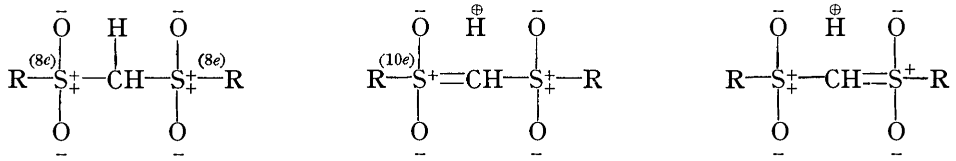
# 64. *Influence of Poles and Polar Linkings on Tautomerism in the Simple Three-carbon System. Part IV. Activation by Sulphonyl Groups.*

By Eugene Rothstein.

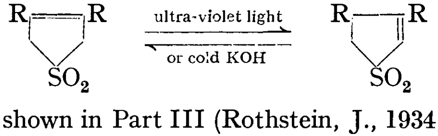
When a methylene group is activated by a sulphonyl radical $\overset{++}{-SO_2}R$, its reactivity is in many respects comparable with that in a β-diketone. The greater part of the activation, however, arises from the two positive charges on the sulphur atom, which promote the loosening of the C–H bond of the methylene group in contradistinction to the diketones, where enolisation is the main factor (compare Arndt and Martius, *Annalen*, 1932, **499**, 228; *Ann. Reports*, 1934, 193). There have, in recent years, been several suggestions that the sulphur atom may in certain cases expand its valency shell (Ingold and Jessop, J., 1930, 708; Kohler and Larson, *J. Amer. Chem. Soc.*, 1935, **57**, 1448; Connor, Fleming, and Clayton, *ibid.*, 1936, **58**, 1386), and there are other cases where an expansion of the sulphur octet is indicated. Both bis(ethylsulphonyl)phenylthiomethane, $(Et{\cdot}SO_2)_2CH{\cdot}SPh$ (Laves, *Ber.*, 1890, **23**, 1414), and bis(phenylsulphonyl)phenylthiomethane (Fromm, *Annalen*, 1889, **253**, 1386) are sufficiently strong acids to decompose warm sodium carbonate solution, the corresponding bissulphonylmethanes being soluble in alkali hydroxide only (Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060).

It is suggested that in addition to the $-I$ effect of the sulphonyl group, there is a mesomeric effect arising from the resonance between the canonical structures:



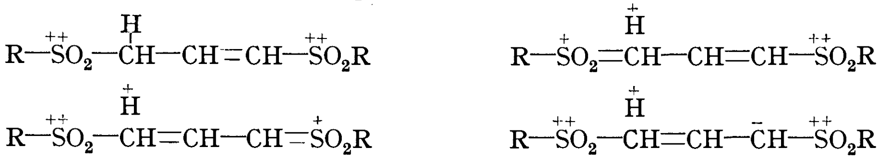
This must be interpreted, not that the hydrogen atom is for any appreciable moment of time actually ionised, but that the electron pair of the C–H bond tends to be distributed over the whole system. Since the contributions of the wave functions of the second and third canonical structures are probably small, the actual effect will be a loosening of the proton involved, with a consequent localisation of a small negative charge on some other part of the system. Although small, the effect appears appreciable. For instance, whereas a bissulphonylmethane, $(R{\cdot}SO_2)_2CH_2$, will dissolve in sodium hydroxide solution but will not react with diazomethane, trimethylenetrisulphone, $CH_2{<}\genfrac{}{}{0pt}{}{SO_2-CH_2}{SO_2-CH_2}{>}SO_2$, is methylated (Arndt and Martius, *loc. cit.*), and similarly, whilst bis(phenylsulphinyl)methane, $(Ph{\cdot}SO)_2CH_2$, will only react with alkali hydroxide in alcoholic solution, trimethylenetrisulphoxide, $CH_2{<}\genfrac{}{}{0pt}{}{SO-CH_2}{SO-CH_2}{>}SO$, easily dissolves in 10% sodium hydroxide solution to give the sodio-derivative (Hinsberg, *J. pr. Chem.*, 1912, **85**, 337), the extra resonance in the ring system leading to a greater fractional ionisation of the hydrogen atom.

This view receives confirmation from the interconvertibility of the cyclic butadienes and their derivatives (Böeseken and van Zuydewijn, *Proc. K. Akad. Wentsch. Amsterdam*, 1934, **37**, 760; 1936, **39**, 31; *Rec. trav. chim.*, 1934, **53**, 673; Backer and Strating, *ibid.*, 1935, **54**, 618):



On the other hand it was shown in Part III (Rothstein, J., 1934, 684) that benzyl-$\Delta^{\alpha}$- and -$\Delta^{\beta}$-propenylsulphones, $CH_2Ph{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_3$ and $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CH_2$, are not tautomeric.

It follows, therefore, that a three-carbon unsaturated system terminated by sulphonyl groups should be considerably more mobile than the corresponding bis-ammonium salts (Ingold and Rothstein, J., 1931, 1666), because in addition to the enhanced polar effect of the sulphonyl radicals, resonance between the following canonical structures (not possible with the ammonium salts) is to be expected :



$$\mathrm{R{-}\overset{++}{S}O_2{-}\overset{H}{C}H{-}CH{=}CH{-}\overset{++}{S}O_2R} \qquad \mathrm{R{-}\overset{+}{S}O_2{=}CH{-}\overset{\overset{+}{H}}{C}H{=}CH{-}\overset{++}{S}O_2R}$$

$$\mathrm{R{-}\overset{++}{S}O_2{-}CH{=}\overset{\overset{+}{H}}{C}H{-}CH{=}\overset{+}{S}O_2R} \qquad \mathrm{R{-}\overset{++}{S}O_2{-}CH{=}\overset{\overset{+}{H}}{C}H{-}\overset{-}{C}H{-}\overset{++}{S}O_2R}$$

