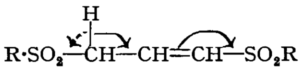
817. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part III.* Reactions of Propenedisulphonamides.*

By Denis C. Nicholson and Eugene Rothstein.

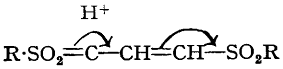
NNN'N'-Tetraethyl-propene-1 : 3-disulphonamide and -but-2-ene-1 : 3-disulphonamide have been prepared. The first can be *C*-monomethylated, yielding the second compound, or trimethylated, affording *NNN'N'*-tetraethyl-4-methylpent-2-ene-2 : 4-disulphonamide. All these substances are crystalline. In addition, both the propene and butene derivatives can be mono- and di-*C*-alkylated, to give syrups. The electronegative character of the sulphonamido-group is further shown by measuring the volume of methane which is evolved when the above compounds are treated with methylmagnesium iodide, up to two molecules of the gas being obtained. The polar character of these compounds, relative to that of the analogous sulphones, is discussed.

In many respects the polar character of derivatives of sulphonic acids is not very different from that of sulphones. The similarity between 1 : 1-bisalkylsulphonylalkanes and 1 : 1-disulphonic esters, for instance, is illustrated by the easy alkylation of methyl methanedisulphonate by potassium and methyl iodide (Schröter and Herzberg, *Ber.*, 1905, **38**, 3391), the resulting methyl ethane-1 : 1-disulphonate affording sodium butane-2 : 2-disulphonate when boiled with sodium ethoxide and ethyl iodide (Merzelius, *Ber.*, 1888, **21**, 1552). Neither ethylene- nor trimethylene-disulphonic acid derivatives contain a replaceable hydrogen atom, and propenemonosulphonic acids are similarly inactive; this suggests that alkylation is due to π-bond formation resultant on the delocalisation of the electron pair forming the carbon–hydrogen bond. The presence of a second sulphonic acid group in the propene system stabilises the mesomeric structures (II) and (III), *i.e.*, it facilitates the separation of a proton as indicated in (I) :



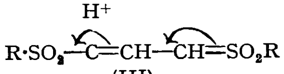
$$R{\cdot}SO_2{-}\overset{H}{CH}{-}CH{=}CH{-}SO_2R$$

(I)



$$R{\cdot}SO_2{=}\overset{H^+}{C}{-}CH{=}CH{-}SO_2R$$

(II)



$$R{\cdot}SO_2{-}\overset{H^+}{C}{=}CH{-}CH{=}SO_2R$$

(III)

($R = OH, NH_2$ etc.)

Confirmatory evidence is provided by the near-ultra-violet absorption of aminobenzenesulphonamides (Kummler and Strait, *J. Amer. Chem. Soc.*, 1943, **65**, 2344). The absorption

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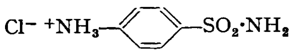
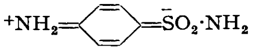
* Part II, preceding paper.

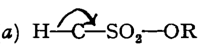
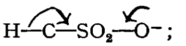
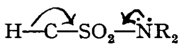
curve of *m*-aminobenzenesulphonamide resembles that of aniline in neutral and of benzenesulphonamide in acid solution, since the quaternary ammonium group does not affect the light absorption of benzene. Acid solutions of sulphanilamide (IV) are similar to the *meta*-compound, but in neutral or alkaline solution the intensity of absorption is much greater than for aniline or *m*-aminobenzenesulphonamide and is ascribed to the presence of the quinonoid structure (V):

(IV) 

 (V)

Kummler and Halverstadt (*J. Amer. Chem. Soc.*, 1941, **63**, 2182) furthermore found that the dipole moments of sulphanilamide and of 4′-aminodiphenyl-4-sulphonamide were greater by 0·81 and 0·69 unit, respectively, than those calculated for compounds without a separation of charges.

The relatively small tendency of bicovalent oxygen to share its non-bonding electrons makes it appear that, on the whole, sulphonic esters should not differ greatly from the corresponding sulphones in their tendency to form π-bonds (*a*). On the other hand the sulphonate ion (*b*) and the sulphonamides (*c*) may raise the energy necessary for the

(*a*)  ; (*b*)  ; (*c*) 

separation of the proton, and consequently some diminution in the ease of tautomeric interchange compared with that of the corresponding sulphones could be expected. Very little work has been done on this aspect. Suter and Bordwell (*ibid.*, 1943, **65**, 507) sulphonated a solution of methallyl chloride in dioxan with sulphur trioxide, obtaining a mixture of 2-chloromethylprop-2-ene-, 2-chloromethylprop-1-ene-, and 3-chloro-2-methylprop-2-enesulphonic acid, the last of which could have been obtained by a prototropic change.

In order to minimise the experimental difficulties it was decided to work with the amides rather than with the free sulphonic acids, but even so it was impossible to synthesise by unambiguous methods pairs of unsymmetrically substituted compounds such as propene- and butene-1 : 3-disulphonamides $NR_2{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SO_2{\cdot}NR'_2$ and $NR_2{\cdot}SO_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}SO_2{\cdot}NR_2'$. Thus neither 3-chloroprop-1-ene-1- nor 4-chlorobut-2-ene-2-sulphonamide could be prepared whilst the corresponding 2- and 3-enyl compounds (VI and VII) resisted further reaction with alkali sulphite; the inactivity of the vinyl halogen atom could not in these cases be overcome (compare Part II).

