

**283.** *Aliphatic Nitro-compounds. Part IV. Addition of Thiols to  $\alpha$ -Nitro-olefins.\**

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Thiols and hydrogen sulphide react with  $\alpha$ -nitro-olefins under basic conditions, giving 2-nitroalkyl sulphides or thiols. The former can be oxidised to 2-nitroalkyl sulphones (also formed from the nitro-olefin and, *e.g.*, sodium *p*-toluenesulphinate) or reduced to 2-aminoalkyl sulphides, which on oxidation give 2-aminoalkyl sulphones. In certain cases the 2-nitro-alcohols or their esters can be used as convenient substitutes for the nitro-olefins.

\* Patent application pending.

As a logical extension of the synthesis of alkyl 2-nitroalkyl ethers by interaction of an  $\alpha$ -nitro-olefin with an alcohol (see Part III of this series), the addition of thiols and hydrogen sulphide to nitro-olefins was investigated. This addition was found to be of wide application, and was more facile than the corresponding addition of alcohols.

In the presence of sodium methoxide, 2-nitroprop-1-ene and methylthiol gave an 86% yield of *methyl 2-nitropropyl sulphide*; similarly *methyl 2-nitro-1-methylpropyl sulphide* was obtained from 2-nitrobut-2-ene and methylthiol, *2-nitropropyl butyl sulphide* from 2-nitroprop-1-ene and butylthiol, *methyl 2-nitro-1-phenylethyl sulphide* from  $\beta$ -nitrostyrene and methylthiol, and *phenyl 2-nitroisopropyl sulphide* from 1-nitroprop-1-ene and thiophenol.

That thiols add to nitro-olefins with greater facility than do alcohols is well illustrated by the interaction of *n*-butylthiol with 2-nitroprop-1-ene; in the absence of a catalyst, this yielded 20% of 2-nitropropyl *n*-butyl sulphide, whilst only traces of methyl 2-nitropropyl ether are formed by refluxing methyl alcohol and the nitro-olefin; further, interaction of equimolecular proportions of sodium methoxide and 2-nitroprop-1-ene gave, in addition to the expected methyl 2-nitropropyl ether, some methyl 2 : 4-dinitro-2-methylamyl ether, formed by addition of the nitro-ether to unchanged nitro-olefin (cf. Part III of this series), but in the corresponding reaction with sodium thiomethoxide in place of sodium methoxide, this type of side reaction does not occur.

In the presence of piperidine as catalyst, nitro-*tert.*-butyl alcohol behaved as 1-nitro-2-methylprop-1-ene, and with butylthiol afforded *butyl nitro-tert.-butyl sulphide*; as in many examples cited in other parts of this series, 2-nitroethyl nitrate could be used as a convenient source of nitroethylene, and reacted with sodium thioalkoxides to give alkyl (or aryl) 2-nitroethyl sulphides. *Methyl, p-tolyl, p-n-butylphenyl, and carboxymethyl 2-nitroethyl sulphides* were prepared by this method, and sodium thiolacetate gave *2-nitroethyl thiolacetate*.

The addition of water to nitro-olefins in the presence of a basic catalyst is known to yield, in certain cases, 2-nitro-alcohols. It has been found that hydrogen sulphide reacts with nitro-olefins more readily than does water, and in the absence of catalysts, 2-nitrothiols are formed many of which react further with the nitro-olefin, giving di-(2-nitroalkyl) sulphides. The yields of thiol and sulphide vary widely from case to case, and are tabulated below.

