

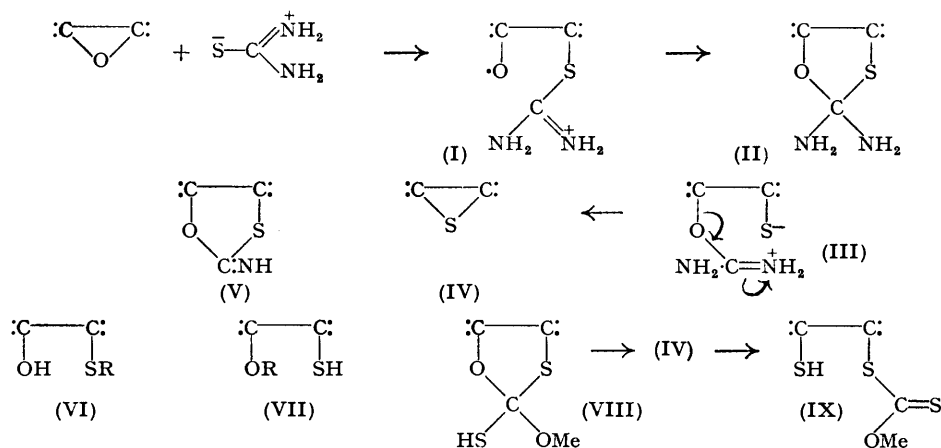
858. The Conversion of Ethylene Oxides into Ethylene Sulphides.

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The mechanism of the formation of ethylene sulphides by the interaction of ethylene oxides with certain actual or potential thiols, RSH, is discussed and shown to involve a transformation of the type $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{SR} \longrightarrow \text{CH}_2(\text{OR})\cdot\text{CH}_2\cdot\text{SH}$. The requirements of R for ethylene sulphide formation are defined and the wide scope of the reaction indicated. It is found that 2-(2:4-dinitrophenylthio)alkan-1-ols and other related nitro-compounds decompose in the same way in the presence of alkali to give ethylene sulphides which are largely polymerised, together with the corresponding nitrophenol. The reaction is also shown by 2-hydroxyethyl ethyl thiocarbonate.

THE study of the conversion of ethylene oxides into ethylene sulphides by means of alkali thiocyanates (van Tamelen, *J. Amer. Chem. Soc.*, 1951, **73**, 3444; see also Ettlinger, *ibid.*, 1950, **72**, 4792) prompts the recording of our own observations on the above conversion by a variety of reagents.

An examination of the preparation of ethylene sulphides from ethylene oxides and thiourea (Dachlauer and Jackel, D.R.-P. 636,708) led to the following reaction mechanisms being developed (Culvenor, Ph.D. Thesis, Melbourne, 1948, p. 20). The existence of thiourea in the zwitter-ion form (Sidgwick's "Organic Chemistry of Nitrogen," 1937, pp. 286, 291) accounts for its ready attack on the ethylene oxide ring by means of a nucleophilic displacement reaction. The initially formed 2-hydroxy-sulphide (I) is then considered to rearrange through the cyclic intermediate (II) into the 2-mercapto-ether (III), which finally decomposes into urea and the ethylene sulphide (IV).



The formation of (IV) is therefore due to two favourable factors, first, the ability of R in $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{SR}$ to migrate to the oxygen atom to form $\text{CH}_2(\text{OR})\cdot\text{CH}_2\cdot\text{SH}$, and secondly, the ready displacement of OR in this substance by the negatively charged sulphur atom. In general this is not the case, *e.g.*, if R = H or alkyl, compounds of this type are stable to ordinary alkaline conditions, but when R = $\text{C}(\text{NH}_2)_2$, as in (III), there is a weakening of the C-O bond (as shown) by an electron shift towards the amidine group, and hence the displacement of OR by the sulphur atom is facilitated. Thus the decomposition into urea and an ethylene sulphide may be viewed as the simple electron redistribution shown in (III). Since this is quite different from the normal hydrolysis of an O-alkylurea, it is evident that a considerable part of the driving force is associated with the displacement of the urea grouping from carbon by the sulphur. There is another driving force in this formation of ethylene sulphides, *viz.*, the remarkable tendency to form a three-membered hetero-

cycle. This has not yet been satisfactorily explained, any more than in the case of the formation of ethylene oxides, where, contrary to ordinary conceptions of strain, an ethylene oxide can be formed as readily as a five-membered ring (Wilson, *J.*, 1945, 49). Finally, the fact that the ethylene sulphide produced is mainly the monomer is due to the alkali in the medium being so mild that the polymerisation to which ethylene sulphide is prone in alkali of somewhat higher concentration (Culvenor, Davies, and Heath, *J.*, 1949, 284; Coltof, U.S.P. 2,183,860, 1939; B.P. 508,932) occurs here only to a moderate extent.

