# **69.** *The Reactions of Propylene Sulphide with Acetyl Chloride and Related Compounds.*

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Acetyl chloride and propylene sulphide rapidly form 2-chloropropyl thiolacetate (II). Acetyl bromide behaves similarly, but acetic anhydride in the presence of pyridine gives 2-*acetylthiopropyl acetate* (X). These esters are converted into the corresponding mercaptopropanols, of which the structures have been proved by the properties of their crystalline derivatives. The two mercaptopropanols are converted by aqueous hydrochloric acid into the same chloropropanethiol [considered to be 2-chloropropane-1-thiol (IX)], which is also formed by the interaction of propylene sulphide and aqueous hydrochloric acid.

The usual or " normal " interaction of compounds containing active hydrogen with asymmetrical ethylene oxides is to form derivatives of secondary alcohols, and the rare fission of asymmetrical ethylene oxides to form derivatives of primary alcohols is regarded as the abnormal process (Kadesch, *J. Amer. Chem. Soc.*, 1946, **68**, 41; Chitwood and Freure, *ibid.*, p. 680; Gilman and Fullhart, *ibid.*, 1949, **61**, 1478). This use of the terms " normal " and " abnormal " is adopted in the present paper with reference to the fission of ethylene sulphides to form secondary or primary thiols, respectively, or derivatives of them. Thus the conversion of propylene sulphide (I) into the derivative (X) of propane-2-thiol results from normal ring fission, as the sulphur atom retains its link with $C_{(2)}$.

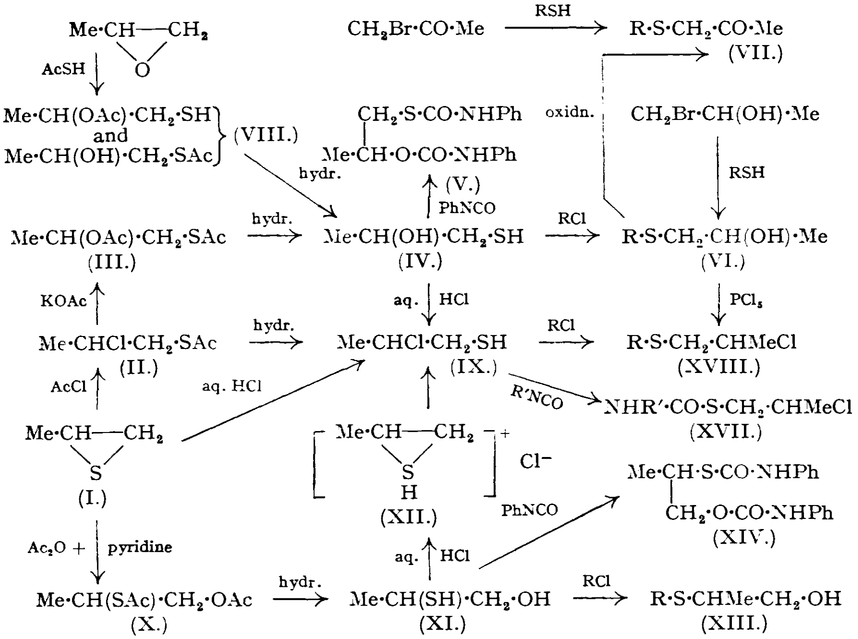
Propylene sulphide (I) reacts spontaneously with acetyl chloride to give 2-chloropropyl thiolacetate (II) in theoretical yield. This abnormal product shows no evidence of being a mixture of isomers. The compound (II) has already been described by Culvenor, Davies, and Heath (*J.*, 1949, 286), but its structure has not been proved. Its conversion into known crystalline derivatives is difficult, for it is inert to sodium iodide in boiling acetone, and is converted by zinc and acetic acid into viscous material; Raney nickel removes both sulphur and chlorine, and concentrated nitric acid gives an almost theoretical yield of sulphuric acid together with a small amount of oxalic acid. However, (II) is converted by potassium acetate in glacial acetic acid into 1-*acetylthio*-2-*propyl acetate* (III), which is hydrolysed by 1% methanolic hydrochloric acid to 1-mercaptopropan-2-ol (IV), a liquid characterised as the *derivative* (V) (obtained by interaction with 2 moles of phenyl *iso*cyanate) and as the 2 : 4 : 6-*trinitrophenyl thioether* (VI; R = picryl). The structure of (IV) is shown by its reaction with 1-chloro-2 : 4-dinitrobenzene and alkali to form 1-(2 : 4-*dinitrophenylthio*)*propan*-2-*ol* [VI; $R = 2:4\text{-}(NO_2)_2C_6H_3$], also obtained from 2 : 4-dinitrothiophenol and 1-bromopropan-2-ol and oxidised by chromic acid to (2 : 4-*dinitrophenylthio*) *acetone* (VII), which is identical with the reaction product from bromoacetone and 2 : 4-dinitrothiophenol.

