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THE REACTION OF TRIPHENYLPHOSPHINE WITH UNSYMMETRICAL DIALKENYL DISULPHIDES AND WITH SYMMETRICAL DIALKENYL TRISULPHIDES

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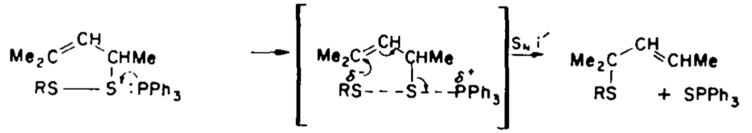
Abstract—The rate and course of the reaction of triphenylphosphine (Ph_3P) with dialkenyl sulphides (RS_XR'; R,R′ = alkenyl, X = 2 or 3) at 80° depend on the structures of the alkenyl groups and the value of X. Symmetrical dialkenyl trisulphides (RS_3R) are converted to two disulphides: RS_2R and RS_2R', the latter having an alkenyl group R′ which is isoallylic with R. Further desulphuration to monosulphides by Ph_3P occurs *via* an S_Ni' process, as previously described, involving an allylic rearrangement of one of the alkenyl groups: $RS_2R \rightarrow RSR'$; $RS_2R' \rightarrow RSR$ and R′SR′. The relative rates of these competing reactions have been derived and the mechanisms are discussed.

PREVIOUS work has shown that dialkenyl- or alkenyl–alkyl disulphides are converted by triphenylphosphine (Ph_3P) to dialkenyl- or alkenyl–alkyl monosulphides with allylic rearrangement of an alkenyl group,[1] and it was proposed that the reaction proceeds by nucleophilic attack by Ph_3P at a sulphur atom in the disulphide followed by an S_Ni' reaction of the polarized complex (e.g. II):



(1)

I II III

(R = alkyl or alkenyl)

That the allylic rearrangement occurs as in reaction (1) and not before or after the desulphuration reaction is now confirmed (a), by the fact that reaction of (I, R = $Me_2C{:}CH{\cdot}CHMe$-) (1 mole.) with a deficiency of Ph_3P (0·5 mole.) at 80° gave the anticipated monosulphide (III, R = $Me_2C{:}CH{\cdot}CHMe$-) but caused no allylic rearrangement in the unreacted disulphide; and (b), by the observation that treatment of bis-(1,3-dimethylbut-2-enyl) monosulphide with either Ph_3P or Ph_3PS for 96 hr at 80° did not effect any allylic rearrangement of the monosulphide.

We now report extensions of the above work to studies of the reaction of Ph_3P with an unsymmetrical dialkenyl disulphide and with symmetrical dialkenyl trisulphides.

Reaction of unsymmetrical dialkenyl disulphides

Reaction of allyl 1,3-dimethylbut-2-enyl disulphide (IV) with Ph_3P at 80° follows the course:

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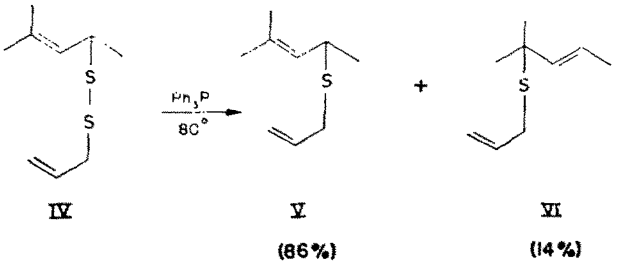
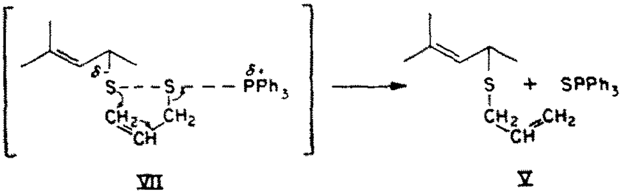
[1] C. G. Moore and B. R. Trego, *Tetrahedron* **18**, 205 (1962).