This mechanism indicates that ethylene sulphides should result from the interaction of ethylene oxides with any thiol, RSH, and hence from the general initial product (VI), provided the nature of R be such that the proposed electron shifts can occur—first, to permit the transient formation of the oxathiole ring intermediate and so effect rearrangement to (VII), and secondly, to produce the necessary weakening of the C—O linkage. The main purpose of the present paper is to demonstrate not only the limitations but also the wide scope of this reaction. Ethylene sulphide formation has already been shown to occur when ethylene oxides condense with potassium thiocyanate, thioamides [$R = CMe:NH$, $CPh:NH$, and $C(OEt):NH$], or substituted thioureas [$R = C(NHPh):NH$ and $C:N\cdot CO\cdot CH_2\cdot CO\cdot NH$] (Culvenor, Davies, and Heath, *loc. cit.*), and in each of these instances R fulfils the requirements for the above mechanism to be applied. Thus with potassium thiocyanate, the hypothetical oxathiole derivative (V), which rearranges and yields (IV) and potassium cyanate, is postulated. This is the mechanism suggested for this particular reaction by Ettliger (*loc. cit.*) and more fully expounded by van Tamelen (*loc. cit.*).

The preparation of ethylene sulphide by the interaction of aqueous sodium sulphide with 2-chloroethyl thiocyanate (Delépine, *Bull. Soc. chim.*, 1920, **27**, 740) involves a similar process—the thiocyanate instead of the cyanate ion being produced. This, and Delépine's reaction (*loc. cit.*) of sodium sulphide with ethylene dithiocyanates, are instances of the displacement from carbon, by a negatively charged sulphur atom, of sulphur attached to an electrophile.

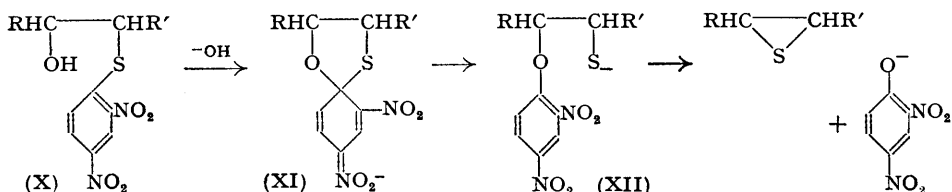
The mechanism of the interaction of ethylene oxide with potassium methyl xanthate [$R = \cdot C(:S)OMe$] to form ethylene trithiocarbonate (Culvenor, Davies, and Pausacker, *J.*, 1946, 1050) involves an intermediate (VIII) to explain the formation of (IV), which then reacts with more xanthate to give (IX), and thence the trithiocarbonate and potassium methoxide or hydroxide.

This trithiocarbonate formation can be faster than the polymerisation of an ethylene sulphide; for example, whilst early attempts to make styrene sulphide gave material of high molecular weight, styrene oxide with potassium methyl xanthate gave styrene trithiocarbonate in 77% yield (Culvenor, Davies, and Pausacker, *loc. cit.*; cf. Guss and Chamberlain, *J. Amer. Chem. Soc.*, 1952, **74**, 1342). It is considered then that the essential reaction pattern is the same, *viz.*, the transformation (VI) \longrightarrow (VII) \longrightarrow (IV), regardless of whether (IV) is isolated as the monomer, as a polymer, or as a trithiocarbonate as above—or even if isolated in the form of its decomposition products, as exemplified by the conversion of stilbene oxide by thiourea into stilbene and sulphur (together with urea) (cf. Culvenor *et al.*, *J.*, 1949, 2573).