Nitro-olefin.	Products and yield.
Nitroethylene .....	2-Nitroethylthiol (18%) and di-(2-nitroethyl) sulphide (48%)
2-Nitroprop-1-ene .....	2-Nitropropylthiol (7%)
1-Nitro-2-methylprop-1-ene .....	Nitro- <i>tert.</i> -butylthiol (31%) and di(nitro- <i>tert.</i> -butyl) sulphide (trace)
2-Nitrobut-2-ene.....	Di-(2-nitro-1-methylpropyl) sulphide (25%)
$\beta$ -Nitrostyrene .....	Di-(2-nitro-1-phenylethyl) sulphide (37%)

The low yield of 2-nitropropylthiol obtained from 2-nitroprop-1-ene was due to the formation of much unstable high-boiling material. In the condensation of 2-nitrobut-2-ene with hydrogen sulphide, some thiol was formed but could not be obtained pure by distillation. The product from  $\beta$ -nitrostyrene was a mixture from which only one stereoisomeride of *di-(2-nitro-1-phenylethyl) sulphide* could be isolated.

In addition to their formation from nitroethylene and hydrogen sulphide, *2-nitroethylthiol* and *di-(2-nitroethyl) sulphide* were also obtained from 2-nitroethyl nitrate with potassium hydrogen sulphide and potassium sulphide respectively, and hydrolysis of 2-nitroethyl thiolacetate (from thiolacetic acid and 2-nitroethyl nitrate) also gave 2-nitroethylthiol in small yield. 1-Nitro-2-methylprop-1-ene and sodium sulphide gave *di(nitro-tert.-butyl) sulphide* and nitro-*tert.*-butylthiol.

Oxidation of nitroalkyl sulphides with hydrogen peroxide in acetic acid afforded the nitroalkyl sulphones in good yield. Thus, *p*-tolyl 2-nitroethyl sulphide gave *p*-tolyl 2-nitroethyl sulphone, which is also obtained by reaction of sodium *p*-toluenesulphinate with 2-nitroethyl nitrate or nitroethylene. Catalytic reduction (Raney nickel) of the nitro-sulphones yielded amino-sulphones, and these were also formed by similar reduction of the nitroalkyl sulphides to aminoalkyl sulphides, followed by oxidation with hydrogen peroxide.

#### EXPERIMENTAL.

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

*Methyl 2-Nitro-1-methylpropyl Sulphide*.—A solution of sodium methoxide [from sodium (9.6 g.) in methyl alcohol (100 c.c.)] was added slowly with stirring to a solution of methylthiol (24 g.) in methyl alcohol (60 c.c.) at  $-5^{\circ}$ . 2-Nitrobut-2-ene (42 g.; see Part III of this series) was then added dropwise during 40 minutes with stirring at  $0-5^{\circ}$ , and, after being stirred for a further hour, the solution was poured into ice-water (400 c.c.), acidified with dilute acetic acid, and extracted with ether. Fractionation

of the dried extract gave *methyl 2-nitro-1-methylpropyl sulphide* (26 g.) as a colourless unpleasant smelling oil, b. p. 91—96°/15 mm. (Found : N, 9.1.  $C_5H_{11}O_2NS$  requires N, 9.4%).

*Methyl 2-Nitropropyl Sulphide*.—2-Nitroprop-1-ene (30 g.; Part I of this series) was brought into reaction with methylthiol (20 g.) as described above. *Methyl 2-nitropropyl sulphide* (40 g.) was obtained as a colourless liquid, b. p. 98—100°/16 mm. (Found : N, 10.2.  $C_4H_9O_2NS$  requires N, 10.4%).

*Methyl 2-Nitropropyl Sulphone*.—Hydrogen peroxide (30%; 45 c.c.) was added quickly with shaking to a boiling solution of methyl 2-nitropropyl sulphide (10 g.) in glacial acetic acid (40 c.c.). The mixture was boiled for 1 hour and evaporated to dryness under reduced pressure at 40—50°. Crystallisation of the residue from benzene gave *methyl 2-nitropropyl sulphone*, m. p. 69—70° (Found : C, 28.8; H, 5.1; N, 7.9.  $C_4H_9O_4NS$  requires C, 28.7; H, 5.4; N, 8.4%).