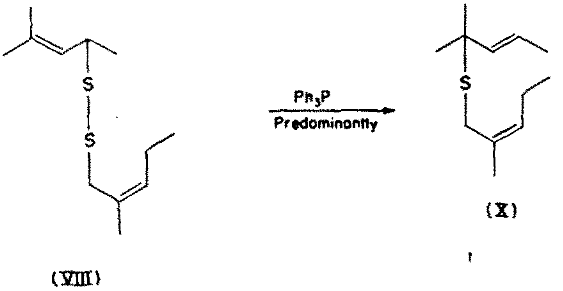
(2)

This is consistent, when taken in conjunction with previous work,[1] with the desulphuration proceeding mainly by an S_Ni' reaction involving attack of the incipient ion $Me_2C{:}CH{\cdot}CHMe{\cdot}\overset{\delta-}{S}$ at the γ-carbon atom of the allyl group:

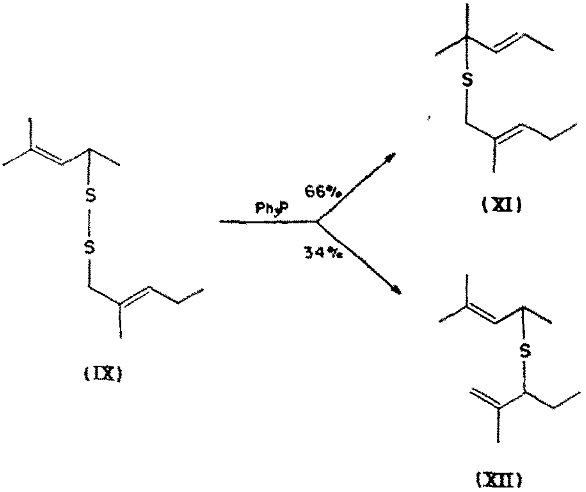


(3)

This contrasts with the course of reaction of Ph_3P with 1,3-dimethylbut-2-enyl *cis*- and *trans*-2-methylpent-2-enyl disulphides (VIII) and (IX), respectively, where the desulphuration involves predominant attack of the incipient ion $MeCH_2{\cdot}CH{:}CMeCH_2{\cdot}\overset{\delta-}{S}$ at the γ-carbon atom of the 1,3-dimethylbut-2-enyl group, i.e. the most substituted γ-carbon atom in the system:[2]



(4)



(5)

(6)

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[2] M. B. Evans, G. M. C. Higgins, B. Saville, and A. A. Watson, *J. Chem. Soc.* 5045 (1962).

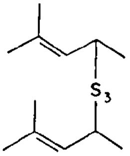
As discussed earlier[1] the relative rates of desulphuration of a series of symmetrical dialkenyl disulphides are equally consistent with the S_Ni' process being controlled by: (i) the electrophilicities of the sulphur atoms of the disulphide bond towards Ph_3P; (ii) the steric accessibility of the γ-carbon atom of the alkenyl group to the incipient thiolate ion, $R\overset{\delta-}{S}$; or (iii) the stability and thus the ease of formation, of the incipient thiolate ion. Which of these factors determines the course of desulphuration of unsymmetrical dialkenyl disulphides appears to depend on the nature of the alkenyl groups present. For the disulphides (VIII) and (IX), the preferred reactions (4 and 5, respectively) are consistent with (iii) being dominant, since $MeCH_2\cdot CH:CMeCH_2\cdot\overset{\delta-}{S}$ will be more stable than $Me_2C:CH\cdot CHMe\cdot\overset{\delta-}{S}$, whereas were (i) or (ii) rate controlling the major product would be expected to be XII. A contributory cause for the insignificant amount of XII formed from VIII is that the ethyl group of VIII, being in *cis*-juxtaposition to the disulphide group, greatly hinders approach of the incipient ion, $Me_2C:CH\cdot CHMe\cdot\overset{\delta-}{S}$, to the γ-carbon atom of the allylic system in the

$MeCH_2\cdot CH:CMe\cdot CH_2$-group.[2]

In contrast to the above, the fact that the disulphide (IV) reacts with Ph_3P mainly *via* reaction (3) suggests that in this system factors (i) or (ii) are dominant, and not (iii) which would require VI and not V to be the major product since the incipient ion, $CH_2:CH\cdot CH_2\cdot\overset{\delta-}{S}$, will be more stable than $Me_2C:CH\cdot CHMe\cdot\overset{\delta-}{S}$.

