414. *The Isomerisation of Diallyl Sulphilimines.*

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Diallyl sulphilimines, $(CH_2{:}CH{\cdot}CH_2)_2S{\rightarrow}N{\cdot}SO_2{\cdot}Ar$ undergo a spontaneous re-arrangement, giving *N*-allyl-*N*-allylthioarylsulphonamides,

$$CH_2{:}CH{\cdot}CH_2{\cdot}N(S{\cdot}CH_2{\cdot}CH{:}CH_2){\cdot}SO_2{\cdot}Ar.$$

The structure of the isomers follows from their hydrolysis to the *N*-allylsulphonamide, hydrogen sulphide, diallyl disulphide, and (presumably) acraldehyde.

When Ar is *p*-tolyl or 4-methyl-3-nitrophenyl, the sulphilimine can be isolated, but when Ar is α-naphthyl the isomer is obtained directly by interaction of diallyl sulphide and *N*-chloro-*N*-sodionaphthalene-1-sulphonamide. The isomerisation is analogous to that of certain alkylbenzyl- or alkylallyl-aniline oxides to *O*-benzyl- or *O*-allyl-hydroxylamines. Dimethyl and di-*n*-propyl, but not diallyl, sulphide can conveniently be regenerated from sulphilimines by reduction.

In a previous communication (*J.*, 1950, 29) two of us stated that the sulphilimine of diallyl sulphide [diallylsulphinetoluene-*p*-sulphonylimine, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}N{\leftarrow}S(CH_2{\cdot}CH{:}CH_2)_2$] is converted without loss in weight into an oil when warmed on the steam-bath or kept for 3—4 days at room temperature. In a refrigerator the compound is stable for 3—4 weeks. The oil (A) which decomposed on attempted distillation at 0·4 mm. and could not be caused to solidify has now been identified as *N*-allyl-*N*-allylthiotoluene-*p*-sulphonamide, by hydrolysis with hot sodium hydroxide whereby hydrogen sulphide, diallyl disulphide, a resin, and *N*-allyltoluene-*p*-sulphonamide are produced. The last-named compound was identical with a specimen synthesised by Wedekind's method (*Ber.*, 1909, **42**, 3939). The course of the hydrolysis may be represented thus (Ar = *p*-tolyl) :

(1) $Ar{\cdot}SO_2{\cdot}N(CH_2{\cdot}CH{:}CH_2){\cdot}S{\cdot}CH_2{\cdot}CH{:}CH_2 \xrightarrow{H_2O} Ar{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2 + CH_2{:}CH{\cdot}CH_2{\cdot}S{\cdot}OH$

(2) $CH_2{:}CH{\cdot}CH_2{\cdot}S{\cdot}OH{\rightarrow}H_2S + CH_2{:}CH{\cdot}CHO$

(3) $4CH_2{:}CH{\cdot}CH_2{\cdot}S{\cdot}OH{\rightarrow}(CH_2{:}CH{\cdot}CH_2{\cdot}S{\cdot})_2 + CH_2{:}CH{\cdot}CH_2{\cdot}SO_2{\cdot}S{\cdot}CH_2{\cdot}CH{:}CH_2 + 2H_2O$

The diallyl " disulphoxide " (allyl allylthiolsulphonate) probably then undergoes hydrolysis to prop-2-enethiol and prop-2-enesulphonic acid.

The decomposition of sulphenic acids, $R{\cdot}CH_2{\cdot}S{\cdot}OH$, to hydrogen sulphide and an aldehyde is well known (Schöberl and Eck, *Annalen*, 1936, **522**, 97). The resin obtained on hydrolysis presumably arose by decomposition or polymerisation of the acraldehyde. The sulphenic acids can also decompose as shown in (3) (Otto, *Ber.*, 1882, **15**, 121; Zincke and Eismayer, *ibid.*, 1918, **51**, 751). The diallyl disulphide was not characterised, as a suitable derivative for melting-point determination is difficult to find, but its odour was very obvious and passing the vapour from the hydrolysis through sodium hydroxide and then into aqueous chloramine-T yielded toluene-*p*-sulphonamide. Authentic diallyl disulphide behaves in a similar manner. No compound analogous to the disulphonamide derivatives (*D*) (Clarke, Kenyon, and Phillips, *J.*, 1920, 1225; Alexander and McCombie, *J.*, 1932, 2087) was detected. Moreover, absorption in mercuric chloride gave an insoluble mercurated product with the properties of that obtained from the authentic disulphide (see p. 1879, and Challenger and Greenwood, *Biochem. J.*, 1949, **44**, 89).