*Methyl 2-Aminopropyl Sulphone*.—Methyl 2-nitropropyl sulphone (12 g.) in methyl alcohol (600 c.c.) was shaken with Raney nickel and hydrogen (75 atms. initial pressure) at room temperature. Distillation of the product gave methyl 2-aminopropyl sulphone (2 g.) as a viscous pale yellow oil, b. p. 110—120°/0.3 mm.; the residue decomposed. The *benzoyl* derivative formed colourless needles from ethyl acetate, m. p. 154° (Found : N, 5.9; S, 13.9.  $C_{11}H_{15}O_3NS$  requires N, 5.8; S, 13.3%).

*Phenyl 2-Nitroisopropyl Sulphide*.—Thiophenol (10 g.) was added to a solution of sodium (2.1 g.) in methyl alcohol (50 c.c.) at 0°. 1-Nitroprop-1-ene (7.9 g.; Part I of this series) was added dropwise with stirring at 0—5° and the product treated as described above for the preparation of methyl 2-nitro-1-methylpropyl sulphide. *Phenyl 2-nitroisopropyl sulphide* (11.5 g.) was obtained as a colourless liquid, b. p. 110—111°/0.1 mm. (Found : N, 6.9.  $C_8H_{11}O_2NS$  requires N, 7.1%).

*Methyl 2-Nitro-1-phenylethyl Sulphide*.—A solution of sodium methoxide [from sodium (9.2 g.) in methyl alcohol (100 c.c.)] was added slowly with stirring to a solution of methylthiol (21 g.) in methyl alcohol at —10°. A solution of  $\beta$ -nitrostyrene (29.8 g.) in dioxan (500 c.c.) was then added dropwise with stirring during  $\frac{1}{2}$  hour at 10°. After being stirred at room temperature for  $\frac{1}{2}$  hour, the mixture was poured into water and extracted with ether. Distillation of the dried ethereal extract gave *methyl 2-nitro-1-phenylethyl sulphide* (19.1 g.) as a yellow oil, b. p. 168—172°/22 mm. (Found : N, 6.7.  $C_9H_{11}O_2NS$  requires N, 6.9%).

*2-Nitropropyl Butyl Sulphide*.—Butylthiol (10.4 g.) was added to a solution of sodium (2.7 g.) in methyl alcohol (50 c.c.) at 0°. 2-Nitroprop-1-ene (10 g.) was then added dropwise with stirring at 0—10° and the product isolated in the usual way. *2-Nitropropyl butyl sulphide* (12 g.) was obtained as a colourless liquid, b. p. 124—128°/13 mm. (Found : N, 7.8.  $C_7H_{13}O_2NS$  requires N, 7.9%). The same product was also obtained by interaction of *n*-butylthiol and 2-nitroprop-1-ene in absence of a catalyst. Equimols. of the reactants were warmed in methyl alcohol solution until reaction commenced, heating was discontinued, and the mixture kept for 12 hours, diluted with ether, washed with sodium hydrogen carbonate and with water, and finally distilled, giving 2-nitropropyl butyl sulphide, b. p. 120—130°/16 mm. in 19% yield. Identity was established by oxidation to the sulphone (see below).

*2-Nitropropyl Butyl Sulphone*.—Prepared from the sulphide by oxidation with hydrogen peroxide in glacial acetic acid, this sulphone separated from methyl alcohol in colourless plates, m. p. 36—37° (Found : N, 6.2; S, 14.7.  $C_7H_{15}O_4NS$  requires N, 6.7; S, 15.3%).

*n-Butyl Nitro-tert.-butyl Sulphide*.—A mixture of *n*-butylthiol (7.0 g.), nitro-*tert.*-butyl alcohol (10 g.; see Part XVIII of this series), and piperidine (1 g.) was kept at 20° for 3 days. The mixture was neutralised with 2*N*-hydrochloric acid, diluted with ether, and washed with water. Distillation of the ethereal solution gave *n-butyl nitro-tert.-butyl sulphide* (8.6 g.) as a colourless liquid, b. p. 124°/11 mm. (Found : C, 50.4; H, 8.6; N, 7.2.  $C_9H_{17}O_2NS$  requires C, 50.3; H, 8.9; N, 7.3%).