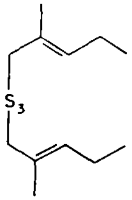
Reaction of symmetrical dialkenyl trisulphides

Reaction of Ph_3P (1 mole) with the trisulphides XIII or XIV (1 mole) under the conditions specified in Table 1 (Expts. 1 and 3, respectively) gives Ph_3PS, unreacted trisulphide, and a mixture of dialkenyl mono- and disulphides, some of which contain the iso-allylic counterparts of the alkenyl groups in the parent trisulphides (Table 2, Expts. 1 and 3); use of excess Ph_3P (> 2 mole per mole of trisulphide) gives dialkenyl monosulphides as the major products, with only minor amounts of the corresponding di- and trisulphides (Tables 1 and 2, Expts. 2 and 4). The composition of the products



XIII

$(A_1S_3A_1)$



XIV

$(B_1S_3B_1)$

indicates that the desulphuration of the trisulphides to disulphides involves in part the allylic rearrangement of an alkenyl group; since the desulphuration of the disulphides to monosulphides is known to proceed virtually entirely by an S_Ni' process as exemplified by reaction (1), the overall conversion of the trisulphides to monosulphides

TABLE 1. REACTION OF TRIPHENYLPHOSPHINE WITH DIALKENYL TRISULPHIDES AT 80°

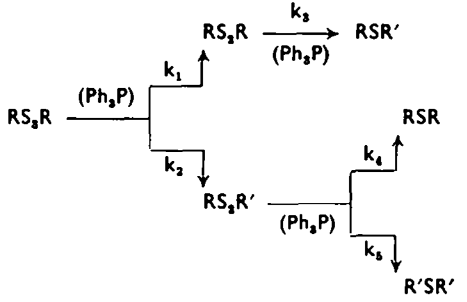
Expt. No.	Trisulphide	Trisulphide (mmoles)	Ph_3P (mmoles)	Reaction time (hr)	Yield of Ph_3PS (%)	Yield of sulphides (%)	Elemental analyses for sulphides (%) C	H	S	P
1	*bis*-(1,3-Dimethylbut-2-enyl)	7·6	7·7	42	93	96	†62·3	9·6	27·8	0·08
2	*bis*-(1,3-Dimethylbut-2-enyl)	3·8	8·1	93	89	88	‡73·0	11·2	16·3	0·02
3	Di-(2-methylpent-2-enyl)	3·8	3·8	20·5	92	97	†61·7	9·8	28·6	0·02
4	Di-(2-methylpent-2-enyl)	19	40	67	90	72*	‡72·5	11·4	15·9	—

* The sulphides were isolated by fractional distillation and not by column chromatography as in Expts. 1–3.

† Calc. for $C_{12}H_{22}S_2$: C, 62·6; H, 9·55; S, 27·85%

‡ Calc. for $C_{12}H_{22}S$: C, 72·6; H, 11·2 ; S, 16·2%.

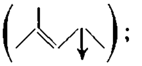
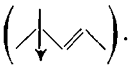
can be represented simply as:

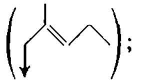
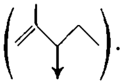


(where R = alkenyl group and R′ its isoallylic counterpart).

TABLE 2. REACTION OF TRIPHENYLPHOSPHINE WITH DIALKENYL TRISULPHIDES AT 80°. COMPOSITION OF THE ORGANIC SULPHIDES FORMED

Sulphides present in bulk sulphidic product*	Expt. 1 (mole %)	Expt. 2 (mole %)	Sulphides present in bulk sulphidic product†	Expt. 3 (mole %)	Expt. 4 (mole %)
A_1SA_2	12·8	33·6	B_2SB_2	(1·0)	(3·1)
A_1SA_1	31·6	58·5	B_1SB_2	25·8	76·0
$A_1S_2A_2$	~0	~0	B_1SB_1	9·2	18·3
$A_1S_2A_1$	6·4	5·5	$B_1S_2B_2$	2·1	~0
$A_1S_3A_1$	49·2	(2·4)	$B_1S_2B_1$	21·2	2·6
			$B_1S_3B_1$	40·7	0

* A_1 = 1,3-dimethylbut-2-enyl (); A_2 = 1,1-dimethylbut-2-enyl ().