$R{\cdot}S{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$ ↓ $N{\cdot}SO_2{\cdot}C_6H_4Me$ (*D.*)

Diallyl sulphide was absent from the products of hydrolysis because no diallyl sulphilimine separated in the chloramine-T solution. The sulphide can readily be detected in a gas stream by formation of the sulphilimine.

The *N*-allyltoluene-*p*-sulphonamide, obtained by alkaline hydrolysis of the oily isomerisation product of the sulphilimine, was oxidized by alkaline potassium permanganate to *p*-sulphamylbenzoic acid (characterised as the methyl ester), thus confirming its structure. The allyl group is eliminated during the oxidation. Oxidation of authentic *N*-allyl- and *N*-methyl-toluene-*p*-sulphonamide with alkaline permanganate was found to give *p*-sulphamylbenzoic acid.

It was decided to seek for further examples of the isomerisation of sulphilimines. By using diallyl sulphide and a " chloramine " of higher molecular weight it was hoped that the product of isomerisation would be a solid which could be purified and characterised. (There is, however, no evidence that the isomerisation to the oil is incomplete; see p. 1880.) The behaviour of diallyl sulphide with *N*-chloro-*N*-sodio-naphthalene-1-sulphonamide $C_{10}H_7{\cdot}SO_2{\cdot}NClNa$ and

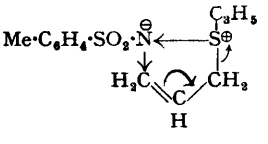
with *N*-chloro-*N*-sodio-4-methyl-3-nitrobenzenesulphonamide (Chattaway, *J.*, 1905, 145) was therefore examined. In the former case no sulphilimine could be isolated, the first product of the reaction being an oil (B). With the nitrotoluene derivative a solid " sulphilimine," diallylsulphine-4-methyl-3-nitrobenzenesulphonylimine was obtained. This was shown to have the normal sulphilimine structure by hydrolysis with hydrochloric acid, whereby 4-methyl-3-nitrobenzenesulphonamide was obtained. Before this hydrolysis the " sulphilimine " was triturated with aqueous sodium hydroxide to remove sulphonamide which is frequently formed during the preparation of sulphilimines, a corresponding amount of sulphide being probably oxidised or chlorinated by the hypochlorous acid simultaneously liberated. When kept for a few days at room temperature the " sulphilimine," without loss in weight, formed an oil (C) (which was turbid if the sulphilimine was contaminated with sulphonamide).

Alkaline hydrolysis of the oils (B) and (C) under the conditions employed in the case of (A) gave *N*-allylnaphthalene-1-sulphonamide and *N*-allyl-4-methyl-3-nitrobenzenesulphonamide respectively (these were prepared by the Schotten–Baumann reaction for comparison). Hydrogen sulphide, allyl disulphide, and resin were formed as before. In the case of (C) the hydrolysis must be conducted at room temperature, otherwise resinification occurs (cf. Schreiber and Schriner, *J. Amer. Chem. Soc.*, 1934, **56**, 114). Migration of allyl from nitrogen to sulphur has, therefore, again been demonstrated but the *N*-allyl-*N*-allylthiosulphonamides could not be caused to solidify.

" Sulphilimines " are useful for the characterisation of aliphatic sulphides (Mann and Pope, *J.*, 1922, **121**, 1052; 1924, **125**, 911) but regeneration of the sulphides does not appear to have been described. This may be effected in the case of the dimethyl and di-*n*-propyl derivatives in 95 and 73% yield respectively by refluxing them with tin and hydrochloric acid, hydrolysis to sulphoxide and sulphonamide and reduction of the sulphoxide readily taking place. The sulphides were characterised as the mercurichlorides. Alkanethiols were shown by the mercuric cyanide test to be absent.