*m-Di(nitro-tert.-butylsulphonyl)benzene*.—Dithioresorcinol (14.2 g.) was added with stirring to a solution of sodium methoxide [from sodium (4.6 g.) in methyl alcohol (160 c.c.)] at 0—10°. 1-Nitro-2-methylprop-1-ene (20.2 g.; Levy and Scaife, in the press) was added dropwise at 0—5°, and the mixture stirred at room temperature for a further 2 hours. The product was poured into ice-water, acidified with dilute acetic acid, and extracted with ether. Distillation of the ethereal extract gave a colourless oil (18.1 g.), b. p. 130°/0.5 mm. The sulphur content of this oil (Found : S, 24.7. Calc. for  $C_{14}H_{20}O_4N_2S$  : S, 18.6%) indicated that it was contaminated with dithioresorcinol. However, on oxidation with hydrogen peroxide in glacial acetic acid pure *m-di(nitro-tert.-butylsulphonyl)benzene* was obtained in 17% yield. It separated from methyl alcohol in colourless needles, m. p. 166—168° (Found : N, 7.1.  $C_{14}H_{20}O_4N_2S_2$  requires N, 6.9%).

*Methyl 2-Nitroethyl Sulphide*.—A solution of methylthiol (9.6 g.) in methyl alcohol (50 c.c.) was added to a solution of sodium methoxide (10.8 g.) in methyl alcohol (30 c.c.) at —10°. 2-Nitroethyl nitrate (27.2 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was added dropwise with stirring at —5°, and, after being stirred for 3 $\frac{1}{2}$  hours at 0°, the solution was filtered and distilled, giving *methyl 2-nitroethyl sulphide*, b. p. 105°/20 mm., in 80% yield (Found : C, 30.2; H, 5.8; N, 11.1.  $C_3H_7O_2NS$  requires C, 29.8; H, 5.8; N, 11.6%).

*Methyl 2-Aminoethyl Sulphide*.—Methyl 2-nitroethyl sulphide (40 g.) in methyl alcohol (700 c.c.) was hydrogenated over Raney nickel at 50—60° and 100 atms. (initial pressure). Fractionation of the product gave methyl 2-aminoethyl sulphide (20 g.) as a colourless liquid, b. p. 90—91°/114 mm. (Schneider, *Annalen*, 1912, 386, 337, gives b. p. 146—148°/760 mm.). The picrate had m. p. 119° (Schneider, *loc. cit.*, gives m. p. 119°).

*Methyl 2-Nitroethyl Sulphone*.—Oxidation of methyl 2-nitroethyl sulphide (12.1 g.) with hydrogen peroxide in boiling glacial acetic acid gave *methyl 2-nitroethyl sulphone* (12.1 g.), colourless needles from alcohol, m. p. 78° (Found : C, 23.3; H, 5.1; N, 9.1.  $C_3H_7O_4NS$  requires C, 23.5; H, 4.6; N, 9.1%).

*Methyl 2-Aminoethyl Sulphone*.—Methyl 2-nitroethyl sulphone (3.06 g.) in methyl alcohol (40 c.c.) was hydrogenated (Raney nickel) at ordinary temperature and pressure. Distillation of the product gave *methyl 2-aminoethyl sulphone* as a colourless liquid, b. p. 160°/0.02 mm., in almost quantitative yield (Found : N, 10.9.  $C_3H_7O_4NS$  requires N, 11.4%). The hydrochloride had m. p. 168° (Schneider, *loc. cit.*, gives m. p. 169°), and the benzoyl derivative, m. p. 134° (Schneider, *loc. cit.*, gives m. p. 134°).

