

296. *Aliphatic Nitro-compounds. Part XVII. Reaction of Nitro-paraffins with Unsaturated Sulphones.**

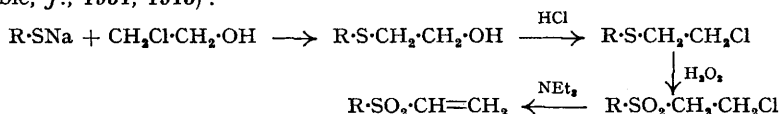
By G. D. BUCKLEY, (Mrs.) J. L. CHARLISH, and J. D. ROSE.

Nitro-paraffins react with vinyl sulphones in the presence of alkaline catalysts to yield 3-nitroalkyl sulphones. The use of small amounts of catalyst results in the replacement of all the α -hydrogen atoms of the nitro-paraffin to give nitro-monosulphones from secondary nitro-paraffins, nitro-disulphones from primary nitro-paraffins, and nitro-trisulphones from nitromethane. The use of sufficient alkali to convert the whole of the nitro-paraffin into its salt results in the formation of mainly mononitro-sulphones from primary nitro-paraffins. 2-Halogenoethyl sulphones with an equivalent of alkali may be used in place of vinyl sulphones. Divinyl sulphone reacts in a similar manner: with secondary nitro-paraffins it gives 3:3'-dinitrodialkyl sulphones, but with primary nitro-paraffins the products are polymeric. Catalytic reduction of the nitro-sulphones affords the corresponding amino-sulphones, and their alkali metal salts give 3-keto-sulphones on treatment with mineral acids.

A convenient synthesis of vinyl sulphones is described.

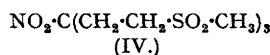
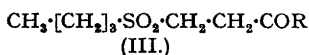
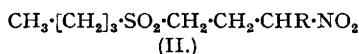
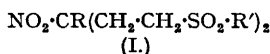
PREVIOUS authors have described the addition of primary and secondary nitro-paraffins to $\alpha\beta$ -unsaturated nitro-compounds (this series, Part VIII), cyanides (Bruson and Riener, *J. Amer. Chem. Soc.*, 1943, **65**, 23), and ketones and esters (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889; Sonn, *Ber.*, 1935, **68**, 148; Michael, *Ber.*, 1896, **29**, 1794), but no attempt to cause them to react with vinyl sulphones appears to have been recorded.

Although divinyl sulphone is a well-known compound, the simple monovinyl sulphones appear to be described only in the patent literature (B.P. 442,524, I.G. Farbenindustrie). Since the method described seemed unsuitable for use on the laboratory scale, the monovinyl sulphones were prepared by the following route based on the usual synthesis of divinyl sulphone (Alexander and McCombie, *J.*, 1931, 1913):



This method gave *methyl*, *n-butyl*, *isobutyl*, and *p-tolyl vinyl sulphones* in satisfactory yield.

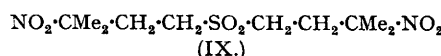
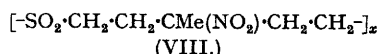
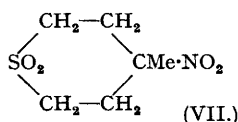
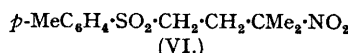
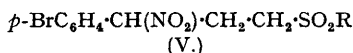
Nitroethane reacted readily with two molecules of *n-butyl vinyl sulphone* in presence of a small amount of potassium hydroxide to give a 75% yield of 3-nitro-1:5-di-(*n-butylsulphonyl*)-3-methylpentane (I; R = Me, R' = Bu) which was reduced catalytically to the corresponding amine. In presence of one equivalent of sodium hydroxide, nitroethane reacted with one molecule of *n-butyl vinyl sulphone* to give 3-nitrodibutyl sulphone (II; R = Me) in 45% yield, together with a 13% yield of the dinitrosulphone (I; R = Me, R' = Bu). It was not possible to suppress completely the formation of the dinitrosulphone even by the use of a large excess of alkali. 3-Nitrodibutyl sulphone was isolated as an oil by acidification of the alkaline solution with acetic or carbonic acids, but acidification with mineral acids precipitated 3-ketodibutyl sulphone (III; R = Me), formed by a Nef hydrolysis (*Annalen*, 1894, **280**, 263), which appears to be unusually facile in the case of γ -nitro-sulphones. The nitro-sulphone could not be purified by distillation or crystallisation, but was reduced catalytically to the easily characterised 3-aminodibutyl sulphone (*hydrochloride*).