The Smiles rearrangement of ether thiols into phenol sulphides in basic media (Warren and Smiles, *J.*, 1931, 914; Kon, *Ann. Reports*, 1933, **30**, 188; Watson, *ibid.*, 1939, **36**, 198) is essentially the reverse of the change (VI) \longrightarrow (VII). The proof (Coats and Gibson, *J.*, 1940, 442) of the reversibility of the Smiles rearrangement shows, however, that it is closely allied to the change (VI) \longrightarrow (VII) (which may itself prove to be reversible). Generally, attachment at a "positive" carbon of an aryl group is a condition of the Smiles rearrangement, and experimental evidence for the inherent analogy of the two processes is now found in the formation of ethylene sulphides from compounds of type (VI) where R is *o*-C₆H₄(NO₂), 2 : 4-C₆H₃(NO₂)₂, or 2 : 4 : 6-C₆H₂(NO₂)₃. Simple ethylene oxides interact with 2 : 4-dinitrothiophenol to give crystalline 2-(2 : 4-dinitrophenylthio)alkan-1-ols (cf. Davies and Savige, *J.*, 1951, 774), which are also obtained from the interaction of the requisite thiol and 1-chloro-2 : 4-dinitrobenzene, in the presence of an exactly equivalent

amount of sodium hydroxide solution, or better by the use of such weak bases as sodium hydrogen carbonate, pyridine, or sodium acetate. (The analogous picryl derivatives are similarly obtained by use of picryl chloride.) Though the resulting sulphides are stable in acid or neutral media, they are converted by dilute alkali even in the cold into the di- or tri-nitrophenol and the corresponding ethylene sulphide. The reaction has been effected starting with ethylene, propylene, *isobutylene*, and *cyclohexene* oxides, although the monomeric sulphides have as yet been detected mainly by means of their highly characteristic odours. The appropriate nitrophenol is readily isolated in high yield, and ethylene sulphide itself is obtained as the solid polymer. If 2-(2:4-dinitrophenylthio)*cyclohexan*-1-ol (X; RR' = $\cdot[\text{CH}_2]_4\cdot$) is warmed with alcoholic alkali in the presence of added carbon disulphide (to form potassium ethyl xanthate), *cyclohexene* trithiocarbonate is obtained in good yield. This product demonstrates the formation of *cyclohexene* sulphide in the reaction mixture since it is not readily formed from 2-mercaptocyclohexanol under the same conditions. Potassium 2:4-dinitrothiophenoxide and stilbene oxide react to give 2:4-dinitrophenol and stilbene, and there is little doubt that the reaction proceeds analogously to that of stilbene oxide and thiourea.

The alkaline decomposition of 2-(2:4-dinitrophenylthio)alkan-1-ols (X) is considered to take the following path:

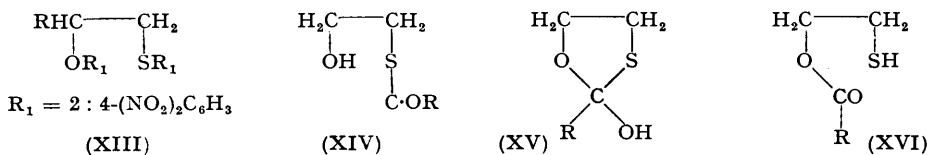


We have obtained definite evidence for the intermediate formation of the mercapto-ether (from ion XI) by carrying out the decomposition of (X; R = R' = H) in the presence of 1-chloro-2:4-dinitrobenzene, the ether sulphide 1-(2:4-dinitrophenoxy)-2-(2:4-dinitrophenylthio)ethane [XIII; R = H] being isolated in 74% yield. Competition occurs between fixation of the intermediate (XII) as the diaryl derivative (as XIII) and the normal decomposition of (XII), since some ethylene sulphide and 2:4-dinitrophenol are also formed. Similarly, treatment of 1-(2:4-dinitrophenylthio)propan-2-ol (X; R = Me, R' = H) with one mole each of 1-chloro-2:4-dinitrobenzene and alkali leads to a 50% yield of 2-(2:4-dinitrophenoxy)-1-(2:4-dinitrophenylthio)propane [XIII; R = Me], together with some of the usual products—propylene sulphide and dinitrophenol. It is clear that the diaryl (XIII) is formed from the ether thiol (as VII), and its isolation in considerable quantity shows that these thiol intermediates are sufficiently stable to persist in the reaction medium for a significant period of time. This conclusion should apply also to the general intermediate (VII) in other cases of ethylene sulphide formation, and it is probable that other thiols of this type can be isolated as derivatives in a similar way.

