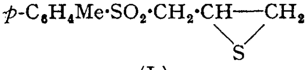
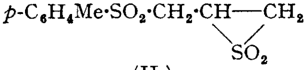
471. *Some Reactions of Arylsulphonylpropane Derivatives.*

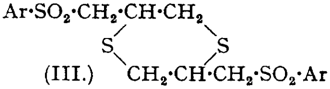
By C. C. J. Culvenor, W. Davies, and W. E. Savige.

It is shown that arylsulphonyl-2 : 3-dibromopropanes react (i) with potassium sulphide to form dithians, and not ethylene sulphides (as I) as reported by Troeger and Hornung (*J. pr. Chem.*, 1897, **56**, 445), and (ii) with water under pressure to give, not the glycol claimed by Troeger and his co-workers, but the olefinic alcohol such as 3-p-*tolylsulphonylprop*-2-*en*-1-ol (V). This alcohol may also be prepared from epichlorohydrin and sodium toluenesulphinate or from 1-*chloro*-3-p-*tolylsulphonylpropan*-2-*ol* (as XI) and cold alkali. It dimerises in the presence of hot alkali to the dioxan (XIV) and is converted by phosphorus pentachloride into the corresponding 3-*chloro*-1-p-*tolylsulphonylprop*-1-*ene* (as VI). Reduction of this chloropropene gives tolyl allyl sulphone, and (VI) is isomerised by catalysts into 1-*chloro*-3-p-*tolylsulphonylprop*-1-*ene* (IV), in both cases migration of the double bond occurring. The chloropropenes (VI) and (IV) both add a molecule of alcohol to give the same ethoxy-chloride. Other ready reactions of this sulphonylpropene type of compound, such as fission of the sulphone linkage with alkali, are described.

It is well known that the interaction of alkali-metal sulphides and dihalogenoethanes usually gives sulphur compounds of high molecular weight, together with dithian derivatives. Occasionally the olefin and sulphur are formed (Delépine and Ville, *Bull. Soc. chim.*, 1920, **27**, 678), but the reported formation of the simple ethylene sulphide is restricted to very few examples, among them being the formation of 3-*p*-tolylsulphonyl-1 : 2-propylene sulphide (I), m. p. 181°, from aqueous potassium sulphide and 1 : 2-dibromo-3-*p*-tolylsulphonylpropane, reported by Troeger and Hornung (*loc. cit.*). It is remarkable also that those authors were able to oxidise their olefinic sulphide with permanganate to the sulphone, for it has been shown (Culvenor, Davies, and Heath, this vol., p. 285) that this is not possible with simple olefin sulphides. A


(I.)

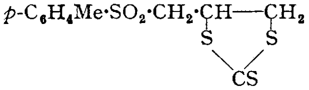

(II.)


(III.)

$p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CHCl$
(IV.)

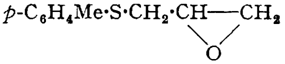
$p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$
(V.)

$p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2Cl$
(VI.)


(VII.)

$(p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2)_2S$
(VIII.)

$p\text{-}C_6H_4Me{\cdot}S{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$
(X.)


(IX.)

repetition of their work shows that their " olefinic sulphide," when purified from much amorphous material of high molecular weight, has m. p. 189—190°, and not 181°, and analysis and a molecular-weight determination show it to be 2 : 5-*bis*-p-*tolylsulphonylmethyl*-1 : 4-*dithian* (III; Ar = *p*-C_6H_4Me). The sulphone (m. p. 200°) which they obtained from this must therefore be 2 : 5-*bis*-p-*tolylsulphonylmethyl*-1 : 4-*dithian* 1 : 1 : 4 : 4-*tetraoxide* and not (II). Troeger and Hornung (*loc. cit.*, p. 448) also similarly condensed 1 : 2-dibromo-3-phenylsulphonylpropane with potassium sulphide, and the analysis and molecular weight of the resulting compound, m. p. 157—158°, indicated the formula $C_{18}H_{20}O_5S_4$; the structural formula ascribed to this contained two ethylene sulphide groups. It is now found that the compound (actual m. p. 158—159°) is also a dithian derivative, viz., 2 : 5-*bisphenylsulphonylmethyl*-1 : 4-*dithian* (III; Ar = Ph). It follows that the product (m. p. >230°) which they obtained from its oxidation with permanganate is 2 : 5-*bisphenylsulphonylmethyl*-1 : 4-*dithian* 1 : 1 : 4 : 4-*tetraoxide*.

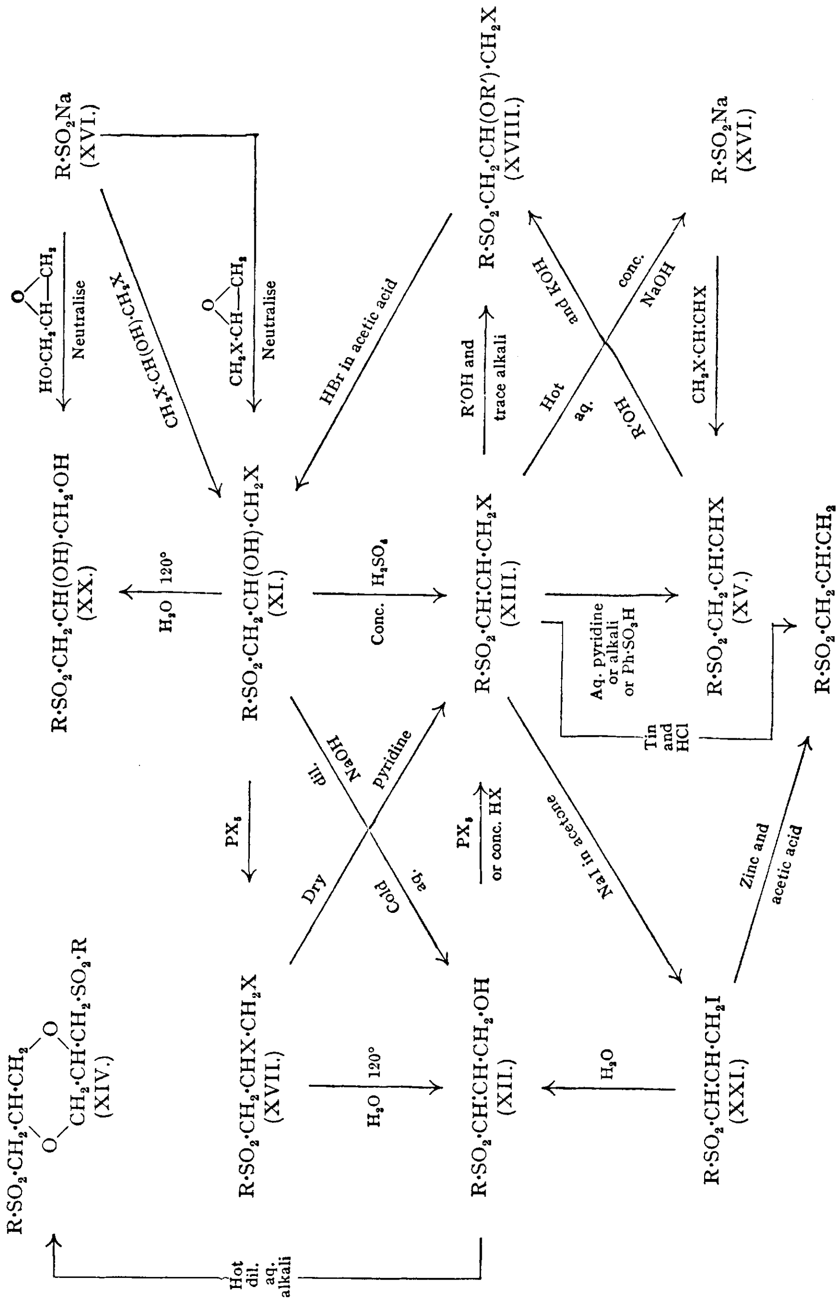
Unsuccessful efforts have been made to prepare *p*-tolylsulphonylpropylene oxide corresponding to (I), from which (I) might be obtained by the action of thiourea. Oxidation with hydrogen peroxide of 1-p-*tolylthio*-2 : 3-*epoxypropane* (IX), prepared from thiocresol and epichlorohydrin, gives an unidentified oil which is not *p*-tolylsulphonylpropylene oxide. Hydrolysis of (IX) with dilute sulphuric acid forms 3-p-*tolylthiopropane*-1 : 2-*diol* (X), which is also formed from potassium thiocresoxide and glycerol monochlorohydrin.

