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THE REACTION OF ALKENETHIOLATE IONS WITH DIALKENYL DISULPHIDES TO GIVE DIALKENYL MONOSULPHIDES

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Abstract—Dialkenyl monosulphide formation accompanies thiolate ion-disulphide interchange during the reaction of sodium alkenethiolates with dialkenyl disulphides at 80° in ethanol. Additional products are organic and inorganic polysulphides and hydrogen sulphide; polysulphide formation can be completely suppressed by use of a large excess of thiol over thiolate ion and disulphide. When identical alkenyl groups are present in the reactants, the monosulphide contains mainly the same alkenyl groups as its precursors, but some allylic rearrangement is also evident. The products are explained by S_N2 reactions of alkenethiolate or alkeneperthiolate ions at S—S bonds with the simultaneous operation of S_N2, S_N2' and S_Ni' reactions of alkenethiolate or incipient alkenethiolate ions at the carbon atoms of the allylic system.

DURING the preparation of the unsymmetrical dialkenyl disulphide, A_1SSB_1 (A_1= $Me_2C{:}CH{\cdot}CHMe$—, B_1=$MeCH_2{\cdot}CH{:}CMeCH_2$—) by the interchange of the corresponding symmetrical disulphides, A_1SSA_1 and B_1SSB_1, catalysed by A_1S^- ion:

$$A_1SSA_1 + B_1SSB_1 \underset{\text{in MeOH}}{\overset{A_1S^-}{\rightleftarrows}} 2A_1SSB_1 \tag{1}$$

it was observed that a complex mixture of *monosulphides* was formed in amount comparable with that of the disulphides. These monosulphides contained mainly the alkenyl groups of the original reactants but also their iso-allylic counterparts (Experimental, Table 2).

This novel formation of monosulphides which accompanies an interchange process of the type:

$$R'S^- + RSSR \rightleftarrows R'SSR + RS^- \rightleftarrows R'SSR + RS^- \tag{2}$$

has prompted a systematic examination of the products derived from the reaction of organic disulphides with thiolate ions of like hydrocarbon structure. By this means the disulphide–thiolate ion exchange process:

$$RS^- + RSSR \rightleftarrows RSSR + RS^- \tag{3}$$

is self-regenerative and thus simplifies the analysis of the other reaction products. Table 1 details the products obtained from the interaction of representative dialkenyl, dialkyl and diaryl disulphides with their corresponding thiolate ions in boiling ethanolic solution under nitrogen. For certain systems control experiments were also performed in which the disulphide or thiol was caused to react with ethanolic sodium ethoxide in the absence of thiolate ion or disulphide, respectively.

The formation of organic monosulphides is seen to be restricted to systems in which R = alkenyl; where R = phenyl and n-butyl the reactants were recovered unchanged. With regard to the former systems ($R =$ alkenyl) additional products included hydrogen sulphide (Expts 1, 4, 5 and 7); organic and sodium polysulphides (Expts 1, 4 and 5); and sodium hydrosulphide (Expt 7). The control experiments 2 and 6 yielded organic monosulphides, but neither in these experiments nor in Expt 3 were inorganic sulphides formed.

The dialkenyl monosulphides contain predominantly the same alkenyl groups as present in the reactants, but monosulphides are also formed in which one of the alkenyl groups is iso-allylic with respect to the original alkenyl group (see Expts 1, 2, 4, 5 and 7). It is significant that monosulphide formation is much more rapid in the but-2-enyl system than in the 1,3-dimethylbut-2-enyl system. Independent experiments proved that both the unrearranged and the rearranged dialkenyl monosulphides result directly from reaction of the disulphides with alkenethiolate or ethoxide ions and not from subsequent isomerization by these ions of an initially formed dialkenyl monosulphide; thus, both bis-(1,3-dimethylbut-2-enyl) sulphide and 1,3-dimethylbut-2-enyl 1,1-dimethylbut-2-enyl sulphide (RSR and RSR*, respectively in Expts 5, 6 and 7) were stable in the reaction environment prevailing in Expt 5. For the systems of Table 1 there was no evidence for allylic rearrangement of the alkenyl groups in the organic di- and polysulphides, or in the thiol when this was present in excess.

