53. *Reduction by Lithium Aluminium Hydride in the Analysis of Mixtures of Alk(en)yl Mono-, Di-, and Poly-sulphides.*

By M. Porter, B. Saville, and A. A. Watson.

Sulphur–sulphur bonds in di[methylpent(en)yl] sulphides * are generally reduced by lithium aluminium hydride in tetrahydrofuran in 5 min. at 65°, with little carbon–sulphur bond fission. This permits semimicro-determination, in mixtures of alk(en)yl mono-, di-, and poly-sulphides, of (*a*) the proportions of di- and poly-sulphides, (*b*) the average sulphur chain length in the polysulphides, and (*c*) the types and relative proportions of the alk(en)yl groups in the di- and poly-sulphides. The method is not generally applicable to diallyl sulphides or to sulphides containing t-alkyl–S groups, for reasons which are discussed.

The generation of thiols from silver mercaptides by an acid–thiourea reagent and silver ion-assisted solvolysis of certain silver mercaptides is described.

In the characterisation of the complex mixtures of organic sulphides formed by heating sulphur with olefins at 100—140° in the absence or presence of accelerators of sulphur vulcanisation and ancillary substances,[1-3] reduction with lithium aluminium hydride (reaction 1) forms the basis of a method for determining the average polysulphide chain length and the proportions of the different types of carbon–sulphur attachments.

$$\mathrm{RS}_x\mathrm{R}' \ (x \geqslant 2) \xrightarrow[\text{(ii) Hydrol.}]{\text{(i) LiAlH}_4} \mathrm{RSH} + \mathrm{R'SH} + (x-2)\mathrm{H_2S} \quad \ldots\ldots\ldots \quad (1)$$

Complete analysis of a mixture of sulphides, $a\mathrm{RSR}' + b\mathrm{RS_2R}' + c\mathrm{RS}_y\mathrm{R}'$ (where a, b, c are mole fractions, $y \geqslant 3$, and R and R′ are alkenyl or alkyl), as applied to the products of sulphuration of 2-methylpent-2-ene under a variety of conditions,[2,3] can be achieved by: (i) determination of the overall composition of the mixture by elemental analysis and ebullioscopic molecular-weight measurement; (ii) determination of $(b + c)$ and $c(y - 2)$ by measurement of the amounts of thiols and hydrogen sulphide, respectively, produced on reduction by lithium aluminium hydride; (iii) independent determination of a and b and of the identities and proportions of the individual mono- and di-sulphides by a combination of gas–liquid chromatography and infrared spectroscopy; and (iv) determination

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* The term " sulphide " is used in this paper to denote mono-, di-, or poly-sulphides.

[1] Bateman and Moore, " Organic Sulfur Compounds," ed. Kharasch, Vol. I, Chapter 20, Pergamon Press, London, 1961.

[2] Evans, Higgins, Moore, Porter, and Watson, unpublished work.

[3] Evans, Higgins, Moore, and Saville, unpublished work.

of the constituent alkenyl and alkyl groups in the di- and poly-sulphides by quantitative gas–liquid chromatography of the thiols formed on reduction; and hence, by combining the results from (iii) and (iv), one obtains the average composition of R and R′ in the polysulphides.

In this paper, we demonstrate the validity of the practical procedures on which steps (ii) and (iv) are based and indicate the extent to which structural changes in R and R′ affect the reactivity of mono-, di-, and poly-sulphides with lithium aluminium hydride.

In earlier work, lithium aluminium hydride was used in the large-scale reduction[4–6] and in the semimicro-determination[7] of sulphide mixtures. A new method for determining thiols[8] has enabled the latter to be improved and to be used when the thiols produced are very susceptible to oxidation or polymerisation or give silver mercaptides which are unstable in the presence of an excess of silver ion. Similarly, gas–liquid chromatography coupled with the synthesis of the relevant thiols[9,10] now allows step (iv) to be made on the semimicro-scale.

