The Reactions of Amines and Sulphur with Olefins. Part II. The Reaction of Diethylamine and Sulphur with Trialkylethylenes.*

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The reaction of diethylamine and sulphur with trialkylethylenes, $R\cdot CMe{:}CHR'$, at 140° yields *tert.*-alkanethiols and di-*tert.*-alkyl disulphides as major products, with only minor amounts of the corresponding polysulphides and sulphurated polymers containing three or more olefin units linked by sulphur bridges. The degree of sulphuration is much lower than with the corresponding *s*-dialkylethylene, *cyclo*hexene (Part I), and monosulphide formation is negligible, both observations indicating that steric influences govern the nature and yield of the sulphurated products.

The use of the diethylamine–sulphur combination for the sulphuration of *cyclo*hexene at 140° (Part I *) has been extended to the trialkylethylenes, $R\cdot CMe{:}CHR'$, which are used as the simplest analogues of rubber hydrocarbon. The reaction characteristics observed with *cyclo*hexene indicated that a major sulphurating agent was hydrogen sulphide, formed by prior interaction of the amine and sulphur, and it was argued that trialkylethylenes would react first to give the intermediate *tert.*-alkanethiol, $R\cdot CMe(SH)\cdot CH_2R'$, by polar addition of hydrogen sulphide, which would combine with a second olefin molecule to give a di-*tert.*-alkyl monosulphide :

$$R\cdot CMe{:}CHR' \xrightarrow{H_2S} R\cdot CMe(SH)\cdot CH_2R' \xrightarrow{\text{Olefin}} S(CMeR\cdot CH_2R')_2 \quad . \quad . \quad . \quad . \quad (1)$$

Examination of the reaction of diethylamine and sulphur with 1-methyl*cyclo*hexene at 140° established the polar nature of the sulphuration process, but also revealed significant differences from the analogous reaction with *cyclo*hexene and the reactions

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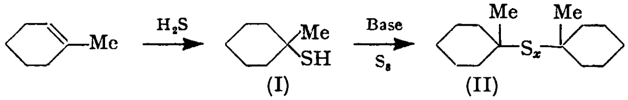
* Part I, preceding paper.

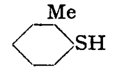
represented by (1) above, *viz.*, (i) a considerably lower yield of sulphurated product comprising 1-methyl*cyclo*hexane-1-thiol (I), a major amount of di-(1-methyl*cyclo*hexyl) disulphide (II; $x = 2$), and a minor amount of the sulphurated polymer typical of that formed in the *cyclo*hexene reaction (Part I); (ii) the absence of di-(1-methyl*cyclo*hexyl) monosulphide (II; $x = 1$); and (iii) the isolation of a considerable amount of diethylammonium hydrogen sulphide, consistent with (i) above. It is noteworthy, however, that the degree of sulphuration effected under the present conditions is much greater than that obtained by Naylor (*J.*, 1947, 1532) by the sulphur-catalysed normal addition of hydrogen sulphide to trialkylethylenes under comparable or even more severe reaction conditions. The structures of the thiol and disulphide as (I) and (II; $x = 2$), respectively, were established by comparison of their chemical properties and infra-red spectra with those of (I) and 2-methyl*cyclo*hexane-1-thiol (III), and their derived polysulphides synthesised by unambiguous means. Such comparison substantiates the polar nature of the sulphuration process which must be represented as occurring mainly by reaction (2) :

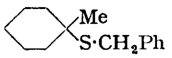


. . . . (2)

The thiol (I) was synthesised by reductive cleavage of benzyl 1-methyl*cyclo*hexyl sulphide (IV) with sodium and liquid ammonia, (IV) being obtained by normal addition of toluene-ω-thiol to 1-methyl*cyclo*hexene in the presence of 75% (w/w) sulphuric acid. Attempted cleavage of (IV) with aluminium bromide (Harnish and Tarbell, *J. Amer. Chem. Soc.*, 1948, **70**, 4123) was unsuccessful, the only products isolated being 1-methyl-1-phenyl*cyclo*hexane and diphenylmethane; the former hydrocarbon apparently arose from attack of the intermediate 1-methyl*cyclo*hexyl carbonium ion on benzene which was used as solvent (cf. Dougherty and Lee, *J. Org. Chem.*, 1939, **4**, 48), and the latter by Friedel–Crafts arylation of the solvent by benzyl bromide. The thiol (III) was synthesised from α-(2-methyl*cyclo*hexyl)thiolacetate by Cunneen's method (*J.*, 1947, 138). The corresponding di- and poly-sulphides of (I) and (III) were obtained by base-catalysed sulphur oxidation of the thiols (Bloomfield, *J. Soc. Chem. Ind.*, 1948, **67**, 14).

