393. *The Syntheses, Characterisation, and some Reactions of Alk(en)yl Dimethylthiocarbamoyl Disulphides and an Alkenyl 2-Benzothiazolyl Disulphide.*

By A. A. Watson.

New procedures for the preparation of alkyl dimethylthiocarbamoyl disulphides are described which are applicable also to the synthesis of alkenyl dimethylthiocarbamoyl disulphides and alkenyl 2-benzothiazolyl disulphides. The reactions of these disulphides with propane-2-thiolate ion and triphenylphosphine, and their reduction with lithium aluminium hydride, are discussed.

Three methods have been described for the preparation of disulphides having the general formula (I), where R and R′ are alkyl, but they fail when R is alkenyl. Interest in *S*-alkenyl derivatives of (I) arises from their presence as intermediates in the formation of sulphides by the interaction of olefins with a thiuram disulphide and zinc oxide at 140°.[1]

$RS{\cdot}S{\cdot}CS{\cdot}NR'_2$ (I)

(II) $R = Et,\ R' = Me$

$EtS{\cdot}CS{\cdot}NMe_2$ (III)

$Me_2C{:}CH{\cdot}CHMe{\cdot}(S)_n{\cdot}CS{\cdot}NMe_2$

(IV) $n = 2$

(V) $n = 1$

Displacement by dialkyldithiocarbamate ion of the thiocyanate ion of an alkanesulphenyl thiocyanate[2] gives (I) but necessitates prior treatment of the thiol RSH with

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[1] Moore and Watson, unpublished results.

[2] Hunt, U.S.P. 2,390,713 (1945).

thiocyanogen to give the starting material. When R is alkenyl, addition to the double bond of the thiol or substitution at an allylic centre also occurs.[3] Similarly, displacement of chloride ion from a sulphenyl chloride [4] by dithiocarbamate ion is not a practicable route to unsaturated derivatives of (I), since the alkenesulphenyl chloride cannot be prepared from the alkenethiol without attack of the double bond by chlorine.

Base-catalysed disproportionation of tetramethylthiuram disulphide, $Me_2N{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}NMe_2$, with a large excess of a dialkyl disulphide has been used [5] to prepare these disulphides. This method was used by the author to prepare ethyl dimethylthiocarbamoyl disulphide (II), but a pure product was not obtained. Attempts to prepare cyclohex-2-enyl dimethylthiocarbamoyl disulphide by this method failed because of the incursion of side-reactions at the elevated temperatures required both for reaction and for isolation of the product.

A successful route for the synthesis of the alk(en)yl thiocarbamoyl disulphides (I; R = Et or $Me_2C{:}CH{\cdot}CHMe$, R′ = Me) is a modification of the general method of Footner and Smiles [6] for the formation of mixed disulphides from sodium alkyl thiosulphates (Bunte salts) by reaction with thiolate ions. In neutral aqueous solutions of Bunte salts and sodium dimethyldithiocarbamate, equilibrium (1) exists, in which the forward reaction

$$RS{\cdot}SO_3^- + Me_2N{\cdot}CS{\cdot}S^- \underset{b}{\overset{a}{\rightleftharpoons}} RS{\cdot}S{\cdot}CS{\cdot}NMe_2 + SO_3^{2-} \qquad (1)$$

(1*a*) is slow owing to the weak nucleophilicity of the dimethyldithiocarbamate ion. Removal of sulphite ion promotes the desired reaction and avoids subsequent reaction of the sulphite ion with the disulphide. This latter complication was anticipated from the observed reactions of certain aliphatic disulphides [7] and of tetramethylthiuram disulphide [8] with sulphite ion, which suggest that the reactions

$$RS{\cdot}S{\cdot}CS{\cdot}NMe_2 \xrightarrow{SO_3^{2-}} RS^- + {}^-O_3S{\cdot}S{\cdot}CS{\cdot}NMe_2 \longrightarrow RS{\cdot}CS{\cdot}NMe_2 + S{\cdot}SO_3^{2-}$$

may take place, resulting in desulphuration of the required product.