Determination of Proportions of Di- and Poly-sulphides in Sulphide Mixtures.—In the new procedure for determination (ii), the mixed sulphides are treated with lithium aluminium hydride for 5 min. at 65° in tetrahydrofuran, and thiols and hydrogen sulphide are liberated from the mixture by decomposition of the excess of hydride with water and addition of aqueous pyridine–sulphuric acid to pH 6. At this pH, hydrolysis of the lithium and aluminium mercaptides and sulphides is complete, but oxidative polymerisation of certain alkenethiols (*e.g.*, 2-methylpent-2-ene-1-thiol), which usually occurs in hot acid, is prevented. Solvation of the thiol by pyridine may also prevent such polymerisation. After expulsion and estimation of the hydrogen sulphide by the previous method,[4] the thiols are co-distilled with the pyridine, tetrahydrofuran, and water into a pyridine–silver nitrate mixture, and the equivalent amount of acid produced on formation of the silver mercaptides is determined alkalimetrically.[8]

TABLE 1.

Reduction of dialkenyl di- and tri-sulphides by lithium aluminium hydride under standard conditions (5 min. at 65° in tetrahydrofuran).

Sulphide	Purity (wt. %)	Contaminants (wt. %)	Polysulphide S * Found	Polysulphide S * Calc.	Disulphide S * Found	Disulphide S * Calc.
Di-(2-methylpent-2-enyl) trisulphide	97·6	Di-(2-methylpent-2-enyl) disulphide (2·4)	33·0	33·0	68·0	66·7
Bis-(1,3-dimethylbut-2-enyl) trisulphide	97·0	Bis-(1,3-dimethylbut-2-enyl) disulphide (3·0)	31·3		65·3	
Di-(2-methylpent-2-enyl) disulphide	98·3	1-ethyl-2-methylallyl 2-methylpent-2-enyl disulphide (1·7)	0·41	0	99·1	100
Bis-(1,3-dimethylbut-2-enyl) disulphide	>99·0	—	<0·2		97·6	
1,3-Dimethylbut-2-enyl 2-methylpent-2-enyl disulphide	96·2	Bis-(1,3-dimethylbut-2-enyl) (2·0) and di-(2-methylpent-2-enyl) disulphide (1·8)	<0·2		99·2	
Dibut-2-enyl disulphide	97·0	But-2-enyl 1-methylallyl disulphide (2·4)	<0·2		98·5	
Dicyclohex-2-enyl disulphide	>99·0	—	1·7		99·0	
Diallyl disulphide	96·5	Diallyl monosulphide (2·0)	8·05		73·2	

* In this and the other Tables these figures are the percentages of the total sulphur present which appear as hydrogen sulphide and thiol, respectively, on reduction.

This method has shown that the majority of di- and poly-sulphides, possessing various

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[4] Farmer, Ford, and Lyons, *J. Appl. Chem.*, 1954, **4**, 554.
[5] Bateman, Glazebrook, Moore, Porter, Ross, and Saville, *J.*, 1958, 2838.
[6] Bateman, Glazebrook, and Moore, *J.*, 1958, 2846.
[7] Moore and Porter, unpublished work.
[8] Saville, *Analyst*, 1961, **86**, 29.
[9] Saville, *J.*, 1962, 5040.
[10] Evans, Higgins, Saville, and Watson, *J.*, 1962, 5045.

TABLE 2.

Reduction of disulphides by lithium aluminium hydride in tetrahydrofuran under non-standard conditions.

Disulphide	Purity (%)	Reaction temp.	Reaction time (min.)	Polysulphide S Found	Polysulphide S Calc.	Disulphide S Found	Disulphide S Calc.
Di-(2-methylpent-2-yl)	99·8	65°	5	$<0{\cdot}3$	0	8·8	100
	,,	,,	300	1·53		83·4	
Bis-(1,3-dimethylbut-2-enyl)	>99	,,	270	4·9		90·2	
Diallyl	96·5	20	15	3·47		88·6	
	,,	,,	<2	1·79		95·6	

TABLE 3.

Reactivity of dialkenyl monosulphides towards lithium aluminium hydride in tetrahydrofuran at 65°.

