190. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part VI.* 1,3-Bisethylsulphonylbutenes.*

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Reactions designed to yield the 1,3-bisethylsulphonylbutenes, Et·SO₂·CHMe·CH:CH·SO₂·Et (1) and Et·SO₂·CMe:CH·CH₂·SO₂·Et (2), yield two isomeric (possibly *cis*- and *trans*-) sulphones, both of whose structures correspond to (2). Although one " active " hydrogen atom per molecule is present in each of the two sulphones (2), the latter are not interconvertible.
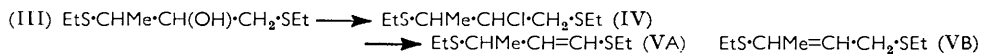
The infrared carbon–carbon and carbon–hydrogen stretching frequencies, and the proton magnetic resonance spectra, of a number of saturated and unsaturated sulphones have been used to confirm the structures of these butene derivatives.

MOST of the simple three-carbon protropic systems activated by sulphonyl groups hitherto investigated have been propene derivatives, although in Part III of this series [1] there was a brief description of the synthesis and reactions of *NNN'N'*-tetraethylbut-2-ene-1,3-disulphonamide. The corresponding disulphonyl compounds, 1,3-bisethylsulphonylbut-1- and -2-ene (I and II) have now been examined. The α-methyl group could be expected

$$\text{Et·SO}_2\text{·CHMe·CH=CH·SO}_2\text{·Et (I)} \rightleftharpoons \text{Et·SO}_2\text{·CMe=CH·CH}_2\text{·SO}_2\text{·Et (II)}$$

to decrease the mobility of the above sulphones and to stabilise the but-2-ene derivative (II) because hyperconjugation of the methyl-hydrogen atoms with the double bond makes this isomer energetically the more stable. It now appears that this isomer (II) is exclusively formed, although there is evidence that the system is potentially mobile. Thus in this respect there is little difference from the 1,3-disulphonamidobutenes.

The initial synthesis was essentially similar to that used for the preparation of the corresponding 1,3-bisalkylsulphonylpropenes [2] except that oxidation to the sulphones was postponed to the final stage. 1,3-Bisethylthiobutan-2-ol (III) was obtained pure but the chloro-derivative (IV) appeared to contain some material resulting from the partial loss of an ethylthio-group, and some further decomposition occurred when dehydrochlorination by potassium t-butoxide to the bisethylthiobutenes (V) was effected. Oxidation of the

(III) EtS·CHMe·CH(OH)·CH₂·SEt ⟶ EtS·CHMe·CHCl·CH₂·SEt (IV)
⟶ EtS·CHMe·CH=CH·SEt (VA)   EtS·CHMe=CH·CH₂·SEt (VB)

thiobutenes (V) afforded a liquid mixture of sulphones, the crystalline content of which

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[1] Nicholson and Rothstein, *J.*, 1953, 4004.
[2] Rothstein, *J.*, 1937, 4012.

varied between 35% and 40%. The non-crystalline material was, however, very similar in properties and continuously deposited the same crystalline mixture over a period of years.

The crystalline sulphones were resolved into two isomeric compounds, m. p.s 80—81° and 90°, respectively, which were not interconvertible and gave a depressed m. p. when mixed. Fission by ozone or potassium permanganate gave mainly alkanesulphonic acids, with traces of carbonyl derivatives whose composition was not determined. Ineffective catalytic reduction was consistent with the presence of a trisubstituted double-bond. The sulphonyl group does not in itself deactivate an unsaturated compound towards hydrogenation since there is no difficulty in reducing 1,1,3,3-tetrakisethylsulphonylpropene [3] or dialkylsulphonylpropenes. Hydrogenation, on the other hand, of $NNN'N'$-tetraethylbut-2-ene-1,3-disulphonamide, $Et_2N \cdot O_2S \cdot CH_2 \cdot CH \vdots CMe \cdot SO_2 \cdot NEt_2$, fails even at 75°/80 atm., and it must be concluded that in the disulphonyl compound (II), also, the methyl group must be attached at the olefinic position.

Zerewitinov determinations for the two isomeric sulphones and the residual oil showed the presence of one active hydrogen atom per molecule, this being characteristic of potentially mobile three-carbon systems. Simple unsaturated sulphones and 1,3-bisalkyl-sulphonylalkane (*e.g.*, 1,3-bisalkylsulphonyl-propane and -butane) react with methyl-magnesium halide only slightly or not at all.[4] The infrared spectra were not incompatible with the structure (II), but, with the exception of some allylsulphonyl derivatives, the published relevant information is scanty and it was necessary to obtain the spectra of a number of related saturated and unsaturated mono- and di-sulphones in order to make useful comparisons. The carbon–carbon and carbon–hydrogen stretching frequencies, together with some of the carbon–hydrogen bending frequencies, are recorded in the experimental portion of this paper. It will be observed that, of all the unsaturated sulphones, only those derived from butene show no absorption on the carbon–hydrogen stretching frequencies characteristic of olefinic double bonds and the lower-melting of the two has only a relatively weak C=C absorption at 1656 cm.$^{-1}$.