*p-n-Butylphenyl 2-Nitroethyl Sulphone*.—2-Nitroethyl nitrate (16.4 g.) was added dropwise to a stirred solution of sodium thio-*p*-butylphenol (22.6 g.) in methyl alcohol (200 c.c.) at —10° to —5°.

After being stirred for 4 hours the mixture was filtered, evaporated to dryness, and extracted with ether. Removal of the ether gave crude *p*-*n*-butylphenyl 2-nitroethyl sulphide as a colourless syrup which on oxidation with hydrogen peroxide gave *p*-*n*-butylphenyl 2-nitroethyl sulphone as colourless needles from alcohol, m. p. 91—92° (Found: C, 53.1; H, 6.4; N, 5.3.  $C_{12}H_{17}O_4NS$  requires C, 53.1; H, 6.3; N, 5.2%).

**Carboxymethyl 2-Nitroethyl Sulphide.**—To a solution of thioglycolic acid (9.2 g.) and sodium methoxide (10.8 g.) in methyl alcohol (150 c.c.), 2-nitroethyl nitrate (13.6 g.) was added dropwise with stirring at 0—5°. After being stirred for 3 hours at 0—20° the mixture was filtered, treated with 2*N*-hydrochloric acid (50 c.c.), evaporated to dryness, and extracted with ether. Removal of the ether gave *carboxymethyl 2-nitroethyl sulphide* (9.9 g.) as a colourless syrup which solidified on standing, and crystallised from toluene, m. p. 47° (Found: C, 29.4; H, 4.0; N, 8.5.  $C_6H_7O_4NS$  requires C, 29.1; H, 4.2; N, 8.5%).

**Carboxymethyl 2-Nitroethyl Sulphone.**—Oxidation of *carboxymethyl 2-nitroethyl sulphide* with hydrogen peroxide in boiling glacial acetic acid gave *carboxymethyl 2-nitroethyl sulphone* in almost quantitative yield. From alcohol—ether—light petroleum (b. p. 40—60°), white crystals, m. p. 115—116°, were obtained (Found: C, 24.7; H, 3.9; N, 7.1.  $C_4H_5O_6NS$  requires C, 24.4; H, 3.6; N, 7.1%). The *ethyl ester*, prepared in almost quantitative yield by heating the acid in alcoholic solution formed colourless crystals from alcohol, m. p. 62° (Found: C, 32.2; H, 4.8; N, 6.3.  $C_6H_{11}O_6NS$  requires C, 32.0; H, 4.8; N, 6.2%).

**Carboxymethyl 2-Aminoethyl Sulphide.**—*Carboxymethyl 2-nitroethyl sulphide* (8.0 g.) in methyl alcohol (200 c.c.) was hydrogenated over Raney nickel at ordinary temperature and pressure. After filtration, removal of the methyl alcohol gave a nickel salt, which was dissolved in water and decomposed by hydrogen sulphide. The solution was filtered from nickel sulphide and evaporated to dryness. Crystallisation of the residue from alcohol gave *carboxymethyl 2-aminoethyl sulphide* (2.8 g.), m. p. 156° (Found: C, 35.3; H, 5.5; N, 10.6.  $C_4H_9O_2NS$  requires C, 35.5; H, 6.6; N, 10.3%).

**2-Nitroethyl Thioliacetate.**—To a solution of thioacetic acid (15.2 g.) and sodium methoxide (10.8 g.) in methyl alcohol (200 c.c.), 2-nitroethyl nitrate (27.2 g.) was added dropwise with stirring at 0—5°. After being stirred for 2 hours, the filtered solution was evaporated and distilled, giving *2-nitroethyl thioliacetate* (23.1 g.), b. p. 68—70°/0.1 mm. (Found: C, 32.0; H, 5.4; N, 9.4.  $C_4H_7O_3NS$  requires C, 32.2; H, 4.7; N, 9.4%).