Discussion of the reactions and their mechanistic interpretation

The formation of dialkenyl mono- and polysulphides during the interaction of dialkenyl disulphides with alkenethiolate or ethoxide ions is novel, particularly regarding the partial occurrence of an allylic rearrangement. Monosulphide formation has hitherto only been observed in alkaline solutions of specially constituted disulphides, e.g., cystine yields lanthionine on refluxing with aqueous sodium carbonate,[1] and this is associated with the special feature of the hydrogen atom β to sulphur being acidic and readily ionizable.[2,3]

In the present systems the effective nucleophil responsible for monosulphide formation is the alkenethiolate ion, RS^- which, under circumstances where thiol is in excess over ethoxide ion, results from the equilibrium:

$$RSH + EtO^- \rightleftarrows EtOH + RS^- \tag{4}$$

and from the reaction:

$$RSSR + EtO^- \rightarrow RSOEt + RS^- \tag{5}$$

when the thiol concentration is low, or when thiol is absent as in Expts 2 and 6. When thiol is in considerable excess, as in Expt 7, the *unrearranged* dialkenyl monosulphide results from an S_N2 displacement at the saturated α-carbon atom of the allylic system:

$$RS^- + R{-}S{-}S{-}R \rightarrow RSR + RSS^- \tag{6}$$

releasing the alkenedithiolate ion (RSS^-) which reacts thus:

$$RSS^- + R{-}SH \rightarrow RSSR + HS^- \tag{7}$$

$$HS^- + EtOH \rightarrow H_2S + EtO^- \tag{8}$$

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[1] M. J. Horn, D. B. Jones and S. J. Ringel, *J. Biol. Chem.* **138,** 141 (1941).

[2] D. S. Tarbell and D. P. Harnish, *Chem. Rev.* **49,** 1 (1951).

[3] J. M. Swan, *Nature, Lond.* **179,** 965 (1957).

TABLE 1. REACTION OF DISULPHIDES WITH THIOLATE IONS IN BOILING ETHANOL UNDER NITROGEN IN PRESENCE OR ABSENCE OF EXCESS THIOL

Experiment No.	System (R=)	Reaction Time hr	Concentration of reactants in ethanol (mole (mole l^{-1})			Recovery of sulphidic material (%)	Organic sulphidic products (wt. %)[c]					
			RSH	RSSR	NaOEt		RSR	RSR*[a]	RSSR	RS_3R[b]	RSH	Unknown components
1	but-2-enyl	1·5	1·0	1·0	0·9	—	80	15	5	—	trace	0
2	but-2-enyl	1·5	0	1·0	0·9	—	83	13	4	—	0	0
3	but-2-enyl	1·5	1·0	0	0·9	—	0	0	0	0	100	0
4	but-2-enyl	1·5	1·0	1·0	0·1	87	42·6	5·8	25·6	22·5	0·5	3·0
5	1,3-dimethylbut-2-enyl	17·0	1·0	1·0	0·1	91	31·4	1·1	34·7	24·1	1·5	7·2
6	1,3-dimethylbut-2-enyl	17·0	0	1·0	0·1	91	1	0	93	0	0	6
7	1,3-dimethylbut-2-enyl	34·0	10·0	0·5	0·1	92	9·8	4·2	14·2	0	71·3	0·5
8	phenyl	24·0	1·0	1·0	0·1	100	—	Reactants	recovered	unchanged	—	—
9	n-butyl	24·0	1·0	1·0	0·1	100	—	Reactants	recovered	unchanged	—	—

[a] R* denotes the isoallylic counterpart of R; e.g. R* = 1-methylprop-2-enyl when R = but-2-enyl.

[b] Designated as trisulphide and calculated from H_2S produced on hydrogenolysis of the sulphidic product by $LiAlH_4$; small quantities of higher polysulphides may be present.

[c] In reactions 1 to 3, weight % refers to relative proportions of products excluding polysulphide which was not determined.

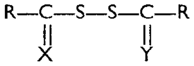
to give inorganic hydrosulphide ion and H_2S. In Expts 1, 4 and 5 where thiol is not in great excess over ethoxide ion and disulphide, the following additional reactions occur giving organic and inorganic polysulphides in addition to dialkenyl monosulphides:

$$\mathrm{RSS^- + RSSR \rightarrow RS_3R + RS^-} \qquad (9)$$

$$\mathrm{RS^- + RS_3R \rightarrow RSR + RS_3^-} \qquad (10)$$

$$\mathrm{RS^- + RS_x^- \rightarrow RSSR + S_{x-1}^{--}} \qquad (11)$$

S_N2 displacement of perthioanions at carbon have been realized previously only when the carbon atom is strongly electrophilic due to the attachment of powerful electron-withdrawing substituents as in I (X and Y = S, O or N);



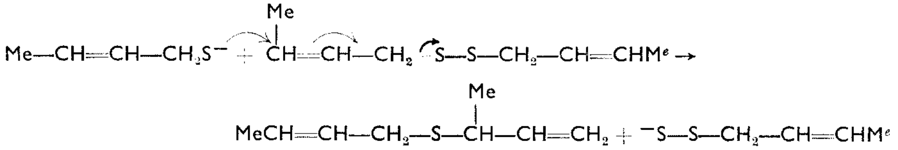
$$\mathrm{R{-}\underset{\underset{X}{\|}}{C}{-}S{-}S{-}\underset{\underset{Y}{\|}}{C}{-}R}$$

(R = aryl, alkylamino, dialkylamino, alkoxy, etc.)

