453. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part VIII.* Further Experiments with 1,3-Bisalkylsulphonylpropenes.*

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The synthesis, positions of equilibrium, and mobilities of 1-n-butylsulphonyl-3-ethylsulphonyl- and of 1-benzylsulphonyl-3-alkylsulphonylpropenes, $R\cdot SO_2\cdot CH_2\cdot CH:CH\cdot SO_2R'$, are discussed in the light of some new results.

THE original investigation[1] of tautomeric change in bisalkylsulphonylpropenes mainly concerned the two 1-benzylsulphonyl-3-ethylsulphonylpropenes (I and II; R = Et), and the present paper records an extension to analogous compounds in which benzyl was replaced by n-butyl and, secondly, where alkyl groups other than ethyl (I and II; R = Me, Pr^n, Bu^n, Bu^t) were used.

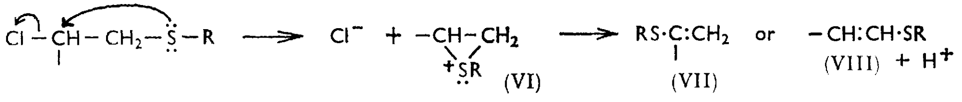
$$\text{(I)}\ Ph\cdot CH_2\cdot SO_2\cdot CH_2\cdot CH:CH\cdot SO_2\cdot R \rightleftharpoons Ph\cdot CH_2\cdot SO\cdot CH:CH\cdot CH_2\cdot SO_2\cdot R\ \text{(II)}$$

The synthesis of 1-n-butylsulphonyl-3-ethylsulphonylpropenes (III; R = Et or Bu^n, R′ = Bu^n or Et) started from 1,3-dichloropropene (IV), and yielded the same equilibrium mixture of bis-sulphones irrespective of the order of introduction of the alkylthio-groups. Owing to the high mobility, complete separation of the isomers was probably not achieved, although two specimens were isolated having m. p.s 101—104° and 67·5—69·5°, respectively, and these gave a mixed melting-point depression. Further attempts at purification, such as recrystallisation from ethyl acetate, led to interconversion (see Experimental section, Tables 2 and 3). The composition of the equilibrium mixture was determined by decarboxylating the alkylsulphonylacetic acids, $R\cdot SO_2\cdot CH_2\cdot CO_2H$, obtained by ozonolysis and estimating the resulting mixture of n-butyl and ethyl methyl sulphone by reference to a melting-point–composition curve as previously described.[1] It was thus found that the equilibrium mixture contained 57% of 1-n-butylsulphonyl-3-ethylsulphonylprop-1-ene, but whether this was the high- or low-melting isomer could not be established.

$$\text{(IV)}\ Cl\cdot CH:CH\cdot CH_2Cl \xrightarrow[\text{EtOH}]{\text{RSNa–}} ClCH:CH\cdot CH_2\cdot SR \xrightarrow[\text{pentanol}]{\text{R'SNa–}}$$
$$R'S\cdot CH:CH\cdot CH_2\cdot SR \longrightarrow R'\cdot SO_2\cdot CH:CH\cdot CH_2\cdot SO_2\cdot R\ \text{(III)}$$

In the benzyl series, the most convenient method of preparation was that outlined below though other methods were also employed. Oxidation of the unsaturated compound (V) gave the disulphones (I) and (II). The chloro-compounds (IV) eliminated hydrogen chloride on storage, presumably through a cyclic intermediate (VI) which could lead to either of the two olefinic derivatives (VII) or (VIII), reactions corresponding to the analogous spontaneous decomposition of 2-bromo-1,1-bisethylthiopropane:[2]

$$Ph\cdot CH_2\cdot SO_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot Cl \longrightarrow Ph\cdot CH_2\cdot SO_2\cdot CH(OH)\cdot CH_2\cdot SR \xrightarrow{PCl_5}$$
$$\text{(IV)}\ Ph\cdot CH_2\cdot SO_2\cdot CHCl\cdot CH_2\cdot SR \xrightarrow{\text{Pyridine}} Ph\cdot CH_2\cdot SO_2\cdot CH\overset{}{=\!=}\overset{(H)}{CH}=\!=CH\cdot SR\ \text{(V)}$$



$$Me\cdot CHBr\cdot CH(SEt)_2 \longrightarrow \left[\begin{array}{l} \longrightarrow Me\cdot CH:C(SEt)_2 \\ \longrightarrow Me\cdot CH(SEt):CH\cdot SEt \end{array}\right. + HBr$$

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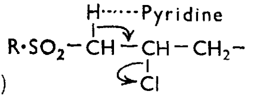
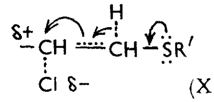
* Part VII, *J.*, 1963, 1036.

[1] Rothstein, *J.*, 1937, 309.

[2] Rothstein, *J.*, 1940, 1553.

Although not conclusive, some evidence of the formation of a rearranged product was provided by the methylthio-derivative (IV; R = Me) which afforded an unsaturated sulphide different from that obtained by the pyridine-catalysed dehydrohalogenation described below. The latter type of reaction was discussed briefly in Part VII, and in the ordinary way should follow the Hofmann rule to yield a prop-1-ene derivative, as in formula (IX) and in fact it occurs, for instance, in the case of 1-benzylsulphonyl-2-chloropropane.[3] An alternative mechanism would be of the Saytzeff type where the unshared electrons of sulphur would be conjugated with the forming double-bond as in formula (X). Usually there was not a clear indication which of the two mechanisms predominated, but an exception was the t-butyl derivative (IV; R = Bu^t) because the intermediate olefin (V) yielded the prop-2-ene disulphone (I) only, and hence the reaction followed the Saytzeff pattern. The isomeric prop-1-ene derivative (II) was not present in the initial product, but boiling the latter in ethyl acetate solution furnished an equilibrium mixture from which it could be isolated by fractional crystallisation. To some extent the methyl analogue (IV; R = Me) behaved in a similar way in that the disulphone (I; R = Me) which was eventually obtained was the prop-2-ene isomer, but " equilibration " led to dimerisation and it was impossible to determine whether the absence of the isomeric compound (II) could be attributed to its instability as a monomer or to its non-formation. Parenthetically it may be remarked that polymerisation is normal in the presence of strong bases and seems consequent on the formation of the mesomeric anion, $R\cdot SO_2\cdot\overset{\ominus}{\overbrace{CH\cdot CH\cdot CH}}\cdot SO_2\cdot R'$, but neutral bases are evidently sufficient to bring this about in the case of the methyl compound.