Use of sodium ethyl thiosulphate in reaction (1*a*), gave the pure disulphide (II) in 66% yield. Attempts to elute the disulphide (II) from a 20% fluorosilicone–Celite gas-chromatography column at 138 and 160° resulted in complete decomposition, but did indicate the absence of any stable impurities such as diethyl disulphide which could easily arise by disproportionation if traces of base were present [reaction (2)]. Elution from a

$$2RS{\cdot}S{\cdot}CS{\cdot}NMe_2 \xrightarrow{\text{base}} RS{\cdot}SR + Me_2N{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}NMe_2 \qquad (2)$$

20% silicone 550–Celite column at 160° provided qualitative identification of the compound, but its variable response to a flame ionisation detector indicated that some decomposition occurred on the column. The infrared spectrum of (II) was closely similar to that of *S*-ethyl dimethyldithiocarbamate (III), the bands at 860 and 738 cm.$^{-1}$ being shifted to 852 and 759 cm.$^{-1}$, respectively. The absence of a band at 738 cm.$^{-1}$ precluded the presence of (III) as a contaminant. The ultraviolet spectrum of (II) showed strong absorption below 235 mμ, an inflexion at 245 mμ, and a maximum at 278 mμ. The inflexion and maximum correspond to the two maxima present in the spectrum of (III), but have lower intensity. Further support for the chemical identity and purity of the product was derived from a study of its reactions, as described below.

An attempt to prepare (I; R = $MeCH_2{\cdot}CH{:}CMe{\cdot}CH_2$, R′ = Me) by the foregoing

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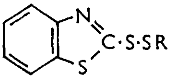
[3] Bacon, Guy, Irwin, and Robinson, *Proc. Chem. Soc.*, 1959, 304.
[4] Schulze, Short, and Crouch, *Ind. Eng. Chem.*, 1950, **42**, 916.
[5] Kleiman, U.S.P. 2,510,893/4 (1950) and 2,610,967/8 (1952).
[6] Footner and Smiles, *J.*, 1925, 2887.
[7] Parker and Kharasch, *Chem. Rev.*, 1959, **59**, 612.
[8] Ginzburg and Derechinskaya, *J. Rubber Ind. U.S.S.R.*, 1936, 310 (*Chem. Abs.*, 1936, **30**, 4790).

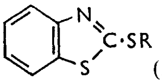
procedure from the appropriate Bunte salt failed because of emulsification; however, barium sulphite precipitation suggested that the desired reaction had occurred. A satisfactory alternative method for the removal of sulphite ions is the formation of the ion $HO{\cdot}CH_2{\cdot}SO_3^-$ at pH 8 by adding formaldehyde and sodium hydrogen carbonate to the Bunte salt solution. This method gave pure 1,3-dimethylbut-2-enyl dimethylthiocarbamoyl disulphide (IV) in 65—77% yield at room temperature.

Gas chromatography of (IV) showed it to be free from stable contaminants such as bis-(1,3-dimethylbut-2-enyl) disulphide[9] and *S*-1,3-dimethylbut-2-enyl dimethyldithiocarbamate (V),[10] but it decomposed on all the stationary phases tried. The infrared spectrum of (IV) was almost identical with that of (V) except for an additional shoulder at 1210 cm.$^{-1}$ and a band-shift from 870 to 853 cm.$^{-1}$. The ultraviolet spectrum was also similar to that of (V), having an inflexion instead of a maximum at 245 mμ, and a maximum at 278 mμ of reduced intensity, both effects consistent with modification of the conjugation of the $S{\cdot}CS{\cdot}NMe_2$ group by the additional sulphur atom. The reactions described below further characterise the product.