*α-Benzylsulphonyl-γ-ethylsulphonyl-$\Delta^{\alpha}$- and -$\Delta^{\beta}$-propene* (I and II) have accordingly been synthesised by various methods,

$$\underset{\text{(I.)}}{\mathrm{CH_2Ph{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SO_2Et}} \rightleftharpoons \underset{\text{(II.)}}{\mathrm{CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}SO_2Et}}$$

which, however, always lead to a mixture of the two isomerides. By careful fractional crystallisation small quantities of each could be obtained, the $\Delta^{\beta}$-sulphone (II) being quite pure, and the other probably containing a small amount of its isomeride. The two sulphones differed in appearance, solubility, and melting point, a mixture of the two showing a depression. Interconversion was exceedingly facile, being rapid in solvents such as methyl alcohol, and rather slower in ethyl acetate or benzene, and also taking place to some extent when the substance was heated above its melting point. It was for this reason that (I), which has the greater solubility and apparently the lower melting point, cannot be obtained quite free from (II), since repeated crystallisations lead to interconversion. The equilibrium mixture contained 40% of the $\Delta^{\beta}$-sulphone, this figure representing a lower limit for this isomeride.

The structure of the sulphones was shown by their reduction with hydrogen in the presence of Adams's catalyst to *α-benzylsulphonyl-γ-ethylsulphonylpropane*, the product being identified by analysis and by comparison with the synthetic bis-sulphone prepared from trimethylene chlorohydrin. Furthermore, fission by ozone showed that the two sulphones were not stereoisomerides, since the corresponding sulphonylacetic acids were isolated (among other products), whereas pure (II) gave *benzylsulphonylacetic acid* only, no ethylsulphonylacetic acid being detected :

$$\mathrm{R{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}\!\vdots\!CH{\cdot}SO_2R'} \longrightarrow \underset{\text{(III, R = benzyl or ethyl.)}}{\mathrm{R{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2H + R'{\cdot}SO_3H + HCHO}}$$

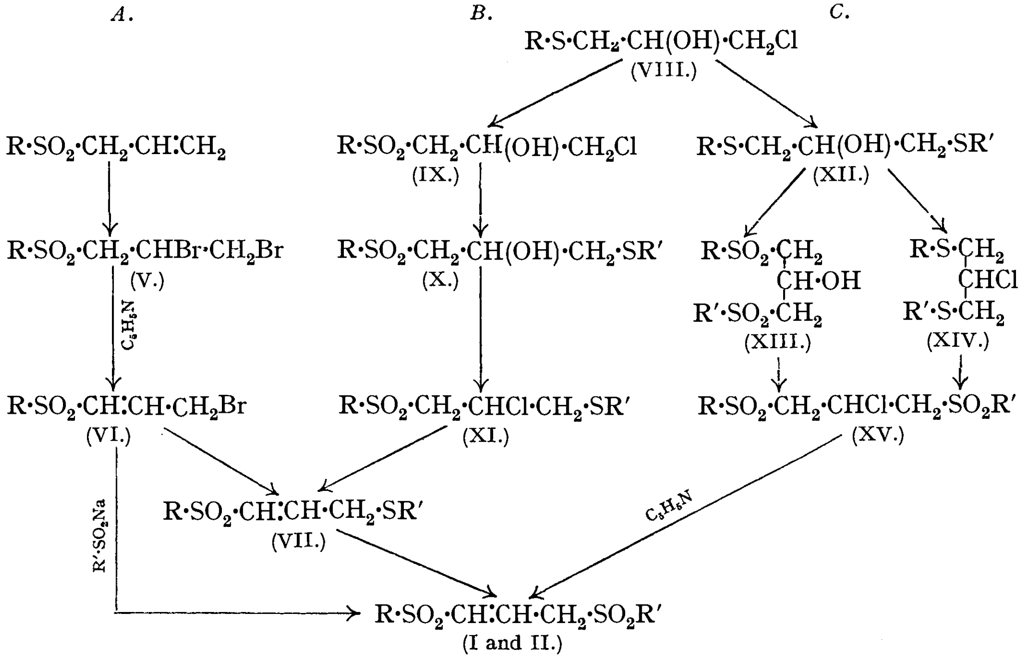
The proportions of these acids were determined by their conversion into the corresponding sulphones, $\mathrm{R{\cdot}SO_2{\cdot}CH_3}$, which were then submitted to thermal analysis. The above fission did not prove a suitable method for estimating the percentage of each isomeride in the original mixture of the sulphones, since among the products obtained were the unchanged sulphones, the corresponding aldehydes and sulphonic acids, together with small quantities of formaldehyde and formic acid. A melting-point curve was therefore constructed from artificial mixtures of the two isomerides and used for this determination. The figures roughly corresponded to those obtained by ozonolysis.

It has been postulated that there are a larger number of wave functions contributing to the mesomeric state of the propene systems than in the case of the bissulphonylmethanes. Consequently an enhanced reactivity might be expected in the former case. Definite evidence of this is provided by the condensation with benzaldehyde in the presence of piperidine with the production of *(βδ)-benzylsulphonylethylsulphonyl-α-phenylbutadiene* (IV) (the orientation of the ethyl and benzyl groups not yet having been determined owing to the experimental difficulties encountered) ; the same condensation product is obtained starting with either of the isomerides :

$$\text{(I) or (II)} + \mathrm{Ph{\cdot}CHO} \longrightarrow \underset{\text{(IV, R and R}' = \text{benzyl or ethyl.)}}{\mathrm{R{\cdot}SO_2{\cdot}CH{:}CH{\cdot}C(SO_2R'){:}CHPh}}$$

Likewise, there is also a reaction with diazomethane (following paper). Bis(phenylsulphonyl)methane will not condense with benzaldehyde or other reagents diagnostic of an active methylene group (Connor, Fleming, and Clayton, *loc. cit.*).