The reversed Smiles rearrangement, (X) \longrightarrow (XII), was tentatively studied by Kent and Smiles (*J.*, 1934, 422) with 2-*o*-nitrophenylthioethanol but they reported this compound to be stable to alkali. Hence they considered 2-hydroxy-sulphides to be the more stable isomers under alkaline conditions. We find that, although 2-*o*-nitrophenylthioethanol is very much more stable than the corresponding dinitro-compound, it does decompose to ethylene sulphide polymer and *o*-nitrophenol when refluxed with alcoholic alkali. The rearrangement cannot be detected with the compound (X; R = CH_2Cl , R' = H) obtained from 2:4-dinitrothiophenol and epichlorohydrin, since it is known to be resistant to cold dilute alkali, and to produce 1-(2:4-dinitrophenylthio)-2:3-epoxypropane with concentrated alkali (Davies and Savige, *loc. cit.*). This is presumably due to the epoxide ring closure's being faster than the rearrangement.

Compounds of the type (VI; R = CO_2Et) also gave ethylene sulphide. Thus mercaptoethanol and ethyl chloroformate in pyridine gave the expected 2-hydroxyethyl thiolcarbonate (XIV; R = OEt), mixed with a smaller amount of the 2-mercaptoethyl

carbonate (XVI; R = OEt). These substances were not separated by distillation, but all fractions obtained produced ethylene sulphide when treated with alkali. An attempt to characterise the thiol (XVI; R = OEt) with chlorodinitrobenzene and alkali led to isolation of a small amount of the bis-2:4-dinitrophenyl compound (XIII; R = H). Evidently this was formed from the expected dinitrophenyl derivative of (XVI; R = OEt) by hydrolysis to give (X; R = R' = H), and subsequent reaction of this substance as described above.



Very recently, Harding, Miles, and Owen (*Chem. and Ind.*, 1951, **42**, 887) * have reported the isolation of monomeric ethylene sulphides from the decomposition of acetylated 2-hydroxy-thiols (VI; R = CO·CH₃) with weak alkali. They also regard the reaction as proceeding in the manner (XIV) → (XV) → (XVI; R = Me). Nylen and Olsen (*Chem. Abstr.*, 1942, **36**, 753) described the formation from ethylene oxide and thiolacetic acid of the thiolacetate (XIV; R = Me) and the isomerisation of the latter to (XVI; R = Me) by long heating with water. This with *n*-sodium hydroxide furnished a compound which the analysis and properties show to be polymeric ethylene sulphide. Sjöberg (*Ber.*, 1941, **74**, 64; 1942, **75**, 15) has also obtained compounds such as (XIV) by condensation of thiolacetic acid with epichlorohydrin, glycidol, and propylene oxide, severally, and although he did not study their behaviour towards alkali, he found that the acetyl group migrated spontaneously from sulphur to oxygen. He postulated for this change the "hypothetical intermediate" of type (XV).

EXPERIMENTAL

2-(2:4-Dinitrophenylthio)alkan-1-ols and Related Compounds.—Ethylene oxide was passed into a solution of 2:4-dinitrothiophenol in aqueous sodium hydrogen carbonate to give an immediate precipitate of 2-(2:4-dinitrophenylthio)ethan-1-ol (X; R = R' = H), m. p. 100° (after recrystallisation from aqueous alcohol), identical with samples prepared from 1-chloro-2:4-dinitrobenzene and mercaptoethanol (Bennett and Whincop, *J.*, 1921, **119**, 1864), and from 2:4-dinitrothiophenol and ethylene chlorohydrin in aqueous sodium hydrogen carbonate.

2-(2:4-Dinitrophenylthio)cyclohexan-1-ol (X; RR' = ·[CH₂]₁·) (0.2 g.) was obtained by adding cyclohexene oxide (0.1 g.) to a solution of 2:4-dinitrothiophenol (0.2 g.) in alcoholic sodium acetate, warming the mixture at 60° for 30 min., and then keeping it at room temperature for 16 hr. with exclusion of air. Crystallisation from aqueous alcohol gave small orange needles, m. p. 135°, undepressed on admixture with a specimen obtained from 2-mercaptocyclohexanol and chlorodinitrobenzene (Culvenor, Davies, and Heath, *loc. cit.*). It may also be prepared by heating cyclohexene oxide and dinitrothiophenol in alcohol for 12 hours at 55–60°. The similar derivatives from reaction of dinitrothiophenol with propylene and isobutylene oxides and epichlorohydrin were prepared according to Davies and Savige (*loc. cit.*).