I

and when the displacing anion is not readily polarizable (e.g. oxy anions).[2,4] The S_N2 displacements of perthiolate ions by alkenethiolate ions at the saturated carbon atom of allylic systems (reactions 6 and 10) seem reasonable on the following grounds: (i) the thiolate ion is a very strong nucleophil for saturated carbon;[5] (ii) perthiolate ions are good leaving groups as evidenced by facile hydrolysis of perthiolesters[6] and by the fact that B_1SS^- is displaced from B_1SSSB_1 (where B_1=MeCH$_2$·CH:CMeCH$_2$—) by Me_2CHS^- at least 650 times faster than B_1S^- is displaced from B_1SSB_1 under identical conditions;[7] and (iii) S_N2 processes at saturated carbon are greatly facilitated when the latter is part of an allylic system,[8,9] for example, the S_N2 reaction of ethoxide ion with but-2-enyl chloride is 95 times faster than that of n-butyl chloride.[10] The more rapid monosulphide formation in the bis-butenyl disulphide system than in the bis-(1,3-dimethylbut-2-enyl) disulphide system (cf. Expts 4 and 5) is consistent with the S_N2 processes now proposed, since methyl substitution at the α-carbon atom in the latter system will sterically hinder attack by thiolate ion. Further evidence of this effect is the observation (Table 2) that B_1SSB_1 (B_1=MeCH$_2$·CH:CMeCH$_2$—) is consumed more rapidly than A_1SSA_1 (A_1=Me$_2$C:CH·CHMe—) to form monosulphides in which the B_1 structure predominates.

With regard to the mechanism of formation of the dialkenyl monosulphides containing an allylically rearranged group (RSR* of Table 1) it is significant that the ratio of normal to rearranged monosulphides is between 28:1 and ca. 2:1, depending on the disulphide and proportions of reactants (Table 1, Expts 1, 2, 4, 5 and 7). An S_N2' process of the type:



$$\mathrm{Me{-}CH{=}CH{-}CH_2S^- + \overset{\overset{Me}{|}}{C}H{=}CH{-}CH_2{-}S{-}S{-}CH_2{-}CH{=}CHM^e \rightarrow}$$

$$\mathrm{MeCH{=}CH{-}CH_2{-}S{-}\overset{\overset{Me}{|}}{C}H{-}CH{=}CH_2 + {}^-S{-}S{-}CH_2{-}CH{=}CHM^e} \qquad (12)$$

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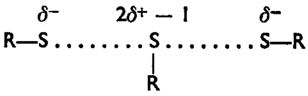
[4] C. G. Moore, B. Saville and A. A. Watson, *J. Appl. Polymer Sci.* **3**, 373 (1960).
[5] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.* 3331 (1952).
[6] H. Böhme and G. Zinner, *Liebigs Ann.* **585**, 142 (1954).
[7] B. Saville, Unpublished work.
[8] E. D. Hughes, *Trans. Faraday Soc.* **37**, 603 (1941).
[9] R. H. DeWolfe and W. G. Young, *Chem. Rev.* **56**, 753 (1956).
[10] C. A. Vernon, *J. Chem. Soc.* 4462 (1954).

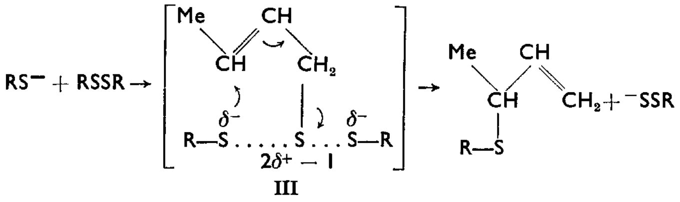
is an obvious route to the rearranged monosulphides. It cannot, however, be the sole route, because of the large proportions of rearranged monosulphides formed and because S_N2' reactions in allylic systems are much slower than the corresponding S_N2 reactions (e.g. rate ratio of 1:28,000 for the S_N2' and S_N2 reactions of bromide ion with but-2-enyl bromide).[11],[12] The following additional and more important route is therefore proposed. The thiolate ion-disulphide interchange reaction (3), which must be proceeding throughout the course of the reactions now described, will involve a transition state (II),[13]



$$\overset{\delta-}{R{-}S}\cdots\cdots\overset{2\delta+\,-\,1}{\underset{R}{S}}\cdots\cdots\overset{\delta-}{S{-}R}$$