Proton magnetic resonance data agreed with these conclusions. The chemical shifts of protons in sulphones was established by examining the proton resonance spectra of a number of " model " derivatives whence it appeared that the shielding constant [5] for an alkylsulphonyl group is near 2·10 p.p.m. The spectrum of the 1,3-bisethylsulphonylbutene showed the following features which agreed with structure (II) but not with structure (I). The line signal for methyl at 7·83 p.p.m. (τ value referred to tetramethylsilane $= 10$) showed the absence of a proton on the carbon atom carrying the methyl group. A methylene doublet centred at 6·05 p.p.m. was similar to that shown by 1,3-bisethyl-sulphonylpropene, $Et \cdot SO_2 \cdot CH_2 \cdot CH \vdots CH \cdot SO_2 \cdot Et$ (6·07 p.p.m.) and allyl methyl sulphone (6·23 p.p.m.), the splitting being a consequence of spin–spin interaction with the adjacent methine proton. Finally, the latter proton gave rise to a triple signal at 3·27 p.p.m. due to spin–spin interaction with the methylene group and this was in contrast to the behaviour of the propene derivative which gave a complex band in this region because of the further coupling with the proton attached to the other olefinic carbon atom.

Characteristic of many of the bisethylsulphonyl derivatives was the duplication of the signals due to the protons of the ethyl groups. It was shown to some extent by 1,3-bis-ethylsulphonylbutene (II) although there was considerable overlapping. The most striking example was 1,1-bisethylsulphonylpropene, $Me \cdot CH \vdots C(SO_2Et)_2$, which gave six lines for the methyl protons and eight for those of methylene, the separation between two consecutive peaks being 4 and 3·5 c./sec., respectively. The methyl protons of 1,3-bisethyl-sulphonylpropene only showed a doubled signal, the methylene protons being represented
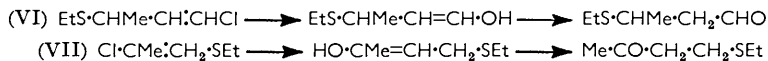
[3] Rothstein and Whiteley, *J.*, 1953, 4012.
[4] Unpublished observations.
[5] Cf. Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 59.

by the usual quartet. There was no doubling in the case of 1-benzylsulphonyl-3-ethyl-sulphonylpropene, or with bisethylsulphonylmethane, but a double quartet for methylene only was observed for 1,1-bisethylsulphonylethane. The phenomenon was partly dependent on unsaturation, because there were eight lines for methylene and the usual three for methyl in 1,1,3,3-tetrakisethylsulphonylpropane whereas the corresponding unsaturated 1,1,3,3-tetrakisethylsulphonylpropene gave sixteen peaks for methylene and nine for methyl, the exact number being a little doubtful because of incomplete resolution. The reason for these duplications, which do not seem to have been described before, is not known. It may be spin–spin interaction between non-equivalent ethylsulphonyl groups or that the latter give rise to independent signals whose chemical shifts differ slightly from one another.

The same two isomeric sulphones (I) and (II) were obtained when attempts were made to synthesise them separately. 1-Chloro-3-ethylthiobut-1-ene EtS·CHMe·CH:CHCl and 3-chloro-1-ethylthiobut-2-ene, Cl·CMe:CH·CH$_2$·SEt, were obtained by condensation of ethanolic sodium ethyl sulphide with 1,3-dichlorobut-1- and -2-ene, respectively. The two compounds were different and it was concluded that rearrangement had not occurred because the former product had a weak infrared absorption band at 3020 cm.$^{-1}$ and a fairly strong one at 3058 cm.$^{-1}$. The 3058 band corresponded to a trisubstituted olefinic C–H stretching frequency increased by the attached halogen. The A.P.I. spectra for *cis*- and *trans*-1,3-dichloropropene show absorptions at 3086 and 3067 cm.$^{-1}$, and 3-chloro-1-ethyl-thioprop-2-ene shows a fairly strong band at 3063 cm.$^{-1}$ as well as less intense ones at 3071 and 3028 cm.$^{-1}$. The isomeric chloro-sulphide gave only one weak absorption peak, at 3024 cm.$^{-1}$; in the remainder of the spectrum (up to 670 cm.$^{-1}$) the absorption was considerably more intense than for the but-1-ene. The vinyl halogen in both the chloro-derivatives was somewhat more reactive than in the corresponding 1,3-dichloropropene derivatives and some replacement appeared to have occurred as there were weak carbonyl absorptions at 1733 and 1721 cm.$^{-1}$:

(VI) EtS·CHMe·CH:CHCl ⟶ EtS·CHMe·CH=CH·OH ⟶ EtS·CHMe·CH$_2$·CHO

(VII) Cl·CMe:CH·CH$_2$·SEt ⟶ HO·CMe=CH·CH$_2$·SEt ⟶ Me·CO·CH$_2$·CH$_2$·SEt

Pentanolic sodium ethyl sulphide converted the chloro-sulphides (VI and VII) into the bisethylthio-derivatives. That obtained from (VI) gave an infrared spectrum practically identical with that derived from the chloro-disulphide (IV), *i.e.*, the bisethylthiopropene from (IV) should be 1,3-bisethylthiobut-1-ene (VA). The bis-sulphide obtained from (VI) yielded on oxidation a mixture of the two sulphones, m. p. 80—81° and 90°, the former in greater proportion. The proton magnetic resonance spectrum of the 1,3-bis-sulphide obtained from the chloro-sulphide (IV) agreed on the whole with the structure (VA), but there were uncertainties which might have resulted from the presence of a small proportion of the isomeric sulphide (VB) in the form of additional peaks. The τ values found for the methyl triplet and methylene quartet of the ethyl groups were, respectively, 8·76 and ~7·4 p.p.m., figures which were comparable with those for the ethyl group of ethyl methyl sulphide, namely, 8·73 and 7·47 p.p.m.[6] Further splitting of the methylene quartet was also present. Three peaks, at 7·95, 8·10, and 8·23 p.p.m., the total integrated area of which was equivalent to one proton, probably represented the methyl of the butene chain, and the splitting indicated that it was not a single isolated methyl group attached to the olefinic position since this would be expected to afford one intense absorption peak only. On the other hand, methyl in the β-position to the olefinic bond should be associated with a doublet and, if the first two peaks were assigned to this, since they were equal in area, it was possible to estimate that the content of the bis-sulphide (VB) was not greater than 25%. A multiplet band at ~6·63 p.p.m.

[6] Bhacca, Johnson, and Shoolery, " N.M.R. Spectra Catalog," Varian Associates, Paolo Alto, California, 1962.

with an area corresponding to one proton was probably due to the single non-olefinic proton. Its position at a somewhat lower field than the doublet representing methylene adjacent to sulphur of allyl sulphide (at 6·92 p.p.m.) [6] was to be expected. By using Shoolery's rules,[5] which are not very accurate for trisubstituted carbon, the resonance position for the proton on the group, $=C \cdot CMeH \cdot S-$, is calculated to be 6·34 p.p.m. Finally, partially resolved bands between 3·9 and 4·7 p.p.m. were probably due to the two olefinic hydrogen atoms, corresponding to the single proton on the carbon atom adjacent to sulphur in vinyl sulphide, which has a chemical shift at 3·57 p.p.m.

If the sulphides had indeed structure (VA), it follows the dehydrochlorination of compound (IV) was a Hofmann-type elimination, *i.e.*, the less substituted olefinic derivative was formed. According to Brown, Moritani, and Okomoto [7] the substitution of t-butoxide for ethoxide ions can lead to Hofmann elimination even when normally the Saytzeff rule is in control. These authors record, for instance, that 2-bromobutane affords 71% of but-2-ene in ethanol but only 27% in t-butyl alcohol. As t-butoxide was also used for removal of hydrogen chloride from the chloro-sulphide (IV), the production of the but-1-ene derivative is not surprising. Further, the Hofmann type of elimination occurs preferentially when the separation of a proton is facilitated by an electronegative pole and this separation tends to be suppressed by an electron-releasing group such as alkyl. In so far as the valency shell of bivalent sulphur is capable of expansion, the elimination may be analogously oriented, so that process (b) rather than (a) is the result:
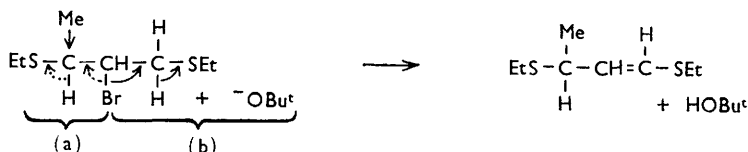
The other bisethylthiobutene, presumably $EtS \cdot CMe \cdot CH \cdot CH_2 \cdot SEt$, obtained from the chloro-sulphide (VII) was somewhat different from the first two. As might be expected from the easier hydrolysis of halogen attached to the same carbon atom as methyl, the compound appears to have an increased proportion of carbonyl derivative showing a rather broad and intense absorption band with maxima at 1742 and 1714 cm.$^{-1}$. The corresponding disulphone was an oil which only after six months began to deposit considerable quantities of the two sulphones previously isolated. Since both the bis-sulphides obtained from the isomeric chloro-sulphides furnish the same pair of disulphones, it is evident that prototropic change had occurred. In particular, it is suggested that two of the syntheses afford 1,3-bisethylthiobut-1-ene which on oxidation yields the disulphone (I) which probably rearranges to the but-2-ene derivative (II).