The methods used for the preparation of the bissulphonylpropenes are summarised in the following diagram. As in any case each of them led to the formation of both isomerides, route B was adopted as the most convenient when further quantities were required, since the product at each stage of the synthesis could be obtained relatively pure. It may be noted that *α-benzylsulphonyl-γ-ethylthio-Δ$^{\alpha}$-propene* (VII, R = benzyl, R′ = ethyl) should have had the structure indicated when prepared from VI (R = benzyl), but fission with ozone yielded products which showed that a considerable proportion of the Δ$^{\beta}$-isomeride was present. Since it is possible that oxidation to the bis-sulphone preceded fission, this is not regarded as conclusive evidence that the presence of a terminal thio-group enhances the mobility of the system.



(R and R′ = benzyl or ethyl.)

## EXPERIMENTAL.

(A) *Preparation of α-Benzyl-γ-ethyl-Δ$^{\alpha}$- and -Δ$^{\beta}$-propenes.—Route A.**—Benzyl-Δ$^{\beta}$-propenylsulphone, prepared from benzylthiol-Δ$^{\beta}$-propene (v. Braun and Engelbertz, *Ber.*, 1923, **56**, 1573) by oxidation with perhydrol, had b. p. 198°/12 mm., and was identical (m. p. and mixed m. p.) with that obtained from sodium benzylsulphinate and allyl bromide (Part III, *loc. cit.*). It was dissolved in chloroform, and the theoretical quantity of bromine in carbon tetrachloride solution slowly added. Heat was developed, and the evolution of a small amount of hydrogen bromide indicated that substitution was taking place. Distillation of the solvent yielded *βγ-dibromo-α-benzylsulphonylpropane* (V, R = $CH_2Ph$), which crystallised from benzene–petrol in prisms, m. p. 85—87°; yield, 70% (Found: C, 33·7; H, 3·6; Br, 44·5. $C_{10}H_{12}O_2Br_2S$ requires C, 33·7; H, 3·4; Br, 44·9%).

*γ-Bromo-α-benzylsulphonyl-Δ$^{\alpha}$-propene* (VI, R = benzyl). The dibromo-sulphone (10 g.) was heated under reflux on the steam-bath for 1 hour with pyridine (2·2 g.) and benzene (40 c.c.). The benzene solution, after being washed with dilute hydrochloric acid and dried, yielded a crystalline solid, which separated from benzene–petrol (b. p. 40—60°) in short needles, m. p.

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* The alternative paths of both route A and B were followed in the expectation of synthesising the Δ$^{\alpha}$- and Δ$^{\beta}$-bissulphones separately. Partly owing to the highly mobile nature of these compounds, this expectation was not realised.

95—97°; yield, 52% (Found: C, 43·4; H, 3·9; Br, 29·1. $C_{10}H_{11}O_2BrS$ requires C, 43·6; H, 4·0; Br, 29·1%). The mother-liquor contained a mixture consisting mainly of unchanged dibromide. The monobromide depressed the m. p. of the initial material and of *γ-bromo-α-benzylsulphonyl-$\Delta^{\beta}$-propene*, m. p. 151—152° (long needles from ethyl alcohol or ethyl acetate), prepared from αγ-dibromopropene and sodium benzylsulphinate (Found: C, 44·1; H, 4·0; Br, 29·0. $C_{10}H_{11}O_2BrS$ requires C, 43·6; H, 4·0; Br, 29·1%). Unlike the $\Delta^{\alpha}$-isomeride, it did not condense with sodium ethylthiol or sodium benzylsulphinate. The terminal position of the bromine atom in the $\Delta^{\alpha}$-compound was shown by the structure of the subsequent condensation products.

The pyridine liquors contained about 40% of the dibromo-compound originally taken. On basification a pale yellow solid was liberated, but its constitution has not yet been determined owing to the rapidity with which it polymerised.

*βγ-Dichloro-α-benzylsulphonylpropane* was obtained in poor yield by passing chlorine through a chloroform solution of benzylsulphonyl-$\Delta^{\beta}$-propene, and crystallising the product from either ether or benzene–petrol (b. p. 40—60°); m. p. 65°, b. p. 215—220°/3 mm. It was identical (m. p. and mixed m. p.) with the product of the reaction between γ-chloro-β-hydroxy-α-benzylsulphonylpropane (IX, R = benzyl) and phosphorus pentachloride (Found: C, 45·2; H, 4·8; Cl, 26·3. $C_{10}H_{12}O_2Cl_2S$ requires C, 44·9; H, 4·5; Cl, 26·6%).

*γ-Chloro-α-benzylsulphonyl-$\Delta^{\alpha}$-propene*, obtained from the dichloro-sulphone by boiling it with pyridine in benzene solution, crystallised from benzene–petrol in feathery clusters of needles, m. p. 75—76° (Found: C, 52·2; H, 4·8; Cl, 15·3. $C_{10}H_{11}O_2ClS$ requires C, 52·0; H, 4·8; Cl, 15·4%).

*Condensation of γ-Bromo-α-benzylsulphonyl-$\Delta^{\alpha}$-propene with sodium ethylthiol. α-Benzylsulphonyl-γ-ethylthiopropene* (VII, R = benzyl, R′ = ethyl), b. p. 190—196°/0·2 mm., was obtained by addition of the bromo-sulphone in alcoholic solution to sodium ethylthiol (10% excess) cooled in ice. It evidently contained benzylsulphonylbis(ethylthio)propane (cf. below), which accounts for the faulty analysis (Found: C, 55·5; H, 6·9; S, 26·4. $C_{12}H_{16}O_2S_2$ requires C, 56·3; H, 6·3; S, 25·0%). It was obtained pure by method B.

