10. *Alkenesulphonic Acids: Preparation and Reactions.*

By A. Lambert and J. D. Rose.

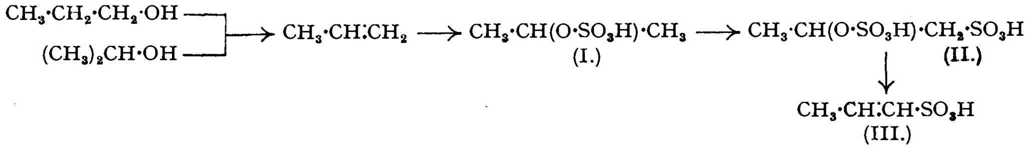
Treatment of both *n*- and *iso*-propyl alcohol with 65% oleum followed by alkali gives *prop*-1-*ene*-1-*sulphonic acid*, also prepared by interaction of sodium 2-hydroxypropane-1-sulphonate (from propylene oxide and sodium hydrogen sulphite) with phosphorus pentachloride, followed by treatment of the product with alkali. *Prop*-1-*ene*-2-*sulphonic acid* is obtained from " acetone bisulphite " and thionyl chloride–pyridine, followed by heating with alkali. Addition reactions of the unsaturated linkage of alkenesulphonic acids are described, including addition of ammonia, piperidine, nitromethane, and ethyl malonate, and Diels–Alder reaction with *cyclo*pentadiene.

ALTHOUGH ethylenesulphonic acid has been known since 1897 (Kohler, *Amer. Chem. J.*, 1897, **19**, 728; 1898, **20**, 680; 1899, **21**, 353), higher homologues do not appear to have been described, and the chemistry of the alkenesulphonic acids has not been extensively investigated.

Arising from other work in these laboratories, an interest in 2-aminoalkanesulphonic acids prompted an investigation into the addition reactions of ethylenesulphonic acid and its esters, and an extension of the work into the field of the propenesulphonic acids and higher homologues.

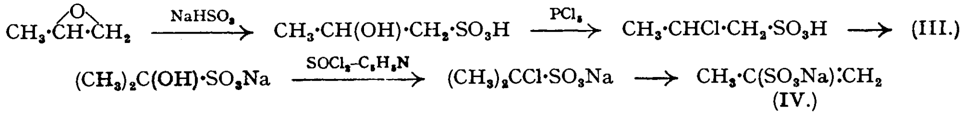
Ethylenesulphonic acid was prepared by hydrolysis of ethane-1 : 2-disulphonyl chloride (Kohler, *ibid.*, 1897, **19**, 734) by the method of Alderman and Hanford (U.S.P. 2,348,705).

Prop-1-*ene*-1-*sulphonic acid* (III) was obtained by treatment of both *n*- and *iso*-propyl alcohol with 65% oleum, followed by interaction of the resulting 1-sulphopropyl-2-sulphate (II) with alkali. The formation of the same propenesulphonic acid from both the normal and the *iso*-alcohol indicates that the intermediate in each case is propylene, to which sulphuric acid adds giving *iso*propyl sulphate (I) which is then sulphonated on the β-carbon atom.



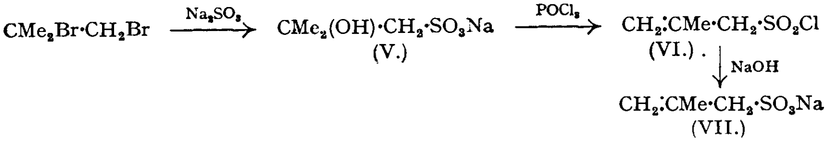
$$\left.\begin{array}{l}\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH}\\ \mathrm{(CH_3)_2CH{\cdot}OH}\end{array}\right] \longrightarrow \mathrm{CH_3{\cdot}CH{:}CH_2} \longrightarrow \underset{\text{(I.)}}{\mathrm{CH_3{\cdot}CH(O{\cdot}SO_3H){\cdot}CH_3}} \longrightarrow \underset{\text{(II.)}}{\mathrm{CH_3{\cdot}CH(O{\cdot}SO_3H){\cdot}CH_2{\cdot}SO_3H}} \longrightarrow \underset{\text{(III.)}}{\mathrm{CH_3{\cdot}CH{:}CH{\cdot}SO_3H}}$$