This proof of the structure of (IV) is independent of previous work, and depends on evidence supplied by the properties of the 2 : 4-dinitrophenyl derivative. Sjöberg (*Ber.*, 1942, **75**, *B*, 27) found that propylene oxide and thiolacetic acid, $CH_3\cdot CO\cdot SH$, formed a mixture (VIII) of 1-acetylthiopropan-2-ol and 2-acetoxypropane-1-thiol, which gave (IV) on hydrolysis. These formulæ seem to have been assumed by Sjöberg by analogy with the products from glycidol and thiolacetic acid. A repetition of his work confirms his formula (IV), and thus proves that the reaction of propylene oxide with thiolacetic acid is a normal one.

Propylene sulphide reacts abnormally with acetyl bromide, and the apparently homogeneous 2-*bromopropyl thiolacetate* (over 95% yield) is converted into (III) by sodium acetate in glacial acetic acid. By analogy, the product from benzoyl chloride (Culvenor *et al.*, *loc. cit.*, pp. 284, 286) is 2-*chloropropyl thiolbenzoate.*

Alderman, Brubaker, and Hanford (U.S.P. 2,212,141) showed that ethylene sulphide reacts with acetic anhydride in the presence of a small quantity of pyridine to give the diacetate of 2-mercaptoethanol. They give, however, no details of the reaction with an asymmetrical sulphide, and it is now found that the main product (over 58% yield) from propylene sulphide is 2-*acetylthiopropyl acetate* (X). Possibly some (III) is also formed, although there is no evidence of its presence. The structure of (X) is proved by converting it into the corresponding 2-*mercaptopropan*-1-*ol* (XI), the boiling point of which is higher than that of the isomeric (IV). The 2 : 4-*dinitrophenyl thioether* [XIII; $R = 2:4\text{-}(NO_2)_2C_6H_3$] derived from (XI) has a much lower melting point than the isomer (VI). Though (XIII) is a primary alcohol, no carboxylic acid was isolated on oxidation with chromic acid, and potassium permanganate gives potassium 2 : 4-dinitrobenzene sulphonate. This permanganate oxidation, perhaps caused by the sulphur atom in (XIII) being attached to a secondary carbon atom, is again different from that of 2-(2 :4-dinitrophenylthio)ethan-1-ol, which gives the disulphone. Further, (XI) reacts with two moles of phenyl *iso*cyanate to form a *derivative* (XIV) different from (V). Hence, the structure of (XI) and the normal ring-opening of propylene sulphide by acetic anhydride in the presence of pyridine are definitely established.