*α-Benzylsulphonyl-γ-ethylsulphonyl-$\Delta^{\alpha}$- and -$\Delta^{\beta}$-propene* (I and II). Oxidation of the above thiosulphone with perhydrol yielded a white semi-solid, which after rubbing with methyl alcohol crystallised from the same solvent in platelets, m. p. 129—130°. This was the $\Delta^{\beta}$-isomeride (section C). The mother-liquors contained a mixture of the two sulphones (Found: C, 49·8; H, 6·1; S, 22·5. $C_{12}H_{16}O_4S_2$ requires C, 50·0; H, 5·6; S, 22·2%).

*α-Benzylsulphonyl-βγ(?)-bis(ethylsulphonyl)propane*, $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH(SO_2Et){\cdot}CH_2{\cdot}SO_2Et$, was furnished by the cold methyl-alcoholic filtrate (above); it separated from methyl alcohol in needles, m. p. 119—120°, depressed by the above bis-sulphone (Found: C, 43·9; H, 5·9; S, 25·4; *M*, 394, 389. $C_{14}H_{22}O_6S_3$ requires C, 44·0; H, 5·8; S, 25·1%; *M*, 382).

The bis-sulphone (together with the tris-sulphone) was also obtained in 78% yield by boiling an alcoholic solution of the bromo-compound with an excess of sodium benzylsulphinate (Found: C, 49·7; H, 5·7%; *M*, 328. $C_{12}H_{16}O_4S_2$ requires *M*, 288).

*α-Ethylsulphonyl-$\Delta^{\beta}$-propene*, $Et{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CH_2$, prepared by the oxidation of the corresponding sulphide (Dawson, *J. Amer. Chem. Soc.*, **1933**, **55**, 2070) with perhydrol in glacial acetic acid solution, had b. p. 129°/11 mm.; yield, 72% (Found: C, 44·7; H, 7·7; S, 23·9. $C_5H_{10}O_2S$ requires C, 44·8; H, 7·4; S, 23·9%).

*βγ-Dibromo-α-ethylsulphonylpropane* (V, R = ethyl). Bromine (24 g.) in carbon tetrachloride (120 c.c.) was slowly added to a cooled solution of α-ethylsulphonyl-$\Delta^{\beta}$-propene (20 g.) in chloroform (100 c.c.). After removal of the solvent, the residue was distilled, b. p. 166°/0·6 mm.; yield, 95% (Found: C, 20·8; H, 3·8; Br, 53·6. $C_5H_{10}O_2Br_2S$ requires C, 20·4; H, 3·4; Br, 54·5%).

*Action of Pyridine on βγ-Dibromo-α-ethylsulphonylpropane.*—Boiling the dibromide with pyridine yielded mixtures of the monobromide with the dibromide. The yield of sulphone was smaller when excess of pyridine was used, but there was little change in the composition of the mixture. In a typical case (yield of sulphones, 55%), distillation gave three fractions, the lowest having b. p. 164°/0·7 mm. (Found: C, 25·2; H, 4·3; Br, 44·2%), and the highest b. p. 171°/0·7 mm. (Found: C, 21·3; H, 3·3; Br, 52·0. $C_5H_7O_2BrS$ requires C, 28·1; H, 4·2; Br, 36·1%), *i.e.*, there was very little separation, and the lower b. p. fraction contained 40—50% of dibromide.

Nevertheless, when an alcoholic solution of the lower fraction was boiled under reflux with twice its weight of sodium benzylsulphinate, an 85% yield of the bis-sulphone (I and II) was obtained. It contained a large proportion of (II), since it had m. p. 127—129° after two recrystallisations from methyl alcohol (Found : C, 49·9; H, 5·5%). No trace of tris-sulphone was detected.

*Route B.*—*γ-Chloro-β-hydroxy-α-benzylthiopropane* (VIII, R = benzyl). Sodium benzylthiol (from 80 g. of benzylthiol), dissolved in ethyl alcohol (200 c.c.), was slowly added to a well-cooled and stirred solution of αγ-dichlorohydrin (200 g.) in ethyl alcohol (200 c.c.). After 1 hour, the mixture was diluted with water (500 c.c.) and extracted with ether. The *chloro-sulphide*, b. p. 123°/0·05 mm. (yield, 72%), usually contained as an impurity benzyl sulphide, which could not be entirely removed by fractional distillation. This accounts for the rather low chlorine content (Found : C, 55·8; H, 6·5; Cl, 14·3. $C_{10}H_{13}OClS$ requires C, 55·4; H, 6·0; Cl, 16·4%).

*γ-Chloro-β-hydroxy-α-benzylsulphonylpropane* (IX, R = benzyl). The chloro-sulphide was warmed on the steam-bath for 45 minutes, in portions not greater than 25 g. at a time, with perhydrol in glacial acetic acid. The precipitate obtained when the liquid was added to excess of water was crystallised from ethyl alcohol, yielding dibenzylsulphone, m. p. and mixed m. p. 150° (Found : C, 68·4; H, 5·5; S, 13·0. Calc. : C, 68·3; H, 5·7; S, 13·0%). The alcoholic filtrate was evaporated to dryness, and the residue again crystallised from alcohol, this process being repeated until no more dibenzylsulphone separated. Finally, the residue was crystallised from benzene, the *chlorosulphone* separating in needles, m. p. 97—98°; yield, 70% (Found : C, 48·2; H, 5·4; Cl, 13·7; S, 13·1. $C_{10}H_{13}O_3ClS$ requires C, 48·3; H, 5·2; Cl, 14·3; S, 12·9%).