† B_1 = 2-methylpent-2-enyl (); B_2 = 1-ethyl-2-methylallyl ().

For the values in brackets the compounds designated were not unequivocally identified but are reasonable assignments.

When RS_3R is $A_1S_3A_1$ (XIII), there is no evidence for the formation of $R'SR'$ (i.e. A_2SA_2) and thus for this system $k_4 \gg k_5$ as expected from the previous consideration of the desulphuration of unsymmetrical dialkenyl disulphides. When RS_3R is $B_1S_3B_1$ (XIV), there is some evidence for the formation of small amounts of $R'SR'$ (i.e. B_2SB_2), but in this case also the yields of B_1SB_1 and B_2SB_2 indicate that $k_4 \gg k_5$ and therefore in the following kinetic analysis it is assumed that in both systems RS_2R' gives RSR exclusively (i.e. $k_5 = 0$). A further slight complication is that the sample of $B_1S_3B_1$ is not isomerically pure; it contains mainly *trans* B_1- groups (89 mole %) with lesser amounts of *cis* B_1-groups (10 mole %) and B_2- groups (1 mole %). It is assumed that the sulphides containing the *cis* and trans B_1 groups will react with Ph_3P at comparable rates, although this will not be strictly true.[2] Within the limits of the above reservations an approximate kinetic analysis is possible of the influence of structure on the relative rates of the reactions specified in the above scheme.

The ratio k_1/k_2 is given by $\{[RS_2R] + [RSR']\}/\{[RS_2R'] + [RSR] + [R'SR']\}$. Accepting that the rates of all reactions are first order with respect to $[Ph_3P]$ and the sulphide concentration, other rate ratios are derivable as follows:

$$-d[\mathrm{RS_3R}]/dt = k_1[\mathrm{Ph_3P}][\mathrm{RS_3R}] + k_2[\mathrm{Ph_3P}][\mathrm{RS_3R}] \qquad \text{(i)}$$

$$-d[\mathrm{RS_2R}]/dt = k_3[\mathrm{Ph_3P}][\mathrm{RS_2R}] - k_1[\mathrm{Ph_3P}][\mathrm{RS_3R}] \qquad \text{(ii)}$$

$$-d[\mathrm{RS_2R'}]/dt = k_4[\mathrm{Ph_3P}][\mathrm{RS_2R'}] - k_2[\mathrm{Ph_3P}][\mathrm{RS_3R}] \qquad \text{(iii)}$$

Dividing (ii) by (i)

$$\frac{d[\mathrm{RS_2R}]}{d[\mathrm{RS_3R}]} = \frac{k_3[\mathrm{RS_2R}] - k_1[\mathrm{RS_3R}]}{(k_1 + k_2)[\mathrm{RS_3R}]}$$

$$= \frac{k_3}{k_1 + k_2}\frac{[\mathrm{RS_2R}]}{[\mathrm{RS_3R}]} - \frac{k_1}{k_1 + k_2}$$

i.e.:

$$\left(\frac{k_3}{k_1 + k_2} - 1\right) \ln\,[\mathrm{RS_3R}] = \ln\left\{1 - \frac{[\mathrm{RS_2R}]}{[\mathrm{RS_3R}]}\frac{(k_3 - k_1 - k_2)}{k_1}\right\} + \text{const.}$$

When $t = 0$, $[\mathrm{RS_3R}] = [\mathrm{RS_3R}]_0$, and $[\mathrm{RS_2R}] = 0$.

Therefore:

$$\left(\frac{k_3}{k_1 + k_2} - 1\right) \ln \frac{[\mathrm{RS_3R}]}{[\mathrm{RS_3R}]_0} = \ln\left\{1 - \frac{[\mathrm{RS_2R}]}{[\mathrm{RS_3R}]}\frac{(k_3 - k_1 - k_2)}{k_1}\right\}$$

or:

$$\left(\frac{k_3/k_1}{1 + k_2/k_1}\right) \ln \frac{[\mathrm{RS_3R}]}{[\mathrm{RS_3R}]_0} = \ln\left\{\frac{[\mathrm{RS_3R}]}{[\mathrm{RS_3R}]_0} - \frac{[\mathrm{RS_2R}]}{[\mathrm{RS_3R}]_0}\left(\frac{k_3}{k_1} - \frac{k_2}{k_1} - 1\right)\right\} \qquad \text{(iv)}$$