Apparently, aqueous hydrochloric acid, like acetyl chloride and bromide, reacts abnormally with propylene sulphide, as a 50% yield of a liquid regarded as 2-chloropropane-1-thiol (IX) is isolated, and this is identical with the product obtained by hydrolysis of 2-chloropropyl thiolacetate (II). It is possible that the fission of propylene sulphide with hydrochloric acid leads to some of the normal isomer which then may give rise to some of the higher-boiling material obtained, just as the necessarily normal opening of ethylene sulphide with hydrochloric acid (Delépine and Eschenbrenner, *Bull. Soc. chim.*, 1923, **33**, 703) also yielded a high-boiling fraction. Samples of (IX), prepared by the four methods indicated in the diagram, seem to be identical, since there is no significant difference in their refractive index or boiling point, and they give identical *thiolurethanes* (XVII) with phenyl and α-naphthyl *iso*cyanate. On attempting to prepare the 2 : 4-dinitrophenyl thioether from (IX), the alkaline conditions required for the reaction result in the conversion of (IX) into propylene sulphide or a polymer (cf. the preparation of ethylene sulphides from 1 : 2-chloro-thiols, Coltof, U.S.P. 2,783,860), and no derivative is formed. However, (IX) obtained from (IV) or (XI) by hydrochloric acid, reacts with picryl chloride in the presence of sodium acetate to form the crystalline *thioether* (XVIII), which is also obtained from (VI) by phosphorus pentachloride. Because of the mild alkaline conditions employed, this production of (XVIII) from different samples of (IX) constitutes the best proof of their identity.



R = 2 : 4-$(NO_2)_2C_6H_3$– or 2 : 4 : 6-$(NO_2)_3C_6H_2$–.
hydr. = hydrolysis by 1% methanolic hydrogen chloride.

The compound regarded as 2-chloropropane-1-thiol (IX) was first prepared by Sjöberg (*loc. cit.*) by the interaction of 1-mercaptopropan-2-ol (IV) and aqueous hydrochloric acid. However, this is no proof of structure, as the same compound is found to be similarly obtained from the isomeric 2-mercaptopropan-1-ol (XI). Apart from the fact that (IX) is obtained on hydrolysis of 2-chloropropyl 1-thiolacetate (II), the formula assigned to it is thought probable for the following reasons. Bennett and Hock (*J.*, 1925, **127**, 2671; Bennett, *Trans., Faraday Soc.*, 1941, **37**, 796) were the first to explain a number of fissions of carbon–sulphur links by means of an intermediary sulphonium ion. Ions of the type (XII) would be expected to be unstable, as it has been shown by Culvenor *et al.* (*loc. cit.*, p. 284) that the ring in aliphatic ethylene sulphides undergoes fission when the higher valency of sulphur is invoked. The rupture of (XII) to form a carbonium ion would, by analogy with the numerous nucleophilic attacks on the $C_{(2)}$ of propylene, be expected to produce (IX) rather than the unknown isomeric chloropropanethiol. This sulphonium ion concept explains the similar conversion (Fuson, Price, and Burness, *J. Org. Chem.*, 1946, **11**, 477), by hydrochloric acid, of both R·S·CHMe·$CH_2$·OH and R·S·$CH_2$·CHMe·OH into R·S·$CH_2$·CHMeCl (where R = Et). A similar rearrangement involving nitrogen instead of sulphur is described by Schultz and Sprague (*J. Amer. Chem. Soc.*, 1948, **70**, 48).

The base-catalysed alcoholysis of propylene oxide (Chitwood and Freure, *loc. cit.*) is analogous to the normal opening of propylene sulphide with acetic anhydride containing pyridine, and can be attributed to the presence of pyridine acetate and to the acetate ion reacting with $C_{(1)}$ which has a lower electron density than $C_{(2)}$. The thiol group formed is then acetylated. It is noteworthy that this normal reaction is very much slower than the abnormal one with acetyl chloride.