**2-Nitroethylthiol.**—(a) *From nitroethylene and hydrogen sulphide.* Nitroethylene (20 g.; Part I of this series) was added slowly with stirring to a saturated solution of hydrogen sulphide in alcohol (350 c.c.) at 0°. The vessel was then sealed and kept at 20° for 2 hours; some di-(2-nitroethyl) sulphide separated at this stage. After removal of the alcohol, distillation of the residue in nitrogen gave *2-nitroethylthiol* (5.2 g.) as a colourless liquid, b. p. 86—87°/14 mm. (Found: C, 22.4; H, 4.3; N, 12.9; S, 29.5.  $C_4H_5O_2NS$  requires C, 22.4; H, 4.7; N, 13.1; S, 29.9%), and *di-(2-nitroethyl) sulphide* (11.8 g.) as a pale yellow oil, b. p. 140—144°/0.2 mm., which darkened on standing (Found: S, 17.8.  $C_4H_8O_4N_2S$  requires S, 17.8%).

(b) *From 2-nitroethyl nitrate and potassium hydrogen sulphide.* 2-Nitroethyl nitrate (13.6 g.) was added dropwise with stirring to a solution of potassium hydrogen sulphide (7.2 g.) in methyl alcohol (100 c.c.) at room temperature. After being stirred for 3 hours, the mixture was filtered, evaporated to dryness, and extracted with ether. Distillation of the ethereal solution gave 2-nitroethylthiol (2.1 g.), b. p. 95°/20 mm.

(c) *By hydrolysis of 2-nitroethyl thioliacetate.* 2-Nitroethyl thioliacetate (7.4 g.) was kept for 1 hour at 20° with a solution of sodium hydroxide (4 g.) in water (70 c.c.). The solution was acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution, washed free of acetic acid with aqueous sodium hydrogen carbonate, was distilled in nitrogen, giving 2-nitroethylthiol (0.5 g.), b. p. 95—100°/20 mm. Mercury 2-nitrothioethoxide, prepared from the thiol and mercuric cyanide in alcohol, separated from alcohol in colourless needles, m. p. 67—68°. It decomposed rapidly on standing. 2 : 4-Dinitrophenyl 2-nitroethyl sulphide was prepared by addition of 1-chloro-2 : 4-dinitrobenzene (1.1 g.) in alcohol (20 c.c.) to a solution of the thiol (0.6 g.) in *n*-sodium hydroxide (5.5 c.c.). The solution was heated to boiling and the product which separated crystallised from benzene, m. p. 196—197° (Found: N, 15.6.  $C_8H_9O_6N_3S$  requires N, 15.4%).

**Di-(2-nitroethyl) Sulphide.**—2-Nitroethyl nitrate (27.2 g.) was added dropwise to a stirred solution of potassium sulphide (11.0 g.) in methyl alcohol (200 c.c.) at 0—5°. After being stirred for 2 hours, the filtered solution was evaporated to dryness, the residue extracted with acetone, and the extract distilled, yielding di-(2-nitroethyl) sulphide (9 g.) identical with that obtained from nitroethylene and hydrogen sulphide. Oxidation of the samples with hydrogen peroxide gave identical specimens of *di-(2-nitroethyl) sulphone*, colourless plates from acetone, m. p. 132° (Found: C, 22.6; H, 3.7; N, 13.2.  $C_4H_8O_6N_2S$  requires C, 22.6; H, 3.8; N, 13.2%).