Similarly, by taking equations (i) and (iii) we obtain:

$$\left(\frac{k_4/k_2}{1 + k_1/k_2}\right) \ln \frac{[\mathrm{RS_3R}]}{[\mathrm{RS_3R}]_0} = \ln\left\{\frac{[\mathrm{RS_3R}]}{[\mathrm{RS_3R}]_0} - \frac{[\mathrm{RS_2R'}]}{[\mathrm{RS_3R}]_0}\left(\frac{k_4}{k_2} - \frac{k_1}{k_2} - 1\right)\right\} \qquad \text{(v)}$$

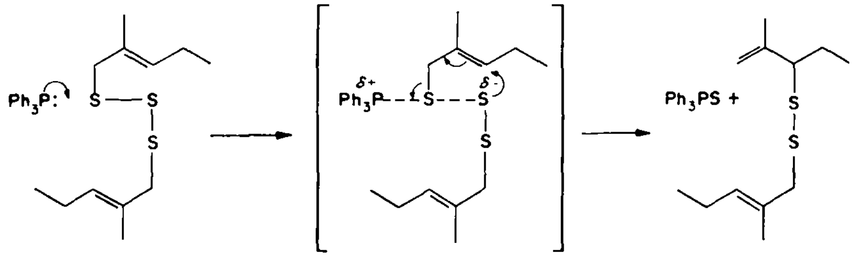
Since k_1/k_2 is calculable as shown above, equations (iv) and (v) can be used to give values of k_3/k_1 and k_4/k_2, respectively (Table 3). Equations (iv) and (v) are soluble graphically yielding two solutions for a given value of k_1/k_2; one solution (when $k_3/k_1 = 1 + k_2/k_1$ and $k_4/k_2 = 1 + k_1/k_2$) is trivial and chemically meaningless.

TABLE 3. KINETIC ANALYSIS OF THE REACTION OF TRIPHENYLPHOSPHINE WITH DIALKENYL TRISULPHIDES

Reaction System		k_1/k_2		k_3/k_1	k_4/k_2
$\mathrm{A_1S_3A_1} + \mathrm{Ph_3P}$	Expt. 1	0·61	Mean	8·9	*
	Expt. 2	0·67	0·64		
$\mathrm{B_1S_3B_1} + \mathrm{Ph_3P}$	Expt. 3	3·8	Mean	2·2	23
	Expt. 4	3·7	3·75		

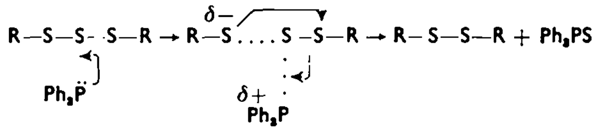
* This cannot be calculated because $[\mathrm{A_1S_2A_2}] \simeq 0$; however, this signifies that $k_4 \gg k_2$.

The product compositions (Table 2) and the kinetic data (Table 3) indicate that desulphuration of the trisulphides to disulphides occurs by two alternative routes, one involving allylic rearrangement of an alkenyl group and the other not involving the alkenyl group. The former reaction clearly proceeds by an $\mathrm{S_N i'}$ reaction, analogous to that observed in the reaction of $\mathrm{Ph_3P}$ with dialkenyl disulphides, e.g.:

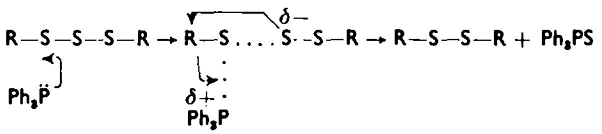


(B$_1$S$_3$B$_1$) (B$_2$S$_2$B$_1$) (7)

The straightforward desulphuration probably proceeds as in reaction (8), but an additional or alternative route (reaction 9) is also possible:



$$R{-}S{-}S{-}S{-}R \rightarrow R{-}\overset{\delta-}{S}\cdots S{-}S{-}R \rightarrow R{-}S{-}S{-}R + Ph_3PS \quad (8)$$



$$R{-}S{-}S{-}S{-}R \rightarrow R{-}S\cdots\overset{\delta-}{S}{-}S{-}R \rightarrow R{-}S{-}S{-}R + Ph_3PS \quad (9)$$

(R = A$_1$ or B$_1$).