An attempt to synthesise the isomeric *prop*-1-*ene*-2-*sulphonic acid* (as IV) by interaction of propylene oxide and sodium hydrogen sulphite followed by indirect dehydration, also yielded (III); (IV) was eventually obtained, although in low yield, from sodium 2-hydroxypropane-2-sulphonate ("acetone bisulphite") by successive treatment with thionyl chloride in pyridine and alkali. An attempt was made to prepare 2-methylprop-1-ene-1-sulphonic acid from 1 : 2-dibromo-2-methylpropane. This was caused to react with sodium sulphite, giving sodium 2-hydroxy-2-methylpropane-1-sulphonate (V), converted by phosphorus oxychloride into the sulphonyl chloride (VI), hydrolysis of which gave sodium 2-methylprop-2-ene-1-sulphonate (VII) identical with that described by Archer, Malkemus, and Suter (*J. Amer. Chem. Soc.*, 1941, **63**, 1597).



$$\mathrm{CH_3{\cdot}\overset{O}{CH{\cdot}CH_2}} \xrightarrow{\mathrm{NaHSO_3}} \mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3H} \xrightarrow{\mathrm{PCl_5}} \mathrm{CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}SO_3H} \longrightarrow \text{(III.)}$$

$$\mathrm{(CH_3)_2C(OH){\cdot}SO_3Na} \xrightarrow{\mathrm{SOCl_2{-}C_5H_5N}} \mathrm{(CH_3)_2CCl{\cdot}SO_3Na} \longrightarrow \underset{\text{(IV.)}}{\mathrm{CH_3{\cdot}C(SO_3Na){:}CH_2}}$$



$$\mathrm{CMe_2Br{\cdot}CH_2Br} \xrightarrow{\mathrm{Na_2SO_3}} \underset{\text{(V.)}}{\mathrm{CMe_2(OH){\cdot}CH_2{\cdot}SO_3Na}} \xrightarrow{\mathrm{POCl_3}} \underset{\text{(VI.)}}{\mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}SO_2Cl}} \xrightarrow{\mathrm{NaOH}} \underset{\text{(VII.)}}{\mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}SO_3Na}}$$

Attempts to obtain αβ-unsaturated sulphonic acids from higher alcohols (*e.g.*, butyl, amyl) by treatment with oleum or with a dioxan–sulphur trioxide complex, followed by alkali, gave only saturated products. Similarly, an attempt to prepare a butenesulphonic acid from but-2-ene and dioxan–sulphur trioxide, followed by alkali, also failed (cf. Suter, Evans, and Kiefer, *J. Amer. Chem. Soc.*, 1938, **60**, 538).

The *methyl* and the *ethyl* ester of prop-1-enesulphonic acid were readily prepared by interaction of the sulphonyl chloride with the sodium alkoxide, but this method, when applied to ethylenesulphonic acid as described by Alderman and Hanford (*loc. cit.*) gave very low yields, and in this case the *methyl* ester was more advantageously prepared from the acid and diazomethane. Prop-1-ene-1-sulphonyl chloride reacted readily with ammonia and aniline, giving respectively the *amide* and anilide; the latter is apparently identical with the anilide obtained by Autenrieth and Rudolph (*Ber.*, 1901, **34**, 3467) from propene-1 : 2-disulphonyl chloride and aniline.

Methyl ethylenesulphonate reacted vigorously with nitromethane in the presence of a little piperidine, giving the adduct, *methyl tri*-(2-*sulphoethyl*)*nitromethane* (VIII). A similar addition reaction occurred with ethyl malonate, the product being a mixture of the *mono*-(IX) and *di-adduct* (X).

$$\underset{\text{(VIII.)}}{\mathrm{NO_2{\cdot}C(CH_2{\cdot}CH_2{\cdot}SO_3Me)_3}} \qquad \underset{\text{(IX.)}}{\mathrm{Me{\cdot}SO_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2}} \qquad \underset{\text{(X.)}}{\mathrm{(Me{\cdot}SO_3{\cdot}CH_2{\cdot}CH_2)_2C(CO_2Et)_2}}$$

Sodium prop-1-ene-1-sulphonate and ammonia, heated together in a sealed tube, gave 2-aminopropanesulphonic acid, identical with that obtained by Heath and Piggott (*J.*, **1947**, 1481) by reduction of 2-nitropropane-1-sulphonic acid. A similar addition reaction occurred with piperidine, but attempts to cause aniline to react were unsuccessful.