Monosulphide	Purity (%)	Contaminant monosulphide (%)	Reaction time (min.)	Poly-sulphides	Disulphide
Di-(2-methylpent-2-enyl)	93	1-Ethyl-2-methylallyl 2-methylpent-2-enyl (7·0)	5	0	0·97
Bis-(1,3-dimethylbut-2-enyl)	96·9	1,1-Dimethylbut-2-enyl 1,3-dimethylbut-2-enyl (3·1)	5	$<0{\cdot}2$	1·4
1-Ethyl-2-methylallyl 2-methylpent-2-enyl	96·8	Di(methylpent-2-enyl) (3·2)	5	$<0{\cdot}2$	2·2
1,1-Dimethylbut-2-enyl 1,3-dimethylbut-2-enyl	97·4	Bis-(1,3-dimethylbut-2-enyl) (2·6)	5	$<0{\cdot}2$	1·6
Dibut-2-enyl	90·0	But-2-enyl 1-methylallyl (10·0)	5	$<0{\cdot}2$	0·8
Dicyclohex-2-enyl	99·3	—	5	$<0{\cdot}2$	1·0
Diallyl	>99	—	60	$<0{\cdot}2$	3·04
		—	312	0·52	6·54

substituted allyl groups, are reduced quantitatively according to reaction (1) in 5 min. at 65° in tetrahydrofuran (Table 1). Dialkyl disulphides may require longer reaction times, particularly if one or both of the alkyl groups are tertiary; *e.g.*, bis-(1,1-dimethylbutyl) disulphide undergoes only 85% reduction in 300 min. at 65° (Table 2). However, with such long reaction times, hydrogen sulphide may be produced from disulphides [*e.g.*, from bis-(1,3-dimethylbut-2-enyl) disulphide (Table 2)], confirming previous indications [7,11,12] that carbon–sulphur bond cleavage (*e.g.*, reaction 2) may accompany sulphur–sulphur bond cleavage in this reduction. The extent of carbon–sulphur cleavage is now found to be critically dependent on the structures of the alk(en)yl groups in the sulphides. For the reduction to be of analytical value the reactivities of the sulphur–sulphur bonds must be at least 500 times greater than those of the carbon–sulphur bonds. This applies for the dialkenyl sulphides of Table 1 (except diallyl disulphide), but not for bis-(1,1-dimethylbutyl) disulphide; in the latter the sulphur–sulphur bonds are relatively unreactive and there is 1·5% of carbon–sulphur bond fission in a time sufficient for reduction of only 83% of the sulphur–sulphur bonds. In diallyl disulphide, both bond types are so reactive that the standard conditions (Table 1) are too vigorous, appreciable hydrogen sulphide being

(2)

formed in less than 2 min. at 20°. In these cases the method is unsuitable. The low reactivity of di-t-alkyl disulphides is probably due to the difficulty of approach of the nucleophil (AlH_4^-) to a sulphur atom bonded on one side to a t-alkyl group (cf. the very

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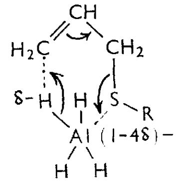
[11] Stahl and Siggia, *Analyt. Chem.*, 1957, **29**, 154.

[12] Studebaker and Nabors, Proc. Internat. Rubber Conf., Washington, 1959, p. 237.

slow exchange of [^{35}S]sulphite ion with t-alkyl thiosulphates compared with n-alkyl thiosulphates[13]).

Monosulphides also undergo a small measure of carbon–sulphur bond fission under the standard conditions (Table 3), but its extent (except with diallyl monosulphide) is less than 2 moles %, with little effect on the determination of di- and poly-sulphides. At longer reaction times, however, such breakdown is more serious (see diallyl monosulphide in Table 3).



(I)

(R = $CH_2{:}CH{\cdot}CH_2$, Li, or Al)

We tentatively suggest that the observed appreciable carbon–sulphur bond fission in diallyl sulphides occurs by S_N2' attack of aluminohydride ion at the γ-carbon atom of diallyl monosulphide or prop-2-ene-1-thiolate ion. Preference for S_N2' rather than S_N2 attack is unusual[14] when there is no hindrance of the latter by α-substituents but it may be favoured by formation of the cyclic transition state (I) in which the carbon–sulphur bond-breaking step is facilitated by formation of an aluminium–sulphur bond.