EXPERIMENTAL

Preparation of 1,3-*Bisethylsulphonylbutenes.*—(a) *From* 1,3-*dibromobutan-2-ol.*[8] A solution of the dibromo-alcohol (80·0 g., 0·345 mole) in ethanol (150 c.c.) was added at room temperature to a stirred solution of redistilled ethanethiol (47 g., 0·76 mole) in ethanol (250 c.c.) containing an equimolecular quantity of sodium ethoxide. In this, as in all experiments conducted with thiols, the reaction was carried out under nitrogen. 1,3-*Bisethylthiobutan-2-ol* was obtained as a yellow oil, b. p. 144—146°/13 mm. (61·2 g., 92%) (Found: C, 49·6; H, 9·4; S, 32·8. $C_8H_{18}OS_2$ requires C, 49·4; H, 9·3; S, 33·0%). A solution of the hydroxy-derivative (19·5 g., 0·1 mole) in benzene (50 c.c.) was boiled under reflux for 30 min. with thionyl chloride (15 g., 0·125 mole), and the product distilled. Two fractions were obtained, analysis showing that each of them was substantially 2-*chloro*-1,3-*bisethylthiobutane*: (i) b. p. 120—125°/15 mm., n_D^{22} 1·5125 (9·4 g., 44%) (Found: C, 47·4; H, 8·6; Cl, 15·5; S, 28·0. $C_8H_{17}ClS_2$ requires C,

[7] Brown, Moritani, and Okomoto, *J. Amer. Chem. Soc.,* 1956, **78**, 2193.
[8] Petrov, *J. Gen. Chem. U.S.S.R.,* 1941, **11**, 713.

45·2; H, 8·1; Cl, 16·7; S, 30·1%); and (ii) b. p. 134—138°/15 mm., n_D^{22} 1·5160 (10 g., 47%) (Found: C, 47·2; H, 8·5; Cl, 15·7; S, 28·6%).

Each of the above chloro-sulphides was converted into, principally, 1,3-bisethylthiobut-1-ene (VA) by boiling them (40 g., 0·188 mole) for 3 hr. under reflux with a solution from potassium (12·5 g., 0·32 g.-atom) in t-butyl alcohol (400 c.c.). It was an oil, b. p. 118°/15 mm., $n_D^{18·5}$ 1·5270 (Found: C, 55·7; H, 8·9; S, 35·6. Calc. for $C_8H_{16}S_2$: C, 54·5; H, 9·1; S, 36·4%). Oxidation by hydrogen peroxide in glacial acetic acid or by monoperphthalic acid in ether yielded oils from which mixed sulphones separated, the crude m. p.s varying between 60° and 80°. The maximum yield of crystalline material was ~35% but further amounts of the solid were slowly deposited. The sulphones are described below.

(b) *From* 1,3-*dichlorobut-2-ene.* The dichloro-compound, b. p. 79·6°/140 mm., n_D 1·4704 (62·5 g., 0·5 mole), was added with stirring to a solution of ethanethiol (33 g., 0·53 mole) and sodium hydroxide (21·3 g., 0·53 mole) in 75% ethanol (250 c.c.). Deposition of sodium chloride was immediate and heat was liberated. The mixture was then boiled for 30 min. and added to water (800 c.c.). 3-*Chloro*-1-*ethylthiobut-2-ene* was isolated, having b. p. 63·5—65·0°/7 mm., n_D^{21} 1·4992 (62·3 g., 83%) (Found: C, 48·3; H, 7·8; Cl, 23·2; S, 20·7. $C_6H_{11}ClS$ requires C, 47·8; H, 7·4; Cl, 23·5; S, 21·3%). The infrared spectrum showed strong absorption at 1667 cm.$^{-1}$ (C=C str.) and weak carbonyl absorption at 1721 cm.$^{-1}$. Oxidation by hydrogen peroxide in glacial acetic acid furnished 3-*chloro*-1-*ethylsulphonylbut-2-ene*, b. p. 102—104°/0·1 mm. (Found: C, 39·2; H, 6·1; Cl, 19·5; S, 17·8. $C_6H_{11}ClO_2S$ requires C, 39·4; H, 6·1; Cl, 19·4; S, 17·5%).

1,3-Bisethylthiobut-2-ene was obtained by boiling under reflux a mixture of the chloro-sulphide (45 g., 0·3 mole), ethanethiol (20 g., 0·323 mole), and sodium pentyloxide solution prepared by dissolving sodium (8·3 g., 0·36 g.-atom) in pentanol (280 c.c.). The resulting sulphide (52 g.) was free from halogen but boiled over a range 53—72°/0·2 mm. Fractionation effected partial separation into two fractions, b. p. 53—60°/0·2 mm., n_D^{21} 1·5069 (4·5 g.), and b. p. 67—72°/0·2 mm., n_D^{21} 1·5240 (29·3 g.). Analysis of the second fraction indicated that it was mainly the required 1,3-bisethylthiobut-e-ene (VB) (Found: C, 52·8; H, 9·6; S, 35·1. Calc. for $C_8H_{16}S_2$: C, 54·5; H, 9·1; S, 36·4%). Oxidation yielded a sulphone, b. p. 145—165°/0·07 mm. After further fractionation, a sulphone, b. p. 162°/0·07 mm., n_D^{21} 1·5076, was obtained and appeared to be the required disulphone (Found: C, 40·2; H, 6·7; S, 26·7. Calc. for $C_8H_{16}O_4S_2$: C, 40·0; H, 6·7; S, 26·7%). The same product was obtained when the sulphide was oxidised by ethereal monoperphthalic acid at −10°. After 6 months, the liquid deposited crystals, m. p. 63—68°, which were subsequently shown to be a mixture of the two isomers described below.