In the case of diallylsulphinetoluene-*p*-sulphonylimine (" diallyl sulphilimine "), although toluene-*p*-sulphonamide can be isolated the sulphide undergoes reduction to hydrogen sulphide and prop-2-enethiol. These products were shown in a separate experiment to be formed on heating of diallyl sulphide with tin and hydrochloric acid.

Dr. J. W. Baker (private communication) suggested that the electron transfer involved in the isomerisation proceeds thus and that the driving force is the attraction of the positive charge on the sulphur atom for the electrons of the S–alkyl link. A rearrangement which is closely analogous to that of the diallyl sulphilimines was observed by Meisenheimer (*Ber.*, 1919, **52**, 1667) and by Meisenheimer, Greeske, and Willmersdorf (*ibid.*, 1922, **55**, 513) who found that in presence of aqueous alkali at 100° allylmethylaniline oxide (I) isomerises to *O*-allyl-*N*-methyl-*N*-phenylhydroxylamine (II). This yielded methylaniline and allyl alcohol on reduction. Hydrolysis with hydrochloric acid gave acraldehyde, methylaniline, and *p*-chloro-*N*-methylaniline (thus establishing its constitution). Allyl alcohol which should also have been produced was not detected. Allylethylaniline oxide and benzylmethylaniline oxide underwent a similar rearrangement, but the products were not examined so closely. Kleinschmidt and Cope (*J. Amer. Chem. Soc.*, 1944,



$C_6H_5{\cdot}MePhN{\rightarrow}O$ (I.) $MePhN{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$ (II.) $CH_2Ph{\cdot}Et_2N{\rightarrow}O$ (III.) $(CH{\cdot}CH{:}CH{\cdot}CH_3){\cdot}MePhN{\rightarrow}O$ (IV.)

66, 1929) confirmed Meisenheimer's results with the latter compounds and proved that their rearrangement was analogous to that of (I); by carrying out a similar change with crotylmethylaniline oxide (IV) they showed that the migrating group undergoes inversion, the product being (V).

They proposed an intramolecular cyclic mechanism for this rearrangement which is similar to that proposed by Dr. Baker (see above) for the rearrangement isomerisation of the sulphilimines.

(IV.)  (V.)

These changes are analogous to the Claisen rearrangements, except that a diad and not a triad system is involved.

Neither sodium hydroxide nor the presence of a phenyl group is necessary for the isomerisation, which has also been effected by the action of heat on various dialkylallylamine oxides and also on benzyldimethylamine oxide (Cope and Towle, *ibid.*, 1949, **71**, 3423), giving *NN*-dialkyl-*O*-allylhydroxylamines and *O*-benzyl-*NN*-dimethylhydroxylamine. Benzyldiethylamine oxide (III) undergoes a similar rearrangement (Cope, Foster, and Towle, *ibid.*, 1949, **71**, 3931), but ethylene and *N*-benzyl-*N*-ethylhydroxylamine are also formed. The latter undergoes *O*-benzylation by migration of benzyl from (III), giving *ON*-dibenzyl-*N*-ethyl- and *NN*-diethyl-hydroxylamine. The authors quote analogous reactions in which quaternary benzyl- and allyl-ammonium halides or bases "alkylate" phenols by migration of allyl or benzyl. Challenger, Taylor, and Taylor (*J.*, 1942, 48) and Challenger and (Miss) Fothergill (*Biochem. J.*, 1949, **45**, xxvii) reported that *N*-methylation of primary aromatic amines occurred when these were heated with quaternary compounds such as betaine or acetothetine $Me_2\overset{+}{S}\cdot CH_2\cdot \overset{-}{CO_2}$.