Similarly, 1-nitropropane reacted with *n-butyl vinyl sulphone* to give 3-nitro-1:5-di-(*n-butylsulphonyl*)-3-ethylpentane (I; R = Et, R' = Bu), *n-butyl 3-nitroamyl sulphone* (II; R = Et), and *n-butyl 3-ketoamyl sulphone* (III; R = Et). Reaction of the sodium salt of *n-butyl 3-nitroamyl sulphone* with aqueous bromine gave *n-butyl 3-bromo-3-nitroamyl sulphone*. Interaction of nitromethane and methyl vinyl sulphone in presence of a little potassium hydroxide gave a 50% yield of *tris*-(2-methylsulphonylethyl)nitromethane (IV), which was reduced catalytically to *tris*-(2-methylsulphonylethyl)methylamine. *p*-Bromophenylnitromethane with methyl vinyl sulphone and a little methyltriethylammonium hydroxide gave *methyl 3-nitro-3-p-bromophenylpropyl sulphone* (V; R = Me) in 50% yield, and the sodium salt of

* Patent application pending.

p-bromophenylnitromethane reacted with isobutyl vinyl sulphone to give isobutyl 3-nitro-3-*p*-bromophenylpropyl sulphone (V; R = CH₂·CHMe₂) in 30% yield. 1- and 2-Nitropropane with *p*-tolyl vinyl sulphone gave respectively 3-nitro-1:5-di-*p*-tolylsulphonyl-3-ethylpentane (I; R = Et, R' = *p*-MeC₆H₄) and 2-nitro-4-*p*-tolylsulphonyl-2-methylbutane (VI).



The behaviour of divinyl sulphone was next examined. It was hoped that interaction of equimolecular proportions of nitroethane and divinyl sulphone would yield the cyclic sulphone (VII), but although a variety of conditions were tried the only products isolated were polymeric, presumably of type (VIII). The expected cyclisation is apparently hindered by steric factors. Divinyl sulphone reacted normally with two molecules of 2-nitropropane to give 3:3'-dinitro-3:3'-dimethyldibutyl sulphone (IX) which, on catalytic reduction, gave 3:3'-diamino-3:3'-dimethyldibutyl sulphone.

Experiments with 2-chloroethyl *n*-butyl sulphone showed that 2-halogenoethyl sulphones with an equivalent of sodium hydroxide could be used instead of vinyl sulphones, but the yields were lower, e.g., 1-nitropropane reacted with 2-chloroethyl *n*-butyl sulphone to give 8% of 3-nitro-1:5-di-(*n*-butylsulphonyl)-3-ethylpentane (I; R = Et, R' = Bu) and 32% of *n*-butyl 3-nitroamyl sulphone (II; R = Et).

EXPERIMENTAL

Analyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Preparation of Alkyl Vinyl Sulphones.

