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THE REACTION OF TRIPHENYLPHOSPHINE WITH ORGANIC DISULPHIDES AND POLYSULPHIDES*

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Abstract—The rate and course of reaction of triphenylphosphine (Ph_3P) with organic sulphur compounds ($R{\cdot}S_x{\cdot}R'$; R,R′ = alkyl or alkenyl, $x = 2$ or 4) at 80° or 140° depend on the nature of R and R′ and on the reaction medium. Dialkyl- and diaralkyl tetrasulphides (R=R′ = iso-Pr; n-Bu; t-Bu; $PhCH_2$) yield triphenylphosphine sulphide and dialkyl- or diaralkyl disulphides which are resistant to further attack by Ph_3P, even at 140°. Dialkenyl- and alkenyl-alkyl disulphides at 80° undergo a less facile desulphuration to give monosulphides which result from the allylic rearrangement of an alkenyl group; the yield of allylically-unrearranged monosulphide is negligible. The rates of the Ph_3P–disulphide reactions increase with increasing solvent polarity and decrease with increasing alkyl substitution at γ-carbon atoms of the alkenyl groups or the α-carbon atom of the alkyl groups. The Ph_3P–tetrasulphide reactions are believed to involve nucleophilic substitutions at the S—S bonds, initially by the reagent and then by a resultant incipient alkanethiolate or alkaneperthiolate ion. The rates and course of the Ph_3P–disulphide reactions are only consistent with nucleophilic attack of the Ph_3P on sulphur yielding an intimate ion-pair which then undergoes an almost exclusive S_Ni' process.

Previous work has shown that no reaction occurs when triphenylphosphine (Ph_3P) is heated in dry benzene at 80° with dialkyl-, diaralkyl- and diaryl disulphides.[1,2] Contrasting with this, reaction of Ph_3P with diallyl disulphide under comparable conditions gives triphenylphosphine sulphide and diallyl monosulphide.[2] We now report extensions of this work to quantitative studies of the reaction of Ph_3P with dialkyl- and diaralkyl tetrasulphides and with dialkenyl- and alkenyl-alkyl disulphides.

Reactions of organic tetrasulphides

The anaerobic reaction of Ph_3P (4 moles) with the tetrasulphides ($R{\cdot}S_4{\cdot}R$; R = iso-Pr; n-Bu; t.-Bu; $PhCH_2$) (1 mole) in dry benzene in the dark at 80° or 140° was followed by determining unreacted Ph_3P by the method of Bartlett and Meguerian.[3] The data (Table 1) indicate that under the specified reaction conditions the stoichiometry of reaction (1) is observed:

$$R{\cdot}S_4{\cdot}R + 2Ph_3P \rightarrow R{\cdot}S_2{\cdot}R + 2Ph_3PS \qquad (1)$$

Confirmation that the resultant disulphides are resistant to Ph_3P is the fact that no Ph_3P is consumed when it is heated with dibenzyl disulphide in dry benzene for extended periods at 140°.

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* Some of this work has been reported elsewhere in preliminary form (M. B. Evans, G. M. C. Higgins C. G. Moore, M. Porter, B. Saville, J. F. Smith, B. R. Trego and A. A. Watson, *Chem. & Ind.* 897 (1960).

[1] A. Schönberg and M. Z. Barakat, *J. Chem. Soc.* 892 (1949).

[2] F. Challenger and D. Greenwood, *J. Chem. Soc.* 26 (1950).

[3] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.* **78**, 3710 (1956).

TABLE 1. REACTION OF ORGANIC TETRASULPHIDES WITH TRIPHENYLPHOSPHINE IN BENZENE IN VACUO

Tetrasulphide	Moles of tetra-sulphide (× 10^4)	Moles of Ph_3P (× 10^4)	Reaction temp (°C)	Reaction time (hr.)	% of Sulphur in tetrasulphide removed by Ph_3P	Calc. % of removable sulphur for conversion of polysulphide to disulphide
Di-isopropyl (Found by analysis: $C_6H_{13\cdot9}S_{4\cdot15}$)	0·561	1·99	80·0	0·5	41·0	51·9
	0·561	1·99	80·0	5·5	54·0	
	0·561	1·99	80·0	16·5	52·4	
	0·561	1·99	80·0	121·0	54·6	
	0·561	1·96	140·0	24·0	53·8	
	0·561	1·98	140·0	28·0	51·9	
Di-t.-butyl	0·50	1·98	80·0	0·5	16·2	50·0
	0·50	2·00	80·0	2·0	34·0	
	0·50	1·97	80·0	4·0	47·9	
	0·50	1·97	80·0	48·0	45·0	
	0·50	2·00	80·0	96·0	45·7	
	0·50	1·95	80·0	126·0	46·8	
Di-n-butyl (Found by analysis: $C_8H_{18\cdot1}S_{3\cdot88}$)	0·50	1·98	80·0	1·0	51·9	48·5
	0·50	2·00	80·0	2·0	50·9	
	0·50	1·99	80·0	4·5	52·9	
	0·50	1·97	80·0	24·0	53·2	
Dibenzyl	0·50	1·97	80·0	0·25	17·7	50·0
	0·50	1·99	80·0	1·0	20·8	
	0·50	1·98	80·0	2·0	40·6	
	0·50	1·99	80·0	47·5	46·0	
	0·50	1·99	80·0	76·0	50·7	
	0·50	1·98	80·0	122·0	50·0	
	0·50	1·99	80·0	143·0	49·8	
	0·50	1·97	140·0	5·0	52·7	
	0·50	1·98	140·0	48·0	52·0	
	0·50	1·97	140·0	48·0	50·2	

Reactions of dialkenyl- and alkenyl-alkyl disulphides

Reaction of symmetrical dialkenyl disulphides ($R'{\cdot}S_2{\cdot}R'$; $R' = CH_2{:}CH{\cdot}CH_2$—; $MeCH{:}CH{\cdot}CH_2$—; $Me_2C{:}CH{\cdot}CH_2$—; $Me_2C{:}CH{\cdot}CHMe$—; $MeCH_2{\cdot}CH{:}CMe{\cdot}CH_2$—) with Ph_3P at 80° in the dark leads to the formation of dialkenyl monosulphides and triphenylphosphine sulphide:

$$\text{Alkenyl—S—S—Alkenyl} + Ph_3P \rightarrow \text{Alkenyl—S—Alkenyl} + Ph_3PS \qquad (2)$$