(c) *From* 1,3-*dichlorobut-1-ene.*[9] Condensation of the dichlorobutene with ethanethiol yielded 1-*chloro*-3-*ethylthiobut-1-ene* as two distinct fractions which had identical infrared spectra and gave correct analytical figures. These were: (i) b. p. 63—65°/13 mm., n_D^{21} 1·4910 (~40% of the total obtained) (Found: C, 47·3; H, 7·5; Cl, 23·8; S, 21·5. $C_6H_{11}ClS$ requires C, 47·8; H, 7·4; Cl, 23·5; S, 21·3%); (ii) b. p. 66·5—68·5°/12 mm., n_D 1·4959 (Found: C, 47·9; H, 7·5; Cl, 24·6; S, 21·5%) [the low chlorine analysis of fraction (ii) may indicate slight alcoholysis. There were also higher-boiling fractions which differed in refractive index and analytical figures]; (iii) b. p. 62°/0·1 mm., n_D^{21} 1·4931 (Found: C, 62·6; H, 9·8; S, 27·5%); and (iv) b. p. 65°/0·1 mm., n_D^{21} 1·4961 (Found: C, 55·1; H, 9·8; S, 35·6%). The total yield of the last two fractions was ~8%. Both were free from halogen. The analytical figures for fraction (iv) corresponded to those of the bis-sulphide, but the refractive index was too low.

Conversion into the Bis-sulphide.—The chloro-sulphide, fraction (c ii) (22·5 g.) was boiled under reflux for 12 hr. with a solution from sodium (4·2 g.) and ethanethiol (10 g.) in pentanol (250 c.c.). Three main fractions were obtained when the product was distilled: (a) b. p. 51°/0·05 mm., n_D^{19} 1·5119 (Found: C, 57·2; H, 9·7; S, 34·4%); (b) b. p. 56°/0·05 mm., n_D^{20} 1·5251 (Found: C, 54·8; H, 10·0; S, 35·6%); and (c) b. p. 58°/0·03 mm., n_D^{20} 1·5240 (Found: C, 55·9; H, 9·0; S, 34·2%). It was evident that all three fractions were mainly the bis-sulphide but it was not possible by further fractional distillation to isolate the pure compounds. The condensation of the first chloro-sulphide fraction (c i) with ethanethiol gave similar results. All the specimens of bis-sulphide obtained from 1,3-dichlorobut-1-ene had virtually identical infrared absorption spectra which were also identical with the spectrum of the compound

⁹ Andrews, *J. Amer. Chem. Soc.*, 1946, **68**, 2584.

derived from 1,3-dibromobutan-2-ol. Only a trace of carbonyl derivative was present. Oxidation by perhydrol or monoperphthalic acid yielded the usual liquid mixture of sulphones.

Isolation and Properties of 1,3-*Bisethylsulphonylbutenes*.—The proportion and yields of crystalline material and oils varied according to the method of oxidation and the synthetic route and they are summarised in Table 1.

TABLE 1.

1,3-Bisethylsulphonylbutenes obtained by different routes.

	Starting from 1,3-dichloro-			Starting from 1,3-dichloro-		
	-but-1-ene	-but-2-ene	-butan-2-ol	-but-1-ene	-but-2-ene	-butan-2-ol
	Oxidn. by H₂O₂ in AcOH			Oxidn. by monoperphthalic acid in Et₂O		
Solid, yield (%) ...	18	4	35	31	0 ‡	40
,, m. p.*	75—80°	63—68°	55—77°	72—80°	—	68—81°
Liquid,† yield (%)	48	63	40	46	79	53
,, b. p./mm.	170—210°/0·1	145—165°/0·07	—	—	—	—
,, n_D^{21}	—	1·5076	1·5048	1·5052	1·5042	1·5088

* M. p.s are those of the crude products.   † All the liquids deposited solids or became semi-solid after several years.   ‡ No crystals before 6 months.

The disulphone, m. p. 75—80°, was a nearly pure single isomer.   Pure (*cis?*) 1,3-*bisethyl-sulphonylbut-2-ene*, m. p. 80—81°, separated in large rods after crystallisation from benzene– or ethyl acetate–light petroleum (b. p. 60—80°) (Found: C, 39·8; H, 7·2; S, 26·5. C₈H₁₆O₄S₂ requires C, 40·0; H, 6·7; S, 26·7%).   The sulphone was identical (m. p. and mixed m. p.) with that obtained by isomerisation and oxidation of 3,3-bisethylthiobut-1-ene, (EtS)₂CMe·CH:CH₂, prepared by Rothstein and Whiteley.[10]   It decolorised a cold solution of potassium permanganate in acetone, but did not react with solutions of bromine in water, chloroform, or carbon tetra-chloride.   A condensation product was not obtained with benzaldehyde, and the substance was not hydrogenated in the presence of platinum or nickel catalysts, or reduced by sodium amalgam.   Molecular-weight determinations in benzene showed the substance to be monomeric (Found: M, 257, 246.   C₈H₁₆O₄S₂ requires M, 240).