It has already been shown (Culvenor, Davies, and Heath, this vol., p. 281) that sodium toluene-*p*-sulphinate reacts with simple ethylene oxides to form β-hydroxy-sulphones. Similarly, from propylene oxide 1-p-*tolylsulphonylpropan*-2-*ol* is obtained, oxidisable to *p*-tolylsulphonylacetone, identical with that prepared by Otto and Otto (*J. pr. Chem.*, 1887, **36**, 426) from the sulphinate and bromoacetone. Sodium toluene-*p*-sulphinate and epichlorohydrin give 1-*chloro*-3-p-*tolylsulphonylpropan*-2-*ol* (XI; R = *p*-C_6H_4Me, X = Cl) provided that the alkali formed is continuously neutralised during the reaction. It has also been prepared from sodium toluene-*p*-sulphinate and glycerol 1 : 3-dichlorohydrin, and is converted by cold dilute alkali into 3-p-*tolylsulphonylprop*-2-*en*-1-*ol* (V), m. p. 122°. This product (V) is formed in high yield, along with a little 2 : 5-*bis*-p-*tolylsulphonylmethyldioxan* (XIV; $R = p\text{-}C_6H_4Me$), when the toluenesulphinate and epichlorohydrin are allowed to react without external neutralisation.

The structure of (V) is shown by the formation of a *phenylurethane*, by acetylation with keten to give 1-p-*tolylsulphonyl*-3-*acetoxyprop*-1-*ene* (as XIII; X = OAc), by benzoylation to form 1-p-*tolylsulphonyl*-3-*benzoyloxyprop*-1-*ene* (as XIII; X = O·COPh), and by conversion with phosphorus pentachloride (or concentrated hydrochloric acid under pressure), and phosphorus pentabromide into 3-*chloro*-1-p-*tolylsulphonylprop*-1-*ene* (VI) and 3-*bromo*-1-p-*tolylsulphonylprop*-1-*ene* (as XIII), respectively. Infra-red spectrum determination also indicates that the structure (V) is correct. It is known that the addition of alcohol to αβ-unsaturated sulphones takes place with great ease in the presence of a basic catalyst (*e.g.*, Alexander and McCombie, *J.*, 1931, 1913), and in agreement with this (V) is immediately dimerised by warm dilute sodium hydroxide solution to form the dioxan (as XIV). With potassium ethyl xanthate (V) forms 3-p-*tolylsulphonyl*-1 : 2-*propylene trithiocarbonate* (VII). This seems to be the first recorded instance of trithiocarbonate formation from a compound isomeric with an ethylene oxide and shows that the production of this type of derivative is not always a good test for an ethylene oxide structure. In this case, addition of the xanthate to the double bond produces the same intermediate (or isomer) as would be obtained by opening the oxide ring, and hence the trithiocarbonate is formed. It may also be obtained from potassium xanthate and the chlorohydrin (XI; $R = p\text{-}C_6H_4Me$, X = Cl). Although xanthate reacts easily, thiourea and potassium thiocyanate have no action on (V) unless heated under pressure, and the products are then complex and not identifiable.

The condensation of chloropropylene sulphide with sodium toluene-*p*-sulphinate gives an unidentified oil, and not the desired ethylene sulphide (I). Other attempts to prepare (I) without the use of the corresponding ethylene oxide as intermediary have also been unsuccessful.