(IX)


(X)

The mobility, *i.e.*, the rate of tautomeric interchange between the sulphones (I) and (II), differed greatly from one to the other. Accurate measurements could not be made, but their relative magnitudes for a given concentration (0·84 mole/l.) in boiling ethyl acetate were indicated by the time taken for the conversion of 20% of the high-melting sulphones (I) into their low-melting isomers (II), *i.e.*, by noting the times taken for the appropriate changes in the melting points.

R in $Ph\cdot CH_2\cdot SO_2\cdot CH_2\cdot CH{:}CH\cdot SO_2\cdot R$	Et	Pr^n	Bu^n	Bu^t
Time (min.) for 20% change	240	80	50	405

As with the n-butylsulphonylethylsulphonyl compound (III), the mobility of the benzyl n-butyl derivatives (I and II) was particularly high and it was doubtful whether the individual isomers were in fact completely pure. This became apparent in the determination of the compositions of the equilibrium mixtures which was carried out either by ozonolysis or by the use of melting-point–composition curves. The results obtained by the two methods in any case differed by approximately 15% but the discrepancy was much greater for n-butyl. The figures are given in Table 1 and suggest

TABLE 1.

Percentages at equilibrium (in ethyl acetate) of 1-benzylsulphonyl-3-alkylsulphonylprop-2-enes, $Ph\cdot CH_2\cdot SO_2\cdot CH_2\cdot CH{:}CH\cdot SO_2\cdot R$ determined (i) from m. p. curves and (ii) by ozonlysis.

R:	Ethyl	n-Propyl	n-Butyl	t-Butyl
%:	(i) 39 ± 2	(i) 40 ± 2	(i) 53 ± 3	(i) 60 ± 2
%:	(ii) 33—41 *	(ii) 46·5	(ii) 70	(ii) 68

* In methanol.[1]

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[3] Rothstein, *J.*, 1934, 684.

that the positions of equilibrium were largely dependent on the inductive release of electrons, with $Bu^t > Et \approx Pr^n$.

EXPERIMENTAL

The Synthesis, Separation, and Experiments with 1-*n*-*Butylsulphonyl*-3-*ethylsulphonylpropenes.*

Preparation of 1-*Chloro*-3-*ethylthiopropene Derivatives.*—The chloro-sulphide was prepared by slow addition of 1,3-dichloropropene [4] (1 mol.) to a stirred solution of ethanethiol (1 mol.) in 10% ethanolic sodium hydroxide (400 c.c.) under nitrogen. It was isolated as a yellow oil (80%), b. p. 54·5—58·5°/12 mm. (Found: C, 44·5; H, 7·0. Calc. for C_5H_9ClS: C, 43·9; H, 6·6%). Oxidation in glacial acetic acid with 30% hydrogen peroxide (2·5 mol.) afforded 1-*chloro*-3-*ethylsulphonylpropene*, b. p. 96—100°/0·3 mm. (Found: C, 36·0; H, 5·6; Cl, 21·2; S, 18·6. $C_5H_9ClO_2S$ requires C, 35·6; H, 5·4; Cl, 21·0; S, 19·0%). Crystalline derivatives of the chloro-sulphide were prepared but it was not possible to regenerate the starting material from them and therefore they could not be used for further purification. Reaction with chloramine-T in aqueous acetone [5] yielded S-3-*chloroallyl*-S-*ethyl*-N-*toluene*-p-*sulphonylsulphidimine*, $Cl{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SEt{:}N{\cdot}SO_2{\cdot}C_6H_4Me$-*p*, separating from dilute ethanol in large clear plates, m. p. 89—90·5° (30%) (Found: C, 47·4; H, 5·8; S, 20·7. $C_{12}H_{16}ClNO_2S_2$ requires C, 47·1; H, 5·3; S, 21·0%). The chloro-sulphide (2·73 g.) was converted into a *mercurichloride* by shaking it for 5 min. with aqueous mercuric chloride (8·5 g. in 200 c.c. of water). The precipitated white solid (3·6 g.) separated from benzene in white platelets, m. p. 128—130°, having the apparent composition $(C_5H_9ClS)_2(HgCl_2)_5$ (Found: C, 7·3; H, 0·7. $C_{10}H_{18}Cl_{12}Hg_5S_2$ requires C, 7·3; H, 1·1%).

1-*n*-*Butylthio*-3-*chloroprop*-2-*ene* was prepared in 85% yield by the reaction between 1,3-dichloropropene and ethanolic sodium n-butyl sulphide and was isolated as a yellow oil, b. p. 87—89°/12 mm. (Found: C, 51·5; H, 8·2; Cl, 21·6; S, 19·2. $C_7H_{13}ClS$ requires C, 51·1; H, 8·0; Cl, 21·5; S, 19·4%). Oxidation afforded 1-3′-chloroallylsulphonylbutane, b. p. 108—111°/0·1 mm. (Found: C, 43·3; H, 6·9; S, 16·3. $C_7H_{13}ClO_2S$ requires C, 42·8; H, 6·7; S, 16·3%).

Condensation of 1-*Chloro*-3-*ethylthioprop*-1-*ene with Sodium Butyl Sulphide.*—n-Butanethiol (25 g., 0·028 mol) was dissolved in a warm solution of sodium pentyl oxide (0·5 mol. from 11·5 g. of sodium) under nitrogen and to the solution was added, with stirring, 1-chloro-3-ethylthiopropene (34 g., 0·25 mol.). Within 5 min. a little sodium chloride was deposited but finally the reaction was completed by boiling the mixture under reflux for 5 hr. Water was then added and the organic layer isolated by extraction with ether. After removal of the pentanol (b. p. 52—53°/12 mm.), the residue was distilled, affording after redistillation two major fractions, (*A*) b. p. 57·5—65°/0·1 mm. (14·0 g.) and (*B*) b. p. 72—75°/0·05 mm. (30 g.). These appeared to be mainly isomeric 1-butylthio-3-ethylthiopropenes but it is possible that traces of a pentyloxy-derivative were present [Found (A): C, 56·3; H, 9·9; S, 33·0. (*B*): C, 57·2; H, 9·6; S, 32·2. Calc. for C_9H, S : C, 56·8; H, 9·5; S, 33·7%]. Oxidation, however, to the corresponding disulphones showed the presence of appreciable amounts of side-products.