(III)





(IV)

The overall lower yield of sulphurated product as compared with the *cyclo*hexene reaction (Part I), the isolation of the thiol (I), and the absence of monosulphuide (II; $x = 1$) in the present reaction collectively suggest that the presence of trialkylethylene unsaturation in the olefin introduces some structural feature, probably steric, which impairs the additive capabilities of hydrogen sulphide and the derived *tert.*-thiol (I). The existence of such steric factors is indicated by examination of molecular models of (I) and (II; $x = 1$ and 2) and has been independently confirmed by determining the relative facilities with which (I) and (III) add both normally and abnormally to *cyclo*hexene and 1-methyl*cyclo*hexene.

Although the *tert.*-thiol (I) resists further addition to the parent olefin, its ability to undergo base-catalysed oxidation by sulphur to give the disulphide (II; $x = 2$) remains unimpaired, and thus the isolation of (I) in the present reaction must be attributed to the absence of sulphur, necessary for such thiol oxidation, in the later stages of the sulphuration process through its prior reaction with diethylamine (Part I).

It is clearly of importance to determine if the undesirable inhibition of the hydrogen sulphide and thiol additions to the parent olefin is specific to the trialkylethylene structure in 1-methyl*cyclo*hexene or is general to both cyclic and acyclic olefins of this type. This has been examined by studying the reaction of the diethylamine–sulphur combination with 2-methylpent-2-ene at 140°. In this case such inhibition was much less since a considerably larger yield of disulphide (VI; $x = 2$) was obtained, with little of the monosulphide (VI; $x = 1$) and polysulphide (VI; $x > 2$). A low yield was also obtained of a saturated thiol, $C_6H_{13}\cdot SH$, shown to be (V) by comparison of its chemical properties and infra-red spectrum with those of 2-methylpentane-2-thiol synthesised from the corresponding benzylthio-compound. The reaction course (3) thus closely resembles that followed by 1-methyl*cyclo*hexene :

$$CH_2Me\cdot CH{:}CMe_2 \xrightarrow[H_2S]{} \underset{(V)}{CH_2Me\cdot CH_2\cdot CMe_2\cdot SH} \xrightarrow[\substack{S_8\text{-base}\\(x\text{ mainly }2)}]{\text{Olefin}, x=1} \underset{(VI)}{(CH_2Me\cdot CH_2\cdot CMe_2)_2S_x} \quad . \quad (3)$$

The *tert.*-alkyl nature of the thiol (V) and the disulphide (VI; $x = 2$) again strongly supports the proposed polar course of the reaction.

Abortive attempts were made to effect sulphuration of trialkylethylenes either by means of the diethylamine–sulphur combination at 100° or by treating the olefin at room temperature with the active sulphur liberated from this combination by means of ethanol.

EXPERIMENTAL

Infra-red spectra were recorded on a Grubb–Parsons single-beam spectrometer. Microanalyses were conducted under the supervision of Dr. W. T. Chambers.

Preparation of Olefins.—1-Methyl*cyclo*hexene, prepared by iodine-catalysed dehydration of 1-methyl*cyclo*hexan-1-ol, had b. p. 109—109·8°/762 mm., n_D^{20} 1·4508 (Found : C, 87·35; H, 12·45. Calc. for C_7H_{12} : C, 87·4; H, 12·6%). Infra-red analysis indicated the absence of methylene*cyclo*hexane and ketonic and hydroxyl groups. 2-Methylpent-2-ene, similarly prepared from 2-methylpentan-2-ol, had b. p. 66·4—66·7°/760 mm., n_D^{20} 1·4005 (Found : C, 85·4; H, 14·35. Calc. for C_6H_{12} : C, 85·7; H, 14·3%). Infra-red analysis indicated that *ca.* 3% of vinylidene unsaturation, $CH_2{:}CR_2$, was present.