The diagram on p. 2200 summarises a number of the reactions of products derived from the condensation of sodium sulphinates (XVI) with epichlorohydrin and related compounds. Many of these reactions have been carried out when R is *p*-tolyl, phenyl, and benzyl. The last choice has been made because some compounds which theoretically could be derived from the products of this reaction have already been prepared, though in different ways. Thus 3-chloro-1-benzylsulphonylprop-1-ene and 3-bromo-1-benzylsulphonylprop-1-ene (XIII) have been made by Rothstein (*J.*, 1937, 309) by the action of pyridine on the corresponding dihalides (XVII), and these compounds are identical with those derived from the action of phosphorus pentachloride or pentabromide on 3-*benzylsulphonylprop*-2-*en*-1-*ol* (XII; $R = CH_2Ph$). It is noteworthy that (XIII; $R = p\text{-}Me{\cdot}C_6H_4$, X = Cl) can isomerise in the presence of basic catalysts or benzenesulphonic acid to form 1-*chloro*-3-p-*tolylsulphonylprop*-1-*ene* (IV), m. p. 74°. The structure of this compound, m. p. 74°, is shown by its synthesis from 1 : 3-dichloropropene and sodium toluene-*p*-sulphinate. During this synthesis the reaction mixture was made faintly acid in order to prevent possible isomerisation of the initial product in the presence of traces of alkali. Rothstein (*loc. cit.*) had prepared the analogous 1-bromo-3-benzylsulphonylprop-1-ene (XV; $R = CH_2Ph$, X = Br) in a similar way from 1 : 3-dibromopropene and sodium benzylsulphinate, and subsequent reactions which he carried out show that he assigned the correct structure to this compound. The possibility of (VI) and (IV) being geometrical isomerides is negatived by the experiments recorded on p. 2204, and the chemical properties of the two isomers support the formulæ assigned to them. For example, the chlorine in (VI) is reactive, for with potassium hydrogen sulphide it rapidly gives an unsaturated compound which is probably *di*-(3-p-*tolylsulphonylprop*-2-*enyl*) *sulphide* (VIII). Also, (VI) is very reactive towards sodium iodide, but (IV) is not. This is in conformity with observations by Conant, Kirner, and Hussey (*J. Amer. Chem. Soc.*, 1924, **46**, 232; 1925, **47**, 476, 488) on relative reactivities of allyl and vinyl chlorides with potassium iodide. Moreover, (VI) is less stable towards sodium hydroxide and decolorises aqueous potassium permanganate more rapidly than does the isomeric vinyl chloride (IV). (XIII; $R = CH_2Ph$, X = Br) also isomerises in the presence of dilute alkali. It is surprising that Rothstein (*loc. cit.*), who prepared both of these benzyl isomers by other methods, did not attempt to bring about this interconversion. He had, however, previously found (*J.*, 1934, 684) that no interconversion between the halogen-free benzyl-1- and -2-propenyl sulphones, $CH_2Ph{\cdot}SO_2{\cdot}CH{:}CHMe$ and $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CH_2$, could be effected. In the presence of alkali, the latter compound reacted with alcohol to form the β-alkoxy-derivative. (VI) and (IV) react with alcoholic alkali in the same way, very mild conditions being required, but alkali with increasing concentration and temperature will convert (VI) into the dioxan (as XIV), or finally bring about fission of the sulphone linkage to form sodium toluene-*p*-sulphinate. The isomeric change in alkali is an example of three-carbon prototropy, similar to that encountered by Rothstein (*J.*, 1937, 309) in certain disulphones, and also to that described by Connor (Gilman "Organic Chemistry," 1943, Wiley, p. 876) with respect to certain cyclic sulphones. In regard to the latter, Boëseken and van Zuydewijn (*Proc. Acad. Sci. Amsterdam*, 1937, **40**, 23; *Chem. Abs.*, 1937, **31**, 4953) found that cyclic isoprene sulphones with alkali gave a mixture of isomers, the main one of which had the double bond in the αβ-position to the sulphonyl group.



With unsaturated monosulphones, some added factor, such as existence of a ring, whereby the electron-attracting effect of the sulphonyl group is magnified, is apparently necessary to bring about this allylic rearrangement. It is noteworthy that in the present investigation the effect of alkali on (VI) is to produce (IV), in which the double bond is in the $\beta\gamma$-position. The presence of the halogen may be responsible for this isomerism in this acyclic type of monosulphone, and the $\beta\gamma$-position of the double bond may be due to the $(+T)$ or electromeric effect of the halogen atom (compare Baker, " Tautomerism," 1934, Routledge, pp. 20, 29, 87, 88). However, the rôle of benzenesulphonic acid, which has the same effect as alkali, is not understood, as both isomers are stable to hydrochloric, acetic, and sulphuric acid. Another phenomenon is the " double-bond migration," which occurs also during reduction of (XIII; X = Br or I) with zinc and acetic acid, or of (XIII; R = Cl) with tin and hydrochloric acid, the corresponding allyl sulphone being obtained in each case. This rearrangement possibly occurs in the unstable transition state during the replacement of halogen by hydrogen, *e.g.*,

$$\text{(XIII)} \xrightarrow{\text{H}} \text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{X} \xrightarrow{\text{H}} \text{(XIX)} + \text{HX}$$

To throw more light on the production of the olefinic alcohols from epichlorohydrin, the glycol, 3-p-*tolylsulphonylpropane*-1 : 2-*diol* (XX; R = *p*-C_6H_4Me), was prepared. Troeger and Hinze (*J. pr. Chem.*, 1897, **55**, 213) claimed to have obtained this compound as plates, m. p. 93—95°, insoluble in cold water, by heating 1 : 2-dibromo-3-(*p*-tolylsulphonyl)propane (XVII; R = *p*-C_6H_4Me, X = Br) with water under pressure. A repetition of this reaction has yielded only the olefinic alcohol (V), which has m. p. 122° but, if incompletely dried, melts partially in the range 90—95°. Since the glycol as prepared below has m. p. 74—75°, Troeger and Hinze's product was probably a moist sample of (V). It is easy to overlook the glycol, which tends to retain water, in which it is very soluble, and it is initially difficult to obtain it crystalline except from benzene in the presence of dehydrating agents. On the other hand, the olefinic alcohol is sparingly soluble in cold water. Their work was possibly influenced by the earlier reported conversion under similar conditions of 1 : 2-dibromo-3-phenylsulphonylpropane into 3-phenylsulphonylpropane-1 : 2-diol (XX; R = Ph) by Otto (*Annalen*, 1894, **283**, 189), who also prepared from this product a derivative, m. p. 86—87°, which he regarded as the dibenzoate. However, it was noticed that his supposed glycol had the same physical properties as 3-*phenylsulphonylprop*-2-*en*-1-*ol* (XII; R = Ph), with which, on repetition of the reaction, the product was found to be identical. It was also found that Otto had miscalculated the theoretical analytical data for the " dibenzoate," of which his analysis agreed more closely with the olefinic monobenzoate (XIII; R = Ph, X = OBz). Otto stated that the " glycol " did not react with benzoyl chloride even at 140° and converted it first into the sodium derivative, but it is now found that the alcohol (XII; R = Ph) reacts directly with benzoyl chloride at 100° to form 1-*phenylsulphonyl*-3-*benzoyloxyprop*-1-*ene*, which has the same physical properties as the reported " dibenzoate." Another case of glycol formation, from the reaction of 1 : 2-dibromo-3-benzylsulphonylpropane (XVII; R = CH_2Ph, X = Br) with water under pressure, has been claimed by van Zuydewijn (*Rec. Trav. chim.*, 1938, **57**, 455), who analysed his compound for sulphur only. Once again, it is now found that the product is the olefinic alcohol (XII; R = CH_2Ph), which has essentially the same physical properties (including low solubility in water) as the compound recorded by van Zuydewijn. Furthermore, Troeger and Hinze (*loc. cit.*) and Troeger and Artmann (*J. pr. Chem.*, 1896, **53**, 467) found that the 1 : 2-dibromo-3-α- and -β-naphthylsulphonylpropane (XVII; R = $C_{10}H_7$, X = Br), in the same way, gave compounds, m. p. 127° and 167°, respectively, which analysed correctly for the corresponding ethylene oxides, although these structures were only tentatively given, and they are listed as ethylene oxides in Beilstein (Vol. VI, pp. 622, 658) with a mark of interrogation.