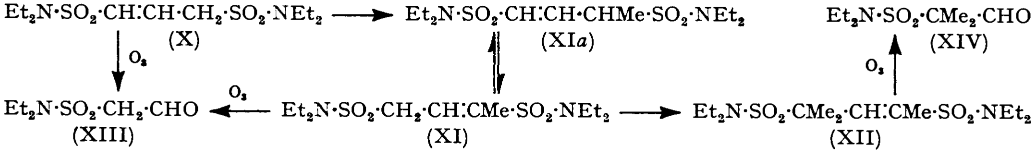
(VI) $CHCl{:}CH{\cdot}CH_2{\cdot}SO_2{\cdot}NEt_2$ $CHCl{:}CH{\cdot}CHMe{\cdot}SO_2{\cdot}NEt_2$ (VII)

The isomerisation of 1-benzylsulphonyl-3-bromoprop-1-ene to the 3-bromoprop-2-ene by alkali is irreversible (Culvenor, Davies, and Savige, *J.*, 1949, 2198) and it was not therefore to be expected that the sulphonamide (VI) would be very different. No isomerisation occurred with either bases or sodium alkoxide. In other respects the sulphonamides differed from the sulphone. Culvenor *et al.* noted that 1-benzylsulphonyl-3-bromoprop-2-ene afforded 1-benzylsulphonyl-3-bromo-2-ethoxypropane when dissolved in cold ethanolic alkali; the chloro-derivative reacts similarly and yields a 1-benzylsulphonyl-2-methoxypropene when it is boiled with three mols. of sodium methoxide (Rothstein, unpublished work). The sulphonamide, on the contrary, scarcely reacts with the reagent in the cold: when the solution is heated, the amide eliminates hydrogen chloride and forms an ethoxypropenesulphonamide which yields acetaldehyde on ozonolysis and there is no sign of an addition product in this case. A slight trace of formaldehyde was noticed, but neither *NN*-diethylsulphamylacetaldehyde nor the corresponding acid could be isolated. Since acetaldehyde could result from the ethoxy-group, either (VIII) or (IX) could represent the structure of the ethoxy-derivative. The formation of (VIII) would be analogous to the formation of 1-ethoxyallyltrimethylammonium salts from 3-chloroallyltrimethylammonium chloride (Ingold and Rothstein, *J.*, 1929, 8) but up to the present it has not been possible to synthesise (VIII) and (IX) for direct comparison.

(VIII) $Me{\cdot}CH{:}C(OEt){\cdot}SO_2{\cdot}NEt_2$ $CH_2{:}C(OEt){\cdot}CH_2{\cdot}SO_2{\cdot}NEt_2$ (IX)

Although direct evidence for interconversion of isomerides was thus not available, that it did occur was a logical inference from the reactions described below. The presence of

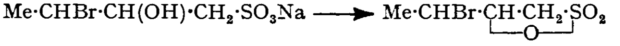
" active " hydrogen in *NNN'N'*-tetraethylpropene-1 : 3-disulphonamide (X) was shown both by its alkylation to the but-2-ene (XI) and the 4-methylpent-2-ene (XII), and also by a Zerewitinov determination with methylmagnesium iodide. The structures of (X), (XI), and (XII) were ascertained by ozonolysis.



The monomethyl derivative (XI) was prepared independently by the reactions :

$$R{\cdot}CHCl{\cdot}CH(OH){\cdot}CH_2Cl \longrightarrow KSO_3{\cdot}CHR{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3K \longrightarrow$$
$$Cl{\cdot}SO_2{\cdot}CHR{\cdot}CHCl{\cdot}CH_2{\cdot}SO_2Cl \longrightarrow (X;\ \textit{i.e.},\ R = H)\ \text{or}\ (XI;\ \textit{i.e.},\ R = Me)$$

The stability of (XI), compared with that of its isomeride (XI*a*), arises from the well-known effect of an alkyl group on the position of a double bond in a tautomeric substance. It depends on the quasi-conjugative effect associated with structural combinations such as $H{-}CH_2{-}CH{=}CH{-}$ (cf. J. W. Baker, " Hyperconjugation," Oxford, 1952). The sulphonamide (XI) was unaffected by alkali or ultra-violet light, although, as the quantity of material available was very small, minute amounts of the isomeride might have escaped detection. As a possible route to (XI*a*) we envisaged dehydrohalogenation of 3-bromo-2-chlorobutane-1-sulphonamide, $Me{\cdot}CHBr{\cdot}CHCl{\cdot}CH_2{\cdot}SO_2{\cdot}NR_2$, followed by reaction with sodium sulphite, analogously to the elimination of hydrogen bromide from 1-benzylsulphonyl-2 : 3-dibromopropane to give 1-benzylsulphonyl-3-bromoprop-1-ene (Rothstein, *loc. cit.*). It was not possible however to prepare the bromochloro-derivative because the reaction of phosphorus pentachloride with sodium 3-bromo-2-hydroxybutane-1-sulphonate (XV) yielded the sultone (XVI) :

(XV)

$$Me{\cdot}CHBr{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3Na \longrightarrow Me{\cdot}CHBr{\cdot}\underbrace{CH{\cdot}CH_2{\cdot}SO_2}_{O}$$
(XVI)

Unlike the bisalkylsulphonylpropenes, the disulphonamides did not condense with benzaldehyde. Propene-1 : 3-disulphonamide did indeed afford the di-*N*-benzylidene derivative, but this was a reaction of the amide-group as was shown by the non-reactivity of the *NNN'N'*-tetraethyl compound (X). Nevertheless carbon tetrachloride solutions of *NN'*-diethyl- and *NNN'N'*-tetraethyl-propene-1 : 3-disulphonamide, the methylated derivative (XI) of the latter, and also the dimethylated compound evolved hydrogen when shaken with " molecular " potassium. Both (X) and (XI) liberated methane when shaken with methylmagnesium iodide. A quantitative determination (Braude and Stern, *J.*, 1946, 404) showed that rather more than one mol. of methane was evolved in the case of the butene derivative, and more than two mols. by the first compound (X) ; the third available hydrogen atom appeared to be inactive towards this reagent.