The abnormal opening of the propylene sulphide ring by acetyl chloride and bromide, and probably by hydrochloric acid, affords interesting implications when compared with the action of such reagents on ethylene oxides. Propylene oxide and hydrochloric acid give the normal product almost entirely (Smith, *Z. physikal. Chem.*, 1919, **93**, 59), though acid-catalysed alcoholysis yields a mixture of normal and abnormal products (Chitwood and Freure, *loc. cit.*). There appears not to be a record of the action of acetyl halides on propylene oxide, but Sjöberg (*Chem. Abstr.*, 1943, **37**, 4363) shows that the product (73% yield) of the interaction of acetyl chloride and epichlorohydrin is normal, and that the product (37% yield) from glycidol is 92% normal. Similar results are obtained in the reaction of glycidol and epichlorohydrin with allyl alcohol in the presence of acid (Swern, Billen, and Knight, *J. Amer. Chem. Soc.*, 1949, **71**, 1152). The sulphur in ethylene sulphides is known to exert its higher valency towards methyl iodide far more easily than does the oxygen in ethylene oxides (Culvenor *et al.*, *loc. cit.*, p. 285) and it is tentatively suggested that hydrochloric acid and acetyl halides likewise form an onium ion to a greater extent with ethylene sulphides than with oxides. This would account for formation of much larger amounts of abnormal products from ethylene sulphides than from ethylene oxides.

Further work on a comparison of reactions of ethylene oxides and sulphides is being carried out. It is already clear that a deduction of the reactions of ethylene sulphides from formal analogy with those of ethylene oxides can be most misleading.

## EXPERIMENTAL.

*Reaction of Propylene Sulphide with Acetyl Halides.*—Propylene sulphide was prepared from propylene oxide and thiourea by a modification of the method described by Culvenor, Davies, and Pausacker (*J.*, 1946, 1050). The preliminary stirring at 0° was omitted, the propylene sulphide added in portions, and the temperature maintained at 20° by efficient stirring and external temperature control during the whole reaction period of 3½ hours. Distillation of the product was effected without undue delay, fractionation giving a product, b. p. 74·5° (yield, 70%).

2-Chloropropyl thiolacetate (II) was prepared from propylene sulphide and acetyl chloride (Culvenor, Davies, and Heath, *J.*, 1949, 286). During fractionation, the b. p. (70—71°/9 mm.) and $n_D^{15}$ (1·491) of the distillate remained constant. (II) was unchanged when boiled with dry pyridine in benzene, but was converted into high-boiling material by interaction with sodium cyanide in alcohol in the presence of a phenol buffer.

(II) (7·6 g.), anhydrous potassium acetate (7 g.), glacial acetic acid (5 ml.), and acetic anhydride (1 ml.) were refluxed until precipitation of potassium chloride ceased (3 hours). The cold mixture was agitated for a short time with water (30 ml.). The washed and dried ethereal extract gave 1-*acetylthio*-2-*propyl acetate* (III) (3·5 g.), b. p. 119—121°/19 mm., having a slight, pleasant odour (Found: C, 47·45; H, 7·05. $C_7H_{12}O_3S$ requires C, 47·7; H, 6·8%). The b. p. and $n_D^{13}$ (1·467) were constant throughout the distillation.

1-Mercaptopropan-2-ol (IV) was obtained when (III) (3 g.) was heated under reflux with 1% methanolic hydrogen chloride (7 ml.) for 6 hours, the mixture being then distilled. (IV), b. p. 70—71°/20 mm., $n_D^{16}$ 1·4815, is completely miscible with water, has an odour resembling that of mercaptoethanol, and gives colour tests characteristic of primary and secondary mercaptans (violet with aqueous sodium nitroprusside, and red with nascent nitrous acid). Sjöberg (*loc. cit.*) recorded b. p. 51°/12 mm. and $n_D^{20}$ 1·4862 for the compound which he assumed to be 1-mercaptopropan-2-ol. (IV) and 2 moles of phenyl *iso*cyanate (cf. Bennett, *J.*, 1922, **121**, 2145) at 100° (2 hours) gave *propylene* 2-*phenylcarbamate* 1-*phenylthiolcarbamate* (V), m. p. 140·5°, prisms from alcohol–light petroleum (Found: N, 8·9. $C_{17}H_{18}O_3N_2S$ requires N, 8·5%). (IV) (0·1 g.) and picryl chloride (0·25 g.) were dissolved in alcohol (10 ml.), and a solution of anhydrous sodium acetate (0·1 g.) in alcohol (5 ml.) was added gradually with thorough mixing, a red colour being produced. After 5 minutes the mixture was warmed on the water-bath for 10 minutes. Addition of water gave 1-*picrylthiopropan*-2-*ol* (VI), m. p. 68°, lustrous light-yellow plates from aqueous alcohol (Found: N, 13·65. $C_9H_9O_7N_3S$ requires N, 13·85%). 1-(2 : 4-*Dinitrophenylthio*)*propan*-2-*ol* [VI; R = 2 : 4-$(NO_2)_2C_6H_3$], m. p. 94°, yellow warts from benzene–light petroleum (Found: N, 11·0. $C_9H_{10}O_5N_2S$ requires N, 10·85%), was obtained from equimolar proportions of (IV), 1-chloro-2 : 4-dinitrobenzene, and sodium hydroxide in alcohol (cf. Bennett and Whincop, *J.*, 1921, **119**, 1863). As shown by a mixed m. p., (VI) was also obtained from 1-bromopropan-2-ol, 2 : 4-dinitrothiophenol, and sodium hydroxide in alcohol, the reactants being warmed on the water-bath for 1 hour (cf. Willgerodt, *Ber.*, 1885, **18**, 328).