It is now clear by analogy that the compounds are actually 3-α- and -β-*naphthylsulphonylprop*-2-*en*-1-*ol*. Similarly, the two " naphthylsulphonylpropylene sulphides," formed from the same $\beta\gamma$-dibromo-derivatives and potassium sulphide, cannot have the three-membered sulphide ring. These amorphous substances are undoubtedly of high molecular weight and impure. From the present work, there can be no doubt that all the dibromo-sulphones of the type (XVII; R = Ar) are converted by water at high temperatures, not into the ethylene oxide, but into the isomeric unsaturated alcohol, though small amounts of the soluble glycol are not necessarily precluded.

During the study of the mechanism of formation of the unsaturated alcohol (XII; R = *p*-C_6H_4Me), the corresponding glycol (which gives the dibenzoate, 1-p-*tolylsulphonyl*-2 : 3-*dibenzoyloxypropane*), has been made by the oxidation of the sulphide glycol (X) as well as by the methods shown in the diagram. Neither the glycol nor the chlorohydrin (XI), from which it can be derived, can be an intermediate in the conversion of the dihalide (XVII) into (XII), though it has not been proved that the reaction may not proceed through the unknown isomeric chlorohydrin or the unsaturated chloride (XIII). The surprising ease of the conversion of the chlorohydrin (XI) into the unsaturated alcohol may indicate that the oxide is easily formed but quickly isomerises to (XII) This has some analogy with the formation from epichlorohydrin and sodium acetylide of pent-2-en-4-yn-1-ol, $HC{\vdots}C{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$, and the ready conversion of 3-phenylpropylene oxide into cinnamyl alcohol, which it has been suggested may be " brought about by the tendency to form conjugated vinylacetylene and styrene systems respectively " (Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1584).

EXPERIMENTAL.

Preparation of 2 : 5-*Bisarylsulphonylmethyl*-1 : 4-*dithians* (III).—Phenyl allyl sulphone, b. p. 140—145°/0·7 mm., was made from aqueous alcoholic sodium benzenesulphinate and allyl bromide after Otto (*Annalen*, 1894, **283**, 184) who records it only as an oil. During its conversion by bromine in carbon tetrachloride into 1 : 2-dibromo-3-phenylsulphonylpropane, some hydrogen bromide was evolved. A much better yield (92%) of the dibromo-compound was obtained by carrying out the bromination of the allyl sulphone in aqueous suspension (Otto, *loc. cit.*).

2 : 5-*Bisphenylsulphonylmethyl*-1 : 4-*dithian* (III; Ar = Ph). 1 : 2-Dibromo-3-phenylsulphonylpropane (1·1 g.) was dissolved in absolute alcohol (5 ml.) at about 35° and stirred vigorously while a solution of sodium sulphide crystals (1·2 g.) in water (1½ ml.) was added. After 2 hours' stirring, the mixture was kept overnight, and the white powder which separated was filtered off and crystallised from alcohol, giving the *dithian* as glistening needles, m. p. 157—158° (Found : C, 50·6, 50·7; H, 4·9, 5·0. $C_{18}H_{20}O_4S_4$ requires C, 50·6; H, 4·7%). No red coloration appeared at the onset of the reaction as reported by Troeger and Hornung (who used potassium sulphide).

2 : 5-*Bis*-p-*tolylsulphonylmethyl*-1 : 4-*dithian* (III; Ar = *p*-C_6H_4Me). The corresponding dibromopropane (1 g.) and sodium sulphide (1 g.), when brought into reaction as above and kept at 34° for 2 days, yielded the *dithian* (0·3 g.), which formed clusters of minute needles, m. p. 189—190°, after repeated recrystallisation from alcohol [Found: C, 52·3; H, 5·3; *M* (Rast), 473, 476. $C_{20}H_{24}O_4S_4$ requires C, 52·6; H, 5·25%; *M*, 456].

Derivatives of Thio-p-*cresol*.—1-p-*Tolylthio*-2 : 3-*epoxypropane* (IX). Epichlorohydrin (9·3 g.) was added slowly to a stirred solution of thiocresol (12·4 g.) and potassium hydroxide (5·6 g.) in water (75 ml.) and alcohol (75 ml.), and the stirring continued for 2 hours before dilution with water and extraction with chloroform. Distillation gave 1-p-*tolylthio*-2 : 3-*epoxypropane* (14·2 g.), b. p. 107·5°/0·2 mm. (Found : C, 66·45; H, 6·4. $C_{10}H_{12}OS$ requires C, 66·7; H, 6·65%).

3-p-*Tolylthiopropane*-1 : 2-*diol* (X) was obtained when the oxide (IX) was heated under reflux for 2 hours with dilute sulphuric acid, and the aqueous layer decanted from a little oil and cooled. Recrystallisation from benzene–light petroleum gave plates, m. p. 58° (Found : C, 61·0; H, 7·4. $C_{10}H_{14}O_2S$ requires C, 60·8; H, 7·1%). (X) was also obtained by shaking a mixture of glycerol monochlorohydrin (11·1 g.), thiocresol (12·4 g.), and potassium hydroxide (5·6 g.) in water (50 ml.) and alcohol (10 ml.) for 1 hour at room temperature and 1 hour on the water-bath, and then extracting it with chloroform (yield, 14·1 g.).

The *diacetyl* derivative, b. p. 166°/0·3 mm., was obtained by heating the glycol (X) with acetic anhydride at 100° for 5 hours and distilling the product (Found : C, 60·1; H, 6·6. $C_{14}H_{18}O_4S$ requires C, 60·1; H, 6·4%).

Oxidation of (IX). The oxide (IX) (5·4 g.) and 30% hydrogen peroxide (10 ml.) were dissolved in acetone (25 ml.), and a little solid barium carbonate added (to neutralize an acid stabilising agent in the peroxide). After 9 days at 34°, the acetone was removed on a water-bath, water added, and products were extracted with chloroform. Distillation gave an unidentified oil (3·9 g.), b. p. 157°/0·2 mm. (Found : C, 64·8; H, 6·3%), and a higher-boiling residue decomposed. The oil was apparently unaffected by heating it with sulphuric acid or alkali.

Reactions of Some Tolylsulphonylpropane Derivatives.