*β-Hydroxy-γ-ethylthio-α-benzylsulphonylpropane* (X, R = benzyl, R′ = ethyl). The chlorosulphone (66 g.), dissolved in methyl alcohol (400 c.c.), was added to a slight excess of sodium ethylthiol in the same solvent. After 12 hours, the liquid was boiled for ½ hour under reflux. The resulting *sulphide-sulphone* was extracted from the diluted solution with chloroform and had b. p. 225°/0·5 mm. (slight decomp.); yield, 90% (Found : C, 52·4; H, 6·6; S, 23·1. $C_{12}H_{18}O_3S_2$ requires C, 52·6; H, 6·6; S, 23·4%).

*β-Chloro-γ-ethylthio-α-benzylsulphonylpropane* (XI, R = benzyl, R′ = ethyl) was prepared by the cautious addition of phosphorus pentachloride (30 g.) to a hot solution of the hydroxy-compound (33 g.) in chloroform (150 c.c.), the product being then boiled under reflux for 10 minutes. The solvent was removed in a vacuum at the ordinary temperature, since the residue became black when heated and did not subsequently solidify. It crystallised from benzene–petrol (b. p. 40—60°) in long feathery needles, m. p. 56—58°, soluble in ether, alcohol and benzene; yield, about 95% (Found : C, 49·4; H, 5·8; Cl, 11·9; S, 21·8. $C_{12}H_{17}O_2ClS_2$ requires C, 49·2; H, 5·8; Cl, 12·1; S, 21·9%).

*α-Benzylsulphonyl-γ-ethylthiopropene* (VII, R = benzyl, R′ = ethyl). The chloro-sulphone (XI) (40 g.) was boiled under reflux for 2 hours with pyridine (150 c.c.), and the resulting liquid extracted with chloroform after dilution and acidification. The residue obtained after removal of the solvent was distilled in portions of not more than 10 c.c. at a time in order to avoid the decomposition which otherwise usually occurred; b. p. 176°/0·02 mm.; yield, 82% (Found : C, 56·6; H, 6·2; S, 24·6. $C_{12}H_{16}O_2S_2$ requires C, 56·3; H, 6·3; S, 25·0%). Oxidation of (VII) with perhydrol gave the usual mixture of (I) and (II) (Found : C, 50·1; H, 5·6%; *M*, 299).

*γ-Chloro-β-hydroxy-α-ethylthiopropane* (VIII, R = ethyl). Sodium ethylthiol (from 50 g. of ethylthiol), dissolved in 66% aqueous ethyl alcohol (150 c.c.), was slowly added to a cold stirred solution of αγ-dichlorohydrin (200 g.) in the same solvent (200 c.c.), and boiled for 10 minutes. After dilution with water, the *sulphide* was extracted with ether and dried with potassium carbonate. Removal of the solvent left an oil, b. p. 100°/9 mm.; yield, 66% (Found : C, 38·6; H, 7·1; Cl, 23·4. $C_5H_{11}OClS$ requires C, 38·8; H, 7·1; Cl, 23·0%). Unless the fractionation was very carefully carried out, a small amount of dichlorohydrin was subsequently found in the sulphide.

*γ-Chloro-β-hydroxy-α-ethylsulphonylpropane* (IX, R = ethyl). The chloro-sulphide (VIII) (20 g.) was gently warmed with perhydrol (38 c.c.) in glacial acetic acid (100 c.c.) for ¾ hours, water-cooling being used when the reaction became vigorous. The resulting *sulphone* was too soluble in water to be extracted by chloroform or ether, and the liquid was therefore fractionated in a vacuum. The residual oil had b. p. 141°/0·1 mm. (yield, 84%), crystallised on standing, and separated from ether in needles, m. p. 49° (Found : C, 32·4; H, 6·0; Cl, 18·9; S, 16·9. $C_5H_{11}O_3ClS$ requires C, 32·2; H, 5·9; Cl, 19·0; S, 17·2%).

*β-Hydroxy-γ-benzylthio-α-ethylsulphonylpropane* (X, R = ethyl, R′ = benzyl), obtained in 90% yield by the addition of the chloro-sulphone (IX) (32 g.), dissolved in alcohol (50 c.c.), to sodium benzylthiol (from 25 g. of benzylthiol) in 80% aqueous alcohol (120 c.c.), had b. p. 216°/0·3 mm. (Found : C, 52·7; H, 6·9; S, 23·2. $C_{12}H_{18}O_3S_2$ requires C, 52·6; H, 6·6; S, 23·4%).

*Action of phosphorus pentachloride on* (X). A hot solution of the hydroxy-sulphide-sulphone (44 g.) in chloroform (100 c.c.) was slowly treated with phosphorus pentachloride (36 g.). The dark brown residue after distillation of the solvent could not be satisfactorily purified, as it did not solidify, and distillation was attended by decomposition (b. p. 220°/1·3 mm.). It was therefore boiled for 2 hours with pyridine (40 c.c.), and the diluted solution acidified and extracted with chloroform, whence *γ-benzylthio-α-ethylsulphonyl-*$\Delta^{\alpha}$*-propene* (VII, R = ethyl, R′ = benzyl) was obtained as a rather cloudy, pale yellow liquid, b. p. 171°/0·02 mm.; yield, 60% (Found: C, 56·9; H, 6·1; S, 24·8. $C_{12}H_{16}O_2S_2$ requires C, 56·3; H, 6·3; S, 25·0%). Oxidation with perhydrol yielded the bis-sulphones (I and II) (Found: C, 49·7; H, 5·7; S, 22·1%).