The kinetic data (Table 3) indicate that the relative rates of the competing desulphurations are quite sensitive to the structure of the alkenyl group and that the desulphurations of the disulphides are in all cases faster than the desulphurations of their precursor trisulphides, thus emphasizing the extreme facility of the S$_N$i′ process as exemplified by reaction (1). A complete mechanistic explanation of the rate differences shown in Table 3 is not yet possible, although the results are broadly consistent with those to be anticipated from the influence of the factors (i)–(iii) referred to above under the heading of the reaction of unsymmetrical dialkenyl disulphides.

EXPERIMENTAL

Preparation of reactants and reference compounds. Pure triphenylphosphine, m.p. 80·0°, and triphenylphosphine sulphide, m.p. 161·0°, were obtained by crystallization of commercial samples from absolute ethanol.

(i) *Allyl* 1,3-*dimethylbut-2-enyl monosulphide* (*allyl* SA_1). To a solution of allyl chloride (0·1 mole) in ethanol (20 ml) was added with stirring a solution of 4-methylpent-3-ene-2-thiol (A$_1$SH; 0·1 mole) and sodium hydroxide (0·1 mole) in a mixture of water (10 ml) and ethanol (20 ml) and reaction completed by warming for 15 min at 40°. The organic sulphide was taken up in pet ether (b.p. 30–40°), washed with water, dried (MgSO$_4$), and after removal of the solvent distilled to give a main fraction (75%): b.p. 33·5–34·0°/0·02 mm (Found: C, 69·3; H, 10·4; S, 20·8. $C_9H_{16}S$ requires: C, 69·2; H, 10·3; S, 20·5%).

(ii) *Allyl* 1,3-*dimethylbut-2-enyl disulphide* (*allyl* S_2A_1). A solution of allyl chloride (0·2 mole) in ethanol (80 ml) was added to a solution of sodium thiosulphate (0·2 mole) in water (80 ml) and the mixture refluxed for 2 hr when an homogeneous solution was formed. Ethanol was removed under red. press. and the residue washed with chloroform (3 × 25 ml). To the resulting aqueous Bunte salt solution was added a solution of 4-methylpent-3-ene-2-thiol (A$_1$SH; 0·1 mole) and sodium hydroxide (0·1 mole) in a water (25 ml)-ethanol (15 ml) mixture. The product was worked up as in (i) to give the *disulphide* (78% based on thiol), b.p. 65°/0·01 mm (Found: C, 57·5; H, 8·7; S, 33·8. $C_9H_{16}S_2$ requires: C, 57·5; H, 8·5; S, 34·0%), shown by gas-liquid chromatography (GLC) to comprise three components, the major one representing 99% of the total chromatogram area.

(iii) *Di-(2-methylpent-2-enyl) trisulphide* (B$_1$S$_3$B$_1$) (kindly supplied by Dr. B. Saville) was prepared from 2-methylpent-2-enyl chloride as described elsewhere[8] (Found: C, 55·1; H, 8·7; S, 36·4. Calc.

for $C_{12}H_{22}S_3$: C, 54·95; H, 8·4; S, 36·65%). GLC analysis indicated a minimum purity of 95%; the chromatogram contained two additional small peaks of which one could be the corresponding disulphide (~2%). Hydrogenolysis with lithium aluminium hydride[4] indicated the compound to be $(C_6H_{11})_2S_{2\cdot97}$ and yielded a thiol fraction comprising *trans*-2-methylpent-2-ene-1-thiol (*trans*-B_1SH), 89%; *cis*-2-methylpent-2-ene-1-thiol (*cis*-B_1SH), 10%; and 2-methylpent-1-ene-3-thiol (B_2SH), 1%.