II

which is susceptible to an S_Ni' reaction when R = alkenyl, as an alternative to the interchange process, as illustrated below:



(13)

R = but-2-enyl (=RSR*)

Reaction (13) is formally similar to the S_Ni' process proposed for the desulphuration of dialkenyl disulphides by triphenylphosphine to give a dialkenyl monosulphide containing an allylically rearranged alkenyl group.[14,15]

Finally, brief comment is made on the observed influence of structure and concentration of the reactants on the relative proportions of the unrearranged and rearranged monosulphides (RSR and RSR*, respectively). Regarding structural influences, no unequivocal explanation can yet be given for the fact that the rate response of the S_Ni' process to structural changes in the alkenyl group is much greater than that of the S_N2 process; (see[9,15] for discussion of possible rate-determining factors in S_N2 and S_Ni' processes, respectively). Concerning concentration effects, excess thiol, by suppressing organic polysulphide formation, increases the yield of RSR* relative to RSR (cf. Expts 5 and 7). This is attributed to two interrelated effects; (a), in the absence of organic polysulphides reaction (6) is the sole route to RSR, but in their presence will be augmented by the more facile S_N2 reactions of RS^- with RS_3R and RS_xR as in (10), in keeping with the anticipated sequence of leaving group propensities: $RS_x^- > RS_3^- > RS_2^- \gg RS^-$; and (b), the S_Ni' reaction of polysulphides with RS^- or RS_x^- will be less facile than that of the S_Ni' reaction of the disulphide (reaction 13), since the transition state in the former case will involve

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[11] B. D. England and E. D. Hughes, *Nature, Lond.* **168**, 1002 (1951).

[12] B. D. England, *J. Chem. Soc.* 1615 (1955).

[13] A. Fava, A. Iliceto and E. Camera, *J. Amer. Chem. Soc.* **79**, 833 (1957).

[14] 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).

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

the less nucleophilic incipient perthiolate ion ($RS_x^{\delta-}$) as the entity attacking the γ-carbon atom of the allylic system (cf. reaction (13), where the nucleophil is $RS_x^{\delta-}$) and thus RSR* formation will be less when organic polysulphides are present at the expense of disulphide.

EXPERIMENTAL

Materials. The methods of preparation of compounds IV–VIII are described elsewhere.[16] The purities quoted in parentheses are G.L.C. area percentages relative to the total samples.

(IV) 1,3-dimethylbut-2-enethiol (99·5%) A_1SH
(V) (bis)-(1,3-dimethylbut-2-enyl) disulphide (99%) $A_1S_2A_1$
(VI) bis-(2-methylpent-2-enyl) disulphide (91% + 9% 2-methylpent-2-enyl 1-ethyl-2-methylallyl disulphide, $B_1S_2B_2$) $B_1S_2B_1$
(VII) bis-(1,3-dimethylbut-2-enyl) sulphide (96% + 4% (VIII)) A_1SA_1
(VIII) 1,3-dimethylbut-2-enyl 1,1-dimethylbut-2-enyl sulphide (97% + 3% VII) A_1SA_2

trans-but-2-enethiol (IX; 98·4%) was prepared from *trans*-but-2-enol by the method of Lee *et al.*[17] and the corresponding disulphide, (X; 97%) by oxidation of the thiol according to the procedure of McAllan *et al.*[18] Other thiols and disulphides were purified commercial samples. AnalaR quality methanol and ethanol were used throughout.

