; H, 4.7; S, 37.2%). Its identity was confirmed by mixed m. p. with an authentic specimen. The acid which formed the major portion of the oxidation product was fractionally distilled, yielding methanesulphonic acid, b. p. 134°/0.15 mm. (Found: C, 13.4; H, 4.6. Calc. for CH_3O_3S : C, 12.5; H, 4.2%). Conversion into the acid chloride and then treatment with ammonia furnished methanesulphonamide, m. p. 91° (0.5 g., 60.5%).

(e) *Reaction with methyl iodide.* The tetrakisethylthio-derivative (3 g., 0.013 mole) was mixed with methyl iodide (9 g., 0.0063 mole) and kept at room temperature for 5 days. The black crystalline mass was dissolved in water, and the solution filtered and evaporated. The concentrated solution deposited trimethylsulphonium iodide, in needles, decomp. at 218—219° (various decomposition points have been recorded; 215° by Klinger, *Ber.*, 1877, 10, 1879; 203—207° by Steinkopf and Muller, *Ber.*, 1923, 56, 1928). Another specimen obtained by alkylation of 1 : 1 : 3 : 3-tetrakisethylthiopropene decomposed at 215—217° (Found: C, 17.6; H, 4.7; I, 62.6; S, 15.8. Calc. for C_3H_9IS : C, 17.7; H, 4.4; I, 62.3; S, 15.7%).

(f) 1 : 1 : 3 : 3-Tetrakisethylthiopropene was recovered unchanged when heated with: (i) methylmagnesium iodide in ether, (ii) benzaldehyde and piperidine or diethylamine, (iii) acetaldehyde and piperidine or diethylamine, (iv) acrylonitrile and benzyltrimethylammonium hydroxide, (v) "molecular" potassium in xylene, and (vi) sodamide and ethyl bromide in benzene. Likewise a solution of the tetraethylthio-derivative in boiling xylene failed to react with *m*-nitrobenzaldehyde in the presence of piperidine.

Two-stage Preparation of 1 : 1 : 3 : 3-Tetrakisethylthio-propene and -propene.—(a) An ice-cold mixture of 1 : 1 : 3 : 3-tetraethoxypropane (7 g., 0.032 mole), ethanethiol (3 g., 0.048 mole) and ethanol (4 c.c.) containing 4% (w/w) of hydrogen chloride was kept at 0° for 16 hr. and

4018 *Reactions of Organic Derivatives of Elements, etc. Part IV.*

then poured into excess of sodium hydrogen carbonate solution. The oil was extracted with ether, and the extract dried (CaCl_2) and fractionated, affording 1 : 1-diethoxy-3 : 3-bisethylthiopropene, b. p. 94—96°/0.5 mm. (4 g.) (Found : C, 52.7; H, 9.7; S, 25.0. $\text{C}_{11}\text{H}_{24}\text{O}_2\text{S}_2$ requires C, 52.4; H, 9.5; S, 25.4%). 3 : 3-Bisethylthiopropaldehyde 2 : 4-dinitrophenylhydrazone was obtained by the addition of concentrated hydrochloric acid (1 c.c.) to a nearly boiling solution of the diethoxy-derivative (0.4 g.) and 2 : 4-dinitrophenylhydrazine (0.3 g.) in ethanol (15 c.c.). The mixture was cooled and water added until there was a faint turbidity. Separation of the derivative occupied several hours, and it slowly crystallised from ethanol then having m. p. 62.5° (yield, 0.2 g.) (Found : C, 43.6; H, 5.2; N, 15.6; S, 17.6. $\text{C}_{13}\text{H}_{18}\text{O}_4\text{N}_4\text{S}_2$ requires C, 43.5; H, 5.0; N, 15.6; S, 17.9%).