In the Diels–Alder reaction, methyl ethylenesulphonate and *cyclo*pentadiene gave *methyl* 2 : 5-endo*methylene*cyclo*hex*-3-*ene*-1-*sulphonate*. Attempts to cause propene-1-sulphonic acid or ethyl prop-1-ene-1-sulphonate to react with toluene in the presence of aluminium chloride or boron trifluoride were unsuccessful, although Suter *et al.* (*J. Amer. Chem. Soc.*, 1945, **67**, 43) have recorded the successful condensation of 2-methylprop-2-ene-1-sulphonate with alkylbenzenes.

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. All m. p.s are uncorrected.

Prop-1-*ene*-1-*sulphonic Acid*.—(a) *From* iso*propyl alcohol*. *iso*Propyl alcohol (60 g.) was stirred at −5° while oleum (67·5%; 120 g.) was added slowly down the side of the flask. The temperature of the mixture was raised to 20°, and a second portion of oleum (67·5%; 125 g.) added. After being stirred overnight at 20°, the product was poured on ice and neutralised with barium carbonate. It was then heated at 60° for 2 hours with excess of barium hydroxide [$Ba(OH)_2,8H_2O$; 158 g.], filtered, neutralised with carbon dioxide, and again filtered. Evaporation to dryness gave crude barium prop-1-ene-1-sulphonate (75 g.); this was treated with an equivalent amount of sulphuric acid in water, filtered, and evaporated to dryness. Distillation of the product gave *prop*-1-*ene*-1-*sulphonic acid* (21·7 g.) as a colourless liquid, which darkened on keeping, b. p. 135°/0·5 mm. (Found : S, 26·4. $C_3H_6O_3S$ requires S, 26·2%). The *benzyl*iso*thiouronium* salt formed fine colourless needles from acetone, m. p. 159—160° (Found : C, 45·7 ; H, 5·3 ; N, 10·1. $C_3H_6O_3S,C_8H_{10}N_2S$ requires C, 45·8 ; H, 5·6 ; N, 9·7%).

(b) *From* n-*propyl alcohol*. *n*-Propyl alcohol (60 g.) was stirred at 10° while oleum (67·5%; 135 g.) was added slowly down the side of the flask. The mixture was then warmed to 20°, and a second portion of oleum (67·5%; 135 g.) added. After being stirred overnight, the mixture was worked up as described in (a), giving prop-1-ene-1-sulphonic acid (35·4 g.), b. p. 135°/0·5 mm. The benzyl*iso*thiouronium salt had m. p. and mixed m. p. with the specimen described above, 159—160°.

(c) *From propylene oxide*. Propylene oxide (29 g.) was shaken with a solution of sodium hydrogen sulphite (57 g.) in water (135 c.c.) until a clear solution was obtained. Evaporation to dryness and extraction of the residue with 95% alcohol gave *sodium* 2-*hydroxypropane*-1-*sulphonate* (Found : S, 20·0; Na, 14·0. $C_3H_7O_4SNa$ requires S, 19·7; Na, 14·2%). A mixture of sodium 2-hydroxypropane-1-sulphonate (20 g.) and phosphorus pentachloride (55 g.) was ground until reaction ceased, and then poured into iced water. The oily product was separated and boiled for 1 hour with a solution of sodium carbonate (25 g.) in water (100 c.c.). After neutralisation with hydrochloric acid and evaporation to dryness, the residue was extracted with 85% aqueous alcohol. Evaporation of the alcoholic solution gave sodium prop-1-ene-1-sulphonate (13 g.). The benzyl*iso*thiouronium salt had m. p. and mixed m. p. with the specimen described above, 159—160°. The anilide, prepared through the sulphonyl chloride, had m. p. and mixed m. p. with the specimen described below, 91°.