Ozonolysis.   The disulphone, m. p. 80—81° (0·7 g.), dissolved in alcohol-free chloroform, was mixed with water and barium carbonate (0·5 g.; to remove any sulphuric acid formed). After passage of ozonised oxygen for 4·5 hr., the layers were separated.   A recognisable product was not obtained from the aqueous layer.   The sharp-smelling oil obtained from the chloroform layer was converted into the 2,4-dinitrophenylhydrazone, consisting of two compounds, one of which was only slightly soluble in ethanol.   Each was recrystallised once from ethanol, there being insufficient material for further purification.   The more soluble compound crystallised in plates, m. p. 145—148° (Found: C, 39·9; H, 3·5; S, 10·3%).   The second substance crystallised as a yellow powder, m. p. 172° (decomp.) (Found: C, 38·9; H, 4·2; N, 15·9%).   Neither of these corresponded exactly to one of the expected products, namely, the 2,4-dinitrophenyl-hydrazones of ethylsulphonyl-acetaldehyde and -propionaldehyde (Calc. for C₁₀H₁₂N₄O₆S: C, 38·0; H, 3·8; N, 17·7; S, 10·1.   Calc. for C₁₁H₁₄N₄O₆S: C, 40·0; H, 4·3; N, 17·0; S, 9·7%). The non-crystalline sulphone, which in general properties resembled the above disulphone, yielded sulphonic acids only when ozonised.

In order to obtain the second sulphone, the combined mixed crystalline oxidation products were separated by hand-picking under a lens.   The crude plate-like crystals so obtained had a m. p. 78—84°.   When they were mixed with the above " rods," the m. p. was depressed to 63—65° and they also gave a depressed m. p. when mixed with 1,3-bisethylsulphonylbut-1-ene or 1,1-bisethylsulphonylbut-2-ene prepared by Rothstein and Whiteley.[10]   The new compound separated from benzene–light petroleum in parallelopipeds, with the sharp corners missing, m. p. 90°.   It was presumably (*trans?*) 1,3-*bisethylsulphonylbut-2-ene*, isomeric with that of m. p. 80—81° (Found: C, 40·1; H, 6·7; S, 26·7%).

Alkylation or interconversion of the two sulphones was not effected.   Cold sodium methoxide had no effect on the isomer, m. p. 80—81°, but the boiling reagent caused partial

¹⁰ Rothstein and Whiteley, unpublished work.

decomposition. Tri-n-pentylamine in xylene changed the crystalline form but there was no mixed m. p. depression with the original material. The isomeric compound, m. p. 90°, was converted into an oil by cold or boiling sodium methoxide.

Preparation of 1,3-*Bisethylsulphonylbutane.*—1,3-Dibromobutane, b. p. 56—57°/7 mm. (14·5 g., 0·067 mole), was condensed with ethanethiol (9 g., 0·145 mole) in an equimolecular quantity of 5% ethanolic sodium ethoxide. This gave 1,3-*bisethylthiobutane*, b. p. 110—112·5°/ 12 mm. (Found: C, 53·8; H, 10·0; S, 35·6. $C_8H_{18}S_2$ requires C, 53·9; H, 10·2; S, 35·9%). Oxidation by hydrogen peroxide in glacial acetic acid afforded 1,3-*bisethylsulphonylbutane*, m. p. 36—37·5° (from benzene) (Found: C, 39·4; H, 7·8; S, 26·3. $C_8H_{18}O_4S_2$ requires C, 39·7; H, 7·5; S, 26·5%).

Zerewitinov Determinations.[11]—These measurements (Table 2) were carried out in tetrahydrofuran solution owing to the insolubility of the disulphones in ether. The last column gives the theoretical volume of methane that could be evolved under the experimental conditions (16·5°, 760 mm.).

TABLE 2.

Zerewitinov determinations of active hydrogen in 1,3-bisethylsulphonyl-butane and -butenes.

Derivative	Weight (g.)	CH_4 evolved (c.c.)	Calc. vol. for 1H (c.c.)
Butane	0·0512	1·6	10·4
Butene, m. p. 80—81°	0·0262	5·4	5·3
Butene, m. p. 90°	0·0448	10·4	9·1
	0·0645	14·2	13·0
Butene, b. p. 162°/0·07 mm.	0·0474	7·8	9·7
,, ,, ,,	0·0764	16·8	15·4

TABLE 3.

(a) Carbon–hydrogen stretching frequencies (cm.$^{-1}$) of some saturated and unsaturated sulphones.