The method outlined above may be applicable to the preparation of other disulphides where, in equilibrium (1), the attacking thio-anion is only weakly nucleophilic, *e.g.*, the formation of 1,3-dimethylbut-2-enyl 2-benzothiazolyl disulphide (VI) by reaction of sodium 1,3-dimethylbut-2-enyl thiosulphate[11] with sodium 2-benzothiazolyl sulphide at room temperature in the presence of formaldehyde at pH 8. The infrared spectrum of (VI) is consistent with the proposed structure in that only bands occurring in the spectra of di-(2-benzothiazolyl) disulphide (VII) and bis-(1,3-dimethylbut-2-enyl) disulphide were present, as would be expected for the mixed disulphide. The ultraviolet spectrum had a maximum at 272 mμ similar to that of (VII) and to those of methyl (VIII) and but-2-enyl (IX),[12] 2-benzothiazolyl sulphide, respectively, but with less fine-structure in the region 280—300 mμ than exhibited by the last compound.

(VI: R = $Me_2C{:}CH{\cdot}CHMe$)
(VII: R = 2-Benzothiazolyl)





(VIII: R = Me)
(IX: R = $MeCH{:}CH{\cdot}CH_2$)

Results

The Reduction of Ethyl and 1,3-*Dimethylbut*-2-*enyl Dimethylthiocarbamoyl Disulphides by Lithium Aluminium Hydride.*—Reduction of the disulphides and estimation of the products was carried out as previously described.[13] Partly because of practical difficulties, the reduction of the disulphide (II) resulted, in the best case, in yields of only 47 mole % of ethanethiol and 66·5 mole % of hydrogen sulphide [assuming 2 moles per mole of (II)]. A quantitative yield of 4-methylpent-3-ene-2-thiol (X), shown to be isomerically pure by gas chromatography, was obtained by reduction of (IV). The yield of hydrogen sulphide was 42 mole % [assuming 2 moles per mole of (IV)]. This incomplete reduction is ascribed to the formation of tetramethylthiuram disulphide by reaction (3). It was established that, under identical conditions, tetramethylthiuram disulphide gave only

$$\underset{\text{(IV)}}{Me_2C{:}CH{\cdot}CHMe{\cdot}S{\cdot}S{\cdot}CS{\cdot}NMe_2} \xrightarrow{AlH_4^-} \underset{\text{(X)}}{Me_2C{:}CH{\cdot}CHMe{\cdot}SH} +$$

$$^-S{\cdot}CS{\cdot}NMe_2 \xrightarrow{\text{(IV)}} Me_2C{:}CH{\cdot}CHMe{\cdot}S^- + Me_2N{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}NMe_2 \quad (3)$$

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[9] Evans, Higgins, Saville, and Watson, *J.*, 1962, 5045.
[10] Saville, *Proc. Chem. Soc.*, 1961, 214.
[11] Saville, *Proc. Chem. Soc.*, 1962, 18.
[12] Moore and Waight, *J.*, 1952, 4237.
[13] Watson, *J.*, 1962, 4717.

30% of the theoretical yield of hydrogen sulphide. The 4-methylpent-3-ene-2-thiolate ion produced in reactions (3) will rapidly react with (IV) to give bis-(1,3-dimethylbut-2-enyl) disulphide, which is reduced by lithium aluminium hydride in 5 minutes under these conditions.[14]

Reaction of Propane-2-thiol and Piperidine with the Disulphides (II), (IV), *and* (VI).—It was shown [15,16] that a tetra-alkylthiuram disulphide reacts with a thiol [reaction (4)],

$$RS^- + R'_2N\cdot CS\cdot S\cdot S\cdot CS\cdot NR'_2 \longrightarrow R'_2N\cdot CS\cdot S^- + RS\cdot S\cdot CS\cdot NR'_2 \xrightarrow{RS^-} RS\cdot SR + R'_2N\cdot CS\cdot S^- \qquad (4)$$

two successive displacements being postulated. The product of the proposed first displacement is representative of the compounds whose syntheses are described above, and it was expected that rapid reaction of these disulphides would occur with propane-2-thiol in the presence of one molar equivalent of piperidine, to give the alk(en)yl isopropyl disulphide and the piperidinium salt of the displaced thio-anion [reaction (5)]. The

$$RS\cdot SX + [C_5H_{10}NH_2{}^+ \ {}^-SPr^i] \longrightarrow RS\cdot SPr^i + C_5H_{10}NH_2{}^+ \ {}^-SX \qquad (5)$$