EXPERIMENTAL

Salts of 2-*Hydroxypropane*-1 : 3-*disulphonic Acid*.—An aqueous solution of potassium hydroxide (78·2 g.) was saturated with sulphur dioxide, an equal quantity of potassium hydroxide was added, and the liquid evaporated in an atmosphere of nitrogen to crystallisation point. 1 : 3-Dichlorohydrin (90 g.) was added and the mixture boiled under reflux until homogeneous. The cooled solution deposited potassium 2-hydroxypropane-1 : 3-disulphonate, crystallising with two molecules of water. It was recrystallised from water until free from inorganic salts. The variable yield (17—56%) was due partly to differences in purity of the starting material and partly to the large number of recrystallisations necessary for the final purification (Found : C, 10·8 ; H, 2·8 ; H_2O, 10·5, 11·6. Calc. for $C_3H_6O_7S_2K_2,2H_2O$: C, 10·8 ; H, 3·0 ; H_2O, 10·9%). The anhydrous *salt* was formed at 125° in a vacuum (Found : C, 11·8 ; H, 2·5 ; S, 21·3. $C_3H_6O_7S_2K_2$ requires C, 12·2 ; H, 2·0 ; S, 21·6%).

Addition of barium chloride (50 g. in 100 c.c. of water) to the potassium salt (63 g. in 150 c.c. of water) precipitated the barium salt which was washed free from chloride ions, and the barium was precipitated from its aqueous (2 l.) solution by addition of sulphuric acid. Excess of lead carbonate was added to the filtered solution, the insoluble material removed, and the lead precipitated by hydrogen sulphide. Filtration and concentration in a vacuum (100°/18 mm.) yielded an oil which was inert to phosphorus oxychloride even at the b. p. Addition of pyridine precipitated the extremely deliquescent *pyridine* salt with evolution of heat. It crystallised from nitromethane, and, after being washed with ethanol at 0°, was stored in a vacuum-desiccator (exposure to air caused immediate liquefaction) (Found: C, 41·0; H, 4·7; N, 7·4. $C_{13}H_{18}O_7N_2S_2$ requires C, 41·3; H, 4·8; N, 7·4%). Boiling the acid or its potassium or pyridinium salt with thionyl chloride or phosphorus oxychloride did not afford a recognisable product.

2-Chloropropane-1 : 3-*disulphonyl Dichloride*.—The hydrated potassium salt (164 g.) was heated for 3 hr. at 130° yielding the anhydrous compound (146 g.); this was suspended in dry chloroform (300 c.c.) and boiled for 3 hr. under reflux with phosphorus pentachloride (339 g., 10% excess). The liquid was filtered and the residues were washed with chloroform (500 c.c.), the latter being added to the original filtrate. After removal of the solvent at 30° under reduced pressure, phosphorus oxychloride was removed on a water-bath. The *disulphonyl dichloride* (102 g.) was redissolved in chloroform, washed with water, and dried ($CaCl_2$). The compound (crude yield, 99 g.) was redistilled three times (considerable loss by decomposition); it had b. p. 148°/0·4 mm. (yield, 35 g., 26%) (Found: C, 13·7; H, 1·8; Cl, 38·3; S, 23·0. $C_3H_5O_4Cl_3S_2$ requires C, 13·1; H, 1·8; Cl, 38·7; S, 23·2%).

An ethereal solution of the dichloride (10 g.) was saturated by a slow stream of dry ammonia. The precipitated *propene*-1 : 3-*disulphonamide* was washed with ether and water and, recrystallised from the latter, had m. p. 156° (yield, 4 g., 55%) (Found: C, 18·0; H, 4·2; N, 13·8; S, 32·0. $C_3H_8O_4N_2S_2$ requires C, 18·0; H, 4·0; N, 14·0; S, 32·0%). It was very soluble in water in the presence of inorganic ions.

Hydrolysis of Propene-1 : 3-*disulphonamide*.—This compound (9 g.) was heated at 120—150° for 7 hr. with concentrated hydrochloric acid (22·5 g.) (sealed tube). Ammonium chloride was filtered from the product and the filtrate which contained sulphate ion evaporated to complete dryness at 60° in a vacuum. The residual amber-coloured oil was redissolved in water (10 c.c.) and neutralised by the addition of excess of barium carbonate. The solution of the barium salt was quickly cooled in carbon dioxide–acetone, and the temperature allowed to rise gradually. The *barium* 1 : 3-*propenedisulphonate* remained undissolved and was recrystallised several times from dilute alcohol. It contained variable amounts of water of crystallisation: one sample was dried for 3 days at room temperature in a vacuum-desiccator (Found: C, 10·9; H, 1·8; S, 16·4; Ba, 37·2. $C_3H_4O_6S_2Ba,2H_2O$ requires C, 9·6; H, 2·2; S, 17·2; Ba, 36·8%).

Reduction of the Disulphonamide.—The diamide (1 g.), dissolved in water (100 c.c.), was reduced with hydrogen in the presence of platinic oxide (0·25 g.). Nearly the theoretical volume of gas was absorbed in 24 hr. The evaporated solution was extracted with glacial acetic acid (30 c.c.), the platinum filtered off, and the solvent distilled from the filtrate. Propane-1 : 3-disulphonamide was obtained, which was identical (m. p. and mixed m. p.) with the amide prepared from propane-1 : 3-disulphonyl dichloride (Cohen and Clutterbuck, *J.*, 1922, **121**, 120) (Found: C, 17·9; H, 4·9; N, 13·3; S, 31·4. Calc. for $C_3H_{10}O_4N_2S_2$: C, 17·8; H, 5·0; N, 13·9; S, 31·7%).

Addition of ethereal diethylamine (10 c.c.) to a solution of the disulphonyl dichloride (5 g.) in this solvent yielded NNN′N′-*tetraethylpropane*-1 : 3-*disulphonamide* which separated from ethanol in prisms, m. p. 40—42° (1·5 g.) (Found: C, 42·0; H, 8·4; N, 8·8; S, 20·0. $C_{11}H_{26}O_4N_2S_2$ requires C, 42·0; H, 8·3; N, 8·9; S, 20·4%).