Arbuzov and Nikonorov (*J. Gen. Chem., Russia*, 1948, **18**, 2008; *Chem. Abs.*, 1949, **43**, 3802) describe reactions of an opposite type. Attempts to prepare the allyl and benzyl ethers of diphenylphosphinous and -thiophosphinous acids, $Ph_2P\cdot OR$ and $Ph_2P\cdot SR$, yielded only the coresponding phosphine oxides or sulphides $Ph_2RP\rightarrow O$ and $Ph_2RP\rightarrow S$ on distillation or, in the second case, spontaneously on standing. Furthermore, the ether $Ph_2P\cdot OMe$ in presence of methyl iodide or a trace of iodine yielded $Ph_2MeP\rightarrow O$.

Our work will be continued in various directions and the behaviour of dibenzylsulphilimine examined.

The sulphilimines $R_2S\rightarrow N\cdot SO_2\cdot R'$ are hydrolysed by acids by attachment of a proton to the nitrogen atom. The absence of the semipolar link in the isomer $RS\cdot NR\cdot SO_2\cdot R'$ renders this less probable. The sulphur atom can, however, expand its valency shell by accepting a hydroxyl ion. This is facilitated by the attraction of the sulphonyl group for the unshared electrons of the nitrogen, an effect which can be relayed to the sulphur. The isomer is therefore hydrolysed by alkali but not by acid (see p. 1877).

Experimental.

Diallylsulphinetoluene-p-*sulphonylimine*.—Diallyl sulphide (6 g.) was shaken for 20 minutes with chloramine-T (13·6 g.) in water (200 c.c.). The crystalline precipitate, which quickly formed, was washed with water and dried (15·3 g.; m. p. 70°). After three recrystallisations from chloroform–light petroleum (b. p. 40—60°) the *sulphilimine* had the constant m. p. of 72° (Found: C, 54·8; H, 6·1; N, 5·1. $C_{13}H_{17}O_2NS_2$ requires C, 55·1; H, 6·0; N, 5·4%). After 3—4 days at room temperature, it was converted into a clear oil without loss of weight.

Hydrolysis of the sulphilimine. Immediately after preparation, the sulphilimine (1 g.) was heated under reflux for 1 hour with hydrochloric acid (10 c.c.). A small amount of oil separated. After cooling, the clear solution deposited 0·48 g. of solid which, after one recrystallisation from water, had m. p. 137°, alone or mixed with authentic toluene-*p*-sulphonamide.

Hydrolysis of the liquefied sulphilimine. The oil (9 g.) was boiled for 45 minutes under reflux with 25% aqueous sodium hydroxide (50 c.c.). Traces of pale yellow solid, unmelted below 270°, were removed by filtration of the reddish-brown solution (*S*) through glass-wool. The odour of diallyl disulphide was noticed. Neutralisation with hydrochloric acid gave an oil and much hydrogen sulphide was liberated. The oil was extracted with ether, evaporation leaving orange needles. The aqueous solution when evaporated to dryness yielded nothing on extraction with hot acetone and contained only sodium chloride. The orange solid, after decolorisation with charcoal and four recrystallisations from benzene–light petroleum (b. p. 40—60°), formed pale yellow crystals (5·4 g.), m. p. 61—62°. Two recrystallisations from dilute alcohol raised the m. p. to 64—65° alone or on admixture with authentic *N*-allyltoluene-*p*-sulphonamide (Found: C, 56·6; H, 6·1; N, 6·2. Calc. for $C_{10}H_{13}O_2NS$: C, 56·9; H, 6·2; N, 6·6%).

A further quantity of the alkaline liquor (*S*) was acidified in a stream of nitrogen which was passed successively through sodium hydroxide (*a*) (to trap hydrogen sulphide), 10% chloramine-T solution (*b*), and 3% aqueous mercuric chloride solution (*c*). Toluene-*p*-sulphonamide, together with traces of oil, was precipitated in (*b*) and identified by mixed m. p. The precipitate in (*c*) had the properties of the mercurated fission product of an unsaturated disulphide, $ClHg\cdot CHR\cdot CH(OH)\cdot CH_2\cdot S\cdot HgCl$, being insoluble in all common organic solvents and unmelted below 270°. With sodium hydroxide yellow mercuric oxide was precipitated. Hydrochloric acid produced the odour of a thiol. Diallyl disulphide (which was recognised in the nitrogen stream by its strong and characteristic odour after absorption of the hydrogen sulphide) behaves in a similar manner with chloramine-T and mercuric chloride.