(b) Concentrated hydrochloric acid (40 c.c.) was slowly added to a stirred mixture of 2-bromo-1 : 1 : 3 : 3-tetraethoxypropane (40 g., 0.13 mole), ethanethiol (17.5 g., 0.28 mole), and glacial acetic acid (80 c.c.), with ice-cooling. After 2 hr., the product was isolated by dilution with water, extraction with ether, and drying (CaCl_2) of the washed extract. The solvent was removed in a vacuum and the residue heated at 100° for 30 min. with pyridine (50 c.c.), the hydrobromide being rapidly deposited. The yellow oil, isolated in the usual manner, had b. p. 95—160°/0.4 mm. Fractionation through a 70-cm. jacketed Vigreux column yielded impure 1 : 1-diethoxy-3 : 3-bisethylthioprop-2-ene (A), b. p. 113—318°/0.4 mm., together with unchanged bromo-acetal and tetrakisethylthiopropene (complete separation was not possible) (Found : C, 51.4; H, 8.3; S, 28.6. Calc. for $\text{C}_{11}\text{H}_{22}\text{O}_2\text{S}_2$: C, 52.8; H, 8.8; S, 28.6%). The 2 : 4-dinitrophenylhydrazone first separated from ethanol in dark-red needles, m. p. 152—156°. After two further recrystallisations from light petroleum (b. p. 80—100°), followed by another from ethanol, it had m. p. 170—171° (Found : C, 43.7; H, 4.4; S, 18.2. $\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_4\text{S}_2$ requires C, 43.8; H, 4.5; S, 18.0%). Hydrolysis of the diethoxy-compound (2 g.) was carried out by stirring it with hydrochloric acid (5 c.c.) and water (5 c.c.) at 60° for 16 hr. and extracting the dark liquid with ether. A solution of the residual oil in ethanol (8 c.c.) was added to aqueous (3 c.c.) hydroxylamine hydrochloride (0.45 g.) containing sodium hydrogen carbonate (0.8 g.), some ethanethiol being liberated. After 4 hr. at room temperature, $\beta\beta$ -bisethylthioacetaldehyde oxime, $(\text{EtS})_2\text{C}:\text{CH}:\text{CH}:\text{N}:\text{OH}$, was precipitated by the addition of water (20 c.c.). It crystallised from aqueous methanol in pale yellow plates, m. p. 86—87° (Found : C, 44.1; H, 7.0; N, 7.2; S, 33.6. $\text{C}_7\text{H}_{13}\text{ONS}_2$ requires C, 44.0; H, 6.8; S, 33.5; N, 7.3%).

(c) *Removal of hydrogen bromide with potassium tert.-butoxide.* The product of the reaction of bromomalonaldehyde di(ethyl acetal) and ethanethiol, the same quantities being used as in (b), was added to 1.2N-potassium tert.-butoxide (150 c.c., 0.18 mole) and boiled under reflux for 2 hr. Part of the solvent was distilled off, and the remainder removed by addition of the residue to water. A straw-coloured oil (B), b. p. 106—109°/0.3 mm. (7 g.), was obtained which could not be freed from unchanged bromo-acetal (Found : C, 51.3; H, 8.4; S, 17.0; Br, 6.1%). The 2 : 4-dinitrophenylhydrazone separated from ethanol in bright-red needles, m. p. 111° (Found : C, 44.1; H, 4.5; N, 15.6; S, 18.0. $\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_4\text{S}_2$ requires C, 43.8; H, 4.5; N, 15.7; S, 18.0%). The oxime was a non-crystallisable liquid.

Condensation of the Diethoxybisethylthiopropene with Ethanethiol.—(a) The diethoxy-compound (A) (5.1 g.), dissolved in glacial acetic acid (10 c.c.), was mixed with ethanethiol (3.2 c.c.), then cooled in ice, and concentrated hydrochloric acid (10 c.c.) was slowly added to the stirred liquid. After 5 hr., the mixture was added to water and the tetrakisethylthiopropene isolated in the usual way as a yellow oil, b. p. 150—152°/0.2 mm. (3.6 g., 61%) (Found : C, 47.0; H, 8.0; S, 45.2. Calc. for $\text{C}_{11}\text{H}_{22}\text{S}_4$: C, 46.8; H, 7.8; S, 45.4%). Oxidation by 30% hydrogen peroxide and glacial acetic acid failed to yield any sulphone.

(b) The reaction with 3.4 g. of the disulphide (B) was carried out as in (a) and yielded a yellow oil (1.6 g.), b. p. 142—147°/0.2 mm. (Found : C, 47.0; H, 7.9; S, 44.9%). This 1 : 1 : 3 : 3-tetrakisethylthiopropene (1.2 g.), mixed with 30% hydrogen peroxide (10.8 c.c.) and glacial acetic acid (7 c.c.), was kept for 7 days below 20°. It was then evaporated to a syrup, water (5 c.c.) was added to the residue and the whole left below 0° overnight. The solution deposited bisethylsulphonylmethane (0.8 g.), identified by m. p. and mixed m. p. The tetrasulphonyl derivative was not obtained.