Attempted Alkylation of Propene-1 : 3-*disulphonamide*.—Various methods for methylating the sulphonamide employing sodium ethoxide and potassium *tert.*-butoxide were unsuccessful, the original material being recovered. Potassium hydroxide (2 equivs.) in one experiment afforded a homogeneous solid which appeared to be the *dipotassium* derivative (Found: C, 13·1; H, 2·7. $C_3H_6O_4N_2S_2K_2$ requires C, 13·0; H, 2·2%) but when it was boiled with excess of methyl iodide only a small quantity of unchanged amide was obtained.

Fission of Propene-1 : 3-*disulphonamide by Ozone*.—Ozonised oxygen was passed through a solution of the disulphonamide (1 g.) in water (100 c.c.) for 36 hr. Concentration of the liquid precipitated some unchanged amide (0·3 g.), the filtrate yielding *sulphamoylacetaldehyde* 2 : 4-*dinitrophenylhydrazone*, m. p. 198—199° (0·5 g.), crystallising from water (Found: C, 32·0; H, 3·1; N, 23·0; S, 10·5. $C_8H_9O_6N_5S$ requires C, 31·7; H, 3·0; N, 23·1; S, 10·6%).

Condensation of Propene-1 : 3-*disulphonamide with Benzaldehyde*.—Excess of freshly distilled benzaldehyde was mixed with the disulphonamide and a drop of piperidine added. The mixture was heated for 10 min., then extracted with ether, and the insoluble portion stirred with ethanol until it crystallised. Recrystallisation from aqueous acetone furnished the NN′-*dibenzylidene* derivative, m. p. 220—222° (decomp.) (Found: C, 54·2; H, 3·9; N, 7·4; S, 17·1. $C_{17}H_{16}O_4N_2S_2$ requires C, 54·3; H, 4·3; N, 7·5; S, 17·0%). When the mixture was heated for 24 hr., the semi-solid product yielded a stiff syrup after extraction with ether. The *substance* slowly separated from ethanol as a granular powder, m. p. 196°; there appeared to be six benzylidene molecules to one of the disulphonamide (Found: C, 74·0; H, 5·3; N, 3·9; S, 8·4. $C_{45}H_{40}O_4N_2S_2$ requires C, 73·4; H, 5·4; N, 3·8; S, 8·7%).

Preparation and Reactions of N-*Alkylated Propene*-1 : 3-*sulphonamides*.—NN′-*Diethylpropene*-1 : 3-*disulphonamide* was prepared by aspirating dry ethylamine through a cooled ethereal solution of 2-chloropropane-1 : 3-disulphonyl dichloride (1·5 g.) and, after filtration, evaporating the filtrate. The residual syrup (1 g.) rapidly crystallised and the compound, recrystallised from ethanol, had m. p. 68° (yield, 0·3 g.) (Found: C, 32·6; H, 6·3; N, 11·0; S, 25·3. $C_7H_{16}O_4N_2S_2$ requires C, 32·8; H, 6·3; N, 10·9; S, 25·0%). It was soluble in ethanol, but insoluble in water, and decolorised potassium permanganate in acetone.

To the chlorodisulphonyl dichloride (10 g.) in dry ether (200 c.c.), cooled in ice, ethereal diethylamine (20·8 c.c. in 200 c.c.) was slowly added. The insoluble matter was removed and the filtrate evaporated. The residue was redissolved in ether, and the solution washed successively with dilute hydrochloric acid and water until the washings were free from chloride ions, and dried (Na_2SO_4). The liquid was concentrated and cooled in carbon dioxide–acetone. The small amount of colour still present in the precipitated crystals of NNN′N′-*tetraethylpropene*-1 : 3-*disulphonamide* was washed away with a little ice-cold ether, and the product recrystallised from ether either alone or in admixture with ethanol. It had m. p. 57—58° (Found: C, 42·6; H, 7·4; N, 9·2; S, 20·3%; *M*, 336. $C_{11}H_{24}O_4N_2S_2$ requires C, 42·3; H, 7·7; N, 9·0; S, 20·5%; *M*, 312). It did not condense with benzaldehyde, and was insoluble in water but soluble in most organic solvents. Potassium permanganate in aqueous acetone was slowly decolorised by it. The sulphonamide was recovered unchanged from its solution in ethereal diazomethane.

Reactions of NNN′N′-*Tetraethylpropene*-1 : 3-*disulphonamide*.—*Fission by ozone.* This was carried out in chloroform solution, cooled in ice, for 12 hr. The ozonide was decomposed by shaking it with water for 15 min. and then heating it under reflux for a further short period. An unidentified carbonyl compound, yielding a 2 : 4-dinitrophenylhydrazone, m. p. 148—150°, was evolved and a second similar *derivative* was isolated after the aqueous liquid had been steam-distilled, having m. p. 125—127° (from ethanol) (Found: C, 41·9; H, 4·1; N, 22·0%). The residue in the flask furnished NN-*diethylsulphamoylacetaldehyde* 2 : 4-*dinitrophenylhydrazone*, m. p. 168—170° (from ethanol) (Found: C, 40·3; H, 5·0; N, 19·2. $C_{12}H_{17}O_6N_5S$ requires C, 40·1; H, 4·8; N, 19·5%). Sulphate ion and diethylamine were present in the mother-liquors.