Disulphide (V)-*disulphide* (VI) *exchange reaction*

The disulphides (0·01 mole of each) and the thiol (IV; 0·005 mole) were added to sodium methoxide (0·005 mole) in methanol (8 ml) and the mixture heated under reflux conditions, under nitrogen, for 2 hr. The solvent was removed by distillation, water added to the residue and the organic phase separated. The organic sulphidic material after washing with water and drying over sodium sulphate was analysed by G.L.C. on 5% silicone 704/celite columns at 138° using a modified flame-ionisation detector.[19] The "volatile" portion of the product, i.e. that portion which was eluted under the specified conditions contained 40–50 wt. % monosulphides and 50–60 wt % disulphides. The

TABLE 2. DIALKENYL MONO- AND DISULPHIDES DERIVED FROM THE INTERACTION OF DISULPHIDES (V) AND (VI) WITH 1,3-DIMETHYLBUT-2-ENETHIOLATE ION

	Component	Weight Percentage	R_{x9}	Assignment
Monosulphides	1	2·4	7·8	*meso and d,l*-A_1SB_2
	2		8·7	
	3	8·3	9·6	A_1SA_1
	4	5·0	12·9	B_1SB_2
	5	11·2	14·1	A_2SB_1
	6	32·0	15·6	A_1SB_1
	7	41·1	19·1	*cis,cis*-B_1SB_1
	8		21·3	*cis,trans*-B_1SB_1
	9		22·6	*trans,trans*-B_1SB_1
Disulphides	10	1·4	38·0	Unidentified
	11	35·0	44·4	$A_1S_2A_1$
	12	4·1	51·3	$B_1S_2B_2$
	13	44·4	59·3	$A_1S_2B_1$
	14	15·1	75·5	$B_1S_2B_1$

A_1 = 1,3-dimethylbut-2-enyl; B_1 = 2-methylpent-2-enyl;
A_2 = 1,1-dimethylbut-2-enyl; B_2 = 1-ethyl-2-methylallyl.

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[16] M. B. Evans, G. M. C. Higgins, B. Saville and A. A. Watson, *J. Chem. Soc.* in press.
[17] D. F. Lee, B. Saville and B. R. Trego, *Chem. & Ind.* 868 (1960).
[18] D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *J. Amer. Chem. Soc.* **73,** 3627 (1951).
[19] J. F. Smith, *Gas Chromatography* p. 114. Butterworths, London (1960).

retention times quoted in R_{x9} units[20] in Table 2 were the same, within experimental error, as those for the authentic compounds indicated.[16]
The sulphide A_1SA_2 has $R_{x9} = 8{\cdot}5$ and therefore, if present only in small quantity, would not be detected in the presence of A_1SB_2. The "involatile" portion of the product was probably polysulphidic.

General procedure for reaction of disulphides with thiolate ions

The thiol and disulphide were successively added to the ethanolic sodium ethoxide solution (10 ml) and heated under reflux conditions under nitrogen. Concentration and reactant conditions are specified in Table 1. The mixture was then cooled and water (10 ml) added and the organic sulphidic product extracted with light petroleum (b.p. 30–40°). The petrol extracts were dried (Na_2SO_4) and then analysed by G.L.C. either directly or after careful removal of solvent at 15 mm press and room temp.

Stabilities of dialkenyl monosulphides to alkenethiolate ion

Two experiments were carried out in an exactly similar manner to the procedure described above but substituting (i) 0·01 mole of VII and (ii) 0·01 mole of VIII for disulphide. Thiol (IV; 0·01 mole) and sodium ethoxide (0·001 mole) and a reaction period of 24 hr were used in each experiment. After reaction, the sulphides were recovered and found by G.L.C. examination to be unchanged.

Analytical procedures for the organic sulphidic material

(1) *Thiol* content was determined by the method of Saville.[21]

(2) *Estimation of mono-, di- and polysulphide.* The solvent-free product was hydrogenolysed with lithium aluminium hydride in boiling tetrahydrofuran, using the procedure described elsewhere.[22] The relative proportions of sulphidic components were calculated from the yields of hydrogen sulphide and thiol produced. Elemental analyses of the products agreed well with the compositions calculated from the hydrogenolysis results.

(3) *G.L.C. analyses* were carried out as described above using 5% silicone 704/celite and 20% dinonyl phthalate/celite columns at 100° or 138°, dependent on the products examined. The proportions of sulphides present (Table 1) were calculated from the mean area percentages of the components. Identifications of the mono- and disulphides were made by comparison of the R_{x9} values[20] of the products with those of authentic compounds prepared in these laboratories.[16]

(4) *Infra-red analyses* were carried out on capillary films and on standard carbon disulphide solutions using a Hilger H 800 spectrophotometer. These analyses, concerned mainly with the detection of the types of olefinic unsaturation, confirmed the G.L.C. analyses.

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[20] M. B. Evans and J. F. Smith, *J. Chromat.* in press.
[21] B. Saville, *Analyst* **86**, (1018), 29 (1961).
[22] M. Porter, B. Saville and A. A. Watson, forthcoming publication.