Methyl Vinyl Sulphone.—Hydrogen peroxide (300 g. of 30%) was added dropwise to a solution of methyl 2-chloroethyl sulphide (135 g.) (*Org. Synth.*, Coll. Vol. 2, 136) in acetic acid (300 c.c.) at such a rate that the solution refluxed gently without external heating. After a further 3 hours' heating on the steam-bath, the solvents were removed by distillation under reduced pressure. The viscous residue, consisting essentially of methyl 2-chloroethyl sulphone, was added during 1 hour to a stirred solution of triethylamine (175 c.c.) in anhydrous ether (320 c.c.) and the mixture was stirred for a further 18 hours. The ethereal solution was decanted from the dark mass of triethylamine hydrochloride which was then extracted with dry acetone. The ether and acetone solutions were combined and fractionated to give methyl vinyl sulphone as a colourless oil (81 g.), b. p. 115–117°/19 mm. (Found: S, 29·8. C₃H₆O₂S requires S, 30·2%).

***n*-Butyl Vinyl Sulphone.**—2-Chloroethyl *n*-butyl sulphone was prepared by oxidation of the corresponding sulphide according to Whitner and Reid (*J. Amer. Chem. Soc.*, 1921, **43**, 637). The crude sulphone (158 g.) was added during 1 hour to a stirred solution of triethylamine (135 c.c.) in ether (250 c.c.) and the mixture was stirred for a further 18 hours. The solution was then filtered from triethylamine hydrochloride and distilled to give *n*-butyl vinyl sulphone as a colourless oil (104 g.), b. p. 135°/15 mm. (Found: S, 21·3. C₆H₁₂O₂S requires S, 21·6%).

isoButyl Vinyl Sulphone.—Ethylene chlorohydrin (99 g. of 30%) was added to a suspension of isobutylthiol (37 g.) in aqueous sodium hydroxide (115 g. of 15%) and refluxed for 1 hour. The mixture was then freed from volatile impurities by steam distillation and, after cooling, the residual oil, consisting of crude 2-hydroxyethyl isobutyl sulphide (40 g.), was separated, mixed with concentrated hydrochloric acid (60 c.c.) and refluxed for 4 hours. After cooling, the oily product was separated, dried (CaCl₂), and distilled, giving 2-chloroethyl isobutyl sulphide as a vesicant oil (39 g.), b. p. 84–85°/25 mm. (Found: Cl, 23·1. C₆H₁₃ClS requires Cl, 23·3%). The chloroethyl sulphide (38 g.) was oxidised to 2-chloroethyl isobutyl sulphone and this was converted into the vinyl sulphone as described above for the isomer. isoButyl vinyl sulphone was obtained as a colourless oil (22 g.), b. p. 132–133°/19 mm. Found: S, 21·8. C₆H₁₂O₂S requires S, 21·6%).

***p*-Tolyl Vinyl Sulphone.**—Hydrogen peroxide (145 g. of 30%) was added slowly to a boiling solution of *p*-tolyl 2-chloroethyl sulphide (36 g.) (Kohn and Fromm, *Ber.*, 1921, **54**, 322) in acetic acid (105 c.c.) and the mixture was refluxed for 2 hours. Water and acetic acid were removed under reduced pressure, and the residual crude *p*-tolyl 2-chloroethyl sulphone (42 g.) was dissolved in dry ether (80 c.c.) and added cautiously to a solution of triethylamine (40 c.c.) in dry ether (80 c.c.). Separation of triethylamine hydrochloride began at once, and, after standing overnight, the solution was filtered and evaporated to dryness. The residue was washed with cold water, giving a white, crystalline solid (25 g.) which, after crystallisation from alcohol, gave *p*-tolyl vinyl sulphone as white needles, m. p. 66° (I.G. Farbenindustrie, *loc. cit.*, give m. p. 65–66°).

Reaction with Nitro-paraffins.

3-Nitro-1:5-di-(*n*-butylsulphonyl)-3-methylpentane.—Aqueous potassium hydroxide (1 c.c. of 33%) was added to a solution of nitroethane (3·5 g.) and *n*-butyl vinyl sulphone (15 g.) in alcohol (40 c.c.) and refluxed for 16 hours. After cooling, the precipitate was collected (13·25 g.) and crystallised from

alcohol, giving 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane (I; R = Me, R' = Bu) as colourless needles, m. p. 105° (Found : N, 4.1; S, 17.1. $C_{14}H_{29}O_6NS_2$ requires N, 3.8; S, 17.25%).