Condensation of 3-*Butylthio*-1-*chloroprop*-1-*ene with Sodium Ethyl Sulphide.*—Ethanethiol and 3-butylthio-1-chloroprop-1-ene (43 g. of each) reacted in sodium pentoxide solution to give a mixture of sulphides which on fractionation afforded fractions (*C*), b. p. 69—73°/0·5 mm. (13 g.) (Found: C, 60·2; H, 10·7; S, 30·2%), and (*D*), b. p. 80—87°/0·4 mm. (23·5 g.) (Found: C, 58·9; H, 10·6; S, 31·0%). There was also a small amount of material, b. p. 95—108°/0·4 mm. (Found: C, 66·1; H, 11·0; S, 22·7%). Derivatives of the first two compounds could not be obtained but when they were boiled with an aqueous suspension of mercuric oxide a small quantity of acraldehyde and some butanethiol (mercuric salt, m. p. 71—73°) were obtained.

Preparation of 1-*Butylsulphonyl*-3-*ethylsulphonylpropenes.*—The above fractions *A*, *B*, *C*, and *D* were oxidised separately by a solution of 30% hydrogen peroxide in three times its volume of glacial acetic acid, finally at 100° for 1 hr. Nearly identical products were obtained in each case. The chloroform extracts yielded crystalline material which after four recrystallisations from ethyl acetate–light petroleum separated in clusters of plates, m. p. 101°. This

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[4] Hill and Fischer, *J. Amer. Chem. Soc.*, 1922, **44**, 2584.
[5] Tarbell and McCall, *J. Amer. Chem. Soc.*, 1952, **74**, 55.

substance was one of the isomers of 1-*n-butylsulphonyl*-3-*ethylsulphonylpropene* (Found: C, 42·4; H, 7·1; S, 24·9. $C_9H_{18}O_4S_2$ requires C, 42·5; H, 7·1; S, 25·2%). The other, a lower-melting isomer, was in these experiments only once obtained nearly pure. The sulphone from fraction *B*, when crystallised once from ethyl acetate, had a rather low m. p. (92—95·5°), and the mother-liquors, on evaporation to half their volume followed by addition of light petroleum (b. p. 60—80°), deposited a mixture of oil and crystals, m. p. 57·5—62·5°. A trace of the isomer, m. p. 105°, depressed the m. p. by 0·5°. The remaining oil (b. p. 130—155°/0·2 mm.) was not identified (Found: C, 47·7; H, 5·0; S, 19·0%).

Separation of the Isomeric 1-*n-Butylsulphonyl*-3-*ethylsulphonylpropenes.*—The crude mixture of sulphones was boiled in ethyl acetate with a little charcoal and filtered. After 6—12 hr. the crystals were filtered off and recrystallised twice from ethyl acetate, affording the highest-melting sample (101—104°) that was isolated (Found: C, 42·7; H, 6·9%). It was characteristic that because of isomerisation the m. p.s of these disulphones was never sharp (see below). The original ethyl acetate filtrate was heated to the b. p. and light petroleum (b. p. 60—80°) was added until there was a slight cloudiness. A second crop of crystals (m. p. 75—78°) containing a greater proportion of the more soluble and lower-melting isomer was recrystallised again from ethyl acetate. This gave a sample of m. p. 82—83°, the mother-liquors yielding a product, m. p. 69—71°. At each stage a mixed m. p. determination with the highest-melting sample was made, and the process continued until no further separation occurred. Only in one case did a sample, m. p. 67·5—69·5°, show a mixed m. p. depression and this was probably the purest low-melting isomer obtained. Recrystallisation raised the m. p. which was no longer depressed by addition of the other isomer. All the compounds were unsaturated to permanganate and analysis showed that the composition was unaltered, *e.g.*, sulphone, m. p. 86·5—87·5° (Found: C, 42·5; H, 7·2%); sulphone, m. p. 63—65° (Found: C, 42·8; H, 7·1%). An approximate composition–m. p. curve was constructed with samples of m. p. 101—104° and 63—65°. A mixture of the disulphones was pre-fused to obtain a homogeneous melt and allowed to solidify. The m. p.s recorded in Table 2 are the temperatures at which the last trace of solid disappeared from the melt. The rapidity at which interconversion took place can be seen from this Table and Table 3.

TABLE 2.

M. p.s of mixtures of isomeric 1-n-butylsulphonyl-1-ethylsulphonylpropenes.

Isomer of low m. p. ...	100	90	70	50	33	20	12·5	0
M. p. before pre-fusion	64·9°	—	—	—	—	—	—	104·3°
Conditions of pre-fusion (sec.)	5(70°)	10(80°)	10(100°)	10(100°)	10(100°)	10(120°)	10(120°)	10(120°)
M. p. after fusion	65·2°	88·2°	88·9°	92·2°	93·2°	97·4°	98·0°	102·8°

TABLE 3.

Effect of heat on the m. p.s of the isomeric bisalkylsulphones (*a*) at 100°, (*b*) in boiling ethyl acetate solution.

Time of heating	*A* M. p.	*A′* M. p.	*B* M. p.	*B′* M. p.
0 min.	67·5—72·5°	101—104°	63—65°	101—104°
5 min.	70—72·5	99—103	—	—
30 min.	73—77	—	—	—
45 min.	75—77	—	—	—
1 hr.	—	—	78—80	93—98
2 hr.	79—80	94·5—101	—	—
3 hr.	—	—	80—83	—
4 hr.	81—83	—	79—83	93—95
12 hr.	—	—	80—83 †	89—94
24 hr.	83—84·5 *	91—94 *	—	90—92

* The sulphone was slightly discoloured. † Although the equilibrium point was not reached, mixed m. p. with the high-melting isomer showed no depression.

Condensation of 1-*n-Butylsulphonyl*-3-*ethylsulphonylpropene with Benzaldehyde.*—A solution of the bisalkylsulphone, m. p. 90—94·5° (1·5 g.), in freshly distilled benzaldehyde (4 c.c.) was shaken with 3 drops of piperidine. It became cloudy after 20 min. and water collected on the surface after 12 hr. Ether was added, the ethereal solution was washed with aqueous sodium carbonate, water, and aqueous sodium hydrogen sulphite, then dried ($CaCl_2$). Removal of the ether gave a yellowish greasy solid which after two crystallisations from ethyl acetate separated in colourless needles, m. p. 115—116°. This was 2(or 4)-n-butylsulphonyl-4(or 2)-ethylsulphonyl-1-phenylbuta-1,3-diene (Found: C, 55·7, 56·9; H, 7·0, 6·6; S, 18·9. Calc. for $C_{16}H_{22}O_2S_4$: C, 56·1; H, 6·5; S, 18·7%).