**Nitro-tert.-butylthiol and Di(nitro-tert.-butyl) Sulphide.**—(a) *From sodium sulphide.* 1-Nitro-2-methylprop-1-ene (101 g.) was added slowly to a stirred solution of sodium sulphide ( $Na_2S \cdot 9H_2O$ ; 120 g.) in water (450 c.c.) at 0—10°. When homogeneous, the solution was treated with acetic acid (120 c.c. of 50%) and extracted with ether. Distillation afforded a fraction, b. p. 46—64°/7 mm. (38 g.), from which unchanged nitro-olefin was extracted with aqueous sodium hydrogen sulphite, giving *nitro-tert.-butylthiol* (12 g.), b. p. 58—63°/7 mm. (Found: C, 35.9; H, 6.3; N, 11.0; S, 22.9.  $C_4H_9O_2NS$  requires C, 35.6; H, 6.7; N, 10.4; S, 23.7%). Mercury nitro-tert.-thiobutoxide, colourless needles from alcohol, m. p. 108°, decomposes slowly on keeping. The residue, after removal of the fraction, b. p. 46—64°/7 mm., was crystallised from benzene—light petroleum to give *di(nitro-tert.-butyl) sulphide*, m. p. 59—60° (Found: C, 40.8; H, 6.8; S, 13.5.  $C_8H_{16}O_4N_2S$  requires C, 40.7; H, 6.8; S, 13.6%).

(b) *From hydrogen sulphide.* A solution of 1-nitro-2-methylprop-1-ene (20 g.) in alcohol (350 c.c.) was saturated at 0° with hydrogen sulphide and kept in a sealed vessel for 7 days at 20°. The alcohol was distilled and the residue, after extraction with aqueous sodium hydrogen sulphite, was isolated with ether and distilled giving *nitro-tert.-butylthiol* (8.4 g.), b. p. 68°/8 mm., and a residue (0.5 g.) which, after crystallisation from benzene—light petroleum, afforded *di(nitro-tert.-butyl) sulphide*, m. p. 59—60°.

*Di(nitro-tert.-butyl) Sulphone*.—Oxidation of di(nitro-*tert.*-butyl) sulphide with hydrogen peroxide in the manner described above gave *di(nitro-tert.-butyl) sulphone*, long colourless needles from methyl alcohol, m. p. 186° (Found: N, 10.4.  $C_8H_{16}O_4N_2S$  requires N, 10.4%).

*Di-(2-nitro-1-methylpropyl) Sulphide*.—A solution of 2-nitrobut-2-ene (27.4 g.) in alcohol (350 c.c.) was saturated with hydrogen sulphide at 0°. The vessel was then sealed and kept at room temperature for 16 hours. After filtration and removal of the alcohol, distillation of the residue in a stream of nitrogen gave an almost colourless liquid, b. p. 70–90°/15 mm., and *di-(2-nitro-1-methylpropyl) sulphide* (3 g.), b. p. 110°/0.04 mm. (Found: S, 13.4.  $C_8H_{16}O_4N_2S$  requires S, 13.6%). The fraction, b. p. 70–90°/15 mm., appeared to be a mixture of unchanged nitro-olefin and the stereoisomerides of 2-nitro-1-methylpropylthiol, but attempts to separate them by distillation failed. Redistillation of this material after 2 weeks, however, gave more (5 g.) di-(2-nitro-1-methylpropyl) sulphide, indicating reaction between the components.

*Di-(2-nitro-1-methylpropyl) Sulphone*.—Oxidation of the crude sulphide with hydrogen peroxide in the usual way gave a mixture of stereoisomerides of *di-(2-nitro-1-methylpropyl) sulphone* which separated from benzene-light petroleum (b. p. 60–80°) in colourless needles, m. p. 92–98° (Found: C, 35.8; H, 6.0; N, 10.2.  $C_8H_{16}O_4N_2S$  requires C, 35.8; H, 6.0; N, 10.4%).

*2-Nitropropylthiol*.—2-Nitroprop-1-ene (20 g.) was added slowly with stirring to a saturated solution of hydrogen sulphide in alcohol (350 c.c.) at 0°. The vessel was then sealed and kept at 20° for 1½ hours. After removal of the alcohol, distillation of the residue gave 2-nitropropylthiol (2 g.) as a colourless liquid, b. p. 83°/12 mm. (Found: S, 25.8.  $C_3H_7O_2NS$  requires S, 26.4%). The dark residue decomposed on attempted distillation at 0.2 mm.