3-Nitrodibutyl Sulphone.—Aqueous sodium hydroxide (20 c.c. of 32%) was slowly added to a stirred and ice-cooled mixture of nitroethane (15 g.) and water (80 c.c.). When a homogeneous solution had formed, *n*-butyl vinyl sulphone (30 g.) was added and the mixture stirred at 20° for 3 hours. The solid precipitate (10 g.) was collected and washed with water; it was identical with the 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane described above. The alkaline filtrate was washed with ether to remove impurities, acidified with acetic acid (13 c.c.), and extracted with ether. The ethereal extract was dried and evaporated, leaving 3-nitrodibutyl sulphone (II; R = Me) as a pale yellow oil (21 g.) which could not be crystallised and decomposed on attempted distillation. With nitrous acid it gave a blue colouration, indicating the presence of a secondary nitro-group.

3-Aminodibutyl Sulphone.—Crude 3-nitrodibutyl sulphone (23 g.) in methyl alcohol (200 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was distilled, giving 3-aminodibutyl sulphone (8.6 g.) as a colourless, feebly basic oil, b. p. 122°/0.5 mm. The hydrochloride formed colourless granules, m. p. 145° (Found : Cl, 15.8. $C_8H_{18}O_3NS.HCl$ requires Cl, 15.65%). The phenylurea formed colourless granules from benzene, m. p. 107° (Found : N, 9.15; S, 10.1. $C_{15}H_{24}O_3N_2S$ requires N, 9.0; S, 10.25%).

3-Ketodibutyl Sulphone (III; R = Me).—A solution of the sodium salt of 3-nitrodibutyl sulphone, prepared from nitroethane (3.75 g.) and *n*-butyl vinyl sulphone (7.5 g.) as described above, was run into a stirred solution of sulphuric acid (6.5 c.c.) in water (30 c.c.) during 30 minutes, the temperature being kept at 10–15°. The crystalline precipitate was collected (3.8 g.) and recrystallised from a little methyl alcohol at –20°, giving the ketone as colourless plates, m. p. 59° (Found : S, 16.6. $C_8H_{16}O_3S$ requires S, 16.65%). The 2 : 4-dinitrophenylhydrazones, m. p. 147°, formed yellow needles from alcohol (Found : N, 14.85; S, 8.6. $C_{14}H_{20}O_6N_4S$ requires N, 15.05; S, 8.6%).

3-Amino-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane.—3-Nitro-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane (5.8 g.) was suspended in 2-ethoxyethyl alcohol (100 c.c.) and shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased; during the reaction the solid gradually passed into solution. The filtered solution was concentrated under reduced pressure and the residue crystallised from benzene, giving colourless crystals of the amine, m. p. 116° (Found : N, 4.1; S, 19.1. $C_{14}H_{31}O_4NS_2$ requires N, 4.15; S, 18.8%). The acetyl derivative formed colourless needles from water, m. p. 164° (Found : S, 16.35. $C_{16}H_{33}O_6NS_2$ requires S, 16.7%).

3-Nitro-1 : 5-di-(*n*-butylsulphonyl)-3-ethylpentane and *n*-Butyl 3-Nitroamyl Sulphone.—(a) *From n-butyl vinyl sulphone.* Aqueous sodium hydroxide (5 c.c. of 32%) was slowly added to a stirred and ice-cooled mixture of 1-nitropropane (4.5 g.) and water (20 c.c.). When the oil had completely dissolved, *n*-butyl vinyl sulphone (7.5 g.) was added and the mixture was stirred at 50° for 3 hours. After cooling, the solid product was collected (1.65 g.). Crystallisation from alcohol gave 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-ethylpentane (I; R = Et, R' = Bu) as colourless needles, m. p. 104° (Found : N, 3.9; S, 16.8. $C_{15}H_{31}O_6NS_2$ requires N, 3.65; S, 16.6%). The alkaline filtrate was washed with ether, acidified with acetic acid (3.5 c.c.), extracted with ether, and the dried extract concentrated, giving *n*-butyl 3-nitroamyl sulphone (II; R = Et) as a pale yellow oil (6 g.) which could not be purified by crystallisation or distillation. With nitrous acid it gave a positive test for a secondary nitro-group.