Action of Alkali on 2-(2:4-Dinitrophenylthio)ethan-1-ol and Related Compounds.—On mixing at room temperature of alcoholic solutions of (X; R = R' = H) (1.2 g.) and potassium hydroxide (0.28 g., 1 mol.), a bright red coloration was immediately produced, which faded to yellow within 10 seconds. There was a strong odour of ethylene sulphide, and potassium dinitrophenoxide separated. After a few minutes water was added, and the amorphous pale yellow precipitate (0.11 g.) was shown by analysis to be impure ethylene sulphide polymer. The filtrate after acidification yielded 2:4-dinitrophenol (0.82 g.), m. p. and mixed m. p. 111–112°. The first runnings of an aqueous-alcoholic distillate obtained by gently warming a suspension of (X) in 10% alcohol containing more than 1 mol. of sodium hydroxide were shown to contain ethylene sulphide by its odour, its instant reaction with the iodine-sodium azide reagent, and the typical separation of polymer noticeable 5 minutes after the addition of a trace of alkali. After 12

* This work is amplified by Miles and Owen, *J.*, 1952, 817, which arrived after the present paper was prepared for publication.

hours the polymer was washed with water and alcohol. Although the m. p. (165—175°) of the dry substance was high, the substance was practically pure polymer and had the characteristic property of electrifying strongly when rubbed with glass [Found; C, 40.1; H, 6.15. Calc. for $(C_2H_4S)_x$: C, 40.0; H, 6.7%].

A cold aqueous-alcoholic solution of 1-(2:4-dinitrophenylthio)propan-2-ol (Davies and Savige, *loc. cit.*, p. 321) and sodium hydroxide gave a red colour which faded to yellow in less than 1 minute. One portion of the mixture with dilute hydrochloric acid gave 2:4-dinitrophenol, another portion with concentrated hydrochloric acid gave this and the highly unpleasant odour of a 2-chloro-thiol, and a third portion on warming gave the not unpleasant odour of propylene sulphide. Results similar to the above were obtained with 1-(2:4-dinitrophenylthio)-2-methylpropan-2-ol (Davies and Savige, *loc. cit.*, p. 778). Though with cold 40% aqueous sodium hydroxide, 1-chloro-3-(2:4-dinitrophenylthio)propan-2-ol gave the corresponding 2:3-epoxide (Davies and Savige, *loc. cit.*, p. 778), it was unchanged by cold 10% sodium hydroxide, but boiling with this alkali, or with aqueous potassium carbonate, gave a brown, amorphous precipitate. No 2:4-dinitrophenol was isolated, and the odour of chloropropylene sulphide was not detected.

Action of Alkali on 2-(2:4-Dinitrophenylthio)cyclohexan-1-ol.—(i) Addition of an equivalent amount of 10% aqueous sodium hydroxide to an alcoholic solution of (X; $RR' = \cdot[CH_2]_4\cdot$) produced a bright red colour, fading to yellow within 5 min. The odour of cyclohexene sulphide was recognised and crystals which soon separated were identified as sodium dinitrophenoxide since they were water-soluble, exploded before melting, and yielded 2:4-dinitrophenol on treatment with acid.

(ii) A mixture of (X; $RR' = \cdot[CH_2]_4\cdot$) (1.5 g.), carbon disulphide (0.4 ml.), and sodium hydroxide (0.4 g.) in alcohol (20 ml.) was heated for 5 min., kept for another 30 min., and then acidified with dilute sulphuric acid. The resulting oily yellow solid was washed with sodium carbonate solution and then crystallised from benzene to give cyclohexene trithiocarbonate (0.52 g.), m. p. 164—165°, mixed m. p. 166—168°.