$(R = Et \text{ or } Me_2C{:}CH\cdot CHMe,\ X = Me_2N\cdot CS\cdot S \text{ or 2-benzothiazolylthio.}$

expected displacement was effected in light petroleum and light petroleum–benzene solution, using an excess of propane-2-thiol and piperidine at room temperature, the piperidinium salt of the displaced thio-anion being deposited within 1 minute. The amount of disulphide, $RS\cdot SPr^i$, formed was estimated by gas chromatography using an internal standard, and the amount of dithiocarbamate ion was determined by complexometric titration after isolation as the zinc salt. For the reaction of disulphide (VI) quantitative estimates were not carried out, but the products were shown to be 1,3-dimethylbut-2-enyl isopropyl disulphide, a small amount of di-isopropyl disulphide, and piperidinium 2-benzothiazolyl sulphide. The significant amount of di-isopropyl disulphide from (IV) (Table 1) is considered to have originated mainly from further, slower, reaction [17] of the initially formed mixed disulphide with propane-2-thiolate ion [reaction (6)], owing to the prolonged reaction time, rather than from the presence of tetramethylthiuram disulphide or 1,3-dimethylbut-2-enyl dimethylthiocarbamoyl trisulphide as impurities, both of which give di-isopropyl disulphide by successive fast displacements [15,16]

TABLE 1.

Products of the reaction of the disulphides (II) and (IV) with an excess of propane-2-thiol and piperidine.

Disulphide	Reaction time (min.)	$RS\cdot SPr^i$ (mole %)	$Pr^iS\cdot SPr^i$ (mole %)	$Me_2N\cdot CS\cdot S^-$ (mole %)
(II)	30	97·8	trace	101·2
(IV)	50	93·2	3·0	95·2

$$Me_2C{:}CH\cdot CHMe\cdot S\cdot SPr^i \xrightarrow{Pr^iS^-} Pr^iS\cdot SPr^i + Me_2C{:}CH\cdot CHMe\cdot S^- \qquad (6)$$

$$Me_2N\cdot CS\cdot S\cdot S\cdot CS\cdot NMe_2 \xrightarrow{Pr^iS^-} Pr^iS\cdot S\cdot CS\cdot NMe_2 + {}^-S\cdot CS\cdot NMe_2 \xrightarrow{Pr^iS^-} Pr^iS\cdot SPr^i + {}^-S\cdot CS\cdot NMe_2 \qquad (7)$$

$$RS\cdot S\cdot S\cdot CS\cdot NMe_2 \xrightarrow{Pr^iS^-} {}^-S\cdot CS\cdot NMe_2 + RS\cdot S\cdot SPr^i \xrightarrow{Pr^iS^-} Pr^iS\cdot SPr^i + RS\cdot S^- \qquad (8)$$

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[14] Porter, Saville, and Watson, *J.*, 1963, 346.
[15] Scheele and Gensch, *Rubber Chem. Technol*, 1957, **30**, 728.
[16] Saville, *J.*, 1960, 1730.
[17] Evans and Saville, *Proc. Chem. Soc.*, 1962, 18.

[reactions (7) and (8)]. The virtual absence of di-isopropyl disulphide from the reaction products of disulphides (II) and (VI) precludes the presence of trisulphide in both cases, and of tetramethylthiuram disulphide and di-(2-benzothiazolyl) disulphide in the products from (II) and (VI), respectively.

Reaction of Ethyl and 1,3-*Dimethylbut*-2-*enyl Dimethylthiocarbamoyl Disulphides with Triphenylphosphine.*—The products of the reactions of disulphides (II) and (IV) with triphenylphosphine at 80°, in the absence of solvent, are given in Table 2. The dithiocarbamates (III) and (V) were identified by gas-chromatographic and spectroscopic examination. Lithium aluminium hydride reduction [13] of the crude product containing (V) indicated a 92 mole % yield from the amount of thiol (X) estimated.

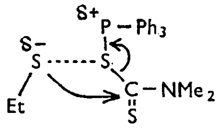
TABLE 2.