(b) *From 2-chloroethyl n-butyl sulphone.* Aqueous sodium hydroxide (12 c.c. of 32%) was added slowly to an ice-cold solution of 1-nitropropane (4.5 g.) in methyl alcohol (20 c.c.). 2-Chloroethyl *n*-butyl sulphone (9.3 g.) was then added and the mixture was stirred at 20° for 18 hours. The solution was diluted with water (50 c.c.) and the precipitate collected (1.45 g.) and recrystallised from alcohol, giving colourless needles, m. p. 104°, not depressed on admixture with 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-ethylpentane. Interaction of an aqueous solution of the sodium salt of *n*-butyl 3-nitroamyl sulphone with bromine at 10–15° gave *n*-butyl 3-bromo-3-nitroamyl sulphone, colourless crystals from alcohol, m. p. 55° (Found : S, 9.95; Br, 25.1. $C_9H_{18}O_4NBrS$ requires S, 10.1; Br, 25.3%).

***n*-Butyl 3-Ketoamyl Sulphone (III; R = Et).**—An aqueous solution of the potassium salt of *n*-butyl 3-nitroamyl sulphone, prepared from 1-nitropropane (4.5 g.) and *n*-butyl vinyl sulphone (7.5 g.) as above, was slowly added to a stirred solution of sulphuric acid (6.5 c.c.) in water (30 c.c.) at 10–15°. Stirring was continued for 30 minutes and the precipitate (4.5 g.) was collected, washed with water, and crystallised from alcohol, giving the ketone as colourless needles, m. p. 89° (Found : S, 15.45. $C_9H_{18}O_6S$ requires S, 15.5%). The 2 : 4-dinitrophenylhydrazones, m. p. 132°, formed yellow needles from alcohol (Found : N, 14.05; S, 7.8. $C_{15}H_{22}O_6N_4S$ requires N, 14.5; S, 8.3%). The ketone was also formed by acidification of the alkaline filtrate obtained in the condensation of 1-nitropropane with 2-chloroethyl *n*-butyl sulphone (see above).

Tris-(2-methylsulphonylethyl)nitromethane (IV).—Nitromethane (6 g.), methyl vinyl sulphone (34 g.), alcohol (80 c.c.), and aqueous potassium hydroxide (1 c.c. of 33%) were refluxed for 6 hours. After cooling, the precipitate (20.6 g.) was collected, washed with alcohol, and crystallised from 2-ethoxyethyl alcohol and from acetic acid, giving colourless crystals of the trisulphone, m. p. 219–220° (Found : N, 3.9; S, 25.0. $C_{10}H_{21}O_6NS_3$ requires N, 3.7; S, 25.3%).

Tris-(2-methylsulphonylethyl)methylamine.—The nitro-compound (10 g.) was suspended in water (250 c.c.) and shaken with hydrogen and Raney nickel at 20°/1 atm. until absorption was complete. The mixture was then heated to the boil, filtered from catalyst, and allowed to cool. The amine separated in colourless needles, m. p. 218° (Found : N, 4.15; S, 27.25. $C_{10}H_{23}O_6NS_3$ requires N, 4.0; S, 27.5%).