1-*Chloro*-3-p-*tolylsulphonylpropan*-2-*ol* (XI; R = *p*-C_6H_4Me, X = Cl).—Sodium toluene-*p*-sulphinate (8·9 g.) and glycerol dichlorohydrin (6·4 g.) were heated under reflux in aqueous alcohol (50 ml.) for 36 hours, the alcohol removed, and the dried benzene extract distilled *in vacuo* to remove unchanged chlorohydrin. The residue, crystallised from benzene, gave the new *chlorohydrin* (XI) (5·1 g.) as small colourless needles, m. p. 84° (Found : C, 48·35; H, 5·5. $C_{10}H_{13}O_3SCl$ requires C, 48·3; H, 5·25%). On warming (XI) with excess of phosphorus pentachloride on the water-bath for 15 minutes, and pouring into water, 1 : 2-dichloro-*p*-tolylsulphonylpropane (XVII; R = *p*-C_6H_4Me, X = Cl) was obtained in good yield. Recrystallisation from benzene–light petroleum gave m. p. 66—69°, which was not depressed on admixture with a specimen, m. p. 70—72°, prepared by treating a solution of tolyl allyl sulphone in carbon tetrachloride with chlorine according to Troeger and Hinze (*J. pr. Chem.*, 1897, **55**, 204).

3-p-*Tolylsulphonylprop*-2-*en*-1-*ol* (V).—(*a*) The chlorohydrin (XI) (1·5 g.) was powdered and stirred for 1½ hours at room temperature with 3% aqueous sodium hydroxide (15 ml.). The *alcohol* (V) (1·2 g.) separated and was crystallised from water (plates or long needles) and from benzene (plates); m. p. 122°. It was also formed on heating the chlorohydrin under reflux with potassium carbonate in aqueous alcohol for 8 minutes [Found : C, 56·9; H, 5·75; *M* (Rast), 216. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·65%; *M*, 212].

(*b*) Epichlorohydrin (4·6 g.) and sodium toluene-*p*-sulphinate (8·9 g.) in water (60 ml.) and alcohol (10 ml.) rapidly became alkaline on admixture. The solution was kept at 32° for 24 hours and gave a semi-solid mass of white plates (9·5 g., 90%) which were identified by mixed m. p. (122°) with the product from the chlorohydrin (XI) and alkali. The crude alcohol (XIV; R = *p*-C_6H_4Me) contained a trace of the dioxan; m. p. 258°. To isolate the intermediate chlorohydrin (XI), the mixture of toluene-sulphinate and epichlorohydrin with phenolphthalein was warmed, and continuously neutralised by titration with 2N-sulphuric acid. After ½ hour, the rate of production of alkali was extremely slow and the reaction practically complete. Cooling produced an oil, which after extraction with chloroform yielded a solid which crystallised from benzene to give (V) (0·8 g.). Concentration of the mother-liquor produced crystals (1·5 g., 25%), m. p. 75—76°, of the chlorohydrin (XI) (above).

The infra-red spectrum of (V) showed a band at 3520 cm.$^{-1}$ due to free OH and a small band at 1634 cm.$^{-1}$ which is probably due to C=C, but may be a vibration frequency of the benzene ring.

Action of Water on 1 : 2-*Dibromo*-3-p-*tolylsulphonylpropane*.—In an attempt to repeat Troeger and Hinze's preparation of the supposed glycol, m. p. 93—95°, the dibromide was heated in a sealed tube with water for (*a*) 17 hours at 120°, (*b*) 48 hours at 110—120°, (*c*) 17 hours at 140—190°. In each case, the product crystallised from water in plates, m. p. between 115° and 120°, and was identified by mixed m. p. with the alcohol (V). The dibromide was unaffected by being heated under reflux with water at ordinary pressure for 12 hours.

Other Reactions for the Preparation of (I).—Chloropropylene sulphide (5 g.) and alcohol (50 ml.) were added to a neutralised and filtered solution of sodium toluene-*p*-sulphinate (10 g.) in water (40 ml.), and the mixture was kept for 3 days at room temperature. The reaction mixture, which did not become alkaline at any stage, was diluted with water and extracted with chloroform. The extract yielded an oil (2·5 g.), b. p. 110—113°/0·3 mm., and a large residue which decomposed on further heating. The oil (Found: C, 57·5; H, 5·35; S, 18·5%) was halogen-free and partly solidified on storage [$C_{10}H_{12}O_2S_2$ (I) requires C, 52·65; H, 5·25; S 21·05%]. It was expected that the thioacetic acid would add to the olefinic chloride (VI) and that the product on acid hydrolysis would yield the 3-chloro-2-mercapto-derivative and thence (I). Thioacetic acid, however, did not combine with this chloride or with the isomeric 1-chloro-3-*p*-tolylsulphonylprop-1-ene (IV) (see p. 2204).

1-p-*Tolylsulphonylpropan*-2-*ol*.—Propylene oxide (3·5 g.) and sodium toluene-*p*-sulphinate (10 g.) in water (60 ml.) were kept at 32° for 20 hours and the alkali thus formed was neutralised with 2N-sulphuric acid (20 ml.; theory, 28 ml.) before the solution was heated on a water-bath to ensure completion of the reaction. On cooling, 1-p-*tolylsulphonylpropan*-2-*ol* (4·8 g.) separated; from benzene it forms needles, m. p. 77—78° (Found: S, 14·8. $C_{10}H_{14}O_3S$ requires S, 14·95%). When it was boiled for 5 minutes with dilute sodium dichromate and sulphuric acid, a solid was obtained which crystallised from benzene and light petroleum in needles, m. p. 50—51°, before and after admixture with tolyl-*p*-sulphonylacetone made from bromoacetone (after Otto and Otto, *loc. cit.*).

Reactions of 3-p-*Tolylsulphonylprop*-2-*en*-1-*ol* (V).—2 : 5-*Bis*-p-*tolylsulphonylmethyldioxan* (XIV) was immediately formed as a copious precipitate of glistening plates when (V) was warmed with very dilute sodium hydroxide. Though sparingly soluble, it crystallises from alcohol or acetone in plates or needles, m. p. 258° (Found: C, 56·5; H, 5·7. $C_{20}H_{24}O_6S_2$ requires C, 56·6; H, 5·7%). It was also formed on heating aqueous potassium carbonate under reflux with (V), on which aqueous pyridine had no effect, but hot concentrated sodium hydroxide in alcoholic solution gave sodium toluene-*p*-sulphinate.

p-*Tolylsulphonylpropylene trithiocarbonate* (VII) was obtained by heating (V) (0·25 g.) or (XI; $R = p\text{-}C_6H_4Me$, $X = Cl$) (0·5 g.) under reflux for 40 minutes with a xanthate solution prepared from potassium hydroxide (0·35 g.) and carbon disulphide (0·5 g.) in alcohol (10 ml.). Readily soluble in benzene and chloroform, less so in alcohol, it forms from the latter solvent a microcrystalline powder, m. p. 128° (Found: C, 42·9; H, 4·2. $C_{11}H_{12}O_2S_4$ requires C, 43·4; H, 4·0%).