Similarly, reaction of alkenyl-alkyl disulphides ($R'{\cdot}S_2{\cdot}R$; $R' = Me_2C{:}CH{\cdot}CHMe$— or $MeCH_2{\cdot}CH{:}CMe{\cdot}CH_2$—, $R = Et$; and $R' = Me_2C{:}CH{\cdot}CHMe$—, $R = t\text{-}Bu$) with Ph_3P at 80° yields alkenyl-alkyl monosulphides and the phosphine sulphide:

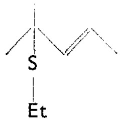
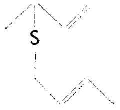
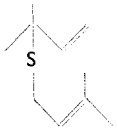
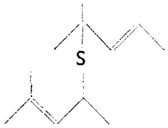
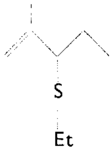
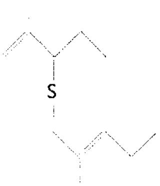
$$\text{Alkenyl—S—S—R} + Ph_3P \rightarrow \text{Alkenyl—S—R} + Ph_3PS \qquad (3)$$

Table 2 details the product yields, together with the physical properties and elemental analyses of the organic monosulphides resulting from reactions (2) and (3) conducted in the absence of solvent. Structural resolution of the dialkenyl- and alkenyl-alkyl monosulphides by a combination of infra-red spectrometry and gas-liquid chromatography (GLC) with reference to relevant synthetic monosulphides, revealed (Table 3 and Experimental section) that the conversions of disulphides to monosulphides involve an almost quantitative allylic rearrangement of an alkenyl group. Thus, the monosulphide derived from ethyl 1,3-dimethylbut-2-enyl disulphide

TABLE 2. REACTION OF TRIPHENYLPHOSPHINE WITH DIALKENYL- AND ALKENYL–ALKYL DISULPHIDES AT 80·0° IN VACUO

Expt. No.	Disulphide	Disulphide (mmoles)	Ph_3P (mmoles)	Reaction time (hr)	Yield of Mono-sulphide (%)	B.p. of monosulphide	n_D^{20}	Elemental analyses of monosulphide (%) C H S	Theoretical analyses for monosulphide (%) C H S	Yield of Ph_3PS (%)
1	Ethyl 1,3-dimethylbut-2-enyl	23	30	41·0	80	52·5/13 mm	1·4718	66·6 11·3 22·5	$C_8H_{16}S$: 66·6 11·2 22·2	—
2	Bis-(but-2-enyl)	23	30	68·0	78	57·5–58·1°/12 mm	1·4870	76·5 9·9 22·7	$C_8H_{14}S$: 67·5 9·9 22·6	—
3	Bis-(3-methylbut-2-enyl)	19·7	30	72·0	82	82·0–82·5°/12 mm	1·4906	70·6 10·6 19·0	$C_{10}H_{18}S$: 70·5 10·7 18·8	—
4	Bis-(1,3-dimethylbut-2-enyl)	17	26·6	72·0	65	47·0°/0·01 mm	1·4862	72·7 11·1 16·0	$C_{12}H_{22}S$: $72{\cdot}6_5$ 11·2 $16{\cdot}1_5$	74
5	Ethyl 2-methylpent-2-enyl	17	22·8	67·5	71	53·7–54·0°/13 mm	1·4700	66·4 11·4 22·0	$C_8H_{16}S$: 66·6 11·2 22·2	77
6	Bis-(2-methylpent-2-enyl)	6·2	9·5	66·5	63	59·0°/0·03 mm	1·4870	72·7 11·4 16·1	$C_{12}H_{22}S$: $72{\cdot}6_5$ 11·2 16·15	—

TABLE 3. STRUCTURAL ANALYSIS OF ORGANIC MONOSULPHIDES DERIVED FROM

Expt. No.	Structure of major component of reaction product	GLC analysis of reaction product				
		No. of components	Stationary phase*	Column temp (°C)	Relative retention times in R_{x9} units†	Mole % of total monosulphide product
1		2	P.E.G.	65	7·8 10·7	98·5 1·5
		2	SIL.	65	3·2 4·2	98·5 1·5
2		2	P.E.G.	100	34·9 38·0	97·0 3·0
		2	SIL.	100	3·9 7·2	97·0 3·0
3		3	P.E.G.	100	18·6 20·3 23·1	2·0‡ 96·0 2·0‡
4		3	SIL.	100	15·1 18·0 19·4	99·0 1·0
5		3	D.N.P.	100	1·45 2·50 4·35	2·0‡ 92·0 6·0
6		2	P.E.G.	100	35·6 69·0	93·5 6·5

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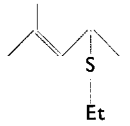
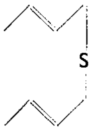
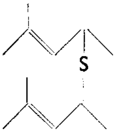
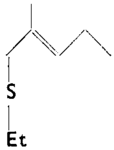
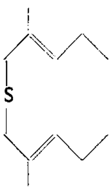
* P.E.G., polyethylene glycol-400–celite; SIL., silicone fluid 704–celite;

† see M. B. Evans and J. F. Smith, *J. Chromat.* in press.

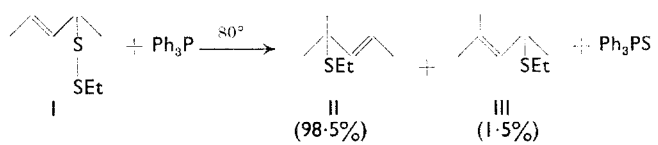
‡ Unidentified product.

THE TRIPHENYLPHOSPHINE—ORGANIC DISULPHIDE REACTIONS OF TABLE 2

GLC data for authentic monosulphide found as minor component of reaction product		Infra-red spectrometric analysis of reaction product		Supplementary structural data
Structure	R_{x9} value†	Region of absorption (cm^{-1})	Types of double bonds and approx. amounts (Exptl. error $\leqslant$ 10%)	
	— 11·0 — 4·4	966	One *trans*-dialkylethylenic group per molecule. No absorption at 837 cm^{-1} indicates absence of trialkylethylenic groups.	Rate of epoxidation with perbenzoic acid indicates one dialkylethylenic group per molecule (Fig. 3).
	— 37·1	960	One *trans*-dialkylethylenic group per molecule.	
	— 7·0	910 990	One vinyl group per molecule	
		842	One trialkylethylenic group per molecule.	Rate of epoxidation with perbenzoic acid indicates two different types of double bonds (Fig. 3).
		910 990	One vinyl group per molecule.	
	—	842	One trialkylethylenic group per molecule.	
	17·6 19·4	968	One *trans*-dialkylethylenic group per molecule.	
	— — 4·43	890	One vinylidene group per molecule.	
	71·0	890	One vinylidene group per molecule.	