(2 : 4-*Dinitrophenylthio*)*acetone* [VII; R = 2 : 4-$(NO_2)_2C_6H_3$], m. p. 139°, pale yellow needles from aqueous dioxan (Found: N, 11·2; S, 12·85. $C_9H_8O_5N_2S$ requires N, 10·95; S, 12·5%), was obtained (*a*) when (VI) (0·5 g.) was dissolved in the minimum volume of glacial acetic acid, and a solution of sodium dichromate (0·7 g.) in dilute sulphuric acid (5 ml.) added gradually, the mixture being then boiled for 5 minutes, and (*b*) on warming equimolar quantities of bromoacetone, 2 : 4-dinitrothiophenol, and sodium hydroxide in alcohol for 10 minutes, as evinced by a mixed m. p. determination. (VII) is sparingly soluble in alcohol and its dioxan solution gives a red precipitate on treatment with a warm solution of *p*-nitrophenylhydrazine hydrochloride and does not decolourise cold dilute permanganate.

1-Mercaptopropan-2-ol (IV), prepared according to the method of Sjöberg (*loc. cit.*), had properties similar to those of a sample prepared by hydrolysis of (III) (*e.g.*, $n_D^{16}$ 1·484, b. p. 50—55°/10 mm.). It reacted with 1-chloro-2 : 4-dinitrobenzene to give (VI), as evinced by a mixed m. p. determination.

2-*Bromopropyl thiolacetate* was obtained in 95% yield when propylene sulphide (14·8 g.) was added in small portions with slight agitation and external cooling to freshly distilled acetyl bromide (15·3 ml.), and the mixture was kept at 35° for 2½ hours before distillation (Found: S, 15·65. $C_5H_9OSBr$ requires S, 16·25%). This liquid, b. p. 45°/0·2 mm. (85—88°/10 mm. with slight decomposition), $n_D^{13}$ 1·521, if freshly distilled has the pleasant odour characteristic of thiol esters. However rapid decomposition occurs in air with development of the highly unpleasant odour of a halogeno-thiol and formation of hydrogen bromide. 2-Bromopropyl thiolacetate is stable in contact with aqueous sodium hydrogen carbonate. The pure liquid may be stored without decomposition in a sealed ampoule. Reduction of the ester with zinc dust and glacial acetic acid at 100° gave a halogen-free oil with an unpleasant odour, b. p. 96—104°/15 mm., $n_D^{14}$ 1·458, which was apparently *not* the desired propyl thiolacetate as it is unchanged on attempted hydrolysis. Reduction of the ester with tin and hydrochloric acid caused rapid hydrolysis and subsequent polymerisation. Treatment with sodium acetate, using the method as described for the chloro-ester and potassium acetate, also yielded 1-acetylthio-2-propyl acetate (III), b. p. 112—114°/15 mm. (55% yield, the balance being polymer); its identity was established by hydrolysis with 1% methanolic hydrogen chloride to give 1-mercaptopropan-2-ol (IV), b. p. 58—60°/15 mm., identified by a mixed melting point determination of its 2 : 4-dinitrophenyl thioether (VI) which was obtained in 80% yield.