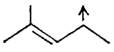
Determination of Hydrocarbon Groupings in Di- and Poly-sulphides.—The alk(en)yl groups of the di- and poly-sulphides present in sulphide mixtures [determination (iv)] can also be identified and estimated on the semimicro-scale by distillation of the thiols formed on reduction into light petroleum, followed by gas–liquid chromatography of the resulting solution after removal of pyridine. The thiols can also be examined after regeneration from the filtered silver mercaptides obtained in determination (ii). This is achieved by adding the silver mercaptides to an aqueous-tetrahydrofuran solution of thiourea and sulphuric acid which displaces the silver by reactions (3) and (4):

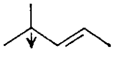
$$\mathrm{RSAg} + \mathrm{H}^+ \rightleftharpoons \mathrm{RSH} + \mathrm{Ag}^+ \qquad \ldots\ldots\ldots\ldots \quad (3)$$

$$\mathrm{Ag}^+ + \mathrm{S{:}C(NH_2)_2} \rightleftharpoons \mathrm{AgS{\cdot}C(NH_2){:}NH_2}^+ \qquad \ldots\ldots\ldots \quad (4)$$

Acid alone is insufficient to force equilibrium (3) completely to the right, as the affinity of silver ions for thiol-sulphur is very high. However, complex-formation with thiourea [equilibrium (4)] removes free silver ions from participation in (3) and quantitatively liberates the thiol which can be extracted by light petroleum to give a solution amenable to chromatography. The validity of this technique has been confirmed by using known mixtures of isomeric methylpentane- and methylpentene-thiols.

This regeneration procedure is not quantitative if the sulphide mixture being analysed contains a high proportion of monosulphides since they co-distil with the thiols and dissolve some silver mercaptides, *e.g.*, silver 4-methylpent-3-ene-2-thiolate, thus preventing effective filtration.


(II)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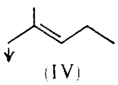
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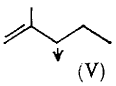
(V)

The assignment of peaks in gas–liquid chromatograms of thiols from di[methylpent(en)yl]di- and poly-sulphides has been confirmed by subsequent removal of 4- and 2-methylpent-3-ene-2-thiol by silver ion-assisted solvolysis (see below and Experimental section), followed by regeneration of 2-methylpent-2-ene-1-thiol and -1-ene-3-thiol and methylpentanethiols from the unsolvolysed silver mercaptides and re-examination by gas–liquid chromatography.

For di[methylpent(en)yl] sulphide mixtures, a chemical method for the estimation of groups (II) and (III) has been devised. This is based on extension of the silver ion-assisted solvolysis of monosulphides containing such groups to silver mercaptides containing similar groups;[10] that is, it depends on the fact that the overall rate of production of

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[13] Fava and Iliceto, *J. Amer. Chem. Soc.*, 1958, **80**, 3478.

[14] DeWolfe and Young, *Chem. Rev.*, 1956, **56**, 753.

protons in reaction (5) is controlled by the stability of R^+, which is much greater when R is (II) or (III) than when it is (IV), (V), or methylpentyl. Hence, conditions may

$$RSAg + Ag^+ \longrightarrow R{-}^+SAg_2 \xrightarrow{\text{slow}} Ag_2S + R^+ \xrightarrow{H_2O} ROH + H^+ \quad . \; . \; . \; . \quad (5)$$

be found where decomposition of silver mercaptides containing groups (II) and (III) is substantially complete whilst those containing (IV), (V), and methylpentyl groups remain virtually unaffected. Treatment of the mercaptides with an excess of 0·2N-silver perchlorate in 75% aqueous tetrahydrofuran for 10 min. at 20° is satisfactory in this respect (use of silver perchlorate rather than silver nitrate avoids the formation of an insoluble 1 : 1 silver mercaptide–silver nitrate complex which prevents complete reaction). The proportion of groups (II) and (III) in the mercaptides is then measured by estimation of the protons produced during solvolysis.[10]

Application of these techniques to a number of known mixtures of authentic methylpentenyl sulphides (Tables 4 and 5) indicates the accuracy obtained; their use with many similar unknown mixtures has been successful,[2,3,15] but has not as yet been extensively studied for other alk(en)yl sulphides.

TABLE 4.

Determination of polysulphide and disulphide sulphur in known mixtures of di(methylpentenyl) sulphides.