Synthesis of Reference Compounds for the 1-*Methyl*cyclo*hexene Reaction.*—(1) *Benzyl* 1-*methyl*cyclo*hexyl sulphide* (IV). 1-Methyl*cyclo*hexene (96 g., 1 mole) was added dropwise with stirring to 75% (w/w) sulphuric acid (500 g.) at 0—5°. Toluene-ω-thiol (62 g., 0·5 mole) was then added, with continued stirring, during 1 hr. at 0—5° and then during 2 hr. at room temperature. The product was decomposed with ice and extracted with ether, and the extract washed successively with water, alkali, and water, dried (K_2CO_3), and distilled. The main distillate, b. p. 83—93°/0·3 mm., n_D^{20} 1·5470 (106 g.), on repeated fractionation, gave the pure *sulphide* (IV), b. p. 100—101°/0·1 mm., n_D^{20} 1·5538 (76·0 g.) (Found : C, 76·4; H, 9·25; S, 14·5. $C_{14}H_{20}S$ requires C, 76·4; H, 9·1; S, 14·5%). Use of 75% (v/v) sulphuric acid in the above reaction gave little of the desired sulphide (IV), the major products being dibenzyl disulphide (58·0 g.), m. p. 69—70° (Found : C, 68·45; H, 6·0; S, 25·55. Calc. for $C_{14}H_{14}S_2$: C, 68·3; H, 5·7; S, 26·0%), and a fraction (34·0 g.), b. p. 53°/0·05 mm., n_D^{20} 1·4950, containing a polymer of 1-methyl*cyclo*hexene [Found : C, 87·15; H, 12·25; S, 0·4. Calc. for $(C_7H_{12})_n$: C, 87·4; H, 12·6%].

(2) 1-*Methyl*cyclo*hexane*-1-*thiol* (I). (*a*) The sulphide (IV) (22·0 g., 0·1 mole), suspended in liquid ammonia (400 ml.), was treated with small portions of sodium (5·5 g., 0·23 g.-atom) with rapid stirring until the solution became permanently blue. Ammonium chloride (14 g.) was then added, and the ammonia allowed to evaporate overnight, the last traces being removed on the water-pump. The product was made just acid with ice-cold 2N-hydrochloric acid and extracted with ether, and the extract fractionated, to give the *thiol* (I), b. p. 48°/11 mm., n_D^{20} 1·4853 (9·2 g.) (Found : C, 66·3; H, 10·7; S, 22·85. $C_7H_{14}S$ requires C, 64·6; H, 10·8; S, 24·6%), containing, as revealed by infra-red analysis, a trace of toluene not removed by further fractionation. Treatment of a neutral solution of the sodium salt of (I) with chloro-2 : 4-dinitrobenzene gave 2 : 4-*dinitrophenyl* 1-*methyl*cyclo*hexyl sulphide* as yellow flakes, m. p. 59—59·5°, from ethanol (Found : C, 52·65; H, 5·45; N, 9·8. $C_{13}H_{16}O_4N_2S$ requires C, 52·7; H, 5·4; N, 9·5%). Hot aqueous mercuric cyanide with (I) gave the *mercuric* derivative as feathery needles (from ethanol), m. p. 106—107° (Found : Hg, 43·4. $C_{14}H_{26}S_2Hg$ requires Hg, 43·7%).

(*b*) Treatment of the sulphide (IV) (11·0 g., 0·05 mole) during 2 days at room temperature with a solution of aluminium bromide (15·0 g., 0·056 mole) in benzene (100 ml.) and fractionation of the product gave only two hydrocarbon fractions : (i) b. p. 56—60°/0·05 mm., n_D^{20} 1·5462 (4·5 g.) (Found : C, 90·8; H, 9·2. Calc. for $C_{13}H_{12}$: C, 92·9; H, 7·1%. Calc. for $C_{13}H_{18}$: C, 89·6; H, 10·4%), and (ii) b. p. 60°/0·05 mm., n_D^{20} 1·5610 (4·7 g.) (Found : C, 91·4; H, 7·95%).