2-*Chloropropane*-2-*sulphonic Acid*.—Thionyl chloride (47·6 g.) was added dropwise with stirring to a mixture of powdered sodium 2-hydroxypropane-2-sulphonate ("acetone bisulphite"; 32·4 g.), anhydrous pyridine (31·6 g.), and dry ether (60 c.c.) at 0°. After being stirred at 0° for 16 hours, the mixture was heated at 30—35° for 1 hour and poured on ice. Evaporation of the ethereal solution gave a dark brown oil (3 g.) which decomposed on attempted distillation. The aqueous solution was made strongly alkaline with sodium hydroxide, distilled in steam to remove the pyridine, and evaporated to dryness. Extraction of the residue with 85% aqueous alcohol gave *sodium* 2-*chloropropane*-2-*sulphonate* which crystallised from absolute alcohol in colourless plates (7 g.) (Found : Cl, 19·3; S, 18·4. $C_3H_6O_3ClSNa$ requires Cl, 19·4; S, 17·8%). The *benzyl*iso*thiouronium* salt formed colourless needles from acetone, m. p. 175—176° (Found : C, 40·8; H, 5·6; N, 8·9. $C_3H_7O_3ClS,C_8H_{10}N_2S$ requires C, 40·7; H, 5·2; N, 8·7%).

Propene-2-*sulphonic Acid*.—Sodium 2-chloropropane-2-sulphonate (1 g.) was heated at 100° with a solution of potassium hydroxide (1·6 g.) in methyl alcohol (5 c.c.) for 2½ hours. After neutralisation with hydrochloric acid, the product was evaporated to dryness and extracted with 95% alcohol. Evaporation of the alcoholic solution gave crude sodium propene-2-sulphonate. The *benzyl*iso*thiouronium* salt formed colourless needles from acetone, m. p. 137—138° (Found : C, 46·2; H, 5·5; N, 10·0. $C_3H_6O_3S,C_8H_{10}N_2S$ requires C, 45·8; H, 5·6; N, 9·7%).

Sodium 2-*Methylprop*-2-*ene*-1-*sulphonate*. *Attempted Preparation of Sodium* 2-*Methylprop*-1-*ene*-1-*sulphonate*.—1 : 2-Dibromo-2-methylpropane (108 g.) was added slowly with stirring to a boiling solution of sodium sulphite (anhydrous; 136 g.) in water (290 c.c.). After refluxing for 7 hours, the solution was filtered, extracted with ether, and concentrated, giving sodium 2-hydroxy-2-methylpropane-1-sulphonate (56 g.). A portion of this (25 g.) was heated at 100° with phosphorus oxychloride (50 g.) for 2½ hours; after cooling, excess of phosphorus oxychloride was decomposed with iced water and the product extracted with chloroform. The chloroform solution was dried ($CaCl_2$) and distilled, giving 2-methylprop-2-ene-1-sulphonyl chloride (6 g.), b. p. 84—85°/15 mm. (Archer, Malkemus, and Suter, *loc. cit.*, give b. p. 83—84°/15 mm.). Hydrolysis of this product by boiling N/1-sodium hydroxide solution gave sodium 2-methylprop-2-ene-1-sulphonate. The benzyl*iso*thiouronium salt formed colourless needles from water, m. p. 154° (Archer *et al.*, *loc. cit.*, give m. p. 154°).

Methyl Ethylenesulphonate.—A solution of ethylenesulphonic acid (4·3 g.) in dry ether (100 c.c.) was treated at 0° with a solution of diazomethane in ether prepared from nitrosomethylurea (10 g.) (Arndt, *Org. Synth.*, Coll. Vol. II, p. 165). The solution was washed with water, dried ($CaCl_2$), and distilled, giving *methyl ethylenesulphonate* (2·85 g.), b. p. 84—85°/12 mm. (Found: C, 30·5; H, 5·1; S, 26·0. $C_3H_6O_3S$ requires C, 29·5; H, 4·9; S, 26·2%).