3-Nitro-1 : 5-di-*p*-tolylsulphonyl-3-ethylpentane (I; R = Et, R' = *p*-MeC₆H₄).—1-Nitropropane (3 g.), *p*-tolyl vinyl sulphone (10 g.), and aqueous potassium hydroxide (1 c.c. of 33%) in alcohol (40 c.c.) were refluxed for 16 hours, cooled, and the solid sulphone which separated was crystallised from acetone, giving white needles, m. p. 151° (Found : C, 55.6; H, 5.8; N, 3.25. $C_{21}H_{27}O_6NS_2$ requires C, 55.6; H, 6.0; N, 3.1%).

2-Nitro-4-*p*-tolylsulphonyl-2-methylbutane (VI).—2-Nitropropane (6 g.), *p*-tolyl vinyl sulphone (10 g.), alcohol (40 c.c.), and aqueous potassium hydroxide (1 c.c. of 33%) were refluxed for 16 hours. After cooling, the separated solid was collected and crystallised from alcohol, giving white needles of the

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sulphone, m. p. 122° (Found: C, 52.95; H, 6.2; N, 4.85. $C_{12}H_{17}O_4NS$ requires C, 53.15; H, 6.25; N, 5.15%).

Methyl 3-Nitro-3-p-bromophenylpropyl Sulphone (V; R = Me).—*p*-Bromophenylnitromethane (6 g.) and methyl vinyl sulphone (8 g.) were dissolved in alcohol (40 c.c.) and a few drops of a 33% aqueous solution of methyltriethylammonium hydroxide were added. After 18 hours at 20°, the precipitate (6 g.) was collected and washed with alcohol. Recrystallisation from alcohol gave colourless needles of the *sulphone*, m. p. 142° (Found: N, 4.45; Br, 25.25; S, 10.1. $C_{10}H_{12}O_4NBrS$ requires N, 4.35; Br, 24.85; S, 9.95%).

isoButyl 3-Nitro-3-p-bromophenylpropyl Sulphone (V; R = CH_2CHMe_2).—*iso*Butyl vinyl sulphone (2.5 g.) was added to a solution of the sodium salt of *p*-bromophenylnitromethane (4.0 g.) in water (40 c.c.) and the mixture was stirred at 50° for 6 hours, cooled, and washed with ether. The aqueous solution was treated with acetic acid (2 c.c.), and the separated oil, which solidified on standing, was collected and washed with alcohol. The crude product (2.0 g.) was repeatedly crystallised from alcohol, giving the *sulphone* as colourless needles, m. p. 92° (Found: N, 4.3; Br, 22.2; S, 9.2. $C_{13}H_{18}O_4NBrS$ requires N, 3.85; Br, 22.0; S, 8.8%).

3 : 3'-Dinitro-3 : 3'-dimethyldibutyl Sulphone (IX).—Aqueous potassium hydroxide (1 c.c. of 33%) was added to a solution of 2-nitropropane (8.9 g.) and divinyl sulphone (5.9 g.) in alcohol (40 c.c.). The solution was refluxed for 3 hours, cooled, and the precipitate (7.85 g.) collected and recrystallised from alcohol, giving the *sulphone* as colourless leaflets, m. p. 135° (Found: N, 9.45; S, 10.55. $C_{10}H_{20}O_4N_2S$ requires N, 9.45; S, 10.85%).

3 : 3'-Diamino-3 : 3'-dimethyldibutyl Sulphone.—3 : 3'-Dinitro-3 : 3'-dimethyldibutyl sulphone (7.8 g.), suspended in 2-ethoxyethyl alcohol (100 c.c.), was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption was complete. The filtered solution was concentrated under reduced pressure, and the residue, a viscous semi-solid mass, was dissolved in water, acidified with hydrochloric acid and evaporated to dryness. After extraction with acetone, the *hydrochloride* remained as a white powder (7.2 g.), m. p. 252—255° (Found: N, 8.9; S, 10.3; Cl, 23.0. $C_{10}H_{24}O_2N_2S \cdot 2HCl$ requires N, 9.05; S, 10.35; Cl, 23.0%).

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