(3) *Di*-(1-*methyl*cyclo*hexyl*) *polysulphide* (II; $x = 3$—4). When the thiol (I) (5·2 g.) was mixed with sulphur (0·64 g.) and diethylamine (0·1 g.) at room temperature hydrogen sulphide was slowly evolved. Fractionation gave : (i) unchanged (I), b. p. 52°/15 mm., n_D^{20} 1·4879

(2·60 g.), and (ii) the polysulphide (II; $x = 3$—4), " molecularly " distilled as a yellow liquid, n_D^{20} 1·5810 (1·90 g.) (Found: C, 54·6; H, 8·35; S, 36·4. Calc. for $C_{14}H_{26}S_3$: C, 57·9; H, 8·97; S, 33·1. Calc. for $C_{14}H_{26}S_4$: C, 52·2; H, 8·1; S, 39·7%).

(4) *2-Methyl*cyclo*hexane-1-thiol* (III). This compound, prepared according to Cunneen's method (*loc. cit.*), had b. p. 54—56°/10 mm., n_D^{20} 1·4950 (68%) (Found: C, 64·4; H, 10·7; S, 24·5. Calc. for $C_7H_{14}S$: C, 64·6; H, 10·8; S, 24·6%). It gave 2 : *4-dinitrophenyl 2-methyl*cyclo*hexyl sulphide* as yellow prisms (from ethanol), m. p. 87—88° (Found: C, 52·65; H, 5·35; N, 9·5. $C_{13}H_{16}O_4N_2S$ requires C, 52·7; H, 5·4; N, 9·5%). Oxidation of (III) (5·2 g.) with sulphur (0·64 g.) in the presence of diethylamine (0·1 g.) or *N*-ethylthioacetamide (0·1 g.) at room temperature gave hydrogen sulphide and a product which on fractionation yielded: (i) unchanged thiol, b. p. 55—56°/10 mm., n_D^{20} 1·4932 (2·52 g.); and (ii) a " molecular " distillate, n_D^{20} 1·5852 (2·1 g.), of mixed di-(2-methyl*cyclo*hexyl) polysulphides (Found: C, 53·5; H, 8·4; S, 38·6. Calc. for $C_{14}H_{26}S_4$: C, 52·2; H, 8·1; S, 39·7%).

(5) *Di-(2-methyl*cyclo*hexyl) monosulphide.* The thiol (III) (4·0 g., 1 mol.), 1-methyl*cyclo*hexene (3·25 g., 1·1 mol.), and acetone (0·5 g.) were sealed *in vacuo* in a Pyrex tube, and irradiated with ultra-violet light for 16 hr. with water-cooling. Fractionation of the product gave: (i) unchanged thiol (III), b. p. 64—66°/20 mm., n_D^{20} 1·4940 (2·3 g.); and (ii) almost pure *monosulphide*, b. p. 62—64°/0·05 mm., n_D^{20} 1·5120 (1·80 g.) (Found: C, 73·9; H, 11·4; S, 14·25. $C_{14}H_{26}S$ requires C, 74·3; H, 11·5; S, 14·2%). Acid potassium permanganate oxidation of the monosulphide gave the corresponding *sulphone* as colourless prisms, m. p. 111—113°, from ethanol (Found: C, 64·9; H, 10·1; S, 12·25. $C_{14}H_{26}O_2S$ requires C, 65·1; H, 10·1; S, 12·4%).

Normal and Abnormal Additions of Thiols to Olefins.—(1) *Polar addition of* (I) *to 1-methyl*cyclo*hexene.* The olefin (9·6 g.) was added slowly to sulphuric acid (50 g., 75% w/w) at 0—5° with vigorous stirring; the thiol (I) (6·5 g.) was then added, and stirring continued at room temperature for a further 15 min. Fractionation of the product gave: (i) a mixture (5·2 g.) of unchanged thiol (I) and olefin, b. p. 45—53°/12 mm., n_D^{20} 1·4670; and (ii) b. p. 58—67°/0·05 mm., n_D^{20}1·5130 (6·1 g.) (Found: C, 77·85; H, 12·0; S, 10·35. Calc. for $C_{14}H_{26}S$: C, 74·3; H, 11·5; S, 14·2%), shown by infra-red analysis to be a mixture of di-(1-methyl*cyclo*hexyl) monosulphide and 1-methyl*cyclo*hexene polymer.