D.N.P., di-nonylphthalate-celite; 75% hydrogen–25% nitrogen used as carrier gas.

(I) contains 98·5 per cent of (II) and 1·5 per cent of the unrearranged monosulphide (III):



(4)

These findings are confirmed by studies of the rate of reaction of perbenzoic acid with the monosulphide (Experimental, Fig. 3) and the comparison of this rate with the rates of reaction of perbenzoic acid with various dialkenyl- and alkenyl-alkyl monosulphides.[4]

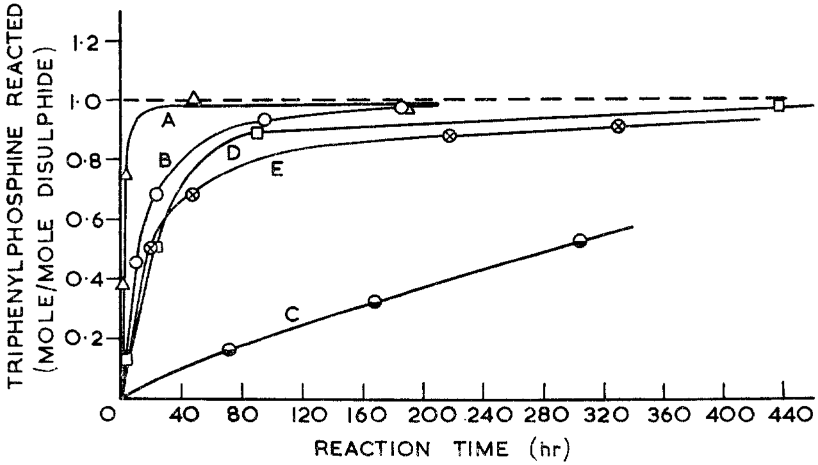


FIG. 1. Reaction of dialkenyl- and alkenyl-alkyl disulphides (0·10 mmole) with triphenylphosphine (0·20 mmole) in benzene (11·0 ml) at 80°.
(A) Diallyl-; (B) Bis-(but-2-enyl)-;
(C) Bis-(3-methylbut-2-enyl)-;
(D) Bis-(cycloHex-2-enyl)-; and
(E) Ethyl 2-methylpent-2-enyl disulphide.

Limited extensions of the above structural studies to reactions in solvents (methanol and benzene) indicate that essentially similar processes occur. Further, the reaction of Ph_3P with an equimolar mixture of diallyl disulphide and bis-(but-2-enyl) disulphide at 80° in benzene gives diallyl monosulphide and 1-methylallyl but-2-enyl monosulphide as the major products, with negligible mixed monosulphides containing both allyl and butenyl groups.

The rates of reactions (2) and (3) in the dark at 80° in benzene and in ethanol–benzene were followed by determining unreacted Ph_3P. The data (Figs. 1 and 2) confirm the stoichiometries of reactions (2) and (3) for certain of the disulphides studied and reveal the marked dependence of rate on disulphide structure and reaction medium. Increased alkyl substitution on the γ-carbon atom of the alkenyl group causes a large *decrease* in the rate of reaction (2) in benzene, e.g.: alkenyl = $CH_2{:}CH{\cdot}CH_2{—} > MeCH{:}CH{\cdot}CH_2{—} > Me_2C{:}CH{\cdot}CH_2{—}$ (Fig. 1); alkyl substitution on the α-carbon atom has much less effect, e.g.: alkenyl = $Me_2C{:}CH{\cdot}CH_2{—} \simeq Me_2C{:}CH{\cdot}CHMe{—}$ (cf. Fig. 1, curve C with Fig. 2, curve 3). The rate of reaction (3)

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[4] C. G. Moore and M. Porter, forthcoming publication.

in benzene is markedly decreased by increasing alkyl substitution on the α-carbon atom of the alkyl group, e.g. for alkenyl = $Me_2C{:}CH{\cdot}CHMe$—, alkyl = Et > t-Bu (Fig. 2). Use of ethanol–benzene in place of benzene results in a significant increase (ca. 6–10 fold) in reaction rate (Fig. 2, compare curves 1 with 2 and 3 with 4).

Finally, the stoichiometry of reaction (2) for diallyl disulphide was confirmed by GLC analysis of the products derived from the reaction in benzene at 80° and 140°; diallyl monosulphide was the sole volatile product (Experimental, Table 4). Incidental to this work, but of particular relevance to the use of Ph_3P for determining polysulphide and cyclic monosulphide structures in natural rubber–sulphur vulcanisates,[5] it was shown that the cyclic monsulphides derived from the reaction of 2,6-dimethylocta-2,6-diene with sulphur at 140°,[6] do not react with Ph_3P at 80° in benzene.

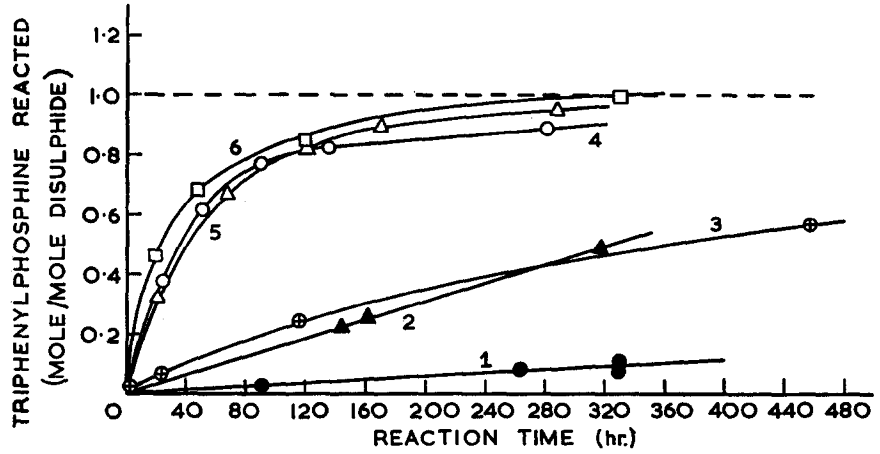
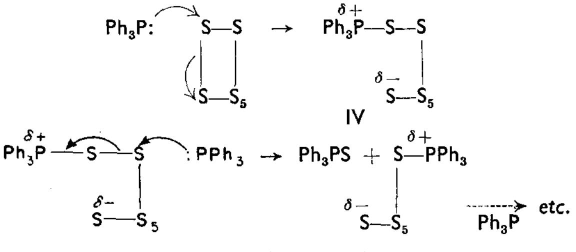