(iv) *Bis*-(1,3-*dimethylbut*-2-*enyl*) *trisulphide* ($A_1S_3A_1$), also supplied by Dr. B. Saville, was prepared as described previously[5] (Found: C, 55·1; H, 8·8; S, 36·3. Calc. for $C_{12}H_{22}S_3$: C, 54·95; H, 8·4; S, 36·65%). GLC analysis indicated a purity of 97·8% and the presence of 2·2% of the corresponding disulphide ($A_1S_2A_1$). Hydrogenolysis with lithium aluminium hydride indicated the compound to be $(C_6H_{11})_2S_{2\cdot96}$ and yielded a thiol fraction comprising 4-methylpent-3-ene-2-thiol (A_1SH), 98%; and 2-methylpent-3-ene-2-thiol (A_2SH), 2%.

The preparation of the other sulphides used has been described previously.[1,2]

(1) *Reactions of bis*-(1,3-*dimethyl-but*-2-*enyl*) *monosulphide*

(a) A mixture of the monosulphide (5·0 mmoles) and triphenylphosphine (10·1 mmoles) was degassed once and heated *in vacuo* for 96 hr at 80°. From the product was isolated triphenylphosphine (84·3%) and a sulphide fraction (87%) shown by I.R. spectrometry to be unchanged monosulphide.

(b) Reaction of the monosulphide (2·4 mmoles) with triphenylphosphine sulphide (2·46 mmoles) in ethanol (5 ml) for 96 hr at 80° gave completely unchanged monosulphide.

(2) *Reaction of triphenylphosphine with dialkenyl disulphides*

(a) *Bis*-(1,3-*dimethylbut*-2-*enyl*) *disulphide*. A mixture of the disulphide (4·28 mmoles) and triphenylphosphine (2·14 mmoles) was heated *in vacuo* for 96 hr at 80° in the dark. The product was treated with pet ether (b.p. 30–40°) and the precipitated material filtered off and crystallized from ethanol to give triphenylphosphine sulphide (97%). The organic sulphides (98%) were isolated from the filtrate by chromatography on an alumina column, using pet ether (b.p. 30–40°) as eluting solvent, followed by careful removal of the solvent. GLC analysis showed that the residue comprised a mixture of the monosulphides previously observed[1] together with unchanged disulphide.

(b) *Allyl* 1,3-*dimethylbut*-2-*enyl disulphide*. A mixture of the disulphide (5·4 mmoles) and triphenylphosphine (7·8 mmoles) was degassed once and heated *in vacuo* in the dark for 96 hr at 80°. Triphenylphosphine sulphide (98%) and a sulphide fraction (0·705 g; 83%) were isolated as in (a) above. GLC analyses of the sulphide fraction revealed the presence of allyl 1,3-dimethylbut-2-enyl monosulphide (V; 86%) and allyl 1,1-dimethylbut-2-enyl monosulphide (VI; 14%) and the absence of disulphide. I.R. spectrometric analysis confirmed the above assignments: absorption at 840 cm^{-1} consistent with the presence of the 1,3-dimethylbut-2-enyl group; absorption at 960 cm^{-1} indicated the presence of the 1,1-dimethylbut-2-enyl group (13 mole % of the methylpentenyl groups); and absorption at 910 and 990 cm^{-1} indicated the presence of the allyl group (100% based on the intensity of the band at 910 cm^{-1}).

(3) *Reaction of triphenylphosphine with dialkenyl trisulphides*

The general procedure used is illustrated by reference to:

Reaction of triphenylphosphine (1 *mole*) *with bis*-(1,3-*dimethylbut*-2-*enyl*) *trisulphide* (1 *mole*). A mixture of triphenylphosphine (7·7 mmoles) and the trisulphide (7·6 mmoles) was sealed *in vacuo* after one degassing and heated for 42 hr at 80° in the dark. The product was worked up as in (2a) and the organic sulphide fraction analysed by GLC using a 5% silicone 704-celite column at 138° and using 75% hydrogen–25% nitrogen as carrier gas; the products were identified and estimated by reference to relevant synthetic sulphides and by using di-n-hexyl monosulphide as an internal standard. Table 1 details the reaction conditions used for the various triphenylphosphine–dialkenyl trisulphide reactions, together with the yields of products and elemental analyses of the bulk organic sulphide fractions. The yields of the individual compounds in the organic sulphide fractions are given in Table 2.

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