Fission by Ozone of the Equilibrated 1-*n-Butylsulphonyl*-3-*ethylsulphonylpropenes.*—This was carried out essentially as for the 1-benzylsulphonyl analogue [1] except that the solvent was pure dry chlorform. A mixture of n-butyl and ethyl methyl sulphone, m. p. 12·5°, was obtained from the two fission products, n-butyl- and ethyl-sulphonylacetic acid. The composition was obtained from a m. p. curve derived from the data in Table 4. The m. p. of the mixed sulphones from the ozonolysis corresponded to 57% of ethyl methyl sulphone since a mixture of the product (5·3 mg.) and ethyl methyl sulphone (0·8 mg.) had m. p. 14·6°, and when 6·8 mg. was mixed with n-butyl methyl sulphone (1·2 mg.) the m. p. was 7·0°. That is, the equilibrium mixture of the disulphonylpropenes contained ~57% of 1-n-butylsulphonyl-3-ethylsulphonylpropene.

TABLE 4.

M.p.s of mixtures of n-butyl and ethyl methyl sulphone.*

$Bu^n\cdot SO_2\cdot Me$ (%)	100	75	70·6	59	55·5	51·7	47·7	39·0	24·5	0·0
M. p.	28·3°	15·6°	11·6°	7·0°	4·7°	8·2°	7·4°	14·1°	20·5°	35·0

* Deposition of moisture made the m. p.s uncertain near the eutectic.

Reduction of the Mixed 1-*n-Butylsulphonyl*-3-*ethylsulphonylpropenes.*—A solution of the disulphones (0·5 g.) in glacial acetic acid (20 c.c.) was hydrogenated in the presence of platinic oxide (0·05 g.). The product was identical (m. p. and mixed m. p.) with that described below.

A mixture of 1-chloro-3-ethylthiopropane [1] and an equivalent quantity of 95% ethanolic sodium n-butyl sulphide was boiled under reflux for 1 hr., affording 1-*n-butylthio*-3-*ethylthiopropane*, b. p. 78—79°/0·05 mm. (Found: C, 56·8; H, 10·5; S, 32·9. $C_9H_{20}S_2$ requires C, 56·2; H, 10·5; S, 33·3%). The corresponding disulphone was obtained by oxidation with 40% hydrogen peroxide in glacial acetic acid at 100°. 1-*n-Butylsulphonyl*-3-*ethylsulphonylpropane* separated from ethyl acetate in plates, m. p. 154·5°, only slightly soluble in benzene or chloroform (Found: C, 42·2; H, 7·9; S, 24·7. $C_9H_{20}O_4S_2$ requires C, 42·2; H, 7·9; S, 24·9%).

Zerewitinov determinations in tetrahydrofuran [6] gave the following figures for " active " hydrogen: 1-n-butylsulphonyl-3-ethylsulphonyl-propane, 0; -propene, m. p. 101—104°, 1·93; -propene, m. p. 72—76°, 2·06.

Preparation of 1-*Benzylsulphonyl*-3-*alkylsulphonylpropenes.*

1-*Benzylthio*-3-*chloropropan*-2-*ol.*—This was best prepared [1] from toluene-ω-thiol and 1,3-dichloropropan-2-ol (Found: C, 55·8; H, 6·5; S, 14·5. Calc. for $C_{10}H_{13}ClOS$: C, 55·4; H, 6·1; S, 14·8%). The principal product was accompanied by a large proportion of 1,3-bisbenzylthiopropan-2-ol which was identified by oxidising it with 40% hydrogen peroxide in acetic acid to the corresponding 1,3-bisbenzylsulphonylpropan-2-ol, m. p. 204—204·5°. The benzylthiochloropropanol was also obtained from 3-chloro-1-mercaptopropan-2-ol, which was prepared by addition of epichlorohydrin to thiolacetic acid and hydrolysing the resultant thiolacetate (b. p. 65—68·5°/0·2 mm.) with methanolic hydrogen chloride.[7] Ethanolic sodium ethoxide (from 28·9 g. of sodium in 500 c.c. of ethanol) was added to a mixture of the thiol (159 g.), redistilled benzyl chloride (141·5 g.), and ethanol (200 c.c.), and the liquid was boiled under reflux with vigorous stirring. The major product, b. p. 132°/0·1 mm. (100 g., 41%) (Found: C, 56·4; H, 6·3; Cl, 15·6; S, 14·6. Calc. for $C_{10}H_{13}ClOS$: Cl, 16·4%), was accompanied by a *substance*, b. p. 145°/0·1 mm. (11 g.) having an identical composition (Found: C, 56·0; H, 6·4; Cl, 15·9; S, 14·6%). Extensive polymerisation occurred during distillation and there were ~100 g. of unidentified resin. Oxidation of 1-benzylthio-3-chloropropan-2-ol prepared by either of the above methods yielded the corresponding sulphone,[1] but the product derived from 1,3-dichloropropan-2-ol was more easily isolated pure.

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[6] Braude and Slein, *J.*, 1946, 404.

[7] Sjoberg, *Ber.*, 1941, **74**, 64.

Preparation of 1-*Alkylthio*-3-*benzylsulphonylpropan*-2-*ols*.—These compounds were prepared by addition of methanolic 1-benzylsulphonyl-3-chloropropan-2-ol (0·2 mol.) to a stirred solution of the appropriate thiol (0·256 mol.) in an equivalent quantity of methanolic sodium methoxide at 0° under nitrogen. The liquid was stirred for 12 hr. and then boiled under reflux for a further 2 hr. after which the mixture was mixed with an excess of water, and the product was extracted with chloroform. The extract was washed with water and dried (Na_2SO_4), and the solvent removed in a vacuum through a short fractionating column. The residue, in the form of a clear oil, was usually used without further purification, but in the case of the t-butyl derivative crystallisation occurred and the resulting 1-*benzylsulphonyl*-3-t-*butylthiopropan*-2-*ol* separated from ether (two recrystallisations) in large parallelepipeds, m. p. 87° (Found: C, 60·3; H, 7·3; S, 20·9. $C_{14}H_{22}O_3S_2$ requires C, 59·6; H, 7·3; S, 21·2%).