FIG. 2. Reaction of dialkenyl- and alkenyl-alkyl disulphides (0·10 mmole) with triphenylphosphine (0·20 mmole) at 80° in benzene (11·0 ml) (curves 1, 3, 5 and 6), or in a mixture of ethanol (9·0 ml)–benzene (2·0 ml) (curves 2 and 4).
Curves (1) and (2), t-Butyl 1,3-dimethylbut-2-enyl-; curves (3) and (4), Bis-(1,3-dimethylbut-2-enyl)-; curve (5), Ethyl 1,3-dimethylbut-2-enyl-; and curve (6) Bis-(2-methylpent-2-enyl) disulphide.

Mechanism of reaction of Ph_3P *with organic di- and polysulphides*

Bartlett and Meguerian[3] have shown convincingly that the anaerobic reaction of Ph_3P with elemental sulphur (S_8 ring) in benzene to give triphenylphosphine sulphide involves an initial rate determining nucleophilic displacement by the Ph_3P at an S—S bond to give the dipolar ion (IV) which then undergoes a sequence of rapid nucleophilic displacements as depicted below:



(5)

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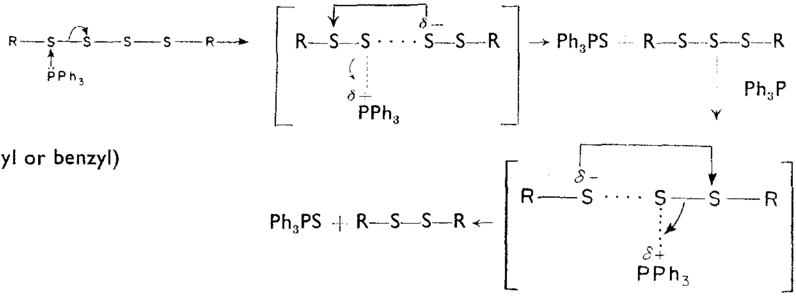
[5] C. G. Moore and B. R. Trego, *J. Appl. Polymer Sci.* 5, 299 (1961).
[6] L. Bateman, R. W. Glazebrook and C. G. Moore, *J. Chem. Soc.* 2846 (1958).

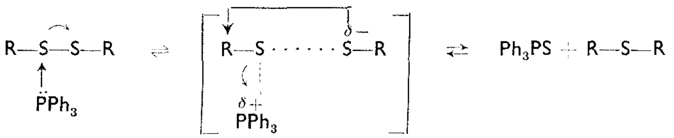
By analogy with (5), the desulphuration of dialkyl- and dibenzyl tetrasulphides by Ph_3P is represented as in reaction (6):



(R = alkyl or benzyl)

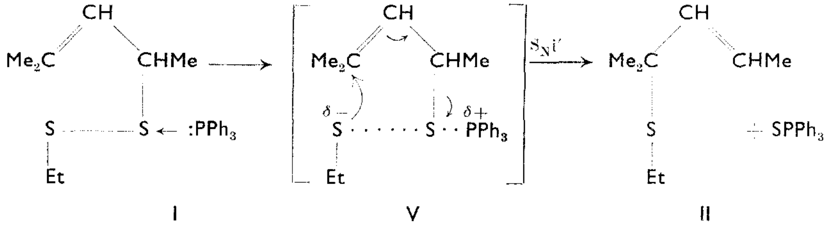
(6)

The inability of Ph_3P to desulphurize dialkyl- and diaralkyl disulphides to the corresponding monosulphides (even at 140°, Table 1 and refs.[1,2]) supports the precise nucleophilic displacements given in (6) and suggests that comparable S_N2 displacements by $\overset{\delta-}{\mathrm{RS}}$ and $\overset{\delta-}{\mathrm{RS}_x}$ species at saturated carbon, as in reaction (7), are energetically much less favourable:



(7)

Contrasting with the unreactivity of saturated disulphides, the ability of Ph_3P to desulphurize dialkenyl- and alkenyl-alkyl disulphides to monosulphides is clearly associated with the observed rearrangement of an alkenyl group during the conversion. This feature, and the fact that the co-reaction of diallyl- and bis-(but-2-enyl) disulphides with Ph_3P gives negligible mixed allyl butenyl monosulphides, are consistent with the Ph_3P undergoing a prior nucleophilic attack at sulphur in the disulphide to give an intimate ion-pair or polarized complex (e.g. V) which then reacts by an S_Ni' process as exemplified by reaction (8):



(8)

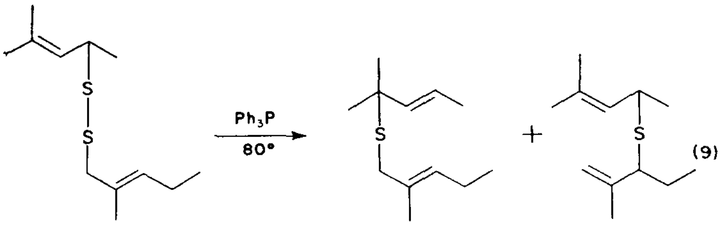
Nucleophilic substitutions of the S_Ni' type are uncommon,[7] and the present examples are particularly novel in that they occur, even in a polar environment (methanol as solvent, or absence of solvent, or in the presence of added alkenethiolate ion in methanol), with negligible competitive intervention of S_N1, S_N2 or S_Ni processes (cf. the stringent requirements for the sole occurrence of S_Ni' processes in other systems described by DeWolfe and Young).[7]

The polar mechanism now proposed is consistent with the enhancement in rate on

[7] R. H. DeWolfe and W. G. Young, *Chem. Rev.* **56**, 753 (1956) and references therein.