3-p-*Tolylsulphonylprop*-2-*enyl carbanilate* (1·3 g.) resulted when phenyl *iso*cyanate (0·7 g.) and (V) (1·06 g.) were heated in benzene (10 ml.) in a sealed tube at 100° for 3½ hours, and the product precipitated with light petroleum. From ether–light petroleum, it forms long needles, m. p. 104—105° (Found: C, 62·0; H, 5·4; N, 4·2. $C_{17}H_{17}O_4NS$ requires C, 61·6; H, 5·15; N, 4·2%).

1-p-*Tolylsulphonyl*-3-*acetoxyprop*-1-*ene* (XIII; $R = p\text{-}C_6H_4Me$, $X = OAc$) was best obtained by dissolving (V) in excess of acetyl chloride, heating the solution at 50° for 2½ hours, evaporating off the excess of acetyl chloride, and rubbing the residue with water. Though very difficult to crystallise from the usual solvents, it formed long, massive prisms (up to 1 inch long), m. p. 50—51°, when crystallised from ether–light petroleum by slow evaporation of the ether (Found: C, 56·6; H, 5·6; S, 12·7. $C_{12}H_{14}O_4S$ requires C, 56·7; H, 5·5; S, 12·6%). The product obtained from (V) by heating it with acetic anhydride at 100° for 3 hours or with acetic acid for 18 hours, or passing an excess of keten through a solution in dry acetone, was identified with this acetate by mixed m. p. The acetate was completely hydrolysed to (V) by heating it under reflux with 2N-sulphuric acid for 20 minutes or by shaking it in ethereal solution with an equimolecular amount of aqueous sodium hydroxide for 18 hours.

The corresponding benzoate, 1-p-*tolylsulphonyl*-3-*benzoyloxyprop*-1-*ene*, was formed when (V) was heated in excess of benzoyl chloride at 100° for 3½ hours and the excess of halide removed by heating with sufficient dilute sodium hydroxide. Recrystallisation from alcohol gave long needles, m. p. 95° (Found: C, 64·8; H, 5·1. $C_{17}H_{16}O_4S$ requires C, 64·5; H, 5·05%).

3-*Bromo*-1-p-*tolylsulphonylprop*-1-*ene* (XIII; $R = p\text{-}C_6H_4Me$, $X = Br$) was obtained when (V) (4 g.) and phosphorus pentabromide (10 g.) were ground together, warmed for a few minutes, and poured into water (yield: 5·2 g., 100%). Recrystallisation from light petroleum and a little benzene gave needles, m. p. 65—66° (Found: C, 43·8; H, 4·1. $C_{10}H_{11}O_2SBr$ requires C, 43·6; H, 4·0%).

3-*Chloro*-1-p-*tolylsulphonylprop*-1-*ene* (VI) was obtained when the alcohol (V) (5·9 g.) and phosphorus pentachloride (6·3 g.) were mixed, and warmed for a few minutes after the main reaction had subsided, the product being separated by extraction with ether and allowing the solvent to evaporate off at room temperature. Recrystallisation from light petroleum and a little benzene gave plates, m. p. 58° (Found: C, 51·85; H, 5·2. $C_{10}H_{11}O_2SCl$ requires C, 52·05; H, 4·8%). The propene (VI) was also obtained on treatment of (V) with excess of concentrated hydrochloric acid for 23 hours in a sealed tube at 120°, though not at 100° at ordinary pressure for 1 hour; it was also formed by dehydrating the chlorohydrin (XI) with excess of concentrated sulphuric acid at 100° for 2 hours, though not with boiling 70% sulphuric acid. An emulsion of (VI) with cold water instantly decolorised aqueous potassium permanganate but not bromine water. Reduction with tin and hydrochloric acid gave *p*-tolyl allyl sulphone, identified by m. p. and mixed m. p. (VI) is essentially unchanged at 70° with excess of 70% sulphuric acid, or at 60° with concentrated sulphuric acid, although dissolution rapidly occurs. When 0·2 g. is heated on the water-bath for 1 hour with 4 ml. of 20% potassium hydroxide, cooled, and neutralised, a small amount of unidentified product, m. p. *ca.* 200°, probably the dioxan (XIV), is obtained. Acidification of the filtrate gave toluene-*p*-sulphinic acid, m. p. and mixed m. p. 89—90°. This is obtained in better yield by using 40% alkali.

The propene (VI) (0·2 g.) was dissolved in aqueous alcohol (2 ml.), and the solution exposed, in a silica tube, to direct sunlight for 48 hours. On evaporation of the solvent, little change in m. p. (or mixed m. p.) had occurred. On use of light petroleum as solvent (and a few drops of benzene) and increase in the time of exposure to 100 hours, similar results were obtained.

When (VI) (0·2 g.) was heated under reflux in a solution of light petroleum (20 ml.) containing a trace of iodine, and the solvent allowed to evaporate after 5 hours, (VI) was recovered, m. p. 56—57°.

1-*Chloro*-3-p-*tolylsulphonyl*-2-*ethoxypropane* (as XVIII) was formed when (VI) and 5% of its weight of potassium hydroxide were kept for 2 hours in ethanol solution at 50°. Recrystallisation from benzene–light petroleum gave large cubes, m. p. 79° (Found: C, 52·3; H, 6·35; OEt, 16·75; S, 12·2. $C_{12}H_{17}O_3SCl$ requires C, 52·1; H, 6·15; OEt, 16·3; S, 11·6%). On treating (VI) with a 20% solution of potassium hydroxide in aqueous alkali at 35°, the dioxan (as XIV) was obtained in small yield, together with an unidentified compound, probably 1-*p*-tolylsulphonyl-2 : 3-diethoxypropane, m. p. 40—41°, which was halogen-free and did not decolorise aqueous permanganate. (XVIII; X = Cl) gave a 10% yield of the alcohol (V) when heated under reflux with hydriodic acid in glacial acetic acid, but when 0·2 g. was dissolved in glacial acetic acid (2 ml.), 60% hydrobromic acid (1 ml.) added, and the mixture heated under reflux for 3 hours, the chlorohydrin (XI), identified by mixed m. p., was obtained, *i.e.*, normal de-ethylation had occurred.

Di-(3-p-*tolylsulphonylprop*-2-*enyl*) *sulphide* (VIII) was obtained when the chloride (VI) (1·38 g.) in alcohol (6 ml.) was shaken with a solution of potassium hydrogen sulphide, prepared by saturating the hydroxide (0·28 g.) in ethanol (5 ml.) with hydrogen sulphide at 0°. The product, collected after 15 minutes, crystallised from alcohol in thick needles, m. p. 125—126° (Found: C, 56·6; H, 5·2; S, 23·4. $C_{20}H_{22}O_4S_3$ requires C, 56·9; H, 5·2; S, 22·8%). It gave negative tests for thiol groups and was unaffected when heated under reflux in aqueous alcohol with sulphuric acid, but was converted by hot dilute sodium hydroxide into a viscous, semi-solid material.