Methyl Tri-(2-*sulphoethyl*)*nitromethane.*—A mixture of nitromethane (0·6 g.) and methyl ethylenesulphonate (1·2 g.) was treated with a saturated solution of potassium hydroxide in methanol (2 drops). When the reaction had ceased, the product was neutralised with dilute acetic acid, washed with water, and crystallised from methyl ethyl ketone, giving *methyl tri-*(2-*sulphoethyl*)*nitromethane* in colourless needles (0·5 g.), m. p. 175° (Found: C, 28·6; H, 5·0; N, 3·4. $C_{10}H_{21}O_{11}NS_3$ requires C, 28·1; H, 4·9; N, 3·3%).

Methyl 3 : 3-*Dicarbethoxypropane*-1-*sulphonate and* 3 : 3-*Dicarbethoxypentane*-1 : 5-*disulphonate.*—A mixture of methyl ethylenesulphonate (1·65 g.) and ethyl malonate (2·16 g.) was treated with 5 drops of a 5% solution of sodium ethoxide in alcohol. When the exothermic reaction was complete, the mixture was kept at room temperature for 45 minutes, then washed successively with dilute aqueous hydrochloric acid, dilute aqueous sodium hydrogen carbonate, and water, and dried ($CaCl_2$). Distillation gave *methyl* 3 : 3-*dicarbethoxypropane*-1-*sulphonate* as a colourless liquid (0·6 g.), b. p. 132—134°/0·2 mm. (Found: C, 42·5; H, 6·4; S, 11·8. $C_{10}H_{18}O_7S$ requires C, 42·5; H, 6·4; S, 11·3%). Crystallisation of the residue (1·5 g.) from ether–methanol ("Drikold") gave *methyl* 3 : 3-*dicarbethoxypentane*-1 : 5-*disulphonate,* m. p. 46—47° (Found: C, 38·7; H, 5·9; S, 16·2. $C_{13}H_{24}O_{10}S_2$ requires C, 38·6; H, 5·9; S, 15·8%).

Methyl 2 : 5-endo*Methylene*cyclo*hex*-3-*ene*-1-*sulphonate.*—A mixture of methyl ethylenesulphonate (6·7 g.), *cyclo*pentadiene (4 g.), and toluene (15 c.c.) was heated in a sealed tube at 140—150° for 10 hours. Distillation then gave *methyl* 2 : 5-endo*methylene*cyclo*hex*-3-*ene*-1-*sulphonate* as a colourless liquid (7·7 g.), b. p. 84—86°/0·08 mm. (Found: C, 51·3; H, 6·4; S, 16·8. $C_8H_{12}O_3S$ requires C, 51·1; H, 6·4; S, 17·0%).

Methyl and Ethyl Prop-1-*ene*-1-*sulphonate.*—A solution of sodium methoxide from sodium (0·93 g.) in methyl alcohol (25 c.c.) was added dropwise with stirring to a solution of prop-1-ene-1-sulphonyl chloride (5·2 g.) in ether (20 c.c.) at 0—10°. After being stirred for 45 minutes at 20°, the product was filtered, neutralised with 50% aqueous acetic acid, and evaporated to dryness. The residue was extracted with ether, and the ethereal solution distilled, giving *methyl prop*-1-*ene*-1-*sulphonate* (4·1 g.) as a colourless liquid, b. p. 110—112°/10 mm. (Found: C, 35·7; H, 6·6. $C_4H_8O_3S$ requires C, 35·3; H, 5·9%). The *ethyl* ester formed similarly by using sodium ethoxide had b. p. 118—122°/14 mm. (Found: C, 39·3; H, 6·7. $C_5H_{10}O_3S$ requires C, 40·0; H, 6·7%).