*Di-(2-nitro-1-phenylethyl) Sulphide*.—A solution of  $\beta$ -nitrostyrene (30 g.) in alcohol (350 c.c.) was saturated with hydrogen sulphide at 0°. The vessel was then sealed and kept at 20° for 2 hours. On cooling to 0°, *di-(2-nitro-1-phenylethyl) sulphide* (9.5 g.) separated as a colourless solid which crystallised from alcohol in large prisms, m. p. 106–107° (Found: N, 8.3; S, 9.5.  $C_{16}H_{16}O_4N_2S$  requires N, 8.4; S, 9.6%). The bulk of the product remained in the mother liquors as a viscous oil, b. p. 80–120°/0.08 mm.; this mixture of stereoisomerides was not separated.

*p-Tolyl 2-Nitroethyl Sulphone*.—(a) *From nitroethylene*. Nitroethylene (3.7 g.) was added slowly to a stirred solution of sodium *p*-toluenesulphinate (8.9 g.) in water (25 c.c.) at 0°. After being stirred at 0° for 3 hours, the mixture was filtered from polynitroethylene, acidified with acetic acid, and extracted with ether. Concentration of the ethereal solution gave *p-tolyl 2-nitroethyl sulphone* (0.6 g.) as colourless needles, m. p. 114° (from alcohol) (Found: C, 46.8; H, 5.0; N, 6.6.  $C_9H_{11}O_4NS$  requires C, 47.2; H, 4.8; N, 6.1%).

(b) *From 2-nitroethyl nitrate and sodium p-toluenesulphinate*. 2-Nitroethyl nitrate (13.6 g.) was added dropwise to a stirred solution of sodium *p*-toluenesulphinate (17.8 g.) in water (50 c.c.) at 20°. The product was filtered off and crystallised from alcohol, giving *p-tolyl 2-nitroethyl sulphone* (18.3 g.), m. p. and mixed m. p. 114°.

(c) *From p-tolyl 2-nitroethyl sulphide*. A solution of sodium methoxide [from sodium (2.3 g.) in methyl alcohol (50 c.c.)] was added to a solution of thio-*p*-cresol (12.4 g.) in methyl alcohol (100 c.c.) at 0°. 2-Nitroethyl nitrate (13.6 g.) was then added dropwise with stirring at –10° to –5°. After being stirred for 3 hours the filtered solution was evaporated, giving crude *p-tolyl 2-nitroethyl sulphide* as a colourless oil, which on oxidation with hydrogen peroxide in acetic acid gave *p-tolyl 2-nitroethyl sulphone* (21 g.), m. p. and mixed m. p. 114°.

*p-Tolyl 2-Aminoethyl Sulphone*.—*p*-Tolyl 2-nitroethyl sulphone (2.3 g.) in methyl alcohol (40 c.c.) was hydrogenated over Raney nickel at ordinary temperature and pressure. Evaporation of the filtered solution gave *p-tolyl 2-aminoethyl sulphone* as a colourless syrup. The *benzoyl* derivative had m. p. 158° (Found: C, 63.2; H, 5.7; N, 4.7.  $C_{16}H_{17}O_2NS$  requires C, 63.3; H, 5.6; N, 4.6%).

*p-Tolyl 2-Aminoethyl Sulphide*.—Crude *p-tolyl 2-nitroethyl sulphide* (5 g.) in methyl alcohol (50 c.c.) was hydrogenated over Raney nickel at ordinary temperature and pressure. Removal of the methyl alcohol gave a colourless syrup, which with ethereal hydrogen chloride yielded *p-tolyl 2-aminoethyl sulphide hydrochloride* (4.1 g.), colourless crystals from alcohol-ether, m. p. 132° (Found: C, 53.3; H, 6.9; N, 6.8.  $C_9H_{13}NS.HCl$  requires C, 53.1; H, 6.9; N, 6.9%).

The authors wish to acknowledge the interest and advice of Dr. H. A. Piggott and Mr. J. D. Rose in this work.