3-*Iodo*-1-p-*tolylsulphonylprop*-1-*ene* (as XXI) was formed in good yield by heating the chloride (VI) and excess of sodium iodide in acetone under reflux for 3 hours. Recrystallisation from aqueous alcohol gave needles, m. p. 75° (Found: C, 37·15; H, 3·65; S, 10·5. $C_{10}H_{11}O_2SI$ requires C, 37·3; H, 3·45; S, 9·95%). In working up one preparation, the aqueous acetone mixture, after a week, deposited crystals of the alcohol (V) in over 10% yield, and this mobility of the iodine atom is confirmed by the rapid production of potassium iodide on treatment with hot dilute alcoholic potash. (XXI) was reduced in dilute acetic acid solution at 100°, by adding twice its weight of zinc dust during 2 hours, to *p*-tolyl allyl sulphone (Found: C, 60·9; H, 6·35. Calc. for $C_{10}H_{12}O_2S$: C, 61·2; H, 6·1%), m. p. 52°, undepressed on admixture with authentic *p*-tolyl allyl sulphone, but depressed by tolyl propyl sulphone, both of which were made by condensing sodium toluene-*p*-sulphinate with the corresponding aliphatic bromide (Otto, *Annalen*, 1894, **283**, 184; *J. pr. Chem.*, 1890, **40**, 562).

Isomeric Change of (VI) *into* 1-*Chloro*-3-p-*tolylsulphonylprop*-1-*ene*.—1-*Chloro*-3-p-*tolylsulphonylprop*-1-*ene* (IV) was obtained when 3-chloro-1-*p*-tolylsulphonylprop-1-ene (VI) (2 g.) was dissolved in benzene (5 ml.) and stirred vigorously with a solution of potassium hydroxide (0·01 g.) in water (20 ml.) at 50° for 1 hour, followed by addition of ether (20 ml.) and stirring for an additional 2 hours at 30°. After the ether had been allowed to evaporate off at room temperature, the product was collected and recrystallised from light petroleum containing a few drops of benzene. 0·9 G. (45%) of needles, m. p. 73°, containing halogen, was obtained (Found: C, 51·9; H, 5·1; S, 14·3. $C_{10}H_{11}O_2SCl$ requires C, 52·05; H, 4·8; S, 13·9%). Mixtures of (IV) with the isomer (VI) or the chlorohydrin (XI) gave considerable depressions in m. p. An emulsion of (XV) decolorised cold aqueous potassium permanganate after a few seconds. (IV) was unchanged on treatment with a solution of sodium iodide in boiling acetone (3 hours), on treatment with hot hydrochloric, sulphuric, or acetic acid, on vigorous stirring of a benzene solution with cold saturated aqueous sodium hydroxide for 3 hours, on exposure of an aqueous alcoholic or benzene–light petroleum solution to direct sunlight for 48 and 100 hours, respectively, or on heating it under reflux for 5 hours in light petroleum containing a trace of iodine. Treatment of (IV) with dilute ethanolic sodium hydroxide at 30° for 3 hours yielded the chloro-ether (XVIII), m. p. 78—79°, identified by mixed m. p., together with a small amount of the dioxan (XIV).

The propene (IV) was also obtained when the isomer (VI) (1 g.) was dissolved in 50% aqueous pyridine (10 ml.) and warmed at 70° for 2 hours and the mixture cooled and neutralised (yield, 0·4 g.). A difficultly separable mixture of (IV) and (VI) was obtained when (VI) was heated at 100° for 3 hours in aqueous benzenesulphonic acid solution; (IV) was isolated by virtue of its lower solubility in aqueous alcohol.

Synthesis of 1-*Chloro*-3-p-*tolylsulphonylprop*-1-*ene*.—1 : 3-Dichloropropene was prepared according to the method of Hill and Fisher (*J. Amer. Chem. Soc.*, 1922, **44**, 2584), by dehydration of *s*-glycerol dichlorohydrin with phosphoryl chloride. Sodium toluene-*p*-sulphinate (8·9 g.) and 1 : 3-dichloropropene (5·5 g.) were dissolved in aqueous alcohol (30 ml.), and the mixture made slightly acid to litmus, warmed on the water-bath for 3 hours, and cooled; an oil separated which solidified on storage. The mixture remained slightly acid. Recrystallisation from alcohol containing a drop of hydrochloric acid gave needles (7·0 g.), m. p. 65—68° undepressed on admixture with (IV). The compound contained halogen and decolorised cold aqueous permanganate in a few seconds.

3-p-*Tolylsulphonylpropane*-1 : 2-*diol* (XX; R = *p*-C_6H_4Me).—(*a*) Sodium toluene-*p*-sulphinate (8·9 g.) and glycidol (3·7 g.) in water (50 ml.) were warmed on a water-bath, and the solution was kept neutralised by titration with 2N-sulphuric acid as the reaction proceeded (phenolphthalein as indicator). After 5 hours, the reaction appeared to be complete (acid added, 18 ml.; theory, 25 ml.) and the solution was evaporated *in vacuo* to a small volume and extracted with chloroform. The extract yielded a viscous, water-soluble syrup which crystallised only when the hot benzene solution was treated with a considerable amount of anhydrous magnesium sulphate and filtered hot. Further purification gave the glycol as plates, m. p. 74—75° (Found : C, 52·5; H, 5·9. $C_{10}H_{14}O_4S$ requires C, 52·2; H, 6·1%).

(*b*) The chlorohydrin (XI; R = *p*-C_6H_4Me, X = Cl) was heated with water in a sealed tube at 110—120° for 24 hours, and the resultant aqueous layer decanted from a little black oil, filtered, and evaporated on a water-bath. The residue partly solidified, and on drying on a porous tile and re-crystallising from benzene with magnesium sulphate, it formed needles, m. p. 74—75°; mixed m. p. with product in (*a*) 73—75°.

(*c*) 3-*p*-Tolylthiopropane-1 : 2-diol (X) (2 g.) and 30% hydrogen peroxide (3 ml.) were dissolved in acetic acid (12 ml.) and kept for 8 days at 36°. The acetic acid was distilled off *in vacuo*, and the residue set aside on a watch-glass in the air. After 2 weeks, it crystallised, and rubbing with ether gave a white powder. Crystallisation from benzene with magnesium sulphate gave the glycol (XX; R = *p*-C_6H_4Me), m. p. 74—75° (not depressed by admixture with the glycol prepared as above).

This glycol (XX) with benzoyl chloride at 100° for 20 hours gave the *dibenzoyl* derivative, small needles, m. p. 133°, from alcohol (Found : C, 65·45; H, 4·95. $C_{24}H_{22}O_6S$ requires C, 65·75; H, 5·0%).