(2) *Abnormal addition of* (I) *to 1-methyl*cyclo*hexene.* Irradiation of a mixture of (I), the olefin, and acetone with ultra-violet light for 17 hr. at 15° gave no sulphide, the product being a mixture of unchanged reactants, as confirmed by infra-red analysis. Similar abnormal addition of *tert.*-butanethiol to 1-methyl*cyclo*hexene gave a sulphide yield of only 8—9% after 17 hours' irradiation at 15°.

(3) *Abnormal addition of* (I) *to* cyclo*hexene.* The thiol (I) (4·0 g., 1 mol.), the olefin (2·77 g., 1·1 mol.), and acetone (0·5 g.), irradiated as in (2) above, gave unchanged thiol (I) (2·50 g.), and slightly impure cyclo*hexyl 1-methyl*cyclo*hexyl sulphide* (1·70 g.), b. p. 66°/0·05 mm., n_D^{25} 1·5110 (Found: C, 74·1; H, 11·6; S, 14·5. $C_{13}H_{24}S$ requires C, 73·6; H, 11·3; S, 15·1%).

*Reaction of Diethylamine and Sulphur with 1-Methyl*cyclo*hexene at* 140°.—The amine (30·0 g.), sulphur (10·0 g.), and the olefin (40·0 g.) were heated *in vacuo* for 24 hr. at 140° ± 1°. Diethylammonium hydrogen sulphide (8·5 g.) and a small amount of tar were separated from the product by filtration, and the filtrate was freed from unchanged amine and olefin by evaporation on the steam-bath under nitrogen. The residue was taken up in ligroin and extracted with 10% sodium hydroxide solution (3 × 25 ml.). The alkaline extract was acidified (hydrochloric acid) and extracted with ether, and the extract dried (Na_2SO_4) and fractionated to give: (i) b. p. 54—106°/12 mm., n_D^{20} 1·5090 (0·5 g.) (Found: C, 60·2; H, 9·5; N, 0·56; S, 28·1%); (ii) b. p. 106—110°/12 mm., n_D^{20} 1·5448 (1·1 g.) (Found: C, 51·65; H, 8·65; N, 3·3; S, 35·05%); and (iii) b. p. 46°/0·1 mm., n_D^{20} 1·5594 (1·1 g.) (Found: C, 47·9; H, 8·8; N, 11·5; S, 30·15. Calc. for C_4H_9NS: C, 46·4; H, 8·7; N, 13·6; S, 31·1%). Fractions (i) and (ii) contained the thiol (I), identified (m. p.s and mixed m. p.s) by its 2 : 4-dinitrophenyl sulphide derivative and its mercuric derivative. Infra-red analysis of (i) and (ii) confirmed that (I) was a major constituent, the isomeric thiol (III) being definitely absent; di-(1-methyl*cyclo*hexyl) sulphides (II) were present in minor amount. Infra-red analysis of (iii) indicated that it was nearly pure *N*-ethylthioacetamide, the thiol form of which presumably accounts for its solubility in aqueous alkali.

The ligroin fraction was washed with 50% hydrochloric acid (5 × 20 ml.) to remove remaining thioamides, and then with aqueous bicarbonate and water. Fractionation of the product gave: (iv) unchanged olefin (14·2 g.) containing a trace of (I), b. p. 50°/30 mm., n_D^{20} 1·4512 (Found: S, 1·6%); (v) pure (I) (1·90 g.), b. p. 50—51°/12 mm., n_D^{20} 1·4880 (Found:

C, 64·8; H, 10·75; N, 0·02; S, 24·3. Calc. for $C_7H_{14}S$: C, 64·6; H, 10·8; S, 24·6%), identified (m. p.s and mixed m. p.s) by its 2 : 4-dinitrophenyl sulphide and mercuric derivatives and by comparison of its infra-red spectrum with that of synthetic (I) and (III); and (vi) b. p. 56—85°/0·07 mm., n_D^{20} 1·5310 (3·6 g.) (Found: C, 62·9; H, 9·75; N, 1·6; S, 25·45. Calc. for $C_{14}H_{26}S_2$: C, 65·1; H, 10·1; S, 24·8%). Infra-red analysis of (vi) showed that it was mainly the disulphide (II; $x = 2$) with minor amounts of higher polysulphides (II; $x > 2$) and indicated the absence of thiols (I) and (III), di-(2-methyl*cyclo*hexyl) polysulphides, *N*-ethylthioacetamide, and all types of C:C unsaturation; weak bands were also present due to a minor amount of *NN*-diethylthioacetamide. The reddish-brown viscous residue (6·85 g.) on molecular distillation gave: (vii) n_D^{20} 1·5602 (Found: C, 63·6; H, 9·25; N, 1·35; S, 25·35%); (viii) n_D^{20} 1·5718 (Found: C, 62·4; H, 8·65; N, 1·2; S, 27·3%); and (ix) a residue which on chromatography on alumina yielded a clear yellow glass (Found: C, 60·65; H, 8·4; N, 0·55; S, 30·15%). Fractions (vii)—(ix) were mixtures of polysulphides (II; $x = 2$—3) together with polymeric material typical of that observed in the *cyclo*hexene reaction (Part I).

Synthesis of Reference Compounds for the 2-*Methylpent*-2-*ene Reaction.*—(1) *Benzyl* 1 : 1-*dimethylbutyl sulphide*, prepared (yield 90%) by a method analogous to that used for the synthesis of (IV), had b. p. 84—88°/0·5 mm., n_D^{20} 1·5230 (Found: C, 74·8; H, 9·5. $C_{13}H_{20}S$ requires C, 75·0; H, 9·6%).

(2) 2-*Methylpentane*-2-*thiol* (V). (i) Reduction of the above sulphide (18·0 g.) with sodium in liquid ammonia, as described above for the synthesis of (II), yielded the slightly impure *thiol* (V) (71%), b. p. 36—38°/12 mm., n_D^{25} 1·4412 (Found: C, 62·35; H, 12·1; S, 25·75. Calc. for $C_6H_{14}S$: C, 61·0; H, 11·9; S, 27·1%). Infra-red analysis showed that the impurity was toluene. The thiol (V) gave a *mercuric* derivative as colourless needles, m. p. 75—76° (Found: S, 14·7; Hg, 46·9. $C_{12}H_{26}S_2Hg$ requires S, 14·7; Hg, 46·2%), from ethanol. Attempts to prepare the 2 : 4-dinitrophenyl sulphide derivative gave only 2 : 4-dinitrophenetole, m. p. 85°. Rheinboldt's test (*Ber.*, 1926, **59**, 1131) confirmed that (V) was a *tert.*-thiol.

(ii) Resublimed aluminium bromide (2·0 g.), in carbon disulphide (50 ml.), was treated with dry hydrogen sulphide at room temperature with the simultaneous addition of 2-methylpent-2-ene (16·8 g.). Hydrogen sulphide addition was continued for a further 15 min., and the mixture decomposed with ice and dilute hydrochloric acid and worked up in the usual way, to give the thiol (V) (6·8 g.), b. p. 36—37°/11 mm., n_D^{20} 1·4430 (Found: C, 59·2; H, 11·65; S, 25·55%). The infra-red spectrum was very similar to that of the thiol obtained in (i) above, though additional bands were present, due to some unidentified impurity. The thiol gave a mercuric derivative, m. p. and mixed m. p. with that from (i) 75—76°.

(3) *Di*-(1 : 1-*dimethylbutyl*) *polysulphide* (VI). The thiol (V) (4·72 g.) and sulphur (0·64 g.) on treatment with diethylamine (0·1 g.) during 10 hr. at room temperature gave unchanged (V) (2·4 g.), b. p. 40°/15 mm., and the polysulphide (VI; $x \sim 4$) obtained by molecular distillation as a pale yellow liquid (1·75 g.), n_D^{25} 1·5460 (Found: C, 49·4; H, 9·05; S, 41·7. Calc. for $C_{12}H_{26}S_4$: C, 48·3; H, 8·7; S, 42·9%).