Products of the reaction of the disulphides (II) and (IV) with triphenylphosphine at 80°.

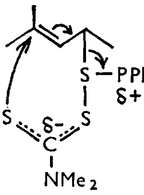
Disulphide	Reaction time (hr.)	$RS{\cdot}CS{\cdot}NMe_2$ * (mole %)	$RS{\cdot}SR$ (mole %)	$Ph_3P{:}S$ (mole %)
(II)	6·5	94	1·2	96
(IV)	5·5	90	none	99·5

* Yield of pure material isolated by distillation from the crude material containing an excess of triphenylphosphine.

The reaction in both cases was therefore a simple desulphuration, analogous to that undergone by tetramethylthiuram disulphide with the same reagent.[18] For the reaction of disulphide (II) it is proposed that the induced incipient or fully developed thiolate ion, produced by co-ordination of the phosphine on the sulphur atom adjacent to the thiocarbamoyl group, attacks the thiocarbamoyl carbon atom as represented in the transition state (XI). The small amount of diethyl disulphide formed shows the reaction either to proceed by way of a cyclic assembly or to involve closely associated ion-pairs. If free ethanethiolate ion were present it would preferentially attack a polarisable electrophilic centre, *i.e.*, the sulphur atom adjacent to the ethyl group in another molecule of disulphide (see previous section) and disproportionation would occur to give diethyl disulphide and tetramethylthiuram monosulphide, the latter being formed from the thiuram disulphide [18] [reactions (9)]. Disproportionation would also be the initial result of attack by the phosphine at the more electrophilic sulphur atom adjacent to the ethyl group, but again the products show that this mechanism is not operative.



(XI)



(XII)

$$EtS^- + EtS{\cdot}S{\cdot}CS{\cdot}NMe_2 \longrightarrow EtS{\cdot}SEt + Me_2N{\cdot}CS{\cdot}S^- \xrightarrow{(II)} EtS^- + Me_2N{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}NMe_2$$

$$\xrightarrow{Ph_3P} Me_2N{\cdot}CS{\cdot}S{\cdot}CS{\cdot}NMe_2 + Ph_3P{:}S \quad (9)$$

The reaction of triphenylphosphine with (IV) can, in principle, occur by two routes, depending upon the sulphur atom in the disulphide group to which the phosphine co-ordinates. The observed products can then be formed either (i) by the process described

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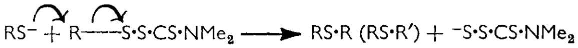
[18] Schönberg and Barakat, *J.*, 1949, 892.

above for (II), or (ii) by attack of incipient dimethyldithiocarbamate ion at the α-carbon of the alkenyl group. Such a displacement by a thio-anion at the α-carbon atom of dialkenyl disulphides has been demonstrated [19] but was always accompanied by some allylic rearrangement, postulated to occur by attack at the γ-carbon atom of the allylic system, by an S_Ni' process. This route is also closely similar to that shown for the conversion of dialkenyl disulphides by triphenylphosphine into monosulphides [20,21] in which allylic rearrangement of one alkenyl group occurs, and appears to be increasingly favoured in the reaction described here by consideration of the transition state (XII). The total absence of the allylic isomer of (V) leads to the conclusion that only mechanism (i) is



$$RS^- + R{-}S{\cdot}S{\cdot}CS{\cdot}NMe_2 \longrightarrow RS{\cdot}R\ (RS{\cdot}R') + {}^-S{\cdot}S{\cdot}CS{\cdot}NMe_2 \qquad (10)$$

$R = Me_2C{:}CH{\cdot}CHMe,\ R' = Me_2C{\cdot}CH{:}CHMe)$

operative. The absence of monosulphide, which could be produced by reaction (10), reinforces the opinion that free thiolate ions are not present in the triphenylphosphine desulphuration reaction.