Composition of mixture		Polysulphide S		Disulphide S	
Sulphide	Wt. %	Found	Calc.	Found	Calc.
(A) Di(2-methylpent-2-enyl) trisulphide	10·2	6·6	5·3	63·7	63·7
(B) Bis-(1,3-dimethylbut-2-enyl) disulphide	44·8				
(C) 1,3-Dimethylbut-2-enyl 2-methylpent-2-enyl monosulphide	45·0				
(A)	51·3	20·0	20·4	74·0	72·2
(B)	34·6				
(C)	14·1				
Di-(2-methylpent-2-enyl) disulphide	9·8	<0·2	0	30·3	29·8
Bis(1,3-dimethylbut-2-enyl) disulphide	9·6				
1,3-Dimethylbut-2-enyl 2-methylpent-2-enyl disulphide	10·4				
2-Methylpent-2-enyl 2-methylpent-2-yl monosulphide	4·8				
1,1-Dimethylbut-2-enyl 2-methylpent-2-enyl monosulphide	14·4				
1,3-Dimethylbut-2-enyl 1-ethyl-2-methylallyl monosulphide	41·0				

TABLE 5.

Relative proportions of thiols obtained on reduction of known mixtures of di(methylpentenyl) sulphides.*

			Relative wt. %	
Composition of mixture	Wt. %	Thiol	Found	Calc.
Di-(2-methylpent-2-enyl) disulphide	9·8	2-Methylpent-2-ene-1-thiol 4-Methylpent-3-ene-2-thiol	52·9 47·1	50·5 49·5
Bis-(1,3-dimethylbut-2-enyl) disulphide	9·6			
1,3-Dimethylbut-2-enyl 2-methylpent-2-enyl disulphide	10·4			
2-Methylpent-2-enyl 2-methylpent-2-yl monosulphide	4·8			
1,1-Dimethylbut-2-enyl 1,3-dimethylbut-2-enyl monosulphide	14·4			
1,3-Dimethylbut-2-enyl 1-ethyl-2-methylallyl monosulphide	41·0			
Di-(2-methylpent-2-enyl) trisulphide †	48·9	2-Methylpent-2-ene-1-thiol	47·3	46·4
Bis-(1,3-dimethylbut-2-enyl) trisulphide	32·3	2-Methylpent-1-ene-3-thiol	1·2	1·2
Bis-(1,3-dimethylbut-2-enyl) disulphide	18·8	4-Methylpent-3-ene-2-thiol	51·5	52·4

* Direct gas–liquid chromatography. † Contained 5% of 1-ethyl-2-methylallyl 2-methylpent-2-enyl trisulphide.

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[15] Porter, unpublished work.

EXPERIMENTAL

Materials.—Tetrahydrofuran was passed through alumina to remove oxygen-containing impurities, dried (Na), and distilled from lithium aluminium hydride; pyridine, light petroleum, and silver nitrate were of " AnalaR " grade, the light petroleum being distilled (b. p. 30—40°) before use; thiourea was recrystallised. " Filter aid " refers to Johns-Manville " Hyflo Super-Cel." Lithium aluminium hydride was used as purchased; different samples varied appreciably in their reducing power, the most active being used in this work. The sulphides were prepared by published methods or have recently been described.[9,10,16]

Reduction with Determination of Thiols and Hydrogen Sulphide.—The sulphide mixture (150—400 mg.) is weighed into a suspension of an equal quantity of lithium aluminium hydride in tetrahydrofuran (7—10 ml.) contained in a three-necked 50-ml. flask fitted with nitrogen inlet, 10-ml. dropping funnel, and water-cooled reflux condenser packed with glass helices and fitted with a delivery tube leading into aqueous buffered cadmium acetate.[17] The flask is surrounded for 5 min. by a water-bath pre-heated to 70—75°, then cooled in ice-water, the excess of reagent is destroyed by dropwise addition of water (10 ml.), and the products are hydrolysed at 70—80° for 1·5 hr. with pyridine–sulphuric acid mixture [20 ml. of a mixture of sulphuric acid (20 ml.), water (230 ml.), and pyridine (250 ml.)]. The liberated hydrogen sulphide is displaced into the cadmium acetate solution by a slow stream of nitrogen, and the precipitated cadmium sulphide estimated iodometrically [17] to give the " polysulphide sulphur " content {$=320{\cdot}6t$ (ml. of N-iodine)/[2 × sample wt. (g.) × sulphur content of sample (wt. %)]}.