Trimethylation. A solution of the tetraethyldisulphonamide (4 g.) in *tert.*-butanol (48 c.c.) was warmed to just above the m. p. of the solvent and mixed with a solution of potassium (2 g.) also in the alcohol (50 c.c.). Methyl iodide (7·3 g.) was added, the mixture shaken at room temperature for 16 hr., the liquid centrifuged, and the remaining potassium iodide washed out with a little water. Removal of the volatile products from the dried (K_2CO_3) solution afforded an oil which quickly crystallised. Recrystallisation from ether yielded NNN′N′-*tetraethyl*-4-*methylpent*-2-*ene*-2 : 4-*disulphonamide*, m. p. 47—48° (4·4 g., 97·8%) (Found: C, 47·6; H, 8·5; N, 7·5; S, 17·6%; *M*, 285. $C_{14}H_{30}O_4N_2S_2$ requires C, 47·4; H, 8·6; N, 7·9; S, 18·1%; *M*, 354).

The trimethylated derivative was ozonised in chloroform solution and the ozonide decomposed by boiling water. The quantity of aldehyde evolved during the decomposition was too small to be identified. There was a residual low-melting solid and after addition of water (100 c.c.) it was steam-distilled and the α-NN-*diethylsulphamoyl*iso*butyraldehyde* 2 : 4-*dinitrophenylhydrazone* recrystallised from ethanol (ice-cooling necessary); this had m. p. 168—170° (yield, 0·34 g.) (Found: C, 43·6; H, 5·6; N, 18·4; S, 8·1. $C_{14}H_{21}O_6N_5S$ requires C, 43·6; H, 5·4; N, 18·1; S, 8·3%).

Mono- and di-alkylation in tert.-*butanol solution.* All the products, with one exception, in this group of reactions were oils which however gave good analyses. The results of some of the experiments suggest that dealkylation followed by dimerisation or realkylation occurs in *tert.*-butoxide solution.

Potassium *tert.*-butoxide solution (28·7 c.c.; 3·5% w/v) was slowly added to a solution of the bisdiethylsulphonamide (8 g.) in the same solvent (35 c.c.) and shaken for 5 min. Methyl iodide (15 c.c.) was added and shaking continued for a further 2 hr., after which the volatile constituents were distilled off at 60° in a vacuum. Water was added to the residue and the NNN′N′-*tetraethylbut*-2-*ene*-1 : 3-*disulphonamide* extracted with ether. The ethereal extract was washed free from potassium iodide, the ether distilled, and the residue dried at 100°/20 mm. The yield of non-crystallisable syrup was 7·9 g. (95%) (Found: C, 44·2; H, 8·4; N, 8·4; S, 19·5%; *M*, 309. $C_{12}H_{26}O_4N_2S_2$ requires C, 44·2; H, 8·0; N, 8·6; S, 19·7%; *M*, 326).

This amide was ozonised in chloroform at 0°. A small quantity of unidentified aldehyde (2 : 4-dinitrophenylhydrazone, crystallised from ethanol, m. p. 156—157°) was obtained together with diethylsulphamoylacetaldehyde, identified through its dinitrophenylhydrazone (m. p. and mixed m. p.) (Found: C, 40·1; H, 4·8%).

Methylation of the butenedisulphonamide. The oil (1 g.) was mixed with *tert.*-butanol (10 c.c.) and methyl iodide (excess), and potassium *tert.*-butoxide solution (3 c.c. of 4%) added. The first drop of the latter produced a red colour which later disappeared. The mixture was shaken for 14 hr. and the product isolated in the usual way. Addition of ethanol to the residual syrup cooled in ice precipitated colourless crystals, having m. p. 140—141° after recrystallisation from ethanol containing a trace of water (yield, 0·18 g.). The structure could not be ascertained but the analytical figures corresponded to a monomethylated dimeride of the original disulphonamide (Found: C, 43·5; H, 7·9; N, 8·5; S, 19·7. $C_{23}H_{50}O_8N_4S_4$ requires C, 43·2; H, 7·9; N, 8·8; S, 20·1%). This *substance* was always isolated when the butenedisulphonamide was further alkylated. The main product from this reaction was probably a NNN′N′-*tetraethylpentenedisulphonamide*, but it did not crystallise (Found: C, 45·6; H, 8·0; N, 7·2%; *M*, 355. $C_{13}H_{28}O_4N_2S_2$ requires C, 45·9; H, 8·3; N, 8·0%; *M*, 340).

Reaction of the butenedisulphonamide with ethyl iodide. The butenedisulphonamide (7·5 g.) was shaken with potassium *tert.*-butoxide solution (26 c.c. of 3·5% solution) and ethyl iodide (8 c.c.). The product yielded a small quantity of the substance, m. p. 140—141°, together with an apparently diethylated derivative, possibly a NNN′N′-*tetraethylheptenedisulphonamide*, b. p. 205°/0·1 mm. (some decomp.). It did not crystallise (Found: C, 48·9; H, 8·7; N, 7·7; S, 17·3. $C_{15}H_{32}O_4N_2S_2$ requires C, 48·9; H, 8·7; N, 7·6; S, 17·4%).

Preparation of a crystalline monomethylated derivative from tetraethylpropenedisulphonamide. Sodium ethoxide (13·4 c.c. of 0·25% w/v solution in ethanol) was added to a solution of the disulphonamide (0·5 g.) in dry ether (350 c.c.). The white gelatinous precipitate of the *sodio*-derivative was centrifuged and dried in a desiccator (Found: C, 38·8; H, 7·2; N, 7·7; S, 18·9; Na, 7·1. $C_{11}H_{23}O_4N_2S_2Na$ requires C, 39·5; H, 6·9; N, 8·4; S, 19·2; Na, 6·9%). The sodio-derivative (0·6 g.) was boiled under reflux with excess of methyl iodide for 30 min., and the ethereal solution of the product washed with water until free from iodide ion and dried (Na_2SO_4). After distillation of the ether, the residue was cooled in ice, yielding a form of NNN′N′-*tetraethylbut*-2-*ene*-1 : 3-*disulphonamide*, m. p. 55° (0·2 g.) (Found: C, 44·0; H, 8·0; N, 8·4; S, 20·1. $C_{12}H_{26}O_4N_2S_2$ requires C, 44·2; H, 8·0; N, 8·6; S, 19·7%). It was identical (mixed m. p.) with the butenedisulphonamide described below and depressed the m. p. of the starting material. There was a residual oil which afforded similar analytical figures and crystallised during several months (Found: C, 44·4; H, 8·1; N, 8·4; S, 19·6%).