EXPERIMENTAL

Gas chromatography was carried out with an apparatus previously described,[22] using stationary phases (quoted individually) supported on acid-washed Celite. Reaction products were identified by comparing their retention volumes with those of authentic compounds. Infrared spectra were recorded using a Hilger H.800 double-beam spectrophotometer; quantitative measurements refer to solutions in carbon disulphide. Ultraviolet spectra were recorded for ethanol solutions, using a Hilger Uvispek spectrophotometer.

Materials and Intermediates.—Dicyclohex-2-enyl disulphide was prepared by oxidising [23] the corresponding thiol, prepared by reaction of 3-bromocyclohexene [24] with alkaline hydrogen peroxide. 1-Chloro-2-methylpent-2-ene,[14] *S*-(1,3-dimethylbut-2-enyl)thiouronium bromide,[25] and *S*-(1,3-dimethylbut-2-enyl)dimethyldithiocarbamate [11] were recently described. 1,3-Dimethylbut-2-enyl isopropyl disulphide and ethyl isopropyl disulphide were prepared from sodium 1,3-dimethylbut-2-enyl thiosulphate [Bunte salt in preparation of (IV) below] and sodium ethyl thiosulphate, respectively, by reaction with propane-2-thiol.[6] Light petroleum was AnalaR and had b. p. 30—40°. Other compounds were either commercially available or prepared by conventional procedures. Benzothiazole-2-thiol (Imperial Chemical Industries, Vulcafor M.B.T.) was freed from di-2-benzothiazolyl disulphide by hot extraction for 4 days with acetone–chloroform–methanol azeotrope. Tetrahydrofuran was dried and purified [14] before use.

Ethyl Dimethylthiocarbamoyl Disulphide (II).—(*a*) The product obtained by use of the the published procedure [5] had b. p. 100—102°/0·005 mm., n_D^{20} 1·6119 (Found: C, 32·9; H, 6·0; N, 6·5; S, 54·9. Calc. for $C_5H_{11}NS_3$: C, 33·15; H, 6·1; N, 7·7; S, 53·05%). Spectroscopic or gas-chromatographic analysis of the product did not reveal the impurity which is inferred to be present from the nitrogen and sulphur analyses.

(*b*) Sodium dimethyldithiocarbamate (35·7 g. of a 40% solution, 0·10 mole) in water (100 ml.) was added dropwise, with stirring at room temperature, under nitrogen, during 2 hr. to a mixture of sodium ethyl thiosulphate (18·1 g., 0·11 mole), light petroleum (150 ml.), and barium chloride dihydrate (24·4 g., 0·10 mole) dissolved in water (200 ml.), barium sulphite being deposited throughout the reaction. After stirring for a further 2 hr., the organic phase was

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[19] Moore and Watson, *Tetrahedron*, 1962, **18**, 219.

[20] Evans, Higgins, Moore, Porter, Saville, Smith, Trego, and Watson, *Chem. and Ind.*, 1960, 897.

[21] Moore and Trego, *Tetrahedron*, 1962, **18**, 205.

[22] Evans and Smith, *J. Chromatog.*, 1961, **6**, 293.

[23] McAllan, Cullum, Dean, and Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3627.

[24] Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80.

[25] Saville, *J.*, 1962, 5040.

separated, washed well with water, and dried (Na_2SO_4). Removal of the solvent left an evil-smelling yellow liquid, m. p. *ca.* 9°, n_D^{20} 1·6278 (Found: C, 33·3; H, 6·0; N, 7·5; S, 52·9%). No attempt was made to distil the product.

Attempted Preparation of Cyclohex-2-enyl Dimethylthiocarbamoyl Disulphide.—Using the procedure described by Kleiman,[5] the product was an undistillable brown tar. During the removal of the excess of dicyclohex-2-enyl disulphide, considerable quantities of dimethylammonium dimethyldithiocarbamate (m. p. 130—131°, mixed m. p. 130—132°) and lesser amounts of carbon disulphide and hydrogen sulphide were formed.