Preparation of 1-*Benzylsulphonyl*-3-n-*butylsulphonylpropene by Route C*.[1]—1-Benzylsulphonyl-3-n-butylthiopropan-2-ol (~34 g.) was oxidised in the usual way by 40% hydrogen peroxide in glacial acetic acid, to yield the corresponding *hydroxy-disulphone* (25 g., 72%), which after four recrystallisations from ethyl acetate separated from benzene in colourless needles, m. p. 104·5°. It was soluble in hot water but not in light petroleum (Found: C, 50·8; H, 6·6; S, 18·9. $C_{14}H_{22}O_5S_2$ requires C, 50·3; H, 6·6; S, 19·2%). Phosphorus pentachloride (20 g.) was added to a solution of the disulphone (20 g.) in chloroform (200 c.c.) and when the initially vigorous reaction had subsided the liquid was boiled under reflux for 10 min. It was then added to vigorously stirred ice–water (500 c.c.) and extracted with chloroform. Two recrystallisations of the product from ethanol yielded a white powder, m. p. 107—113° (14 g., 66%). A further two recrystallisations from benzene yielded pure 1-*benzylsulphonyl*-3-n-*butylsulphonyl*-2-*chloropropane* as plates, m. p. 114—116° (10·2 g., 49%) (Found: C, 48·2; H, 6·2; Cl, 10·1; S, 18·0. $C_{14}H_{21}ClO_4S_2$ requires C, 47·7; H, 6·0; Cl, 10·1; S, 18·2%). The mother-liquors from the above recrystallisation also afforded a small quantity of halogen-free material, m. p. 191—201°, which was not identified.

Removal of hydrogen chloride from the above chloro-sulphone was accomplished by boiling it (10·2 g.) with pyridine (26 g.) for 2 hr. Acidification with 5N-hydrochloric acid (75 c.c.) precipitated a dark oil which was isolated by means of chloroform. Distillation of the extract gave a dark residue which was boiled in ethyl acetate with charcoal. The hot filtered solution deposited a *substance* which was recrystallised twice from ethyl acetate and twice from benzene, from which it separated in feathery needles, m. p. 173·5—175·5°. It was stable to heat (30 min. at 180—200°) and was unchanged when a solution in methanol was boiled for 24 hr. Potassium permanganate was not decolorised in acetone solution. Analysis suggested that it was possibly a dimeric *form* of the sulphone described below (Found: C, 53·6; H, 6·2; S, 19·9%; *M*, 406. $C_{28}H_{40}O_8S_4$ requires C, 53·1; H, 6·4; S, 20·3%; *M*, 632).

Addition of light petroleum (b. p. 60—80°) to the original ethyl acetate mother-liquors yielded 1-benzylsulphonyl-3-n-butylsulphonylprop-1-ene, m. p. 100—102°, which decolorised cold potassium permanganate in acetone. It was identical (m. p. and mixed m. p.) with the disulphone described below. The low overall yield (18%) starting from 1-benzylsulphonyl-3-chloropropan-2-ol led to the use of the alternative synthesis (*B*) for both this and the other disulphones.

Preparation of 1-*Alkylsulphonyl*-3-*benzylsulphonylpropenes by Route B*.[1]—(*a*) 1-*Benzylsulphonyl*-3-n-*butylthio*-2-*chloropropane*. Phosphorus pentachloride (44 g., 0·21 mol.) was slowly added to a stirred solution of 1-benzylsulphonyl-3-n-butylthiopropan-2-ol (40 g., 0·132 mol.) in chloroform (250 c.c.) at 0°. The reaction was completed by heating the mixture at 100° for 10 min. during which it darkened considerably. The phosphorus compounds were decomposed by stirring the mixture with ice–water, the organic layer was washed with water and dried (Na_2SO_4), and the solvent removed in a vacuum. The residual pale brown oil was next dissolved in dry ether (200 c.c.) and shaken with charcoal (1 g.), and dry light petroleum (b. p. 60—80°) (200 c.c.) was added. The precipitated 1-*benzylsulphonyl*-3-n-*butylthio*-2-*chloropropane* was obtained as needles, m. p. 63—64° (36 g., 86%), after two crystallisations from benzene–light petroleum (2 : 1) (Found: C, 52·5; H, 6·8; Cl, 10·9; S, 20·3. $C_{14}H_{21}ClO_2S_2$ requires C, 52·4; H, 6·6; Cl, 11·1; S, 20·0%).

(*b*) 1-*Benzylsulphonyl*-2-*chloro*-3-*methylthiopropane*. Phosphorus pentachloride (60 g., 0·29 mol.) reacted with crude 1-benzylsulphonyl-3-methylthiopropan-2-ol (65 g., 0·24 mol.) to yield 1-*benzylsulphonyl*-2-*chloro*-3-*methylthiopropane* (78 g.) which crystallised from ether (300 c.c.)–light petroleum (b. p. 40—60°; 100 c.c.) in pale mauve nodules, m. p. 65—67° (45 g.). Three further recrystallisations from ether afforded buff crystals, m. p. 71—72° (Found: C, 46·8; H, 5·5; Cl, 12·9; S, 23·1. $C_{11}H_{15}ClO_2S_2$ requires C, 47·4; H, 5·4; Cl, 12·7; S, 23·0%).

The mother-liquors from the first crystallisation yielded a tarry residue which evolved hydrogen chloride on storage. It was left in a vacuum over sodium hydroxide for a year, after which distillation gave a viscous oil having a composition approximating to that of benzylsulphonylmethylthiopropene (see below) though it still contained some chlorine (Found: C, 57·1; H, 6·1; Cl, 2·8; S, 24·5%). Oxidation afforded the sulphone which separated from ethyl acetate in granules, m. p. 124—127°, which softened several degrees below the actual m. p. The infrared spectrum showed considerable differences from the benzylsulphonylmethylsulphonylpropene described below.

(*c*) 1-*Benzylsulphonyl*-2-*chloro*-3-*ethylthiopropane*.[1] This was obtained by the above improved method from 1-benzylsulphonyl-3-ethylthiopropan-2-ol (0·1 mol.) and phosphorus pentachloride (0·135 mol.). The compound (79%) crystallised from benzene–light petroleum in needles, m. p. 58—60° (Found: C, 49·5; H, 6·2; S, 21·9. Calc. for $C_{12}H_{17}ClO_2S_2$: C, 49·2; H, 5·8; S, 21·9%).