Preparation of 2-(2:4-Dinitrophenoxy)-1-(2:4-dinitrophenylthio)propane (XIII; R = Me).—(X; R = Me, R' = H) (1.3 g.) and 1-chloro-2:4-dinitrobenzene (1.0 g., 1 mol.) were dissolved in alcohol (25 ml.) and treated with a solution of potassium hydroxide (0.28 g.) in alcohol (10 ml.). The reaction appeared to be similar to that performed in the absence of chlorodinitrobenzene. The colour of propylene sulphide was again clearly recognised. After 15 min., water was added, and the precipitate (1.9 g.) collected and crystallised from acetone to give 2-(2:4-dinitrophenoxy)-1-(2:4-dinitrophenylthio)propane (0.98 g.), yellow tabular prisms, m. p. 193—194° (Found: C, 42.7; H, 2.8; N, 13.2; S, 7.5. $C_{15}H_{12}O_9N_4S$ requires C, 42.5; H, 2.8; N, 13.2; S, 7.55%). Although sparingly soluble in most solvents, it dissolves to a considerable extent on refluxing in acetone for several hours. The reaction filtrate was concentrated to a small volume and acidified to give 2:4-dinitrophenol (90 mg.), m. p. 110—111°, mixed m. p. 111—112°.

1-(2:4-Dinitrophenoxy)-2-(2:4-dinitrophenylthio)ethane (XIII; R = H).—(X; R = R' = H) (0.6 g.) and chlorodinitrobenzene (0.5 g., 1 mol.) were dissolved in alcohol (15 ml.) and treated with potassium hydroxide (0.15 g.) in alcohol (10 ml.). Water was added after 30 min. and the precipitate (0.77 g.) was collected and crystallised from acetone, giving 1-(2:4-dinitrophenoxy)-2-(2:4-dinitrophenylthio)ethane as pale yellow felted needles, m. p. 181—182°, sparingly soluble in alcohol, soluble in dioxan (Found: C, 41.3; H, 2.5; N, 13.2; S, 7.8. $C_{14}H_{10}O_9N_4S$ requires C, 41.0; H, 2.4; N, 13.7; S, 7.8%).

2-(*o*-Nitrophenylthio)ethan-1-ol.—When (X; R = R' = H) (0.2 g.), obtained from mercaptoethanol and *o*-bromonitrobenzene according to Bennett and Berry (*J.*, 1927, 1666), was refluxed for 15 minutes in alcohol (2 ml.) and water (0.25 ml.) containing sodium hydroxide (0.04 g.), it was nearly all recovered unchanged, although on acidification the odour of *o*-nitrophenol was apparent. However, after 3 hours' refluxing, a precipitate of ethylene sulphide polymer (0.06 g.) separated, and concentration and acidification of the filtrate furnished *o*-nitrophenol, m. p. and mixed m. p. 44°.

In this drastic experiment the formation of the ethylene sulphide polymer and not the fission of the sulphur-phenyl link is important. Thus it is found that in a comparable experiment the refluxing for 1 hour of 2:4-dinitrothioanisole with alcoholic potassium hydroxide produced 2:4-dinitrophenol and dimethyl disulphide, as well as an intense darkening of the reaction mixture.

2-Picrylthioethanol and Related Compounds.—2-Picrylthioethanol, m. p. 72°, small yellow needles from benzene-ligroin (Found: N, 14.9. $C_8H_7O_7N_3S$ requires N, 14.55%), was obtained

on gradually adding a solution of sodium acetate (1 g.) in alcohol (20 ml.) to a mixture of picryl chloride (2.5 g.) and 2-mercaptoethanol (0.8 g.) in alcohol (20 ml.), then warming it on the water-bath for 10 minutes, and finally diluting it with water. Each addition of sodium acetate produced a red colour, which soon faded. The same product was obtained when sodium hydroxide (0.4 g.) in alcohol was used in place of sodium acetate, the mixture being well shaken after each addition.

With excess of alcoholic alkali, 2-picrylthioethanol gave a deep crimson colour which did not completely fade during 10 minutes, but rapidly changed to pale yellow on slight warming. A yellowish, polymeric precipitate was obtained, and the odour of ethylene sulphide was detected. Acidification of the mixture with concentrated hydrochloric acid gave rise to the unpleasant odour of a chloro-thiol, together with precipitation of picric acid (identified by mixed m. p.).

2-Picrylthioethanol in glacial acetic acid was warmed at 100° for 6 hours with a slight excess of 30% hydrogen peroxide; the mixture was then diluted with water, and extraction with chloroform gave a large proportion of picric acid. Treatment of 2-picrylthioethanol in acetone with 30% hydrogen peroxide for 2 weeks at 30° brought about the separation of a large quantity of acetone peroxide, prisms, m. p. ca. 95°. No other product was isolated. 1-Picrylthiopropyl-2-ol and 2-chloro-1-picrylthiopropyl (Davies and Savige, *J.*, 1950, 321, 322) gave similar results to 2-picrylthioethanol, on treatment with hydrogen peroxide.