Attempted Preparation of 2-Methylpent-2-enyl Dimethylthiocarbamoyl Disulphide.—Sodium 2-methylpent-2-enyl thiosulphate was prepared by refluxing together, with vigorous stirring, 1-chloro-2-methylpent-2-ene (35·5 g., 0·30 mole), a solution of sodium thiosulphate pentahydrate (82 g., 0·33 mole) in water (90 ml.), and ethanol (100 ml.) for 2·5 hr. until the two phases merged. The procedure used for preparation (*b*) of (II) was then followed, but the product was not isolated because of emulsification.

1,3-*Dimethylbut*-2-*enyl Dimethylthiocarbamoyl Disulphide* (IV).—To sodium thiosulphate pentahydrate (35 g., 0·14 mole) in water (40 ml.) was added finely powdered *S*-(1,3-dimethylbut-2-enyl)thiouronium bromide (24 g., 0·10 mole), and the mixture stirred for 1 hr. at 40°. Methanol (20 ml.) was added and the mixture heated at 65° for 15 min., after which time the absence of thiouronium cation was shown by testing a sample of the mixture with picric acid. Organic impurities were extracted with chloroform (2 × 30 ml.) and light petroleum (2 × 30 ml.). Light petroleum (40 ml.), 40% formaldehyde solution (7·5 ml., 0·10 mole), and sodium hydrogen carbonate (8·5 g., 0·10 mole) were added to the Bunte salt solution, and sodium dimethyldithiocarbamate (7·2 g. of a 40% solution, 0·05 mole) in water (25 ml.) was added during 1 hr. at room temperature with vigorous stirring. After stirring for a further 2 hr., the organic phase was separated, well washed with water, dried (Na_2SO_4), and evaporated at room temperature under reduced pressure, leaving the *disulphide* (9·1 g., 77%) as a yellow crystalline mass, m. p. 44—45·5° (Found: C, 46·1; H, 7·3; N, 5·9; S, 40·3. $C_9H_{17}NS_3$ requires C, 45·9; H, 7·3; N, 5·95; S, 40·85%).

1,3-*Dimethylbut*-2-*enyl* 2-*Benzothiazolyl Disulphide* (VI).—A solution of sodium 1,3-dimethylbut-2-enyl thiosulphate was prepared on a 0·10-molar scale, as described above, and diluted with water (100 ml.). Light petroleum (200 ml.) and 40% formaldehyde solution (7·5 ml., 0·10 mole) were added and a solution of the sodium salt of benzothiazole-2-thiol [prepared by dissolving benzothiazole-2-thiol (8·3 g., 0·05 mole) in acetone (50 ml.), adding sodium hydrogen carbonate (12·75 g., 0·15 mole) in water (400 ml.), warming, and adding acetone (100 ml.) until the precipitated solid had dissolved] was added during 1 hr. with vigorous stirring. The mixture was stirred for 1 hr., the petroleum layer separated, washed with water, dried (Na_2SO_4), and the solvent removed at room temperature under reduced pressure leaving the *disulphide* as a viscous yellow liquid (3·5 g., 25%) (Found: C, 55·4; H, 5·5; N, 4·7; S, 33·7. $C_{13}H_{15}NS_3$ requires C, 55·4; H, 5·4; N, 5·0; S, 34·2%).

Reductions with Lithium Aluminium Hydride.—These were carried out as previously described,[13] on 200 mg. samples for 2 hr. at 65°. Ethanethiol, which was produced on reduction of (II), was identified gas chromatographically (20% dinonyl phthalate at room temperature). It partly co-distilled with the hydrogen sulphide and was trapped with the hydrogen sulphide in buffered cadmium acetate solution as cadmium ethyl sulphide. It was removed from this mixture by boiling, re-trapped in ice-cooled buffered cadmium acetate solution, and estimated iodometrically. 4-Methylpent-3-ene-2-thiol (X), produced on reduction of (IV), was identified by gas chromatography (20% dinonyl phthalate at 65°).