Oxidation of N-*Allyltoluene*-p-*sulphonamide*.—The product of the hydrolysis of the liquefied sulphilimine (2 g.) was boiled under reflux for 1 hour with excess of alkaline 6% potassium permanganate solution (200 c.c.). After decolorisation with sulphur dioxide, the solution was evaporated. The residue was washed with water, dissolved in sodium carbonate solution, and reprecipitated by dilute hydrochloric acid. The product (1·15 g.), after three recrystallisations from water, had m. p. 283° (decomp.) alone or on admixture with authentic *p*-sulphamylbenzoic acid, m. p. 281° (Found: C, 42·2; H, 3·8; N, 7·1. Calc. for $C_7H_7O_4NS$: C, 41·8; H, 3·5; N, 6·9%).

Characterisation of the oxidation product. The acid (0·6 g.) was treated with ether (20 c.c.) containing diazomethane prepared from nitrosomethylurea (1 g.; excess), and left for 1 hour. The mixture was then refluxed for 1 hour and the ether evaporated. Unchanged *p*-sulphamylbenzoic acid was removed with aqueous sodium hydrogen carbonate. The ester (0·3 g.; m. p. 176—178°), recrystallised twice from water, had m. p. 181—182°, alone or on admixture with authentic methyl *p*-sulphamylbenzoate (Found : C, 44·9; H, 4·5. Calc. for $C_8H_9O_4NS$: C, 44·7; H, 4·2%).

Oxidation of N-*Allyltoluene*-p-*sulphonamide.*—Authentic *N*-allyltoluene-*p*-sulphonamide (6 g.) (see p. 1881) was refluxed for 2 hours with alkaline 6% potassium permanganate solution (500 c.c.; excess). Decolorisation with sulphur dioxide gave the corresponding crude carboxylic acid. A further quantity was obtained by concentration of the filtrate. The combined precipitates were treated with sodium hydrogen carbonate solution and filtered. Acidification of the filtrate precipitated an acid which, after two recrystallisations from hot water, had m. p. 280—281° (decomp.) alone or on admixture with authentic *p*-sulphamylbenzoic acid. The portion (0·8 g.) insoluble in sodium hydrogen carbonate, when recrystallised from hot water, had m. p. 137° alone or mixed with toluene-*p*-sulphonamide.

Preparation of N-*Chloro*-N-*sodionaphthalene*-1-*sulphonamide.*—The sulphonamide, prepared from sodium naphthalene-α-sulphonate, was converted into the "chloramine" compound through the corresponding dichloroamide (Chattaway, *J.*, 1905, 145) (Found : available Cl, 9·2. Calc. for $C_{10}H_7O_2NSClNa$: available Cl, 13·4%).

Preparation of N-*Chloro*-N-*sodio*-4-*methyl*-3-*nitrobenzenesulphonamide.*—Toluene-*p*-sulphonic acid was nitrated in a freezing mixture with concentrated nitric acid in acetic anhydride (Hirwe and Jambhekar, *J. Indian Chem. Soc.*, 1933, **10**, 42). The sodium salt of the nitrated acid was converted into the sulphonamide (Fichter and Bernoulli, *Ber.*, 1909, **42**, 4308), and the "chloramine" compound prepared as usual (Found : available Cl, 9·35. Calc. for $C_7H_6O_4N_2SClNa$: Available Cl, 13·0%). The chloramine is particularly susceptible to warm alkali; Chattaway (*loc. cit.*) attributes this to the effect of the nitro-group.