*Route C.*—*β-Hydroxy-α-benzylthio-γ-ethylthiopropane* (XII, R, R′ = benzyl, ethyl) was prepared by the addition of γ-chloro-β-hydroxy-α-ethylthiopropane (76 g.) to sodium benzylthiol (from 70 g. of benzylthiol) in 75% alcohol (200 c.c.); b. p. 162—163°/0·2 mm.; yield, 86% (Found: C, 58·9; H, 7·6; S, 27·0. $C_{12}H_{18}OS_2$ requires C, 59·5; H, 7·4; S, 26·4%). Owing to the presence of some unchanged dichlorohydrin in the chloro-sulphone, a fraction, b. p. 215°/0·2 mm., was obtained. This was mainly *β-hydroxy-αγ-bis(benzylthio)propane* (Found: C, 65·0; H, 6·7; S, 22·2. $C_{17}H_{20}OS_2$ requires C, 67·1; H, 6·6; S, 21·5%), since oxidation with perhydrol yielded the corresponding *β-hydroxy-αγ-bis(benzylsulphonyl)propane*, which crystallised from glacial acetic acid in small plates, m. p. 204—205° (Found: C, 55·3; H, 5·4; S, 17·6. $C_{17}H_{20}O_5S_2$ requires C, 55·4; H, 5·4; S, 17·4%). It was insoluble in ethyl acetate, acetone, alcohol and chloroform.

*β-Hydroxy-α-benzylsulphonyl-γ-ethylsulphonylpropane* (XIII), obtained by the oxidation of (XII) with perhydrol, separated from ethyl acetate in needles, m. p. 143—144°. It did not condense with benzaldehyde in the presence of piperidine (Found: C, 47·4; H, 6·3; S, 21·0. $C_{12}H_{18}O_5S_2$ requires C, 47·1; H, 5·9; S, 20·9%).

*β-Chloro-α-benzylthio-γ-ethylthiopropane* (XIV). The hydroxy-bis-sulphide (XII) (16 g.) was warmed under reflux with thionyl chloride (6 c.c.) in benzene (10 c.c.). Fractional distillation gave the *chloro-sulphide*, b. p. 144—145°/0·2 mm., in 88% yield (Found: C, 56·0; H, 7·2; S, 24·4. $C_{12}H_{17}ClS_2$ requires C, 55·3; H, 6·5; S, 24·6%). It was stable to boiling pyridine.

*β-Chloro-α-benzylsulphonyl-γ-ethylsulphonylpropane* (XV). The chloro-bis-sulphide (45 g.) was cautiously oxidised by perhydrol (100 c.c.) in glacial acetic acid (300 c.c.), water-cooling being employed when the reaction became vigorous. The resulting *sulphone*, which contained a considerable amount of unidentified by-product, crystallised from ethyl alcohol in platelets, m. p. 105—107°; yield, 48% (Found: C, 44·6; H, 5·5; Cl, 10·8; S, 18·9. $C_{12}H_{17}O_4ClS_2$ requires C, 44·4; H, 5·2; Cl, 10·9; S, 19·7%). It was also obtained by the action of phosphorus pentachloride (12 g.) on the hydroxy-bis-sulphone (12 g.) dissolved in chloroform (100 c.c.). The hydrogen chloride was eliminated in the usual way by boiling pyridine to yield the bis-sulphones (I) and (II).

(B) (i) *Preparation of α-Benzylsulphonyl-γ-ethylsulphonylpropane.*—*γ-Hydroxy-α-ethylthiopropane*, $SEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 104°/15 mm., was prepared in 76% yield from trimethylene chlorohydrin (35 g.) and sodium ethylthiol (from 25 g. of ethylthiol) (Found: C, 49·8; H, 10·3; S, 26·4. $C_5H_{12}OS$ requires C, 50·0; H, 10·0; S, 26·7%). The corresponding chloro-sulphide was obtained in 64% yield by boiling under reflux a mixture of the hydroxy-sulphide (20 g.), dissolved in benzene (10 c.c.), with thionyl chloride (15 c.c.); b. p. 73°/14 mm.

*γ-Benzylthio-α-ethylthiopropane*, $SEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2Ph$, prepared from the chloro-sulphide and sodium benzylthiol, had b. p. 135°/0·3 mm.; yield, 88% (Found: C, 63·1; H, 7·8; S, 28·0. $C_{12}H_{18}S_2$ requires C, 63·7; H, 8·0; S, 28·3%). Oxidation with perhydrol gave *γ-benzylsulphonyl-α-ethylsulphonylpropane* in 91% yield. It crystallised from ethyl acetate in needles, m. p. 153—154° (Found: C, 49·6; H, 6·4; S, 22·2. $C_{12}H_{18}O_4S_2$ requires C, 49·7; H, 6·2; S, 22·1%). It did not react with alkali alkoxide, and no condensation product was formed when it was mixed with benzaldehyde and piperidine.

(ii) *Preparation of ethylsulphonylacetic acid* (III, R = ethyl). Ethyl ethylthioacetate was prepared from ethyl chloroacetate and sodium ethylthiol (Klason, *Bull. Soc. chim.*, 1875, **23**, 444); b. p. 65°/9 mm. (Found: C, 48·7; H, 8·2. Calc.: C, 48·6; H, 8·1%). Oxidation with perhydrol gave the corresponding sulphone, b. p. 110°/0·3 mm. (not previously recorded) (Found: C, 40·2; H, 6·7; S, 17·9. Calc.: C, 40·0; H, 6·7; S, 17·8%). Hydrolysis was best accomplished by warming the ester with concentrated hydrochloric acid and evaporating the resulting solution to dryness. A nearly theoretical yield of the acid was obtained, and it solidified when kept in a desiccator for some time, having m. p. 62—64°. It has not previously been isolated in crystalline form (Found: C, 31·5; H, 5·5; S, 20·6. Calc.: C, 31·6; H, 5·3; S, 21·1%). The acid lost carbon dioxide when heated, decomposition commencing at 210° and being complete at 240—250°. The yield of methylethylsulphone was over 84%, this being a minimum figure owing to the difficulty of keeping the original acid completely water-free.