*Reaction of Propylene Sulphide with Acetic Anhydride.*—Propylene sulphide (14·8 g.), freshly distilled acetic anhydride (25 g.), and pyridine (1·5 ml.) were heated under reflux on the water-bath for 6 hours and then in an oil-bath at 130° for a further 3 hours. The product distilled over the range 97—103°/10 mm., further fractionation yielding 2-*acetylthiopropyl acetate* (X), b. p. 103—105°/11 mm., $n_D^{15}$ 1·4702 (20·6 g.) (Found : C, 47·5; H, 7·0. $C_7H_{12}O_3S$ requires C, 47·7; H, 6·8%). It has a slight, pleasant odour. Hydrolysis [method as for isomer (III)] yielded 2-*mercaptopropan*-1-*ol* (XI), b. p. 60—62°/12 mm., 68°/25 mm., $n_D^{17}$ 1·4818 (Found : C, 37·85; H, 8·6. $C_3H_8OS$ requires C, 39·1; H, 8·7%). Like its isomer (IV), it is completely miscible with water, has a slightly unpleasant odour, and gives a mauve colour with sodium nitroprusside and a red colour with nitrous acid. During distillation of (X) and (XI) no change occurred. On heating (XI) at 100° for 2 hours with two moles of phenyl *iso*cyanate *propylene* 1-*phenylcarbamate* 2-*phenylthiolcarbamate* (XIV), m. p. 157·5°, prisms from aqueous alcohol (Found : N, 8·7. $C_{17}H_{18}O_3N_2S$ requires N, 8·5%), were obtained.

2-(2 : 4-*Dinitrophenylthio*)*propan*-1-*ol* [XIII; R = 2 : 4-$(NO_2)_2C_6H_3$], m. p. 64°, yellow warts from benzene–light petroleum (Found : C, 41·8; H, 3·7. $C_9H_{10}O_5N_2S$ requires C, 41·85; H, 3·85%), was obtained from (XI), 1-chloro-2 : 4-dinitrobenzene, and sodium hydroxide in alcohol [method as for (VI), crystallisation being difficult]. Oxidation of (XIII) with chromic acid gave a polymer and water-soluble material which is difficult to extract. Oxidation at 70° with 3% aqueous potassium permanganate gave potassium 2 : 4-dinitrobenzenesulphonate (Found : N, 10·15. Calc. for $C_6H_3O_7N_2SK$ : N, 9·8%), which explodes on heating and is soluble in water. 1-(2 : 4-Dinitrophenylthio)propan-2-ol, prepared by the method of Bennett and Whincop (*loc. cit.*) from mercaptoethanol, 1-chloro-2 : 4-dinitrobenzene, and sodium hydroxide in alcohol, when similarly oxidised with potassium permanganate yielded white plates, m. p. 183—185°, on extraction with ether. The m. p. was not depressed on admixture with an authentic specimen of 2 : 4-dinitrophenylsulphonylmethane.