Independent Synthesis of Butenedisulphonic Acid Derivatives.—Preparation of 1 : 3-*dibromo- and* 1 : 3-*dichloro-butan*-2-*ol.* But-2-enyl alcohol was obtained from crotonaldehyde by reduction with aluminium *iso*propoxide (Young, Hartung, and Crossley, *J. Amer. Chem. Soc.*, 1936, **58**, 100). Addition of the appropriate halogen yielded the 2 : 3-dihalogenobutan-2-ol which with aqueous potash afforded 3-halogeno-1 : 2-epoxybutane and thence by addition of halogen halide the dihalogenobutanol (Petrov, *J. Gen. Chem.*, *U.S.S.R.*, 1941, **11**, 712). The physical properties of the compounds at each stage of the synthesis agree with the published figures and the intermediates gave correct analyses.

Condensation with potassium sulphite. Reasonable yields starting from the dibromobutanol were unobtainable owing to the difficulty of separating the potassium disulphonate from the potassium bromide formed.

A solution of potassium hydroxide (7·9 g.) in water (100 c.c.) was saturated with sulphur dioxide, and an equal amount of potassium hydroxide added, followed by 1 : 3-dichlorobutan-2-ol (20 g.). The mixture was boiled under reflux for 6 hr., then cooled; the excess of organic material was extracted with ether, and the liquid filtered from the inorganic salts which had crystallised. Addition of ethanol to the filtrate precipitated *potassium* 2-*hydroxybutane*-1 : 3-*disulphonate* which was purified by repeated precipitation from its aqueous solution until completely free from inorganic salts (yield, 2·2 g., 7·5%) (Found: C, 15·3; H, 2·3; S, 19·9. $C_4H_8O_7S_2K_2$ requires C, 15·5; H, 2·6; S, 20·6%).

Condensation with ammonium sulphite. The dibromo-alcohol (212 g.) was boiled for 5 hr. under reflux and vigorous stirring with 4 equivs. (970 g.) of ammonium sulphite monohydrate, and water (300 c.c.). After dilution to 3 l., barium hydroxide (2·2 kg. of the octahydrate) was added and the liquid boiled until free from ammonia, the volume of the solution being maintained by further addition of water. Undissolved material was removed by filtration, the precipitate was washed by water, and the washings were added to the filtrate. The combined solutions were saturated with carbon dioxide, the precipitated barium carbonate was filtered off, and the filtrate shaken with silver oxide (from 680 g. of silver nitrate). After removal of the silver halide, the barium hydroxide was precipitated as the carbonate by passage of carbon dioxide through the solution, and the filtrate reduced to a small bulk by evaporation. Addition of ethanol precipitated the *barium* salt which was recrystallised from water (yield, 243 g.) (Found: C, 12·8; H, 2·6; S, 16·4; Ba, 35·5; H_2O, 4·3. $C_4H_8O_7S_2Ba,H_2O$ requires C, 12·4; H, 2·6; S, 16·6; Ba, 35·5; H_2O, 4·6%).

The *sodium* salt, prepared from an aqueous solution of the barium salt (200 g.) and sodium carbonate, was washed with alcohol and ether (yield, 123 g.) and recrystallised from aqueous ethanol (Found: C, 17·2; H, 3·2; S, 22·7. $C_4H_8O_7S_2Na_2$ requires C, 17·3; H, 2·9; S, 23·1%). It reacted neither with thionyl chloride nor with phosphorus trichloride.

Preparation of the sulphonyl chloride. A suspension of the above sodium salt (50 g.) in dry chloroform (100 c.c.) was boiled under reflux for 2 hr. with phosphorus pentachloride (96 g.). The crude product (42 g.) had b. p. 150—170°/2 mm. (much decomp. and evolution of sulphur dioxide and hydrogen chloride). Redistillation afforded *but-2-ene-*1 : 3-*disulphonyl dichloride*, b. p. 134—140°/1 mm. (decomp.) (yield, 12·5 g.), evidently containing a trace of 2-chlorobutane-1 : 3-disulphonyl chloride (Found: C, 19·0; H, 2·9; Cl, 29·4; S, 25·3. $C_4H_{16}O_4Cl_2S_2$ requires C, 19·0; H, 2·4; Cl, 28·1; S, 25·3%).

Reaction of the sulphonyl chloride with ammonia. An ethereal solution of the disulphonyl chloride (15 g.) was saturated with dry ammonia, and the precipitate filtered off, washed with ether, and digested with dry boiling acetone (150 c.c.) for 2 hr. Removal of the insoluble portion and evaporation of the solvent afforded an oil (8 g.) which was rubbed with ether and then water. *But-2-ene-*1 : 3-*disulphonamide* (2·3 g.) was gradually deposited, having m. p. 144—145° (Found: C, 22·6; H, 4·7; N, 12·8; S, 29·4. $C_4H_{10}O_4N_2S_2$ requires C, 22·2; H, 4·7; N, 13·1; S, 29·9%). After removal of the amide, the residual syrup was washed with acetone and dried in a vacuum. A highly deliquescent crystalline *substance* was obtained which could not be identified (Found: C, 37·4; H, 6·8; N, 9·1%).

Reaction of the sulphonyl chloride with diethylamine. Ethereal solutions of the pure sulphonyl chloride (8 g.) and diethylamine (18 c.c.) were carefully mixed, the insoluble material was filtered off, and the filtrate washed with water and dried ($CaCl_2$). Removal of the solvent yielded *NNN′N′*-tetraethylbut-2-enedisulphonamide, m. p. 55° (2·5 g.) (Found: C, 44·1; H, 8·0; N, 8·6; S, 19·6%). A rather smaller yield of the substance was obtained when starting with the crude sulphonyl chloride.