Reaction of Diethylamine and Sulphur with 2-*Methylpent*-2-*ene at* 140°.—The amine (30·0 g.), sulphur (10·0 g.), and olefin (50·0 g.) were heated *in vacuo* at 140° ± 1° for 21 hr. with gentle rocking. After removal of diethylammonium hydrogen sulphide (0·6 g.), the product was treated with ligroin (b. p. 40—60°) and a tar (1·1 g.) separated. The ligroin solution was evaporated on the water-bath under nitrogen to remove unchanged amine and olefin, diluted with more ligroin, and extracted with cold 50% hydrochloric acid (4 × 25 ml.) to remove thioamides. The resultant ligroin fraction on distillation gave: (i) b. p. 45—50°/12 mm., n_D^{20} 1·4448 (2·3 g.), containing about 79% of the thiol (V) and a little monosulphide (VI; $x = 1$) (Found: C, 61·7; H, 11·95; N, 0·1; S, 26·3; SH, by copper butyl phthalate titration, 22%; C : H = 12 : 27·8. Calc. for $C_6H_{14}S$: C, 61·0; H, 11·9; S, 27·1; SH, 28%); the thiol in (i) was identified as (V) by its mercuric mercaptide, m. p. and mixed m. p. with synthetic sample (above) 74—75·5° (Found: C, 32·9; H, 6·05; Hg, 46·9%), by the green coloration in Rheinbold's test, and by the close identity of infra-red spectrum of (i) with that of synthetic (V); (ii) b. p. 50—77°/0·05 mm. (15·85 g.); and (iii) a final residue (3·90 g.) which was purified by chromatography on alumina to yield a reddish-brown oil consisting mainly of polymer of the type $C_6H_{13}{\cdot}S_x{\cdot}C_6H_{12}{\cdot}S_x{\cdot}C_6H_{13}$ [Found: C, 55·95; H, 9·65; N, 1·4; S, 33·1%; *M* (ebullioscopic in benzene), 351, 355, 364. Calc. for $C_{18}H_{38}S_4$: C, 56·5; H, 9·9; S, 33·5%; *M*, 382]; infra-red analysis of (iii) indicated that it was fully saturated.

Infra-red analysis of fraction (ii) showed the presence of traces of thiol and *NN*-diethylthioacetamide. A portion of (ii) was therefore purified by extraction first with 20% sodium hydroxide solution (2 × 25 ml.) and then with 50% hydrochloric acid (4 × 25 ml.), and the product fractionated to give: (ii*a*) b. p. 50—65°/0·2 mm., $n_{\rm D}^{20}$ 1·4860 (Found: C, 62·6; H, 11·5; N, 0·27; S, 25·5%; *M* (ebullioscopic in benzene), 208. Calc. for $C_{12}H_{26}S_2$: C, 61·55; H, 11·1; S, 27·35%; *M*, 234]; and (ii*b*) b. p. 65—74°/0·2 mm., $n_{\rm D}^{20}$ 1·5055 [Found: C, 60·0; H, 10·8; N, 0·94; S, 28·95%; *M* (ebullioscopic in benzene), 225]. Fractions (ii*a*) and (ii*b*) are therefore mainly di-(1 : 1-dimethylbutyl) disulphide (VI; $x = 2$) together with minor amounts of the mono- and poly-sulphide; this was confirmed by the close identity of their infra-red spectra with that of synthetic (VI; $x \sim 4$); C:C type of unsaturation was absent. A band at 1536 cm.$^{-1}$ due to S═C–N probably indicated traces of the dithio-oxalodiamide $(Et_2N{\cdot}CS)_2$, since thioamides on being heated with sulphur and amines occasionally form this type of compound (cf. Levesque, U.S.P. 2,525,075, 1950).

Attempted Low-temperature Sulphurations.—(1) 2-Methylpent-2-ene (40 ml.) was added to the complex derived from *n*-butylamine (50 ml.) and sulphur (5·0 g.) in nitrogen. The complex was decomposed with ethanol at room temperature, and the mixture stirred for a further 30 min. Filtration of the product gave unreacted sulphur (4·7 g.) and a filtrate which on evaporation yielded no sulphurated product.

(2) A mixture of piperidine (15 g.), sulphur (5·0 g.), and 1-methyl*cyclo*hexene (25 g.) was refluxed in nitrogen for 5 hr. at 100°. The reddish liquid was decanted from some tar, the latter extracted with ligroin, and the ligroin solution of the main product extracted with cold hydrochloric acid. Fractionation of the neutral ligroin solution gave only unreacted olefin.

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