increasing the polar nature of the medium (Fig. 2), and the magnitude of this effect suggests that there must be only slight charge separation in (V) in the transition state, as is required for an S_Ni' process. The relatively small influence of medium on rate in these systems contrasts with the considerable rate enhancement on increasing the polar nature of the medium in the $Ph_3P—S_8$ reaction where a transition state with large charge separation is proposed;[3] it conforms, however, with the slight response in rate to change in polarity of the medium observed for the reaction of Ph_3P with episulphides[8] and with t.-alkyl peresters,[9] The rate effects observed in the systems described here reinforce the conclusions from the structural features of the reaction products that a competing S_N2 process involving a free alkenethiolate or alkanethiolate ion in the transition state (as implied previously[2]) must be of negligible importance relative to the S_Ni' process, and they suggest further that there must be minimal competition by an S_N2' process involving free thiolate ions. Certainly, both the structural and rate features of the present reactions are inconsistent with the early concept[1,10] that Ph_3P–disulphide reactions to give monosulphides involve a prior thermal homolysis of the disulphide bond. It is not implied, however, that free radical desulphurations cannot occur in these systems under certain reaction conditions, since in the comparable trialkylphosphite–dialkyl disulphide system Walling and Rabinowitz[11] have shown that when reaction conditions conducive to prior homolysis of the disulphide bond are imposed on the system (e.g., irradiation with ultra-violet light or the introduction of an external free radical source such as an organic peroxide) then dialkyl monosulphide and trialkylphosphorothionate are formed by a free radical chain process.

Finally, it is of interest to consider in the context of the S_Ni' mechanism the factors which might be responsible for the rate differences observed with the different dialkenyl- and alkenyl-alkyl disulphides (Figs. 1 and 2), and in the case of unsymmetrical dialkenyl disulphides (e.g. VI) the cause of the preferred direction of desulphuration as exemplified by the products of reaction (9).[12] The influence of disulphide structure on rate (p. 210) is equally consistent with the rate of the S_Ni' process being controlled by : (a) the electrophilicities of the sulphur atoms of the disulphide bond towards Ph_3P; (b) the steric accessibility of the incipient ion, $\overset{\delta-}{RS}$, at the γ-carbon atom of the alkenyl group; and (c) the stability, and, therefore, ease of formation, of



VI VII (75%) VIII (25%)

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[8] D. B. Denney, W. F. Goodyear and B. Goldstein, *J. Amer. Chem. Soc.* **83**, 1726 (1961).
[9] D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.* **82**, 4736 (1960).
[10] A. Schönberg, *Ber. Dtsch. Chem. Ges.* **68**, 163 (1935).
[11] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.* **81**, 1243 (1959).
[12] M. B. Evans, G. M. C. Higgins, B. Saville and A. A. Watson, *J. Chem. Soc.* in press.

the incipient ion, RS. However, the proportions of the products obtained in reaction (9) clearly suggest that (c) is the dominant factor controlling the rate and course of the reaction, since the incipient ion $\mathrm{MeCH_2{\cdot}CH{:}CMeCH_2{\cdot}\overset{\delta-}{S}}$ will be more stable than $\mathrm{Me_2C{:}CH{\cdot}CHMe{\cdot}\overset{\delta-}{S}}$, whereas were (a) or (b) rate controlling they would require (VIII) and not (VII) to be the predominant product.

EXPERIMENTAL

Materials. Pure triphenylphosphine, m.p. 80·0° (99·0% pure by iodometric assay[3]), and triphenylphosphine sulphide, m.p. 161·0°, were obtained by crystallization from absolute ethanol of samples kindly supplied by Albright and Wilson (Mfg.) Ltd. The triphenylphosphine was stored in the dark *in vacuo.* 2,6-Dimethylocta-2,6-diene, prepared by the method of Naylor,[13] had b.p. 58·0°/14 mm, n_D^{20} 1·4501 (Found: c, 86·7; H, 12·9. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%) and was 98·5% pure by GLC analysis. Diallyl, b.p. 59·6–59·7°/757 mm, n_D^{20} 1·4046, was prepared by the method of Turk and Chanan.[14] AnalaR benzene was rigorously dried by distillation over sodium wire.

Preparation of Organic Tetrasulphides

(i) *Di-t.-butyl tetrasulphide.* A solution of sulphur monochloride (0·25 mole) freshly distilled over sulphur, in carbon tetrachloride (200 ml) was added with stirring at room temp to a solution of pure 2-methylpropan-2-thiol (0·525 mole) in carbon tetrachloride (250 ml). The solvent was removed under red. press. and the residue fractionated to give the tetrasulphide (44·1 g, 70%), b.p. 76–82°/0·05–0·06 mm, n_D^{20} 1·5660 (Found: C, 39·6; H, 7·5; S, 53·0. Calc. for $C_8H_{18}S_4$: C, 39·6; H, 7·5; S, 52·9%). (ii) *Dibenzyl tetrasulphide,* prepared as in (i), m.p. 53–54° (Found: C, 54·0; H, 4·7; S, 41·0. Calc. for $C_{14}H_{14}S_4$: C, 54·15; H, 4·55; S, 41·3%). Slightly impure samples of : (iii) di-isopropyl tetrasulphide (Found: C, 32·9; H, 6·4; S, 60·8. Calc. for $C_6H_{14}S_4$: C, 33·6; H, 6·6; S, 59·8%), and (iv) di-n-butyl tetrasulphide (Found: C, 40·1; H, 7·6; S, 52·0. Calc. for $C_8H_{18}S_4$: C, 39·6; H, 7·5; S, 52·9%) were prepared by the method of Bloomfield.[15]