*Reaction of Propylene Sulphide with Hydrochloric Acid.*— A solution of propylene sulphide (14·8 g.) in methanol (20 ml.) was added with shaking and external cooling to a solution of concentrated aqueous hydrochloric acid (25 ml.) in methanol (30 ml.), and the mixture set aside for 19 hours, after which an unpleasant-smelling oil separated. Water (100 ml.) was added and the oil extracted with chloroform without delay, washed, dried ($CaCl_2$), and distilled. A small amount of propylene sulphide distilled and then a fraction, b. p. 59—61°/80 mm. Redistillation gave 2-chloropropane-1-thiol (IX), b. p. 124—125°/760 mm., 60°/80 mm. ; $n_D^{13}$ (1·484) of the distillate did not vary during the distillations, even when a fractionating column was used. The yield was 11·0 g., higher-boiling halogen-containing liquids comprising the balance. Sjöberg (*loc. cit.*) records b. p. 125—125·5°/764 mm., $n_D^{20}$ 1·4852 for the compound which he assumes to be 2-chloropropane-1-thiol, and reports it to be decomposed immediately by aqueous alkali. Though (IX) does not form a derivative with 1-chloro-2 : 4-dinitrobenzene and sodium hydroxide, or with 1-fluoro-2 : 4-dinitrobenzene and sodium acetate, the unpleasant odour of the halogeno-thiol is replaced by the rather fragrant odour of propylene sulphide, and sodium chloride is precipitated. (IX) is comparatively inert to phenyl *iso*cyanate, heating in a sealed tube at 160° for 3 hours being necessary to effect conversion into 2-*chloropropyl* 1-*phenylcarbamate* (XVII), m. p. 91·5°, prisms from light petroleum containing a few drops of benzene (Found : N, 6·3; S, 14·35. $C_{10}H_{12}ONSCl$ requires N, 6·1; S, 13·95%); this derivative is obtained in good yield from both first and last fractions of the distillate. Similarly (IX) reacts with α-naphthyl *iso*cyanate to give 2-*chloropropyl* 1-α-*naphthylthiolcarbamate*, m. p. 110° (Found : N, 5·0. $C_{14}H_{14}ONSCl$ requires N, 5·0%). 2-Chloropropane-1-thiol (IX) was again obtained when 2-chloropropyl thiolacetate (II) (7·6 g.) was heated under reflux for 2 hours with 2% methanolic hydrogen chloride. Distillation gave 3·4 g. of product, b. p. 67—68°/85 mm., 124—125°/760 mm., $n_D^{14}$ 1·484, which yielded with phenyl and α-naphthyl *iso*cyanates, respectively, the derivatives reported above. The residue from the distillation was a mobile, halogen-containing liquid of very high b. p. Distillation of a crude sample of (IX) at atmospheric pressure resulted in profound decomposition and the product contained hydrogen chloride and a liquid (b. p. 77°) with the odour of propylene sulphide; this, on storage, was replaced by that of the chloro-thiol.

2-Chloropropane-1-thiol (IX), prepared according to Sjöberg (*loc. cit.*) by treatment of 1-mercaptopropan-2-ol (IV) with concentrated aqueous hydrochloric acid, had b. p. 58—60°/80 mm., 124—125°/760 mm., $n_D^{16}$ 1·486, and $n_D^{14}$ 1·487. The yield was 66%, the residue consisting of high-boiling halogen-containing liquid. (IX) prepared by this method also gives derivatives with phenyl and α-naphthyl *iso*cyanates identical with those from (IX) prepared from propylene sulphide and hydrogen chloride. Also, (IX) (0·15 g.), picryl chloride (0·24 g.), and anhydrous sodium acetate (0·2 g.) in alcohol (5 ml.), on storage for 16 hours and dilution with water, yielded 2-*chloro*-1-*picrylthiopropane* (XVIII; R = picryl), m. p. 86°, small yellow needles from benzene–light petroleum (Found : N, 12·85. $C_9H_8O_6N_3SCl$ requires N, 13·05%). (XVIII), which contained halogen, gave an appreciable depression in m. p. on admixture with picryl chloride, but not with the product obtained on treatment of (VI) in chloroform with phosphorus pentachloride, followed by evaporation of the solvent and pouring of the mixture into water.

2-Mercaptopropan-1-ol (XI) (4·2 g.) and concentrated aqueous hydrochloric acid (17 ml.) were warmed on the water-bath. An immediate turbidity developed, and after 15 minutes the mixture was cooled and the oily layer extracted with ether, dried ($CaCl_2$), and distilled. The distillate, b. p. 41°/30 mm., 55°/50 mm., 62°/70 mm., $n_D^{14}$ 1·488, gave steady boiling points when distilled at different pressures. With phenyl *iso*cyanate and picryl chloride respectively it gave derivatives identical with those obtained from (IX) prepared by the interaction of (IV) and hydrogen chloride.

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