Sulphone	Ph or C=C<H\H	Ph or C=C<H/H	Me	CH_2	Me
Et·SO₂·CHMe·CH₂·SO₂·Et	—	—	2981s	2942s	2882w
(Et·SO₂)₂CH·CH₂·CH(SO₂·Et)₂	—	—	2980m	2946m / 2918vs	2880w
Ph·CH₂·SO₂·CH₂·CH₂·CH₂·SO₂·Et	3012w	3043w	2990m	2934s	—
Me·SO₂·CH₂·CH:CH₂ *	3089w	3025s	2991w	2927s	—
Ph·CH₂·SO₂·CH₂·CH:CH₂	3092w	3035m / 3045m	—	2963m / 2909s	—
Ph·CH₂·SO₂·CH:CHMe	—	3036m	2973m	2923s	—
Et·SO₂·CMe:CH·CH₂·SO₂·Et,† m. p. 80—81°	—	—	2991s / 2966s	2945s / 2926m	2882w
Et·SO₂·CMe:CH·CH₂·SO₂Et,† m. p. 90°	—	—	2995s / 2978s	2948s / 2931m	2881w
Et·SO₂·CH₂·CH:CH·SO₂·Et	—	3051vs	2984s	2952m / 2921m	2895m
Buⁿ·SO₂·CH₂·CH:CH·SO₂·Et	—	3047vs	2981s	2952s	2885m
Ph·CH₂·SO₂·CH₂·CH:CH·SO₂·Me	—	3062s	9297s	2930s	—
Ph·CH₂·SO₂·CH₂·CH:CH·SO₂·Et	—	3047s / 3031s	2976s	2941vs / 2946vs	—
Ph·CH₂·SO₂·CH:CH·CH₂·SO₂·Et	—	3047s / 3034w	2984vs	2946vs	—
Ph·CH₂·SO₂·CH₂·CH:CH·SO₂·Buᵗ	—	3049vs	2985s / 2971m	2936s	—
Ph·CH₂·SO₂·CH:CH·CH₂·SO₂·Buᵗ	—	3049s / 3030w	2978s	2934s	2872w
(Et·SO₂)₂C:CH·CH(SO₂·Et)₂	—	3002w ‡	2981m	2936s	2880w

* Thin film. † Assumed structures. ‡ May be a side-band on methyl. § Cf. Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257; 1940, *A*, **175**, 208.

[11] Braude and Stein, *J.*, 1946, 404.

TABLE 3. (*Continued.*)

(*b*) Carbon–carbon and oxygen–sulphur stretching frequencies (cm.$^{-1}$) of some saturated and unsaturated sulphones.

| | Assignments * | | |
	C=C	S=O † asym.	S=O † sym.
Sulphone			
Et·SO$_2$·CHMe·CH$_2$·CH$_2$·SO$_2$·Et	1645w	1307 1282sb	1139
(Et·SO$_2$)$_2$CH·CH$_2$·CH(SO$_2$·Et)$_2$	---	1323 1290sb	1143—1164 1117
Ph·CH$_2$·SO$_2$·CH$_2$·CH$_2$·CH$_2$·SO$_2$·Et	—	1312	1124
Me·SO$_2$·CH$_2$·CH:CH$_2$	1642m	1290	1133
Ph·CH$_2$·SO$_2$·CH$_2$·CH:CH$_2$	1645m	1311 1285	1136 1119
Ph·CH$_2$·SO$_2$·CH:CHMe	1647s	1297 1289	1117
Et·SO$_2$·CMe:CH·CH$_2$·SO$_2$·Et, m. p. 80—81°	1656w	1307 1282sb	1139 1130sb
Et·SO$_2$·CMe:CH·CH$_2$·SO$_2$·Et, m. p. 90°	1639s	1290 1264	1129 1145, 1109sbs
Et·SO$_2$·CH$_2$·CH:CH·SO$_2$Et	1642m	1282	1136 1119
Bu^{n}·SO$_2$·CH$_2$·CH:CH·SO$_2$·Et	1647m	—	—
Ph·CH$_2$·SO$_2$·CH$_2$·CH:CH·SO$_2$·Me	1642s	—	—
Ph·CH$_2$·SO$_2$·CH$_2$·CH:CH·SO$_2$·Et	1645m	1304 1289	1124
Ph·CH$_2$·SO$_2$·CH$_2$·CH:CH·CH$_2$·SO$_2$·Et	1653m	1307 1276	1151 1124
Ph·CH$_2$·SO$_2$·CH$_2$·CH:CH·SO$_2$·Bu^{t}	1639m	1326, 1300 1282	1144 1111
Ph·CH$_2$·SO$_2$·CH:CH·CH$_2$·SO$_2$·Bu^{t}	1639m	1316, 1300 1282	1112 1156, 1144sbs
(Et·SO$_2$)$_2$C:CH·CH(SO$_2$·Et)$_2$	1616s	1323 1282sb	1155, 1134 1126

sb = Side-band.

* Katritzky and Jones (*J.*, 1960, 4497) recently suggested that the carbon–sulphur stretching frequency has a strong absorption at about 970 cm.$^{-1}$. Of the simple sulphones which we have examined, dimethyl sulphone has no absorption in this region, ethyl methyl and benzyl methyl sulphone have an intense absorption, whilst bismethylsulphonyl- and bisethylsulphonyl-methane have a band of medium intensity. † All the sulphur–oxygen stretching frequencies are represented by very intense and broad absorptions and for these measurements the concentration in potassium chloride was somewhat lower than for the remainder of the spectra.