Preparation of Dialkenyl- and Alkenyl-alkyl Disulphides

(i) *Di-but-2-enyl disulphide via but-2-ene-1-thiol.* The thiol was prepared according to the general method of Lee, *et al.*:[16] But-2-ene-1-ol (1·1 moles), b.p. 114–120°/745 mm, 48% hydrobromic acid (140 ml) and thiourea (1·1 moles) were gently refluxed together for 30 min and the product was then cooled overnight at −20° to give crude S-but-2-enyl thiuronium bromide which was filtered off and carefully washed with cold aqueous acetone (yield, 128 g, 55%). The combined mother liquors were treated with *p*-toluene sulphonic acid (70 g, in 125 ml water) and the resultant crystalline tosylate was separated and washed with aqueous acetone (yield, 84 g 25%). The tosylate and bromide salts were combined and added to aqueous sodium hydroxide (60 g of hydroxide in 250 ml water) at room temp. After stirring the mixture for 1·5 hr, the thiol was separated by steam distillation and the distillate then washed (H_2O) and dried ($MgSO_4$) to yield the crude thiol (51 g). Two fractionations of this through a Vigreux column gave but-2-ene-1-thiol (22·4 g, 23%), b.p. 99·1–102·5°/762 mm. (Found: C, 54·6, H, 9·4; S, 36·3. Calc. for C_4H_8S: C, 54·5; H, 9·1; S, 36·4%), shown by GLC analyses to contain 97% of one component. The thiol (20 g) was dissolved in ice-cold aqueous sodium hydroxide (55 g in 250 ml water) and the resultant mercaptide then oxidized to the *disulphide* by the slow addition of 30% hydrogen peroxide (16 ml). The mixture was made just acid with glacial acetic acid, the disulphide extracted with ether and the ether solution rendered neutral by washing with aqueous potassium carbonate. Subsequent removal of the ether and distillation of the residue gave a disulphide fraction (14·1 g, 70%), b.p. 62·0–62·8°/0·01–0·03 mm, n_D^{16} 1·5386 (Found: C, 55·3; H, 8·3; S, 36·8. $C_8H_{14}S_2$ requires: C, 55·1; H, 8·1; S, 36·8%), shown by GLC analysis to contain two main components (95% and 3·8%, respectively). Infra-red spectrometric analysis indicated the major component of the disulphide to be the *trans*-but-2-enyl isomer (absorption at 960 cm^{-1}).

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[13] R. F. Naylor, *J. Chem. Soc.* 1532 (1947).
[14] A. Turk and H. Chanan, *Org. Synth.* **27**, 7 (1947).
[15] G. F. Bloomfield, *J. Chem. Soc.* 1547 (1947).
[16] D. F. Lee, B. Saville and B. R. Trego, *Chem. & Ind.* 868 (1960).

(ii) *Bis-(3-methylbut-2-enyl)disulphide via 3-methylbut-2-ene-1-thiol.* Thiol was prepared by the general method of Saville:[17] A mixture of isoprene (1 mole), thiourea (1·1 moles) and 48% hydrobromic acid (120 ml) was vigorously shaken at room temp for 15 hr and then the product was freed from unreacted diene and treated with aqueous *p*-toluenesulphonic acid (190 g in 400 ml water) to give the tosylate. This was hydrolysed with cold aqueous alkali as in (i) to give the thiol (29 g, 28%), b.p. 125·5–127°/765 mm. (Found: C, 58·8; H, 10·2; S, 31·3. Calc. for $C_5H_{10}S$: C, 58·8; H, 9·8; S, 31·4%), shown by GLC analysis to contain 99% of one component. Oxidation of the thiol as in (i) above gave the *disulphide* (80%), b.p. 87–89°/0·01–0·05 mm, n_D^{17} 1·5378 (Found: C, 59·3; H, 8·9; S, 31·8. $C_{10}H_{18}S_2$ requires: C, 59·4; H, 8·9; S, 31·7%). GLC analysis of the disulphide indicated the presence of 3 components, the area percentage of the main one being 97; infra-red spectrometric analysis showed the principal unsaturation to be trialkylethylenic.

(iii) *Ethyl 1,3-dimethylbut-2-enyl disulphide.* A mixture of 4-methylpent-3-ene-2-thiol,[17] (0·53 mole), b.p, 133·0–133·5°/754 mm, n_D^{20} 1·4741, diethyl disulphide (0·53 mole) and a basic catalyst [2 ml of a solution of the above thiol (2 g) and sodium (0·5 g) in propan-1-ol (10 ml)] was heated under partial reflux at atm press, during which ethane thiol (25 g, 0·40 mole) was distilled off through a Fenske column at a distillate temp maintained at 34·0–34·6°. The residue, after washing with water, drying ($MgSO_4$) and fractional distillation, yielded a disulphide fraction (47 g, 51%), b.p. 92·5–93·1°/10 mm, n_D^{20} 1·5176 (Found: C, 54·4; H, 9·1; S, 36·6. $C_8H_{16}S_2$ requires: C, 54·5; H, 9·1; S, 36·4%), shown by GLC analysis to contain 97·6% of the required *disulphide* and <1% of bis-(1,3-dimethylbut-2-enyl) disulphide.

(iv) *t.-Butyl 1,3-dimethylbut-2-enyl disulphide.* To a solution of 2-methylpropan-2-thiol (0·06 mole) and 4-methylpent-3-ene-2-thiol (0·048 mole) in aqueous sodium hydroxide (14 g hydroxide in 74 ml water) was added aqueous potassium ferricyanide (28 g ferricyanide in 145 ml water) at room temp. Working up the product as usual gave the *disulphide* (2·5 g, 25·5%), b.p. 55·5–56·0°/0·01 mm, n_D^{20} 1·5094 (Found: C, 59·1; H, 10·0; S, 31·4. $C_{10}H_{20}S_2$ requires: C, 58·8; H, 9·85; S, 31·35%); GLC analysis revealed a main component (99%) having the retention time anticipated for the above disulphide.[18]

Samples of the following disulphides were kindly supplied by Dr. B. Saville and Mr. A. A. Watson (details of their synthesis are reported elsewhere[12]): (v) Pure bis-(1,3-dimethylbut-2-enyl) disulphide; (vi) Bis-(2-methylpent-2-enyl) disulphide; (vii) Ethyl 2-methylpent-2-enyl disulphide. The compounds (vi) and (vii) contained 90% and 94%, respectively, of the designated methylpentenyl groups, but disulphides containing the isomeric 1-ethyl-2-methylallyl group were minor contaminants. (viii) Pure bis(cyclohex-2-enyl) disulphide, b.p. 128–130°/0·1 mm, n_D^{20} 1·5854 (Found: C, 63·6; H, 8·0; S, 28·4. Calc. for $C_{12}H_{18}S_2$: C, 63·7; H, 8·0; S, 28·3%), was obtained by the hydrogen peroxide oxidation of the corresponding sodium alkenethiolate.

