813. *The Reaction of Dialkenyl and Alkenyl Alkyl Disulphides with Triethyl Phosphite and of Dialkenyl Disulphides with Cyanide Ion.*

By C. G. Moore and B. R. Trego.

Dialkenyl and alkenyl alkyl disulphides react with triethyl phosphite to give monosulphides having mainly an allylically rearranged alkenyl group. Dialkenyl disulphides react with cyanide ion to give monosulphides; in the case of dibut-2-enyl disulphide the alkenyl groups are mostly unrearranged, although a significant amount of allylic rearrangement is also apparent.

We reported recently the reactions of dialkenyl and alkenyl alkyl disulphides with triphenylphosphine[1] and of dialkenyl disulphides with alkenethiolate ions.[2] Limited extensions of the above studies to the reaction of the disulphides with the nucleophils, triethyl phosphite and cyanide ion, are now reported.

Reaction of Disulphides with Triethyl Phosphite.—Reaction of diallyl disulphide with triethyl phosphite at 80° *in vacuo* in the dark yields a monosulphide fraction containing diallyl monosulphide (97 wt. %) and less than 0·5 wt. % of allyl ethyl monosulphide, indicating that the reaction predominantly follows the course:

$$(\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}S})_2 + (\mathrm{EtO})_3\mathrm{P} \xrightarrow{80^\circ} (\mathrm{CH_2{:}CH{\cdot}CH_2})_2\mathrm{S} + (\mathrm{EtO})_3\mathrm{PS} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

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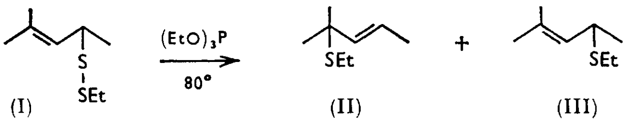
[1] Moore and Trego, *Tetrahedron*, 1962, **18**, 205.

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

Comparable reaction of ethyl 1,3-dimethylbut-2-enyl disulphide (I) with the phosphite gives a monosulphide fraction comprising the sulphides (II) (96·4%) and (III) (2·9%), but no diethyl monosulphide:



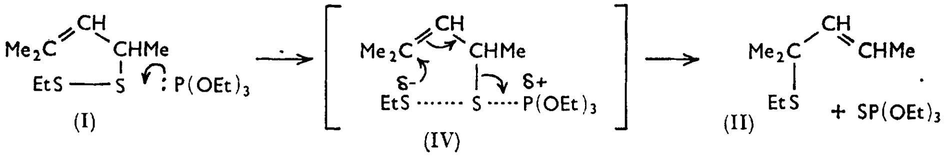
. . . . (2)

These reactions contrast with the thermal (non-homolytic) reactions of dialkyl disulphides with trialkyl phosphites which predominantly follow the course:

$$\mathrm{RS{\cdot}SR + (R'O)_3P \longrightarrow [RS{\cdot}\overset{+}{P}(OR')_3\,{}^{-}SR] \longrightarrow RS{\cdot}P(O)(OR')_2 + RSR'} \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

involving fission of an alkyl-oxygen bond (R'–O) in the phosphite by an alkanethiolate ion (RS^-).[3,4]

Isolation of the sulphide (II) as the major product of reaction (2) indicates that an allylic rearrangement of an alkenyl group accompanies the desulphuration of disulphides by triethyl phosphite, as is also found for the desulphuration of disulphides by triphenylphosphine[1] and we propose therefore that both processes involve a common mechanism in which an intermediate ion-pair (*e.g.*, IV), formed by nucleophilic attack of phosphorus on sulphur undergoes an S_Ni' reaction as illustrated (cf. ref. 1):



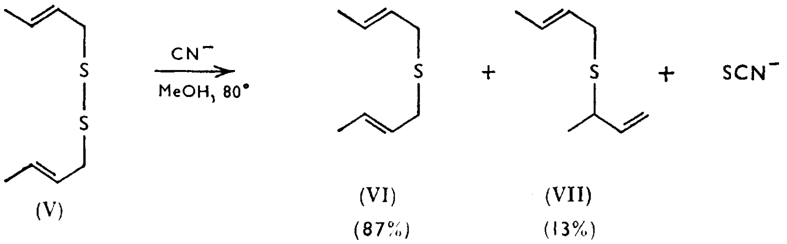
. . (4)