Infrared Absorptions.—Many of the simple saturated and unsaturated bisalkylsulphonyl-propenes and butenes have only been prepared in these laboratories and consequently there is a lack in the literature of infrared absorption spectra which could have been used for comparison purposes. In particular, there appears to be little indication what effect the sulphonyl group has on the absorptions due to the C–H and C=C stretching and the C–H bending frequencies. Table 3*a* contains the C–H stretching frequencies of sixteen sulphones measured on a grating spectrometer. Table 3*b* contains C=C and S–O stretching frequencies. All but one of the absorptions have been measured on an instrument incorporating a rock-salt prism, for potassium chloride discs with 3 mg. of sulphone in 200 mg. of potassium chloride. Since absorptions due to sulphur–oxygen stretching frequencies are very intense compared with those of other groups, the approximate intensities of the latter to be found in Tables 3*a* and *b* are therefore relative to one another and not to that of the sulphonyl groups. The three saturated sulphones were included in the Tables in order to identify the positions of the bands due to the methyl and methylene groups. It is also evident that absorptions associated with phenyl-carbon–hydrogen stretching frequencies and overlapping those due to vinyl-carbon–hydrogen (*i.e.*, at ∼3075 and 3020 cm.$^{-1}$) are always weak and need not be confused with olefinic absorption bands. In fact, the most intense absorptions in this region (3051 and 3048 cm.$^{-1}$) occur with 1,3-bisethylsulphonyl- and 1-n-butylsulphonyl-3-ethylsulphonyl-propene which do not contain phenyl. The bisethyl-sulphonylbutenes are notable because they are the only unsaturated sulphones which show no absorption at 3025—3050 cm.$^{-1}$. This at once suggests a trisubstituted olefin, R·CMe:CH·CH$_2$R

rather than the isomeric R·CHMe·CH:CHR (R = Et·SO₂) which would be expected to exhibit the normal peak. The other exception is the last compound, 1,1,3,3-tetrakisethylsulphonylpropene, which of necessity has a trisubstituted double bond and shows only a weak absorption at a rather low frequency. Absorption due to carbon–carbon (C=C) stretching frequency is shown by both the alkylsulphonylbutenes.

Proton Magnetic Resonance Spectra.—The spectra of sulphones, in deuterochloroform solution with tetramethylsilane as internal reference, were recorded on a Varian A-60 spectrometer operating at 60 Mc./sec. In most cases chemical shifts were large in comparison with spin–spin interactions and it was possible to make empirical correlations of the different species

TABLE 4.

Chemical shifts (p.p.m.) of some sulphones and bisethylthiobutene.

s = singlet; d = doublet; t = triplet; q = quartet; m = multisplitting; dt, dq, mt, mq denote doubling or higher multiplication of the group of absorption peaks.

	$-SO_2 \cdot CH_2 \cdot Me$		$\begin{matrix}\gamma\quad\beta\quad\alpha\\C-C-C-C-SO_2-(C)\end{matrix}$		
Sulphone (sulphide)	$-CH_2$	$-Me$	α-group	β-group	γ-group
Me·SO₂·Me	—	—	s 7·02	—	—
Me·SO₂·CH₂Me	q 7·03	t 8·63	s 7·20	—	—
Me·SO₂·CH₂·CH₂·CH₂Me	—	—	Me s 7·19	—	(Me) t 8·97
			CH₂ t 7·02		
CH₂(SO₂·Et)₂	q 6·55	t 8·55	s 5·55	—	—
Me·CH(SO₂·Et)₂	dq 6·6	t 8·55	q 5·73	d 8·15	—
CH₂:CH·CH₂·SO₂·Me	—	—	Me s 7·12	m 4·2	*cis* 4·6
			CH₂ d 6·23		*trans* 4·4
Me·CH:CH₂(SO₂·Et)₂	dq 6·4	dt 8·6	—	q 2·19	d 8·54
Et·SO₂CH:CH·CH₂·SO₂·Et	d 6·91 *	dt 8·59	CH₂ d 6·07	—HC=CH not assigned	
Et·SO₂·CMe:CH·CH₂·SO₂·Et †	dq 6·92	t 8·59	Me s 7·83	t 3·27	
		t 8·61	CH₂ d 6·05		
Ph·CH₂·SO₂·CH₂·CH:CH·SO₂Et ...	q 6·99	t 8·67	CH₂ d 6·23	—HC=CH not assigned	
			PhCH₂ s 5·71		
(Et·SO₂)₂CH·CH₂·CH(SO₂·Et)₂ ...	dq 6·5	t 8·55	t 4·89	t 6·89	
(Et·SO₂)₂CH·CH:C(SO₂·Et)₂	mq 6·5	mt 8·55	d 2·45	d 3·12	
EtS·CHMe·CH:CH·SEt	q 7·39	t 8·76	Me m 8·0	m 3·9—4·7	
			CH m 6·6		

* In CF₃·CO₂H each signal of the doublet is partially split (separation 1·5 c./sec.). † All three samples, those having m. p. 80° and 90° prepared by the present authors, and that prepared by Rothstein and Whiteley,[10] gave practically identical spectra.

of protons with the positions of the absorption bands, checking them by estimating the number of each kind of proton from the relative integrated areas under the curves. Generally, it was possible to estimate the positions of the simpler multiplet bands to the nearest 1 c./sec. but, as mathematical treatment was not attempted, only approximate assignments could be made in the more complex cases. In Table 4, chemical shifts are given in parts per million with τ values [τ (SiMe₄) = 10] to the nearest 0·01 p.p.m. except in the more uncertain cases. Coupling constants are not given but were usually 7—8 c./sec.

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