(iii) *Preparation of benzylsulphonylacetic acid* (III, R = benzyl). Ethyl benzylthioacetate (Johnson and Guest, *Amer. Chem. J.*, 1909, **42**, 278), b. p. 129°/0·7 mm., was oxidised with perhydrol to give *ethyl benzylsulphonylacetate*, which crystallised from benzene–petrol (b. p. 40—60°) in needles, m. p. 50°; yield, 88% (Found: C, 54·7; H, 5·8; S, 13·2. $C_{11}H_{14}O_4S$ requires C, 54·5; H, 5·8; S, 13·2%). An 80% yield of the corresponding *benzylsulphonylacetic acid* was obtained by hydrolysis with cold 10% aqueous sodium hydroxide, the greater part of the acid being precipitated by acidification of the alkaline solution and the remainder isolated by extraction with chloroform. It was slightly soluble in benzene and soluble in acetone and water, whence it crystallised in plates, m. p. 139—140° (Found: C, 50·5; H, 4·7; S, 14·7. $C_9H_{10}O_4S$ requires C, 50·5; H, 4·7; S, 15·0%). A nearly theoretical yield of methylbenzylsulphone was isolated when the acid was heated at 180—190° until no further carbon dioxide was evolved.

(C) *Properties of α-Benzylsulphonyl-γ-ethylsulphonyl-$\Delta^{\alpha}$- and -$\Delta^{\beta}$-propene.*—(i) The sulphones were soluble in chloroform, less so in ethyl acetate, alcohol, and water, and practically insoluble in ether. Although alkaline permanganate solution was reduced, no addition of halogen acid, halogens, or sulphuric acid took place. They could be distilled without decomposition (b. p. above 220°/0·1 mm.), but no separation of isomerides resulted.

(ii) *Separation of the $\Delta^{\alpha}$- and the $\Delta^{\beta}$-isomeride.* The procedure followed for the separation was to recrystallise the crude product from ethyl acetate. Part of the solvent of the filtrate was removed by evaporation in a vacuum, and excess of petrol (b. p. 40—60°) added to the residue. The precipitate, consisting mainly of the $\Delta^{\alpha}$-sulphone, was rapidly recrystallised three times from benzene, from which it separated in plates, m. p. 105—107° (Found: C, 50·3; H, 5·6; S, 21·9%). Further recrystallisation usually caused isomerisation with a consequent lowering of the melting point.

The crude $\Delta^{\beta}$-sulphone from the first ethyl acetate crystallisation was recrystallised a further three times from ethyl acetate and then from benzene, from which it was obtained in needles, m. p. 131—132°, having a typical soapy feel when crushed with a spatula. This was the highest m. p. usually recorded, but in one case, only, after crystallisation from a very dilute benzene solution the substance had m. p. 137° (Found: C, 49·8; H, 5·4%). The yield from 15 g. of a mixture, m. p. 95—100°, was 0·5 g. of the $\Delta^{\alpha}$-sulphone and 2·0 g. of the $\Delta^{\beta}$-sulphone, the remaining 12·5 g. being a mixture (Found: C, 50·1; H, 5·6%) of the two which could again be partly separated by the same cycle of operations.

(iii) *Catalytic reduction.* The sulphones (1 g.), dissolved in glacial acetic acid, were shaken with Adams's catalyst in the presence of hydrogen until no more absorption took place. The resulting α-benzylsulphonyl-γ-ethylsulphonylpropane was identical (m. p. and mixed m. p.) with that described in section B (i) (Found: C, 50·0; H, 6·4; S, 21·8%).

(iv) *Condensation with benzaldehyde.* Either of the sulphones (2 g.) was shaken with benzaldehyde (6 c.c.) and piperidine (3 drops). The solution became warm and water was eliminated. The cloudy solution was kept for 12 hours, and the *βδ-benzylsulphonylethylsulphonyl-α-phenylbutadiene* (IV) precipitated by the addition of excess of ether. It crystallised from ethyl acetate in fine needles, m. p. 154° (Found: C, 60·4; H, 5·3; S, 17·2; *M*, 379. $C_{19}H_{20}O_4S_2$ requires C, 60·6; H, 5·3; S, 17·0%; *M*, 376).

Complete reduction of the condensation product could not be effected. It was recovered unchanged when treated with hydrogen and Adams's catalyst at ordinary pressures, and boiling under reflux with hydriodic acid (*d* 1·94) for 6 hours appeared to give a *dihydro-compound*, which crystallised from ethyl acetate–petrol (b. p. 60—80°) in needles, m. p. 124° (Found: C, 60·6; H, 5·8; S, 16·4. $C_{19}H_{22}O_4S_2$ requires C, 60·3; H, 5·8; S, 16·9%).

(v) *Equilibration experiments.* A melting-point diagram was constructed from artificial mixtures of the two sulphones. Since an experimental mixture had of necessity to be melted before the composition could be determined, the artificial mixtures were similarly fused and allowed to solidify before determination of the melting point was carried out. This made an automatic allowance for the interconversion that takes place during fusion, and accounts for the rather low melting points of the pure sulphones recorded in the table below:

*Melting Points of Mixtures of the $\Delta^{\alpha}$- with the $\Delta^{\beta}$-Sulphone.*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\Delta^{\beta}$-Sulphone, % ............ | 100 | 72·1 | 50·0 | 37·0 | 24·1 | 16·9 | 0·0 |
| M. p............................ | 126·3° | 117·7° | 108·5° | 101·0° | 91·5° | 95·0° | 103·5° |

The following interconversion experiments were recorded :

(a) The $\Delta^{\beta}$-sulphone (m. p. 131°, 0·1 g.) was boiled under reflux for 2 days with methyl alcohol (10 c.c.), and the solution evaporated to dryness. The residue had m. p. 105°, corresponding to 44% of the $\Delta^{\beta}$-sulphone. This figure was confirmed by the addition of a known quantity of the isomeride to the mixture and redetermination of the m. p.