Ethyl picryl sulphide, m. p. 44–45°, long yellow needles from methanol (Found: N, 15.2. $C_8H_7O_6N_3S$ requires N, 15.35%), was obtained when a solution of pyridine (0.4 g.) in alcohol was added to a mixture of ethanethiol (0.3 g.) and picryl chloride (1.25 g.) in alcohol (a deep red colour was first obtained; this soon disappeared with formation of a black, granular precipitate), then the mixture was warmed on the water-bath for 15 minutes (a clear, yellow solution being obtained), allowed to cool, and diluted with a small amount of water. The sulphide is unchanged on warming with 10% aqueous alcoholic sodium hydroxide. It is converted by 30% hydrogen peroxide in glacial acetic acid (1 hour at 100°) into *ethyl picryl sulphoxide*, m. p. ca. 175° (violent detonation), yellow prisms from acetic acid (Found: N, 14.4. $C_8H_7O_7N_3S$ requires N, 14.55%). *Ethyl picryl sulphone*, m. p. ca. 210° (slight decomp.), pale yellow plates from acetone-ligroin, was obtained on warming ethyl picryl sulphide for 5 hours at 100° with 30% hydrogen peroxide in glacial acetic acid (Found: N, 13.8. $C_8H_7O_8N_3S$ requires N, 13.8%).

Trityl Thioethers.—2-(Triphenylmethylthio)ethanol, m. p. 114–115°, plate-like needles from ligroin (Found: C, 78.75; H, 6.6; S, 10.65. $C_{21}H_{20}OS$ requires C, 78.75; H, 6.25; S, 10.0%), was obtained on warming a mixture of triphenylmethyl chloride (2.4 g.) and mercaptoethanol (0.7 g.) in ligroin on the water-bath for 1 minute (hydrogen chloride being evolved), and crystallising the crude product from aqueous alcohol. It was recovered unchanged after refluxing for 4 hours with alcoholic potassium hydroxide. This stability to alkali contrasts with its conversion into triphenylmethanol in 15 minutes on the water-bath by hydrochloric acid in aqueous dioxan. It also gave triphenylmethanol after long storage with dilute sulphuric acid or by treatment with phosphorus pentachloride in chloroform or by thionyl chloride and pouring the product into water. (The above products were identified by m. p. and mixed m. p. determinations.) Here the side chain in 2-(triphenylmethylthio)ethanol has evidently suffered fission, the triphenylmethyl chloride formed being hydrolysed to the carbinol by the water. This is indicated by the stability of 2:3-dichloropropyl triphenylmethyl sulphide (Davies and Savige, *loc. cit.*, p. 777) to glacial or aqueous acetic acid, and its ready conversion into triphenylcarbinol by chloroformic phosphorus pentachloride followed by aqueous treatment. The contrast between trityl and 2:4-dinitrophenyl thioethers is shown by the ready interaction of chloroformic phosphorus pentachloride and 1-(2:4-dinitrophenylthio)propan-2-ol to yield 2-chloropropyl 2:4-dinitrophenyl sulphide (VI) (cf. Davies and Savige, *loc. cit.*, p. 779).

Reaction of 2-Mercaptoethanol with Ethyl Chloroformate.—Ethyl chloroformate (9.8 ml., 10.85 g.) in dry ether (15 ml.) at 0° was added in portions, with frequent shaking, to a mixture of mercaptoethanol (7.8 g.) and pyridine (9 g.) in dry ether (15 ml.), contained in an ice-bath. A yellow colour was observed after each addition of ester, but this soon faded. The mixture was kept at 10°, with occasional shaking, for ½ hour, and plates of (presumably) pyridine hydrochloride then separated. The mixture was poured into water (50 ml.), and the ethereal layer separated, washed with water, dried (Na_2SO_4), and distilled. Constant-boiling fractions could not be obtained. In the initial distillation, three fractions were collected separately: (1) b. p. 48–50°/0.7 mm., n_D^{20} 1.488 (1 ml.), slightly soluble in cold water; (2) intermediate fraction, n_D^{20} 1.4654 (0.5 ml.); (3) b. p. 85–110°/0.4 mm., n_D^{20} 1.467 (10 ml.), soluble in warm water, but reprecipitated on cooling. The amount of higher-boiling material was negligible. All three fractions were mobile liquids, and each gave a mauve colour with aqueous sodium nitroprusside,

and possessed a mercaptan-like odour. Each of the fractions, when warmed with 10% aqueous sodium hydroxide, gave amorphous polymeric material, and evolved ethylene sulphide. Fraction (1) may have contained some mercaptoethanol: that used had n_D^{18} 1.4985, b. p. 52°/12 mm.