The reflux condenser is washed down with a small quantity of pyridine or tetrahydrofuran and replaced by a distillation unit with a 10 cm. long stillhead (to prevent splashing over of acid by uneven boiling while allowing the tetrahydrofuran–water–pyridine azeotrope to distil) and a 15 cm. water-cooled surface (to ensure complete condensation of the distillate). The thiols and solvents are distilled under a stream of nitrogen (to minimise uneven boiling) into a mixture of aqueous 0·4N-silver nitrate (10 ml.) and pyridine (10 ml.) cooled to −10° to coagulate the silver mercaptides formed. After dilution with water (150 ml.) the mixture is titrated against 0·1N-aqueous sodium hydroxide (phenolphthalein), to give the " disulphide sulphur " content {$=320{\cdot}6t'$ (ml. of N-sodium hydroxide)/[sample wt. (g.) × sulphur content of sample (wt. %)]}.

Reduction with Identification, and Estimation of the Relative Proportions, of Individual Thiols.—(*a*) *Direct method.* The sample is treated as above except that the receiver containing the aqueous silver nitrate–pyridine is replaced by a 30 cm. tube containing light petroleum (1—2 ml.) and cooled to −5°. After completion of the distillation, water (8—10 ml.) is added to the distillate, the tube is stoppered and shaken, and the upper layer is transferred by pipette to a second tube, extracted once with N-sulphuric acid (3 ml.) to remove pyridine (which interferes with the subsequent analysis), and examined by gas–liquid chromatography at 65° with 20% of dinonyl phthalate on acid-washed Celite as stationary phase; the thiols are identified by comparison of their R_{x9} values [18,19] with those of authentic samples and estimated from the relative peak areas.

(*b*) *Regeneration from silver mercaptides.* The precipitated silver mercaptide mixture obtained as above is diluted with water, filtered off (with filter aid), and washed with water (200 ml.) to remove pyridine, and the combined filtrate and washings are titrated against 0·1N-sodium hydroxide as above. About half of the residue is transferred to a 10-ml. test tube and 4 ml. of acid thiourea solution [from thiourea (3·5 g.), sulphuric acid (1·5 ml.), water (10 ml.), and tetrahydrofuran (38 ml.)] are added slowly whilst the solid is agitated with a glass rod. The mercaptides rapidly dissolve; water (4 ml.) is added and the liberated thiols are extracted with light petroleum (1 ml.) and examined chromatographically as above.

Silver Ion-assisted Solvolysis of Silver Mercaptides.—(*a*) *Determination of groups* (II) *and* (III). Filter aid (*ca.* 1 g.) is added to the diluted suspension of silver mercaptides obtained as above, and the solids are then filtered off on a washed pad of filter aid and washed with water. The combined washings and filtrate are titrated as before (t'') and the mercaptides are quantitatively transferred into tetrahydrofuran (15 ml.) and dissolved at 40° (5 min.). After cooling, aqueous 0·8N-silver perchlorate (5 ml.) is added, and reaction allowed to proceed for 10 min., then stopped by addition of 50% aqueous pyridine (30 ml.). The mixture of unchanged

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[16] Milligan, Saville, and Swan, *J.*, 1961, 4850.

[17] B.S. 903: 1950, Section 3·5 (London: British Standards Institution).

[18] Smith, *Chem. and Ind.*, 1960, 1024.

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

mercaptides and silver sulphide is filtered off on a washed pad of filter aid and washed with water (100 ml.), and the combined filtrate and washings are titrated against 0·1N-sodium hydroxide (t'''). The percentage of the 2-methylpent(en)yl groups in the di- and poly-sulphides which are of types (II) and (III) is given by: $100t'''/0{\cdot}97t''$, where 0·97 is the yield factor for the production of protons on solvolysis of RSAg [R = (II) or (III)].

(*b*) *Removal of groups* (II) *and* (III). The petroleum solution of thiols (1 ml.) obtained as in the preceding paragraph is mixed with tetrahydrofuran (2 ml.), and aqueous 0·8N-silver perchlorate (1 drop) is added. After shaking, the unsolvolysed thiols are regenerated by treatment with the thiourea reagent (2 ml.) and water (2 ml.) as above and the petroleum layer is separated and examined by chromatography.

Reduction of Individual and Mixed Authentic Sulphides.—The sulphides and mixtures (Tables 1—4) were treated by the first of the above methods except where otherwise indicated. In the case of diallyl disulphide (last entry of Table 2), water was added to destroy the excess of lithium aluminium hydride as soon as practicable after addition of the disulphide, and the reflux condenser was washed down with pyridine before the heating, in order to retain the volatile propenethiol in the reaction flask at that stage.

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THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48—56 TEWIN ROAD,
WELWYN GARDEN CITY, HERTS.

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