Preparation of Dimethylsulphinenaphthalene-1-*sulphonylimine.*—A mixture of dimethyl sulphide (1·5 g.) and 10% ice-cold aqueous *N*-chloro-*N*-sodionaphthalene-1-sulphonamide (80 c.c.) immediately became turbid, and after an hour's shaking a viscous *sulphilimine* separated. This hardened when the solution was left for a week in the refrigerator, and after four crystallisations from ethyl acetate had m. p. 102—103° (Found : C, 53·7; H, 4·8; N, 5·2. $C_{12}H_{13}O_2NS_2$ requires C, 54·0; H, 4·9; N, 5·25%).

Hydrolysis. The sulphilimine (0·25 g.) was refluxed for 30 minutes with dilute hydrochloric acid (5 c.c.). The solid deposited on cooling was recrystallised from hot water and had m. p. 150° alone or mixed with authentic naphthalene-α-sulphonamide.

Dimethylsulphine-4-*methyl*-3-*nitrobenzenesulphonylimine.*—Dimethyl sulphide (1 g.) reacted almost immediately when shaken with aqueous 10% *N*-chloro-*N*-sodio-4-methyl-3-nitrobenzenesulphonamide (40 c.c.). After an hour's shaking the *sulphilimine* was filtered off, washed with water, and crystallised three times from chloroform–ligroin (b. p. 40—60°). The m. p. was then 120—121°, unchanged by recrystallisation from benzene (Found : C, 39·2; H, 4·2; N, 9·9; S, 23·1. $C_9H_{12}O_4N_2S_2$ requires C, 39·2; H, 4·35; N, 10·1; S, 23·2%).

Hydrolysis. The sulphilimine was hydrolysed with dilute hydrochloric acid as above. The sulphonamide so obtained had m. p. 143° alone or mixed with authentic 4-methyl-3-nitrobenzenesulphonamide.

Attempted Preparation of Diallylsulphinenaphthalene-1-*sulphonylimine. Formation of* N-*Allyl*-N-*allylthionaphthalene*-1-*sulphonamide.*—Allyl sulphide (3 g.) was slowly added with occasional shaking to ice-cold aqueous 10% *N*-chloro-*N*-sodionaphthalene-1-sulphonamide (100 c.c.). A heavy colourless oil (B) separated almost at once but no solid was formed. After the mixture had been shaken for 90 minutes and left for 2 days in the refrigerator, the oil (still no solid was present) was extracted with ether, and the solvent evaporated at room temperature. Some naphthalene-α-sulphonamide, m. p. 150°, together with a trace of naphthalene-β-sulphonamide, m. p. 213° (derived from contaminant in the sodium naphthalene-α-sulphonate), was removed by dissolving the oil in acetone–benzene. Evaporation of the solvent left a clear oil (4·5 g.).

Hydrolysis. The oil (4·5 g.) was identified by hydrolysis with 25% aqueous sodium hydroxide (25 c.c.). Hydrogen sulphide and diallyl disulphide were evolved on acidification and carried into absorption tubes by a stream of nitrogen, as in the case of *N*-allyl-*N*-allylthiotoluene-*p*-sulphonamide. Extraction of the reaction mixture with ether gave orange crystals which, after decolorisation with charcoal and three recrystallisations from aqueous alcohol, had m. p. 81° alone or mixed with authentic N-*allylnaphthalene*-α-*sulphonamide* (see below) (Found : C, 62·9; H, 5·2; N, 6·0; S, 13·8. $C_{13}H_{13}O_2NS$ requires C, 63·1; H, 5·2; N, 5·7; S, 13·0%).

Attempted acid hydrolysis of freshly prepared diallylsulphinenaphthalene-α-*sulphonylimine.* A further quantity of oil (B) was freed from sulphonamide with cold 1% sodium hydroxide and extracted with chloroform, and the solvent evaporated in an air-stream at room temperature. After 10 minutes' heating with hydrochloric acid the oil appeared unchanged and no sulphonamide was obtained on cooling. Under similar conditions, an allylsulphilimine would have been quickly hydrolysed. The specimen had therefore fully isomerised before this experiment. The liquefied diallylsulphinetoluene-*p*-sulphonylimine was also stable to hot hydrochloric acid.