Reactions of Disulphides (II) *and* (IV) *with Propane*-2-*thiol and Piperidine.*—Samples (*ca.* 500 mg.) of the disulphide and internal gas chromatography standard (n-undecane or n-tridecane, *ca.* 200 mg.) were dissolved in n-heptane (5 ml.) and benzene (1 ml.), and a 2-molar excess of propane-2-thiol and piperidine in n-heptane (5 ml.) was added. The mixtures were allowed to stand for the times stated in Table 1, washed twice with water (10 ml.), in which the precipitated salts dissolved, and once with 0·1N-sulphuric acid (10 ml.). The disulphides formed were identified and estimated by gas chromatography (20% neopentane glycol adipate at 100° or 5% silicone 704 at 138°) by comparison with the standards. The detector responses of the disulphide products, relative to the standards, were determined separately. In estimating dimethyldithiocarbamate ion in the aqueous extracts, an excess of zinc acetate was added, and the precipitated crude zinc dimethyldithiocarbamate filtered off and extracted with hot chloroform for 24 hr. Solvent was removed from a sample of the chloroform extract, and drying on a vacuum hotplate (necessary to complete dissociation of the zinc dimethyldithiocarbamate–piperidine complex [26]) gave the salt, m. p. and mixed m. p. 253—255° (without recrystallisation) (Found: C, 24·2; H, 4·1; N, 9·2; S, 40·0; Zn, 21·2. Calc. for $C_6H_{12}N_2S_4Zn$: C, 23·6; H, 3·9; N, 9·2; S, 41·9; Zn, 21·4%). Quantitative determination of zinc dimethyldithiocarbamate in the chloroform extract was carried out by evaporating an aliquot to dryness, digesting the residue with concentrated hydrochloric acid, adding water, and aqueous ammonia to pH 9, and titrating with EDTA to a Solochrome Black end-point.

Reaction of Disulphide (VI) *with Propane-2-thiol and Piperidine.*—The reaction was carried out as described above, for 30 min., but quantitative estimation of the products was not attempted. The precipitated salt was filtered off and washed with light petroleum, and had m. p. 159·5—161°, mixed m. p. with piperidinium 2-benzothiazolyl sulphide 159·5—162·5° (Found: C, 58·0; H, 6·3; N, 10·6; S, 24·9. Calc. for $C_{12}H_{16}N_2S_2$: C, 57·2; H, 6·3; N, 11·1; S, 25·4%). The disulphide products in the organic layer were identified by gas chromatography.

Reaction of Disulphides (II) *and* (IV) *with Triphenylphosphine.*—The disulphide (0·02 mole) was sealed *in vacuo* with triphenylphosphine (0·022 mole) and heated at 80 ± 0·2° for the times stated in Table 2. Some reaction took place at room temperature, the mixture becoming solid at the interface of the two reactants if not mixed immediately. The solid product was treated with light petroleum, filtered, washed well with more petroleum, and dried. The filtered solid had m. p. 162—163°, mixed m. p. with triphenylphosphine sulphide 162—163·5° (Found: S, 10·7. Calc. for $C_{18}H_{15}PS$: S, 10·85%). Solvent was removed from the washings by distillation at atmospheric pressure, the residue distilled at 0·01 mm., and the distillate weighed. A sample (180 mg.) of the crude product from the desulphuration of (IV) was reduced with lithium aluminium hydride [13] before distillation. The amount of thiol formed was estimated [13] and identified by gas chromatography after regeneration [10] from the silver thiolate. Gas chromatography of the thiol (20% dinonyl phthalate at 65°) showed it to be entirely 4-methylpent-3-ene-2-thiol (X). The distilled dimethyldithiocarbamates were identified and shown to be >98% pure by gas chromatography (5% silicone 550 at 118 or 160°). Elemental analyses were carried out on the product (III) from disulphide (II) (Found: C, 40·4; H, 7·4; N, 9·3; S, 42·9. Calc. for $C_5H_{11}NS_2$: C, 40·2; H, 7·4; N, 9·4; S, 42·9%), and on the product (V) from disulphide (IV) (Found: C, 53·1; H, 8·4; N, 6·8; S, 31·5. Calc. for $C_9H_{17}NS_2$: C, 53·2; H, 8·45; N, 6·9; S, 31·45%).

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[26] Higgins and Saville, *J.*, 1963, 2812.