Under reaction conditions conducive to homolysis of the S–S bond in disulphides, trialkyl phosphites have been shown[4] to react with dialkyl disulphides by a free-radical chain process according to the stoicheiometry:

$$\mathrm{RS{\cdot}SR + (R'O)_3P \longrightarrow RSR + (R'O)_3PS} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

We discount reactions (1) and (2) occurring by this free-radical mechanism since it should lead in the case of the reaction of compound (I) with triethylphosphite, not only to the rearranged sulphide (II), but also to substantial amounts of diethyl sulphide, the sulphide (III), and two isomeric di(methylpentenyl) sulphides, which is contrary to fact.

Reaction of Dialkenyl Disulphides with Cyanide Ion.—Diallyl disulphide reacts with cyanide ion in methanol at 80° to give diallyl monosulphide; and di(but-2-enyl) disulphide (V) reacts similarly to give an 80% yield of a mixture of the isomeric monosulphides (VI) (87%) and (VII) (13%):



. . (6)

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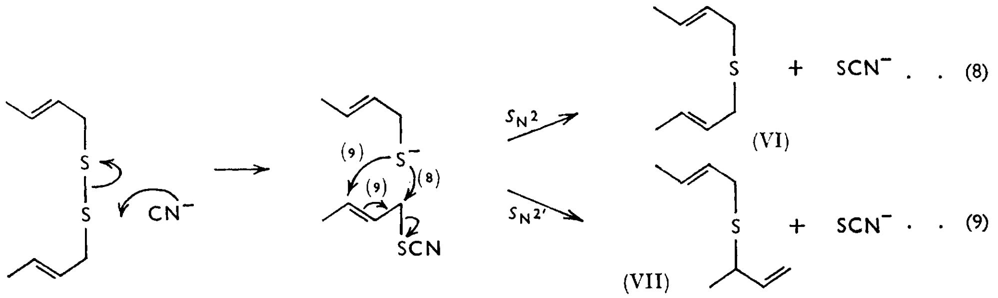
[3] Jacobson, Harvey, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 6064.
[4] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243.

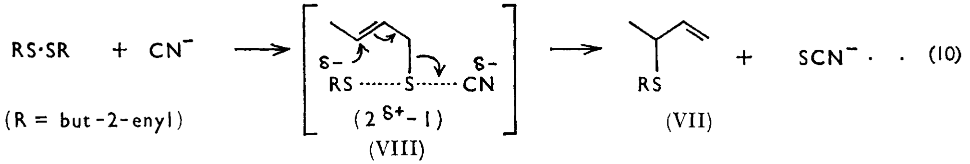
These desulphurations may be explained by an initial reversible S_N2 displacement at sulphur:[5]

$$RS{\cdot}SR + {}^{-}CN \rightleftharpoons RSCN + RS^{-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

followed by attack of the alkenethiolate ion (RS^-) at the α- or γ-carbon atoms of the allylic system in the alkenyl thiocyanate (RSCN):



The predominant formation of the unrearranged monosulphide (VI) is consistent with the known marked preference for S_N2 over S_N2' reactions by charged nucleophils at allylic systems (*e.g.*, rate ratio of 28,000 : 1 for the S_N2 and S_N2' reactions of bromide ion with but-2-enyl bromide).[6,7] The unusual feature of reaction (6) is the relatively high yield of rearranged monosulphide (VII) which is inconsistent with known rate ratios for S_N2 and S_N2' reactions of but-2-enyl systems.[7] It is suggested, therefore, that the major route to the product (VII) is, not reaction (9), but an S_Ni' reaction of the polar intermediate (VIII):



as invoked similarly for the formation of monosulphides with an allylically rearranged alkenyl group from the interaction of dialkenyl disulphides with triphenylphosphine[1] and alkenethiolate ions[2] (cf. also reaction 4).