(b) The $\Delta^{\beta}$-sulphone (1·0 g.) was boiled with methyl alcohol for 24 hours. The residue after removal of the solvent had m. p. 103·5°, corresponding to 41·2% of the $\Delta^{\beta}$-sulphone.

(c) The $\Delta^{\alpha}$-sulphone (0·1 g.) was boiled with benzene (10 c.c.) for 2 days, it then having m. p. 105·5°, equivalent to 44·8% of the $\Delta^{\beta}$-sulphone. This was confirmed as in the case of (a).

(d) Experiment (b) was repeated, leading to 97° for the m. p. of the residue, equivalent to 31·5% of the $\Delta^{\beta}$-sulphone.

The residues from (b) and (d) were subsequently used in the ozone experiments (section D).

(D) *Fission of* (I) *and* (II) *by Ozone.*—The essential requirement was the isolation of the benzyl- and ethyl-sulphonylacetic acids formed by the fission of the $\Delta^{\alpha}$- and the $\Delta^{\beta}$-sulphone respectively from a mixture which contained in addition to these substances the corresponding sulphonic acids, sulphuric acid, benzyl- and possibly ethyl-sulphonylacetaldehyde, unchanged sulphone, and small quantities of formaldehyde and formic acid. Moreover it was found that, though fission did not occur in chloroform solution, it was difficult to prevent complete oxidation to the sulphonic acids when acetic acid was used. The method finally adopted was to pass ozonised oxygen through a water–chloroform solution of the sulphones for 16—24 hours. The chloroform layer contained the unchanged sulphones and benzylsulphonylacetaldehyde, identified by m. p. and by the *p*-nitrophenylhydrazone (Part III, *loc. cit.*) respectively. Ethylsulphonylacetaldehyde was not positively identified, but its presence was inferred from the low analysis figures obtained for the above nitrophenylhydrazone unless it was carefully purified.

The aqueous layer was heated on a water-bath and neutralised with excess of barium carbonate. After filtration, the filtrate was slightly acidified with hydrochloric acid and evaporated to dryness. The barium salts thus obtained were mixed with absolute ethyl alcohol and a slight excess of concentrated sulphuric acid and esterified by the alcohol vapour method. The esters were extracted from the diluted solution with chloroform and dried, and the solvent removed: the residue was heated on the steam-bath for 12 hours with concentrated hydrochloric acid. The acid solution was diluted, boiled with norit, and filtered, and the filtrate evaporated to dryness. The mixed acids were heated in a glycerol bath at 180—250° until decomposition was complete; the resulting sulphones, dissolved in chloroform, were washed with sodium bicarbonate solution and dried. Distillation of the solvent yielded a rather dark residue, which was purified by boiling with norit in ethyl acetate solution. The composition of the mixed sulphones was determined by a fusion curve of artificial mixtures of methylethyl- and methylbenzyl-sulphones. In each case the figure obtained was checked by addition of a known proportion of one of the constituents to the experimental mixture. The applicability of the method was confirmed by preliminary trials with artificial mixtures of benzyl- and ethyl-sulphonylacetic acids with the corresponding sulphonic acids.

*M. p.'s of Mixtures of Methylbenzyl- and Methylethyl-sulphones.*

| Methylbenzylsulphone, % | 0·0 | 9·4 | 20·2 | 34·1 | 48·7 | 65·7 | 82·0 | 100·0 |
|---|---|---|---|---|---|---|---|---|
| M. p. .......................... | 34·6° | 32·0° | 48·4° | 66·2° | 82·3° | 99·0° | 112·5° | 125·6° |

TABLE I.

*Fission by Ozone of Mixtures of the $\Delta^{\alpha}$- and the $\Delta^{\beta}$-Sulphone.*

| M. p. of mixture. | β-Sulphone, %. | Wt. taken, g. | Wt. of mixed sulphone, g. | Methyl-benzyl-sulphone, %. |
|---|---|---|---|---|
| 131° | 100 | 1 | 0·02 | 97·5 |
| 125—126 | 95 | 1 | 0·10 | 95·1 |
| 117 | 68 | 3 | 0·22 | 75·0 |
| 105—108 | *ca.* 47 | 1 | 0·04 | 54·0 |
| 95—100 | ,, 33 | 2 | 0·10 | 43·3 |
| 103·5° * | 41·2 | 1 | 0·02 | 74·0 |
| 97 * | 31·5 | 1 | 0·06 | 62·7 |
| 95—100† | *ca.* 33·0 | 2 | 0·05 | 57·0 |
| 100—104 | ,, 40·0 | 2 | 0·25 | 41·0 |

* Equilibrated sulphones; cf. section C (v,b and v,d respectively). † Equilibrated sulphones.

(E) *Fission by Ozone of the Sulphide-sulphones* (VII).—These were carried out in exactly the same way as with the bis-sulphones. The results are in Table II.

TABLE II.

*Fission of* $R{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SR'$.

| R. | R′. | Wt. taken, g. | Wt. of mixed sulphones, g. | Methylbenzyl-sulphone, %. |
|---|---|---|---|---|
| Benzyl | Ethyl (VII) | 1·0 | 0·08 | 47·0 |
| ,, | ,, ,, | 1·8 | 0·23 | 87·5 |
| ,, | ,, ,, | 1·0 | 0·05 | 91·0 |
| Ethyl * | Benzyl (X) | 1·9 | 0·15 | 70·0 |

* Benzaldehyde was found in the neutral fraction.

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