(*d*) 1-*Benzylsulphonyl*-2-*chloro*-3-*n*-*propylthiopropane*. The corresponding crude hydroxy-compound (35 g., 0·12 mole) in chloroform (200 c.c.) solution was treated with phosphorus pentachloride (36 g., 0·175 mole). The product first crystallised from ether in nodules, m. p. 58—64° (30 g., 73%). Two further crystallisations yielded 1-*benzylsulphonyl*-2-*chloro*-3-*n*-*propylthiopropane* as a mixture of plates and needles, m. p. 71—72° (Found: C, 51·5; H, 6·3; Cl, 11·5; S, 20·5, 21·3. $C_{13}H_{19}ClO_2S_2$ requires C, 50·9; H, 6·2; Cl, 11·6; S, 20·9%). The once recrystallised product was unstable; after a short time it darkened and hydrogen chloride was evolved.

(*e*) 1-*Benzylsulphonyl*-2-*chloro*-3-*t*-*butylthiopropane*. The hydroxy-compound (48 g., 0·20 mole) reacted with phosphorus pentachloride (60 g., 0·29 mole) to yield a mauve-brown product. Three recrystallisations from dry ether yielded colourless plates of 1-*benzylsulphonyl*-2-*chloro*-3-*t*-*butylthiopropane* (50 g., 72%), m. p. 86·5—87° (Found: C, 52·8; H, 6·2; Cl, 11·3; S, 20·4. $C_{14}H_{21}ClO_2S_2$ requires C, 52·4; H, 6·6; Cl, 11·1; S, 20·0%).

(*f*) *Preparation of* 3-*alkylthio*-1-*benzylsulphonylprop*-1-*enes*. The appropriate chloro-derivatives were boiled under reflux with pyridine as described in the case of benzylsulphonyl-chloroethylthiopropane. The bulk of the product was usually oxidised as the crude material because of the extensive decomposition which occurred during distillation. The distillates described below were yellow oils which rapidly darkened and became blue-green.

1-*Benzylsulphonyl*-3-*n*-*butylthiopropene* (77%), b. p. 187—188°/0·07 mm. (decomp.) (Found: C, 58·8; H, 7·4; S, 22·2. $C_{14}H_{20}O_2S_2$ requires C, 59·1; H, 7·1; S, 22·5%).

1-*Benzylsulphonyl*-3-*methylthiopropene*, b. p. 158—163°/0·01 mm. (decomp.) (Found: C, 54·5; H, 5·6; S, 26·2. $C_{11}H_{14}O_2S_2$ requires C, 54·5; H, 5·8; S, 26·5%).

1-*Benzylsulphonyl*-3-*n*-*propylthiopropene* (75%), b. p. 183—185°/0·05 mm. (decomp.) (Found: C, 57·4; H, 6·7; S, 24·0. $C_{13}H_{18}O_2S_2$ requires C, 57·8; H, 6·7; S, 23·7%).

1-*Benzylsulphonyl*-3-*t*-*butylthiopropene* was initially obtained as a brown wax (73%). It separated from ether–light petroleum in irregular rhomboids, m. p. 65—67·5° (Found: C, 59·1; H, 7·0; S, 22·6. $C_{14}H_{20}O_2S_2$ requires C, 59·1; H, 7·1; S, 22·5%).

(*g*) *Preparation of* 3-*alkylsulphonyl*-1-*benzylsulphonylpropenes*. The optimum conditions for oxidising the benzylsulphonylbutylthiopropene are described below. The reaction temperatures had to be carefully controlled and it was inadvisable to increase the scale of the reaction. Oxidations of the other sulphides were carried out similarly.

A solution of 40% hydrogen peroxide (12 c.c., 0·14 mole) in glacial acetic acid (15 c.c.) was added during 1 hr. to the alkylthio-sulphone (15 g., 0·053 mole) in the same solvent (15 c.c.) at $<30°$. The mixture was stirred overnight and then the oxidation completed at 100° for 2 hr. Removal of the solvent under reduced pressure left white crystals which were dissolved in chloroform, washed with water and aqueous sodium carbonate, and dried. Removal of the solvent afforded a yellow solid which was decolorised by boiling its solution in ethyl acetate with charcoal. This yielded 12·5 g. (75%) of mixed isomers which were separated by fractional crystallisation from ethyl acetate and light petroleum (b. p. 60—80°), by the procedure described for n-butylsulphonylethylsulphonylpropene. As the individual compounds reached their limit of purity it was advantageous to recrystallise them from benzene in order to minimise the isomerisation. Even so, there was a practical limit to the effectiveness of separation and a point was reached when further crystallisation gave lower-melting products, *i.e.*, to production of isomers. The m. p.s of all the bisalkylsulphonylpropenes were somewhat indeterminate and most samples softened and collapsed some 10° below the temperature at which the liquid became clear. The latter point, however, was taken as the true m. p. and gave consistent figures.

(*i*) *n-Butylsulphonyl derivatives.* The purest products obtained were 1-*benzylsulphonyl*-3-*n-butylsulphonylprop*-2-*ene*, separating from benzene in plates, m. p. 104—108°, clear at 117° (Found: C, 53·2; H, 6·6; S, 20·6. $C_{14}H_{22}O_4S_2$ requires C, 53·2; H, 6·4; S, 20·3%), and 1-*benzylsulphonyl*-3-*n-butylsulphonylprop*-1-*ene*, separating from benzene in clusters of needles, m. p. 94—99·5°, clear at 102·5° (Found: C, 53·5; H, 6·4; S, 20·6. $C_{14}H_{22}O_4S_2$ requires C, 53·2; H, 6·4; S, 20·3%). Column chromatography with chloroform–benzene failed to separate the isomers; alumina, " low in alkali " silica gel, and " Amberlite " IR-4B (OH) resin adsorbed the sulphones but decomposed them; acidic " Amberlite " IRC-50 (H) resin did not adsorb them.

Ozonolysis.—The main purpose of this was to identify the isomers. (i) The sulphones were ozonised in water–chloroform, and the alkylsulphonylacetic acids were decarboxylated to the corresponding methyl sulphones in the usual way. The chloroform layer afforded benzylsulphonylacetaldehyde which yielded what was essentially the 2,4-*dinitrophenylhydrazone* (although the analysis figure for sulphur was rather too high) which crystallised from 50% aqueous ethanol in needles, m. p. 170—172° (Found: C, 47·9; H, 3·8; S, 9·8. $C_{15}H_{14}N_4O_6S$ requires C, 47·7; H, 3·7; S, 8·5%). The composition of the above mixture of benzyl and n-butyl methyl sulphones was obtained from the m. p.–composition curve (Table 5).