A pure chloroform solution of this substance (2·78 g.) was ozonised at 0° for 56 hr., diethylamine sulphate being deposited. The ozonide and other products were shaken with water for 36 hr. and then mixed with a slight excess of sodium carbonate. Extraction with ether afforded a very small amount of the unchanged amide; the aqueous layer was slightly acidified with dilute hydrochloric acid, a trace of acetic acid removed by extraction of the liquid again with ether, and the 2 : 4-dinitrophenylhydrazone of diethylsulphamoyl acetaldehyde prepared in the usual way. It was identical (m. p. and mixed m. p.) with that previously isolated (Found: C, 40·2; H, 4·4; N, 19·6%). The mother-liquors from the hydrazone were concentrated to about 250 c.c and all the sulphate was precipitated as the barium salt. The weight of the latter (1·9844 g.) was nearly equivalent to the sulphate (1·9900 g.) from one sulphamoyl group.

Reaction of the bisdiethylsulphamoylbutene with potassium *tert.*-butoxide, ethanolic sodium hydroxide, or diazomethane yielded either unchanged material or non-crystalline products. Methylation with *tert.*-butoxide and methyl iodide again yielded a non-crystalline syrup which appeared to contain trimethylated amides (Found: C, 46·2, 47·2; H, 8·7, 7·9; N, 8·1, — ; S, 18·5, 16·6. Calc. for $C_{14}H_{30}O_4N_2S_2$: C, 47·4; H, 8·6; N, 7·9; S, 18·1%). Catalytic hydrogenation was completely unsuccessful, at 75°/80 atm. It was not possible to prepare the reduction product, *NNN′N′*-tetraethylbutane-1 : 3-sulphonamide from 1 : 3-dibromobutane (Farquer and Perkin, *J.*, 1914, **105**, 1356) since, when the latter (30 g.) was boiled under reflux with a solution of hydrated sodium sulphite (75 g.) in water (20 c.c.), sodium 3-bromobutanesulphonate (49 g.) was obtained. This was shown by its conversion into the sulphonyl chloride, b. p. 110—130°/0·1 mm., and thence (in ether) into 3-bromo-*NN*-diethylbutanesulphonamide, b. p. 125°/0·5 mm. (somewhat impure) (C, 36·2; H, 6·9; N, 4·9; Br, 28·8; S, 11·2. Calc. for $C_8H_{18}O_2NBrS$: C, 35·3; H, 6·7; N, 5·1; Br, 29·4; S, 11·8%). Since the second bromine atom would not react further purification was not attempted.

Derivatives of Monosulphonic Acids.—*Reaction of* 1 : 3-*dichlorobut*-2-*ene* ***with potassium sulphite.*** A saturated solution of potassium sulphite, prepared as before from potassium hydroxide (2 × 36 g.) and sulphur dioxide, was boiled for 2 hr. under reflux with the dichlorobutene (20 g.). Cooling the liquid to room temperature afforded *potassium* 3-*chlorobut*-2-*ene*-1-*sulphonate* which was recrystallised from 80% ethanol (Found: C, 22·6; H, 3·2; Cl, 16·9; S, 15·2. $C_4H_6O_3ClSK$ requires C, 23·0; H, 2·9; Cl, 17·0; S, 15·4%). The *sodium* salt was similarly obtained by using sodium sulphite (Found: C, 25·1; H, 3·7; Cl, 18·1; S, 16·2. $C_4H_6O_3ClSNa$ requires C, 24·9; H, 3·1; Cl, 18·4; S, 16·6%).

3-Chlorobut-2-ene-1-sulphonyl chloride, b. p. 64—66°/0·5 mm., was prepared from the finely ground sodium salt (9 g.; dried at 100°) and phosphorus pentachloride (9·7 g.) (yield, 2 g.). Reaction with ammonia furnished 3-*chlorobut*-2-*ene*-1-*sulphonamide,* m. p. 76—78° (from ethanol) (Found: C, 28·6; H, 4·7; N, 8·3; Cl, 20·3; S, 18·8. $C_4H_8O_2NClS$ requires C, 28·3; H, 4·8; N, 8·3; Cl, 20·9; S, 18·9%). The compound was unchanged by being boiled with potassium *tert.*-butoxide. No recognisable product was obtained when it was heated for 2 hr. with concentrated sodium sulphite solution at 130°.

The analogous reaction of 1 : 3-dichlorobut-1-ene with potassium sulphite yielded 4-*chlorobut*-3-*en*-2-*ol,* b. p. 108°/536 mm. (41%) (Found: C, 45·5; H, 6·6; Cl, 32·6. C_4H_7OCl requires C, 45·1; H, 6·6; Cl, 33·3%).

Addition of sodium hydrogen sulphite to 1-*bromo*-2 : 3-*epoxybutane.* A mixture of the epoxy-derivative (15·8 g.), sodium hydrogen sulphite (11 g.) and water (22 c.c.) was shaken for 24 hr. *Sodium* 3-*bromo*-2-*hydroxybutane*-1-*sulphonate* separated with $\frac{1}{2}H_2O$ and was recrystallised from moist acetone (Found: C, 18·2; H, 3·7; Br, 30·3; S, 12·0; Na, 8·7; H_2O, 3·4. $C_4H_8O_4BrSNa,\frac{1}{2}H_2O$ requires C, 18·2; H, 3·4; Br, 30·2; S, 12·1; Na, 8·7; H_2O, 3·4%).