EXPERIMENTAL

Materials.—The organic sulphur compounds were prepared as described elsewhere.[1] Triethyl phosphite had b. p. 153·5—155°/754 mm., n_D^{20} 1·4120 (Found: C, 43·1; H, 9·15. Calc. for $C_6H_{15}O_3P$: C, 43·4; H, 9·0%

Reaction of Disulphides with Triethyl Phosphite.—(1) *Diallyl disulphide.* A mixture of the disulphide (34·2 mmoles) and the phosphite (51 mmoles) was sealed *in vacuo* after one degassing and then heated for 19·5 hr. at 80° in the dark. The product was transferred to water and steam-distilled and the organic phase of the distillate was separated, washed with water, dried ($MgSO_4$), and fractionally distilled to give a sulphide (2·78 g.), b. p. 139—141°/753 mm., n_D^{20} 1·4874 (Found: C, 63·4; H, 9·1; S, 27·4. Calc. for $C_6H_{10}S$: C, 63·1; H, 8·85; S, 28·05%), which was shown by gas–liquid chromatography to contain diallyl monosulphide (97 wt. %) and <0·5 wt. % of allyl ethyl monosulphide; on this basis the yield of diallyl monosulphide was 76%.

(2) 1,3-*Dimethylbut-2-enyl ethyl disulphide* (I). A mixture of the disulphide (22·6 mmoles) and the phosphite (36 mmoles) was heated as in (1) for 48 hr. and the product then treated with dilute ∼N/50-hydrochloric acid (70 ml.) and steam-distilled. Working up the organic phase

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[5] Parker and Kharasch, *Chem. Rev.*, 1959, **59**, 583.

[6] England and Hughes, *Nature*, 1951, **168**, 1002; England, *J.*, 1955, 1615.

[7] DeWolfe and Young, *Chem. Rev.*, 1956, **56**, 753 and references therein.

as in (1) gave a sulphide fraction (1·84 g.), b. p. 52·5—55·0°/13 mm., n_D^{20} 1·4728 (Found: C, 66·2; H, 11·5; S, 22·7. Calc. for $C_8H_{16}S$: C, 66·6; H, 11·2; S, 22·2%), shown by gas–liquid chromatography and infrared spectrometry[1] to contain (II) (96·4%) and 1,3-dimethylbut-2-enyl ethyl monosulphide (III) (2·9%) but to be devoid of diethyl monosulphide. The total yield of (II) and (III) was 57%.

Reaction of Disulphides with Cyanide Ion.—(1) *Diallyl disulphide.* A mixture of the disulphide (27 mmoles) and potassium cyanide (55 mmoles) in dry methanol (100 ml.) was sealed *in vacuo* after degassing and heated for 118 hr. at 80°. The product was added to water (100 ml.), extracted with light petroleum (b. p. 30—40°; 3 × 50 ml.), dried ($MgSO_4$), and distilled to give a first fraction (1·55 g.), b. p. 130—135°/760 mm., n_D^{20} 1·4870 (Found: C, 62·9; H, 9·0; S, 28·1. Calc. for $C_6H_{10}S$: C, 63·1; H, 8·85; S, 28·05%), shown by gas–liquid chromatography to contain 99 wt. % of diallyl monosulphide (50% yield).

(2) *Di(but-2-enyl) disulphide* (V). A mixture of the disulphide (29 mmoles) and potassium cyanide (55 mmoles) in dry methanol (100 ml.) was heated as in (1) for 268 hr. and the product was worked up as in (1), to give a sulphide fraction (3·3 g.), b. p. 57—70°/10 mm., n_D^{20} 1·4966 (Found: C, 67·5; H, 9·9; S, 22·5. Calc. for $C_8H_{14}S$: C, 67·5; H, 9·95; S, 22·55%), shown by gas–liquid chromatography and infrared spectrometry to contain di(but-2-enyl) monosulphide (VI) (87%) and 1-methylallyl but-2-enyl monosulphide (VII) (13%). The total yield of (VI) and (VII) was 80%.

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