TABLE 5.

M. p.s of mixtures of benzyl and n-butyl methyl sulphone.

$CH_2Ph·SO_2·Me$ (%)	100	83·7	69·2	48·8	21·6	17·2	9·0	0
M. p.	125·8°	116°	106·3°	91·5°	57·8°	49·2°	28·0°	30·3°

Two ozonolyses were carried out. A sample of the sulphone, m. p. 115° (1·5 g.), yielded a mixture of benzyl and n-butyl methyl sulphone, m. p. 119° (0·1 g.), corresponding to 88% of benzyl methyl sulphone, *i.e.*, the original disulphone contained 88% of 3-benzylsulphonyl-1-n-butylsulphonylprop-1-ene. Similarly the equilibrated isomers (1·5 g.), m. p. 103—104°, yielded the mixed methyl sulphones (0·05 g.), m. p. 107·5°, representing 70% of benzyl methyl sulphone.

(ii) *Methylsulphonyl derivatives.* Oxidation of 1-benzylsulphonyl-3-methylthiopropene yielded a product which after four recrystallisations from ethyl acetate separated in lustrous plates, m. p. 127° (after softening at 124°). For reasons given below and from infrared spectra, it was concluded that the compound was the required 1-*benzylsulphonyl*-3-*methylsulphonylprop*-2-*ene* (Found: C, 48·3; H, 4·8; S, 23·2. $C_{11}H_{14}O_4S_2$ requires C, 48·1; H, 5·1; S, 23·4%).

The compound appeared to be entirely one isomer. Fractional recrystallisation in the usual way gave products all of which melted in the range 120—127° and showed no depression of the m. p. when mixed with the highest-melting specimen. Ozonolysis of a sample of m. p. 126·5—127°, which easily decolorised potassium permanganate in acetone, yielded mainly benzyl methyl sulphone, the m. p. of which was 124·7° corresponding (Table 6) to 95% of benzyl methyl sulphone.

TABLE 6.

M. p.s of mixtures of benzyl methyl and dimethyl sulphone.

$CH_2Ph·SO_2·Me$ (%)	100	84·9	69·4	51·8	48·0	38·5	30·5	16·0	0
M. p.	125·8°	113·5°	101·1°	86·8°	87·0°	91·0°	95·5°	102·6°	110·2°

Prolonged boiling of the substance in ethyl acetate containing a little charcoal and a trace of quinol converted part of it into a polymer which, after removal of unchanged material, was precipitated by light petroleum in a somewhat jelly-like form. Removal of traces of solvent by filtration left a matt of needles, m. p. 122° which fell to a powder when touched. This decolorised permanganate solution rather more slowly than the starting sulphone but did not depress the m. p. of the latter. There was no change in the composition but the molecular weight [8] in benzene was considerably increased (Found: C, 48·6; H, 5·1; S, 23·2%; *M*, 360,

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[8] Sucharda and Bobranski, " Semimicro-Methods for the Elementary Analysis of Organic Compounds," A. Gallenkamp & Co., Ltd., London, 1936, p. 34.

395, and 473. Calc. for $C_{11}H_{14}O_4S_2$: *M*, 274). Similar results were obtained when the disulphone (2 g.) was boiled under reflux for 6 hr. with 50% ethanolic triethylamine (40 c.c.). The product was a semi-solid which hardened on storage and only slowly discharged the colour of potassium permanganate. " Crystallisation " from benzene furnished a similar substance which shrank at 67—75°, collapsed at 82°, and frothed and cleared to an oil at 82—86° [Found: C, 48·2; H, 5·3; S, 23·1%; *M* (camphor), 416]. A freshly prepared specimen of the sulphone (m. p. 125°) had a normal molecular weight (*M*, 280) but after prolonged boiling in benzene it became partly insoluble and the molecular weight rose to 495.

(iii) *Ethylsulphonyl derivatives.* 1-Benzylsulphonyl-3-ethylsulphonylprop-2- and -1-ene melted, respectively, at 130·5° and 103° after softening 5—8° below these temperatures. Neither of them depressed the m. p. of the corresponding sulphone prepared previously.[1] Zerewitinov determinations showed 2·02 and 1·94 atoms, respectively, of " active " hydrogen per mol.

(iv) *n-Propylsulphonyl derivatives.* Oxidation of 1-benzylsulphonyl-3-n-propylthiopropene afforded, after fractional crystallisation of the product, 1-*benzylsulphonyl*-3-*n-propylsulphonylprop*-2-*ene*, m. p. 115—116° (Found: C, 52·0; H, 5·9; S, 21·1. $C_{13}H_{18}O_4S_2$ requires C, 51·6; H, 6·0; S, 21·1%), and -*prop*-1-*ene*, m. p. 103—105° (Found: C, 51·9; H, 5·8; S, 21·2%). The equilibrium mixture, m. p. 92—94°, of the above two sulphones yielded a mixture of benzyl methyl and methyl n-propyl sulphone, m. p. 91·5°, which from Table 7 corresponded to 53·5% of benzyl methyl sulphone, *i.e.*, 53·5% of 1-benzylsulphonyl-3-n-propylsulphonylprop-2-ene in the original mixture. The higher-melting isomer was evidently the last-named compound since on ozonolysis it gave a mixture, m. p. 120·4°, corresponding to 95% of benzyl methyl sulphone (the remaining 5% of methyl n-propyl sulphone probably resulted from partial isomerisation of the pure compound). Zerewitinov determinations on the two disulphones gave 1·97 and 2·1 atoms of " active " hydrogen per mol. of the higher- and lower-melting isomer, respectively.

TABLE 7.