Preparation of bis-(but-2-enyl)monosulphide. 1-Chlorobut-2-ene, prepared by the method of Hatch and Nesbitt,[19] had b.p. 81·2–83·2°/759 mm, n_D^{20} 1·4338 (Found: C, 53·0; H, 8·0; Cl, 38·8; Calc. for C_4H_7Cl: C, 53·0; H, 7·8; Cl, 39·2%) and contained on the basis of GLC and infra-red spectrometric analyses 90·4% of the *trans* and 9·6% of the *cis* isomers. The chlorobutene (0·056 mole) was added to a stirred solution of but-2-ene-1-thiol (0·056 mole) and sodium (0·069 g atom) in ethanol (40 ml) and the reactants then heated just to reflux. The product was added to water (50 ml) and the organic phase extracted with ether (3 × 20 ml), washed with water, dried ($MgSO_4$) and distilled to give the monosulphide (71%), b.p. 69·0–70·5°/10–11 mm, n_D^{20} 1·4965 (Found: C, 67·4; H, 10·1; S, 22·5. Calc. for $C_8H_{14}S$: C, 67·6; H, 9·9; S, 22·5%), which was shown by GLC and infra-red spectrometric analysis to contain 10% of the isomeric 1-methylallyl but-2-enyl monosulphide.

All other organic sulphur compounds described here were commercial samples purified by fractional distillation or crystallization.

Reaction of Triphenylphosphine with Organic Tetrasulphides in Benzene

General procedure. 5·0 ml Aliquots of standard solutions of the tetrasulphides (ca. 1 mmole) in dry benzene (100·0 ml) were transferred to reaction tubes, using benzene (1·0 ml) to assist transfer. A weighed amount of triphenylphosphine (ca. 1 mole per g atom of sulphur in the tetrasulphide) was washed into each tube by means of benzene (5·0 ml) and the solutions then degassed once, sealed

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[17] B. Saville, *J. Chem. Soc.* in press.

[18] M. B. Evans and J. F. Smith, *J. Chromat.* **5**, 300 (1961).

[19] L. F. Hatch and S. S. Nesbitt, *J. Amer. Chem. Soc.* **72**, 727 (1950).

in vacuo and heated in the dark at either 80·0° or 140·0° for specified times. Unreacted triphenylphosphine was determined by the rapid addition to the solution of a known and excess volume of standard iodine solution (ca. 4M/100 of iodine in benzene containing 20% ethanol (95%) and 5 g pyridine per litre) and estimating the excess iodine by titration against a freshly prepared standard solution of triphenylphosphine in benzene (ca. 4M/300).[3] Corrections were applied for the loss of triphenylphosphine due to its autoxidation during the reaction and subsequent analysis procedure; such loss (amounting to 2·0–3·7%, depending upon reaction conditions) was allowed for by conducting control experiments in which benzene solutions of triphenylphosphine were heated under the specified reaction conditions. The validity of the analytical procedure for determining unreacted triphenylphosphine in the reaction products was checked as follows: It was shown that iodine does not react with di-t.-butyl tetrasulphide nor catalyse its reaction with triphenylphosphine at room temp by adding a known weight of triphenylphosphine to a solution of the tetrasulphide in a known and excess volume of standard iodine solution and back titrating the excess iodine as described above; 100% of the incident triphenylphosphine and iodine were determined. Data are given in Table 1 for the percentage of sulphur in the tetrasulphides which is removed by the triphenylphosphine.

Reaction of Triphenylphosphine with Dialkenyl- and Alkenyl-alkyl Disulphides

(A) *Structural studies of the reaction products*

The general procedure used is illustrated by reference to:

(i) *Reaction of triphenylphosphine with bis-*(1,3-*dimethylbut*-2-*enyl*) *disulphide.* A mixture of triphenylphosphine (26·6 mmoles) and the disulphide (17 mmoles) was sealed *in vacuo* and heated in the dark for 72 hr at 80·0°. The product was separated by filtration into a crystalline portion and a liquid. The former was washed with ether (8ml) and then crystallized from ethanol to give triphenylphosphine sulphide (74%), m.p. 161·5–162·0° and mixed m.p. with authentic compound 161·0–162·0° (lit. m.p. 160·5–161·5°). Careful fractional distillation of the ether solution of the filtrate gave a di-methylpentenyl monosulphide (11·1 mmoles, 65%), b.p. 47·0°/0·01 mm. The analytical data and structural features of this and other monosulphides obtained in comparable manner are recorded in Tables 2 and 3. Structural resolution of the monosulphides was achieved by a combination of GLC and infra-red spectrometric analyses of the reaction products and of authentic monosulphides prepared as described here or elsewhere.[12,17] Details are given in Table 3 of the columns and their operating conditions used in the GLC analyses. For the infra-red analyses, mono- and disulphides were examined on a Hilger H800 double beam spectrometer between 4000-650 cm^{-1} as 100 μ films and as standard solutions in carbon disulphide.

(ii) *Reaction of triphenylphosphine with bis-*(1,3-*dimethylbut*-2-*enyl*) *disulphide in methanol.* (a) A mixture of triphenylphosphine (26·6 mmole), the disulphide (17·3 mmoles) and absolute methanol (10 ml) was heated *in vacuo* for 72 hr at 80·0° and the product then fractionated as described in (i) above to give a monosulphide fraction (9·8 mmoles, 57%), b.p. 49·8–50·0/0·01 mm. (Found: C, 72·65; H, 11·25; S, 16·3. Calc. for $C_{12}H_{22}S$: C, 72·65; H, 11·2; S, 16·15%) which on the basis of GLC analysis contained 96% of 1,1-dimethylbut-2-enyl 1,3-dimethylbut-2-enyl monosulphide (IX) and ca. 3% of bis-(1,3-dimethylbut-2-enyl) monosulphide (X).

(b) Treatment of the reactants as in (a) above, but in the added presence of the sodium salt of 4-methylpent-3-ene-2-thiol (0·17 mmoles), gave a monosulphide fraction (10·1 mmoles, 58%) (Found: C, 72·3; H, 11·0; S, 16·4%) which on the basis of GLC analysis contained 95% of (IX) and 4% of (X).