Prop-1-*ene*-1-*sulphonyl Chloride.*—Crude barium prop-1-ene-1-sulphonate (10 g.) was heated with phosphorus oxychloride (20 g.) at 100° for 3 hours. After cooling, chloroform was added and the whole poured into iced water. When reaction had ceased, the chloroform solution was washed with water, dried ($CaCl_2$), and distilled, giving *prop*-1-*ene*-1-*sulphonyl chloride* (3·4 g.) as a colourless liquid, b. p. 80—82°/12 mm. (Found: C, 26·0; H, 3·9; Cl, 25·1. $C_3H_5O_2SCl$ requires C, 25·7; H, 3·6; Cl, 25·4%). The anilide formed colourless prisms from aqueous alcohol, m. p. 91° (Found: C, 54·7; H, 5·6; N, 7·5; S, 16·6. Calc. for $C_9H_{11}O_2NS$: C, 54·8; H, 5·6; N, 7·1; S, 16·2%). The *amide,* formed by treatment of the chloride in dry ether with excess of dry ammonia at 0—10°, had b. p. 112°/0·2 mm. and crystallised from ether–light petroleum (b. p. 40—60°) in colourless prisms, m. p. 50—52° (Found: C, 29·6; H, 5·9; N, 11·6. $C_3H_7O_2NS$ requires C, 29·7; H, 5·8; N, 11·6%).

2-*Aminopropane*-1-*sulphonic Acid.*—Sodium propene-1-sulphonate (6·8 g.) in water (15 c.c.) was heated in a sealed tube with ammonia solution (*d* 0·88; 33 c.c.) at 150° for 5 hours. The product was evaporated to dryness, and the residue treated with concentrated hydrochloric acid. After filtration and removal of the hydrochloric acid, treatment of the residue with absolute alcohol gave 2-aminopropane-1-sulphonic acid (2·8 g.) which crystallised from aqueous alcohol, m. p. and mixed m. p. with an authentic specimen prepared according to Heath and Piggott (*loc. cit.*) *ca.* 325° (decomp.) (Found: C, 26·6; H, 6·6; N, 10·1; S, 22·9. Calc. for $C_3H_9O_3NS$: C, 25·9; H, 6·5; N, 10·1; S, 23·0%). Gabriel and Ohle (*Ber.*, 1906, **39**, 2891) give m. p. *ca.* 330° (decomp.).

2-*Piperidinopropanesulphonic Acid.*—Crude barium propene-1-sulphonate (5 g.) in aqueous alcohol was boiled under reflux with piperidine (11 c.c.) for 5 hours. The product was evaporated to dryness, treated with concentrated hydrochloric acid, and filtered. After removal of the hydrochloric acid, crystallisation of the residue from aqueous alcohol gave 2-*piperidinopropanesulphonic acid* (2·3 g.) in small colourless needles, m. p. 312° (decomp.) (Found: C, 46·3; H, 7·9; N, 6·8; S, 15·8. $C_8H_{17}O_3NS$ requires C, 46·4; H, 8·2; N, 6·8; S, 15·45%).

2-*Amino*-2-*phenylethane*-1-*sulphonic Acid.*—A suspension of sodium 2-phenylethylenesulphonate (Suter and Milne, *J. Amer. Chem. Soc.*, 1943, **65**, 582; 5 g.) in ammonia solution (*d* 0·88; 30 c.c.) was heated in a sealed tube at 150° for 7 hours. The product was worked up as described above for 2-aminopropane-1-sulphonic acid and crystallised from water, giving 2-*amino*-2-*phenylethane*-1-*sulphonic acid,* m. p. 306—308° (decomp.) (Found: C, 47·8; H, 5·5; N, 7·1. $C_8H_{11}O_3NS$ requires C, 47·8; H, 5·5; N, 7·0%).

2-*Piperidino*-2-*phenylethane*-1-*sulphonic Acid.*—A solution of sodium 2-phenylethylene-1-sulphonate (3 g.) in a mixture of water (15 c.c.) and piperidine (5 c.c.) was refluxed for 16 hours. The product was worked up as described above for 2-aminopropane-1-sulphonic acid and crystallised from alcohol, giving a small yield of 2-*piperidino*-2-*phenylethanesulphonic acid,* m. p. *ca.* 292° (decomp.) (Found: C, 58·1; H, 7·3; N, 5·4. $C_{13}H_{19}O_3NS$ requires C, 58·0; H, 7·1; N, 5·2%).

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