M. p.s of mixtures of benzyl methyl and methyl n-propyl sulphone.

$CH_2Ph{\cdot}SO_2{\cdot}Me$ (%)	100	87·3	68·1	47·5	35·3	15·5	10·0	0
M. p.	125·8°	117·6°	103·7°	86·3°	73·0°	41·9°	29·6°	32·2°

(v) *t-Butylsulphonyl derivatives.* Oxidation in the usual way of 1-benzylsulphonyl-3-t-butylthiopropene afforded in the first instance only the higher-melting isomer. The disulphone was therefore boiled for 17 hr. under reflux in ethyl acetate solution, and the product was fractionally crystallised, the efficiency of separation being checked by mixed m. p. with the highest-melting isomer. This gave 1-*benzylsulphonyl*-3-*t-butylsulphonylprop*-2-*ene* which separated from benzene in needles, m. p. 144·5—145° (Found: C, 52·9; H, 6·0; S, 20·5%. $C_{14}H_{20}O_4S_2$ requires C, 53·1; H, 6·4; S, 20·3%), and 1-*benzylsulphonyl*-3-*t-butylsulphonylprop*-1-*ene*, separating from benzene in plates, m. p. 125—127° (Found: C, 53·1; H, 6·2; S, 20·4%).

The reference curve for the determinations of the proportions of benzyl methyl and methyl t-butyl sulphone obtained by ozonolysis was constructed from the data in Table 8. The isomer, m. p. 144·5—145°, yielded mixed benzyl methyl and methyl t-butyl sulphone, m. p. 117·6°, corresponding to 84·5% of the former, and therefore the high-melting isomer had the structure assigned above. The equilibrium mixture, m. p. 137·3—137·5°, of the two disulphones gave methyl sulphones, m. p. 107°, and hence it contained 68% of the higher-melting isomer. Zerewitinov determinations of the high-melting isomer showed 1·62, and of the low-melting isomer 2·08 atoms of " active " hydrogen per mol.

TABLE 8.

M. p.s of mixtures of benzyl methyl and methyl t-butyl sulphone.

$CH_2Ph{\cdot}SO_2{\cdot}Me$ (%)	100	83·3	62·1	50·0	37·9	24·8	16·2	13·3	8·8	4·8	0
M. p.	125·8°	116·5°	102·0°	92·7°	79·2°	59·8°	47·1°	47·1°	59·4°	73·0°	84·5°

The dialkyl sulphones used for the above mixed m. p. curves were prepared by conventional methods. In some cases the m. p.s were somewhat different from those recorded in the literature which are given in parentheses in the following data: benzyl methyl sulphone,[1]

m. p. 124·5° (125·6°), methyl n-propyl sulphone,[9] m. p. 31·5—32·5° [28° (corr.)], methyl t-butyl sulphone,[10] m. p. 84·5° (78—79°).

Melting-point Curves.—Tables 9—10 indicate m. p.s of mixtures of bisalkylsulphonylpropenes, $\mathrm{R{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}SO_2{\cdot}R'}$. That for R,R′ = benzyl, ethyl, is the one previously published,[1] but as in the present determinations the samples were not "pre-fused" the percentage of the higher-melting sulphone was modified by reducing its value by 10% (Table 9).

TABLE 9.

Modified table of m. p.s of mixtures of 1-benzylsulphonyl-3-ethylsulphonyl-prop-2-ene and -prop-1-ene.

Prop-2-ene (%)	90	64·9	45	33·3	21·7	16·9	0·0
M. p.	126·3°	117·7°	108·5°	101·0°	91·5°	95·0°	103·5°

Equilibrium Compositions of Bisalkylsulphones.—(i) *Benzylsulphonylethylsulphonylpropenes.* Each of the isomeric sulphones was boiled in ethyl acetate under reflux for 7 days, and the solvent was then removed in a vacuum. Both the residues had m. p. 104·3° corresponding to 39(±2)% of 1-benzylsulphonyl-3-ethylsulphonylprop-2-ene and gave correct analyses.

TABLE 10.

M. p.s of mixtures of 3-alkylsulphonyl-1-benzylsulphonyl-prop-2-ene(i) and prop-1-ene (ii).

(a) alkyl = $\mathrm{Pr^n}$		(b) alkyl = $\mathrm{Bu^n}$		(c) alkyl = $\mathrm{Bu^t}$		(a) alkyl = $\mathrm{Pr^n}$		(b) alkyl = $\mathrm{Bu^n}$		(c) alkyl = Bu	
(i) (%)	M. p.	(i) (%)	M. p.	(i) (%)	M. p.	i (%)	M. p.	(i) (%)	M. p.	(i) (%)	M. p.
100·0	110·0°	19·4	90·4°	100·0	111·5°	33·5	96·8°	100·0	144.2°	30·5	128·4°
89·3	107·0	16·5	90·7	86·0	109·7	30·0	95·0	85·0	141·0	21·4	122·8
66·2	103·0	13·9	89·6	67·0	108·0	26·0	95·5	77·5	139·6	18·2	120·2
49·2	99·6	11·5	91·2	66·0	108·4	18·0	97·8	73·6	139·1	11·1	124·2
36·6	96·4	9·7	93·2	57·0	106·3	13·5	98·4	63·0	137·1	0·0	127·1
29·8	95·0	0·0	96·5	51·6	104·7	13·0	99·5	46·7	133·1		
22·8	93·2			44·5	102·8	0·0	101·5				

(ii) *Benzylsulphonyl-n-propylsulphonylpropenes.* Three separate samples of the sulphones dissolved in ethyl acetate were boiled under reflux for 24—52 hr. The m. p.s of the resulting residues were 97·4—97·7°, corresponding to 40(±2)% of 1-benzylsulphonyl-3-n-propylsulphonylprop-2-ene. Analysis again showed that no change other than isomerisation had occurred.

(iii) *Benzylsulphonyl-n-butylsulphonylpropenes.* Because of slight decomposition, attempts to equilibrate the sulphones by heating them at 120° were abandoned. A 10% solution of the higher-melting isomer (111·5°) in ethyl acetate was therefore boiled under reflux for 42 hr. The product, m. p. 103·5—103·7°, was unaltered when it was boiled for a further 48 hr. in the same solvent with a little charcoal. The equilibrium composition was therefore 53(±3)% of 1-benzylsulphonyl-3-n-butylsulphonylprop-2-ene.

(iv) *Benzylsulphonyl-t-butylsulphonylpropenes.* The mixed isomers (2 g.) were boiled in ethyl acetate (75 c.c.) containing a little charcoal for at least 7 days. In a number of experiments the m. p. varied between 136° and 136·7°; consideration of the figures led to 136·3(±0·3)° as the m. p. of the equilibrium mixture. The corresponding composition was then 60(±2)% of 1-benzylsulphonyl-3-t-butylsulphonylprop-2-ene.

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