Fraction (3) was redistilled with the aid of an efficient fractionating column, but again a constant-boiling fraction could not be obtained. The distillate was divided arbitrarily into three equal fractions: (3a) b. p. 133—140°/20 mm.; (3b) b. p. 140—158°/20 mm., n_D^{15} 1.472 (Found: C, 40.15; H, 6.55. Calc. for $C_6H_{10}O_3S$: C, 40.0; H, 6.65%); (3c) b. p. 158—168°/20 mm., n_D^{15} 1.465. These three fractions are each considered to be a mixture, consisting mainly of ethyl S-2-hydroxyethyl thiolcarbonate (XIV; R = OEt), with a smaller amount of ethyl 2-mercaptoethyl carbonate (XVI; R = OEt). Each had properties similar to those described above for fraction (3), except that fraction (3a) partly polymerised to a white solid when kept in a sealed tube for 1 month (possibly caused by the alkali in the glass).

Reaction of the Condensation Product with p-Nitrophenyl isocyanate.—Fractions (3), (3a), (3b), and (3c) all gave the following reaction; it (0.5 g.) was warmed on the water-bath for 1 hour with a filtered solution of *p*-nitrophenyl isocyanate (1.5 g.) in dry benzene (15 ml.), with exclusion of moisture. The cooled mixture was quickly filtered into a dry flask, and ligroin (15 ml.) added. When cooled to 0°, and rubbed with a glass rod, the precipitated oil solidified, giving a crude, pale yellow product, m. p. 95—98° (0.5 g.). Recrystallisation of this from benzene–ligroin gave a compound, considered to be 2-carbethoxythioethyl *p*-nitrophenylcarbamate, *p*-NO₂·C₆H₄·NH·CO₂·CH₂·CH₂·S·CO₂Et, m. p. 100.5°, large, pale ivory needles (Found: C, 46.1; H, 4.4; S, 10.05, 10.35. C₁₂H₁₄O₆N₂S requires C, 45.8; H, 4.45; S, 10.2%); more was obtained on concentration of the original filtrate, but attempts to isolate a second product were unsuccessful.

Reaction of Condensation Product with 1-Chloro-2:4-dinitrobenzene.—Each of fractions (1), (2), (3), (3a), and (3c) gave the following reaction: The fraction (0.15 g.), 1-chloro-2:4-dinitrobenzene (0.2 g.), and sodium hydroxide (0.04 g.) in alcohol (10 ml.) were kept for 5 minutes. The precipitate was washed with alcohol, then with water, and finally recrystallised from glacial acetic acid and then from ethyl acetate, giving 1-(2:4-dinitrophenoxy)-2-(2:4-dinitrophenylthio)ethane, (XIII; R = H), m. p. and mixed m. p. 181—182°, fine, pale yellow needles (0.18 g.) (Found: C, 41.1; H, 2.6; S, 7.7; N, 13.1%). It is sparingly soluble in hot alcohol or in cold benzene, but soluble in dioxan. Addition of water to the original filtrate gave an oil, which appeared to be a mixture of unchanged reactants. However, no additional product was obtained on keeping this mixture.

Action of Potassium 2:4-Dinitrothiophenoxide on Stilbene Oxide.—Stilbene oxide (0.6 g.) was added to a solution of dinitrothiophenol (0.61 g.) and potassium hydroxide (0.17 g.) in alcohol (5 ml.) and kept at 32° for 2 days. The mixture was diluted with water, and the resulting oily precipitate crystallised from a little alcohol and sublimed, to furnish stilbene as colourless prisms, m. p. and mixed m. p. 124°. The aqueous filtrate was evaporated to a small volume, acidified, and extracted with ether. This extract yielded 2:4-dinitrophenol, m. p. 108—110°, mixed m. p. 111°.

The micro-analyses were made in Dr. Zimmermann's laboratory in the Commonwealth Scientific and Industrial Research Organization, Melbourne. One of us (W. E. Savige) acknowledges financial assistance from the Commonwealth Reconstruction Training Scheme.