An intimate mixture of the anhydrous salt (7·2 g., prepared by heating the hydrated compound at 100° for 30 min.) and phosphorus pentachloride (14 g.) was heated at 100° for 15 min., chloroform added to the product, and the warm liquid filtered and then filtered again from the excess of phosphorus chloride which separated after cooling. Distillation of the volatile products afforded a residue of the *sultone,* m. p. 110° (0·5 g.), of the starting sulphonic acid. It was recrystallised from carbon tetrachloride (Found: C, 22·5; H, 3·5; Br, 36·6; S, 14·8. $C_4H_7O_3BrS$ requires C, 22·3; H, 3·3; Br, 37·2; S, 14·9%).

Experiments with 3-*Chloroprop*-2-*ene*-1-*sulphonic Acid Derivatives.*—A vigorously stirred mixture of 3-chloroallyl chloride (100 g.), crystalline sodium sulphite (227 g.), and water (90 c.c.) was boiled for 3 hr. under reflux. After cooling and filtration from deposited salts, the mother-liquor was evaporated to dryness. The combined solids were extracted with boiling 95% ethanol. Cooling the filtered alcoholic solution afforded *sodium* 3-*chloroprop*-2-*enesulphonate monohydrate* which was recrystallised from dilute ethanol (yield, 129 g.) (Found: C, 18·5; H, 3·3; Cl, 18·2; S, 16·2; Na, 11·7. $C_3H_4O_3ClSNa,H_2O$ requires C, 18·3; H, 3·1; Cl, 18·1; S, 16·3; Na, 11·7%). Conversion into the *sulphonyl chloride* was accomplished by mixing the dried (100°) sodium salt (10 g.) with phosphorus pentachloride (15·6 g.). When the spontaneous reaction had subsided chloroform (20 c.c.) was added and the mixture boiled for 30 min. The product had b. p. 66—68°/0·5 mm. (slight decomp.) (yield, 5·5 g., 56%) (Found: C, 20·6; H, 2·8; Cl, 40·5; S, 18·3. $C_3H_4O_2Cl_2S$ requires C, 20·6; H, 2·3; Cl, 40·5; S, 18·3%). The *amide,* m. p. 83° (yield, 61%), was prepared from the sulphonyl chloride in the usual way and recrystallised from ethanol (Found: C, 23·6; H, 4·1; N, 9·0; Cl, 22·8; S, 20·7%; *M*, 160. $C_3H_6O_2NClS$ requires C, 23·1; H, 3·9; N, 9·0; Cl, 22·8; S, 20·6%; *M*, 155·5). Addition of sodium ethoxide to an ethereal solution of the amide precipitated the *N*-sodio-derivative from which the amide was recovered unchanged when acid was added.

3-*Chloro*-NN-*diethylprop*-2-*ene*-1-*sulphonamide* was prepared by mixing ethereal solutions of the sulphonyl chloride (7 g.) and diethylamine (8·3 c.c.). There appeared to be two isomeric products: (i) (3·05 g.), b. p. 94—98°/0·1 mm., n_D^{20} 1·483, d^{20} 1·200 (Found: C, 39·3; H, 6·5; N, 6·8; Cl, 16·8; S, 15·3. $C_7H_{14}O_2NClS$ requires C, 39·7; H, 6·7; N, 6·6 Cl, 16·8; S, 15·2%), and (ii) (1·1 g.), b. p. 102—103°/0·1 mm., n_D^{20} 1·487, d^{20} 1·200 (Found: C, 39·6; H, 6·7; N, 6·9; Cl, 17·0; S, 15·3%). Both these compounds decolorised dilute permanganate solution moderately rapidly and bromine water rather more slowly. Condensation with sodium sulphite could not be effected. Fission by ozone yielded *NN*-diethylsulphamoylacetaldehyde.

3-Chloro-*NN*-diethylprop-2-enesuphonamide (8 g.) was shaken for 16 hr. with a solution from sodium (0·87 g.) in ethanol (25 c.c.). There was only a slight precipitate of sodium chloride and the resulting compound, b. p. 106—108°/0·1 mm., was evidently mainly unchanged starting amide contaminated with some of the compound described below (Found: C, 41·1; H, 7·0; N, 6·6; Cl, 16·3; S, 15·0%).

In a second experiment the mixture of the chlorosulphonamide (5 g.) and sodium ethoxide solution (50 c.c. containing 1 g. of sodium) was boiled for 2 hr. under reflux, affording a nearly quantitative yield of sodium chloride. The major product was 2-*ethoxy*-NN-*diethylprop*-2-*ene*-1-*sulphonamide*, b. p. 120°/0·1 mm. (4·25 g., 81%) (Found: C, 48·2; H, 8·9; N, 6·2; S, 14·3. $C_9H_{19}O_3NS$ requires C, 48·8; H, 8·6; N, 6·3; S, 14·5%). This compound decolorised both permanganate and bromine water. Ozonolysis afforded acetaldehyde (2 : 4-dinitrophenylhydrazone) (Found: C, 43·0; H, 3·9; N, 24·8. Calc. for $C_8H_8O_4N_4$: C, 42·8; H, 3·6; N, 25·0%). Sulphate ion was found in the aqueous solution of the ozonide but no other product could be identified.

"Zerewitinov" Determination of Active Hydrogen in NNN'N'-*Tetraethyl-propane-, -propene-, and -but-*2-*ene*-1 : 3-*disulphonamide.*—The last two columns of the annexed Table give the theoretical volumes of methane that could be evolved under the conditions of the experiment (temp. 18°).

Derivative.	Weight, g.	Pressure, mm.	CH_4 evolved, c.c.	Vol. calc. (c.c.) for 1H	for 2H
Propane	0·077	745	1·6	13·1	26·2
,,	0·098	745	4·6	16·6	33·2
Propene	0·092	753	32·1	15·3	30·6
,,	0·076	745	27·0	12·9	25·8
But-2-ene	0·086	753	15·9	13·7	27·4
,,	0·087	753	16·8	13·9	27·8

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