Phenylsulphonylpropane Derivatives.

3-*Phenylsulphonylprop*-2-*en*-1-*ol* (XII; R = Ph) was obtained as white plates (13·3 g.) when sodium benzenesulphinate (16·4 g.) and epichlorohydrin (9·3 g.) were dissolved in water (60 ml.) and alcohol (15 ml.) and kept at 32° for 2 days; it crystallises in long needles from water; m. p. 139—140° (Found : C, 54·5; H, 4·7. $C_9H_{10}O_3S$ requires C, 54·5; H, 5·05%). The unpurified product is contaminated with an appreciable amount of the dioxan (below). The propenol (XII) is also obtained as silky needles (0·6 g.), m. p. 135—137° (crude), by the action of water (25 ml.) on 1 : 2-dibromo-3-phenylsulphonylpropane (2 g.) in a sealed tube at 110—120° for 23 hours. A mixture with the alcohol (XII; R = Ph) melted at 137—138°. When heated with excess of benzoyl chloride at 100° for 20 hours, followed by removal of the excess with dilute sodium hydroxide, (XII; R = Ph) gave the *benzoyl* derivative, which crystallised from alcohol and a little water in long needles, m. p. 86—86·5° (Found : C, 63·4; H, 4·55. $C_{16}H_{14}O_4S$ requires C, 63·6; H, 4·65%). [Otto (*loc. cit.*) found C, 63·2; H, 5·3, though the dibenzoate of his " glycol," $C_{23}H_{20}O_6S$, requires C, 65·1; H, 4·7%.]

2 : 5-*Bisphenylsulphonylmethyldioxan* (XIV; R = Ph) was precipitated rapidly on warming the alcohol (XII; R = Ph) with dilute alkali. It forms glistening plates, m. p. 244°, from alcohol (Found : C, 54·2; H, 4·7. $C_{18}H_{20}O_6S_2$ requires C, 54·5; H, 5·05%).

3-*Chloro*-1-*phenylsulphonylprop*-1-*ene* was prepared from the alcohol (XII; R = Ph) and phosphorus pentachloride in the same way as for the tolyl homologue. From aqueous alcohol, it forms needles, m. p. 58·5° (Found : C, 49·8; H, 4·2; Cl, 16·3. $C_9H_9O_2SCl$ requires C, 49·9; H, 4·15; Cl, 16·4%). The 3-*bromo*-analogue, prepared from (XII; R = Ph) and phosphorus pentabromide, crystallises from ether–light petroleum in long, massive needles, m. p. 34—35° (Found : C, 41·3; H, 3·6. $C_9H_9O_2SBr$ requires C, 41·4; H, 3·45%).

3-*Iodo*-1-*phenylsulphonylprop*-1-*ene*.—The chloro-compound (2·5 g.) and sodium iodide (2·5 g.) were heated under reflux for 3 hours in acetone (30 ml.), and then water (200 ml.) was added. The *iodide* solidified and recrystallised from aqueous alcohol to form irregular, feathery crystals, m. p. 67—68° (Found : C, 35·2; H, 2·75. $C_9H_9O_2SI$ requires C, 35·1; H, 2·9%).

1-*Chloro*-3-*phenylsulphonyl*-2-*ethoxypropane* (XVIII; R = Ph, R′ = Et, X = Cl) resulted from warming 3-chloro-1-phenylsulphonylprop-1-ene with weak alcoholic alkali at 60° for 15 minutes. It crystallises from aqueous alcohol in prisms, m. p. 79° (Found; C, 51·1; H, 6·0; Cl, 13·9; S, 12·7. $C_{11}H_{15}O_3SCl$ requires C, 50·3; H, 5·7; Cl, 13·5; S, 12·2%).

Benzylsulphonylpropane Derivatives.

3-*Benzylsulphonylprop*-2-*ene*-1-*ol* (XII; R = CH_2Ph), from 1 : 2-dibromo-3-benzylsulphonylpropane (1·95 g.) and water (20 ml.) in a sealed tube at 120° for 3½ hours, was collected after cooling and crystallised from benzene in fine needles, m. p. 113—114° (Found : C, 56·6; H, 5·8. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·65%). The m. p. 110—111° was given to the so-called 1-benzylsulphonylpropane-2 : 3-diol by van Zuydewijn (*loc. cit.*, p. 454), who prepared it in the above way and also by the action of peracetic acid and then water on benzyl allyl sulphone. It has now also been obtained (1·9 g.) from epichlorohydrin (1·2 g.) and sodium benzylsulphinate (2·2 g.) in aqueous alcoholic solution at 35° for 24 hours. It formed 2 : 5-*bisbenzylsulphonylmethyldioxan* (XIV; R = CH_2Ph) when heated in dilute aqueous alkali for several minutes. Insoluble in alcohol, benzene, and acetone, it dissolved readily in dioxan and crystallised from this solvent in short needles, m. p. 248—249° (sinters from 245°) (Found : C, 56·6; H, 5·5. $C_{20}H_{24}O_6S_2$ requires C, 56·6; H, 5·65%).

3-Chloro- and 3-bromo-1-benzylsulphonylprop-1-ene were obtained by the action of the appropriate phosphorus pentahalide on the alcohol (XII; R = CH_2Ph). The former gave needles, m. p. 70—71°, from benzene–light petroleum, and the latter crystallised from the same solvent in long, silky needles, m. p. 95—97°. They did not depress the m. p.s of authentic samples of the halides prepared by heating the corresponding dibromides with pyridine in benzene (Rothstein, *loc. cit.*).

3-Bromo-1-benzylsulphonylprop-1-ene (0·5 g.), isomerised by dilute alkali in the same way as the tolyl analogue, gave a product (0·1 g.) which crystallised from benzene–light petroleum as plates, m. p. 150—151°. Rothstein (*loc. cit.*, p. 312) records the melting point of 1-bromo-3-benzylsulphonylprop-1-ene as 151—152°. The mother-liquors in this case yielded a second *product* (0·3 g.), plates from benzene–light petroleum, m. p. 69°, which is also isomeric with these halides (Found : C, 43·9; H, 4·8. $C_{10}H_{11}O_2SBr$ requires C, 43·6; H, 4·0%).

Benzene solutions of these two compounds, m. p. 69° and 152°, were exposed in silica tubes to sunlight for 100 hours without appreciable change. The possibility of stereoisomerism is being further investigated.

3-Bromo-1-benzylsulphonylprop-1-ene, reduced with zinc and acetic acid in the manner described for 3-iodo-1-*p*-tolylsulphonylprop-1-ene yielded benzyl allyl sulphone, identical with a specimen made after Rothstein (*J.*, 1934, 684).

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