(iii) *Reaction of triphenylphosphine with diallyl disulphide in benzene.* Aliquots of a solution of triphenylphosphine (6·84 mmoles) and the disulphide (3·42 mmoles) in benzene (12·03 g) were sealed *in vacuo* after prior degassing and then heated in the dark under the conditions specified in Table 4. The reaction products were analysed for diallyl mono- and disulphides by GLC examination on a 20% wt/wt polyethylene glycol/celite column operating at 100° using cyclopentanol as an internal standard, and for diallyl by GLC examination on a squalane/celite column at room temp, with 75% hydrogen/25% nitrogen as carrier gas. The data indicate that diallyl monosulphide is the sole reaction product, diallyl and diallyl disulphide being completely absent (Table 4).

(iv) *Reaction of triphenylphosphine with a mixture of diallyl disulphide and bis-*(*but*-2-*enyl*) *disulphide in benzene.* A mixture of the disulphides (1·5 mmoles of each) and triphenylphosphine (3·8 mmoles) in benzene (5·0 ml) was sealed *in vacuo* after one degassing and then heated for 232 hr at 80·0° in the dark. GLC analysis of the reaction product indicated diallyl monosulphide and 1-methylallyl but-2-enyl monosulphide to be the major components; disulphides were absent and the total concentration of unsymmetrical monosulphides (e.g. allyl but-2-enyl monosulphide) cannot exceed 2% of that of diallyl monosulphide.

TABLE 4. REACTION OF TRIPHENYLPHOSPHINE (2 MOL) WITH DIALLYL DISULPHIDE (1 MOLE) IN BENZENE. (DISULPHIDE CONCENTRATION: 0·22 MOLE. $l.^{-1}$)

Time (hr)	Temp (°C)	Diallyl Monosulphide (mole. $l.^{-1}$) (replicate chromatograms)
1·0	80·0	0·22, 0·21, 0·22
3·0	80·0	0·23, 0·23, 0·22
7·0	80·0	0·22, 0·22, 0·21
24·0	140·0	0·18, 0·20, 0·21

(v) *Reaction of triphenylphosphine with t.-butyl* 1,3-*dimethylbut*-2-*enyl disulphide.* A mixture of triphenylphosphine (17 mmoles) and the disulphide (2·5 g, 12 mmoles) was heated *in vacuo* for 480 hr at 80° and the product fractionated as in (i) above to give: (a) a fraction (0·67 g) b.p. 31·5–47·6°/12 mm which was predominantly (70% by infra-red analysis) t.-butyl 1,1-dimethylbut-2-enyl monosulphide (Found: C, 69·1; H, 12·0; S, 19·5. Calc. for $C_{10}H_{20}S$: C, 69·7; H, 11·7; S, 18·6%) admixed with some unreacted disulphide; and (b) a fraction (0·36 g) b.p. 92°/12 mm which was mainly unreacted disulphide (82% by GLC analysis). A considerable amount of unreacted disulphide appeared to be retained in the distillation residue.

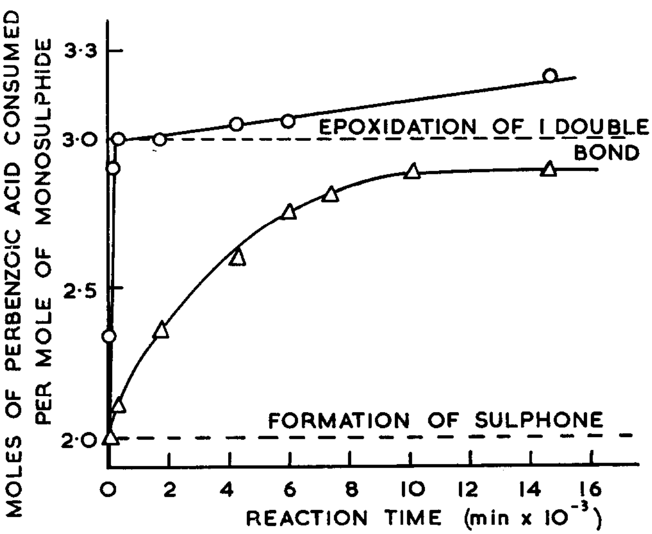

FIG. 3. Reaction of perbenzoic acid in benzene at 20·0° with the monosulphides derived from the interaction of triphenylphosphine with organic disulphides at 80°.

–○–○–○–, Monosulphide of Expt. 3 Table 2.
– – – –, Monosulphide of Expt. 1 Table 2.

(B) *Rate studies in benzene solutions and in ethanol–benzene solutions*

The rate of reaction of triphenylphosphine (2 moles) with the dialkenyl- or alkenyl-alkyl disulphide (1 mole) at 80·0° in either benzene or in ethanol–benzene solutions was studied using the same procedure as described above for the triphenylphosphine–organic tetrasulphide rate studies (*vide* p. 216). The data are presented in Figs. 1 and 2 which also detail the reactant concentrations.

Reaction of Triphenylphosphine with Other Organic Sulphur Compounds

(i) *Dibenzyl disulphide.* No reaction occurred when the disulphide (1 mole) and triphenylphosphine (2 moles) were heated together in benzene for long periods at either 80° or 140° under concentration conditions identical with those specified in Fig. 1.

(ii) *Cyclic monosulphides derived from the interaction of sulphur with* 2,6-*dimethylocta*-2,6-*diene at* 140°. Heating a mixture of sulphur (10 g) and the diene (100 g) for 5 hr at 140° *in vacuo* and subsequent removal of unreacted sulphur (4 g) followed by fractional distillation of the liquid reaction product gave a volatile fraction (2·17 g), b.p. 75–86°/12 mm, n_D^{20} 1·4910 (Found: C, 75·6; H, 11·6; S, 12·4%) shown by spectrometric (infra-red and ultra-violet) and GLC analyses to contain the cyclic monosulphides specified in ref. 6 as the major components together with alloöcimene and unreacted diene. A solution of the above cyclic monosulphide fraction (44·2 mg) and triphenylphosphine (0·20 mmole) in benzene (10·0 ml) was heated *in vacuo* for 96 hr at 80°. Subsequent iodometric assay of the solution indicated that <1% of the triphenylphosphine had reacted.

Rate of Perbenzoic Acid Reaction with Monosulphides derived from the Interaction of Triphenylphosphine with Dialkenyl- and Alkenyl-alkyl Disulphides

The rates of reaction of standard benzene solutions of perbenzoic acid with the monosulphide products obtained in Expts. 1 and 3 (Table 2) were measured using the method of Moore and Porter.[4] The rate curves (Fig. 3) are consistent with the structures of the olefinic groups of the monosulphides as specified in Table 3, Expts. 1 and 3, respectively.

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