Diallylsulphine-4-*methyl*-3-*nitrobenzenesulphonylimine.*—Allyl sulphide (6 g.) was slowly added, with occasional shaking, to ice-cold aqueous 10% *N*-chloro-*N*-sodio-4-methyl-3-nitrobenzenesulphonamide (200 c.c.). A pale yellow precipitate quickly separated. After 30 minutes' shaking the solid was filtered off, washed with 1% sodium hydroxide solution (50 c.c.) (to remove sulphonamide), then with water, and dried (10 g.). After three crystallisations from chloroform–ligroin (b. p. 40—60°), the

sulphilimine had the constant m. p. of 76—77°. Within 2 hours the m. p. began to fall owing to isomerisation. At the end of 3—4 days a clear oil had formed (Found, for a partly isomerised sample: C, 47·2; H, 5·1; N, 8·3; S, 20·1. $C_{13}H_{16}O_4N_2S_2$ requires C, 47·5; H, 4·9; N, 8·5; S, 19·5%). A little 4-methyl-3-nitrobenzenesulphonamide (0·2 g.) was recovered from the alkaline wash-liquors.

Hydrolysis. The sulphilimine (0·5 g.) was heated for a few minutes with hydrochloric acid (10 c.c.). A trace of oil separated. The clear solution on cooling deposited 4-methyl-3-nitrobenzenesulphonamide, m. p. and mixed m. p. 142°, after one recrystallisation from water.

Hydrolysis of N-*Allyl*-N-*allylthio*-4-*methyl*-3-*nitrobenzenesulphonamide.*—Owing to the decomposition which occurs when hot alkali acts on derivatives of *p*-nitrotoluene, milder conditions were employed. The liquefied sulphilimine (4 g.) was left for 12 hours at room temperature with 10% aqueous sodium hydroxide (25 c.c.). The reaction was completed by 10 minutes' warming on the steam-bath. On acidification with hydrochloric acid under nitrogen, hydrogen sulphide and diallyl disulphide were evolved and trapped as before. Solid N-*allyl*-4-*methyl*-3-*nitrobenzenesulphonamide* which separated from the acidified reaction mixture was washed with water and recrystallised once from aqueous alcohol; it had m. p. 70° alone or mixed with a specimen prepared as below (Found: C, 46·2; H, 4·7; N, 11·1; S, 12·8. $C_{10}H_{12}O_4N_2S$ requires C, 46·8; H, 4·7; N, 10·9; S, 12·5%).

Regeneration of the Sulphide from Dimethylsulphinetoluene-p-*sulphonylimine.*—The sulphilimine (1·0 g.) was warmed with tin and 2N-hydrochloric acid (30 c.c.) under reflux. The issuing gases were aspirated through (*a*) 4% mercuric cyanide solution and (*b*) 3% mercuric chloride solution. The sulphilimine dissolved and precipitates soon appeared in the mercuric chloride. No precipitate formed in the mercuric cyanide, showing absence of thiol. After about 45 minutes, when there was no further precipitation, the mercurichloride was separated, washed with water, and dried (1·5 g.; 95%). After three recrystallisations from benzene containing a little acetone, the m. p. was 157° alone or on admixture with authentic dimethyl sulphide mercurichloride. The hot reaction mixture, filtered from excess of tin, deposited a solid (0·5 g.) on cooling. After one recrystallisation from aqueous alcohol this had m. p. 137° alone or mixed with toluene-*p*-sulphonamide.

Regeneration of the Sulphide from Di-n-*propylsulphinetoluene*-p-*sulphonylimine.*—The procedure was as described above, except that aspiration for 3—4 hours was required before sulphide evolution ceased. The sulphilimine (1·0 g.) yielded 0·8 g. (73%) of crude mercurichloride which, after two recrystallisations from alcohol, had m. p. 87° alone and 86·5—87·5° on admixture with authentic di-*n*-propyl sulphide mercurichloride. The m. p. of both samples of this mercurichloride was found to have risen after being left for a few days in corked tubes, presumably owing to loss of *n*-propyl sulphide (which could be recognised by its odour) and resultant conversion of $Pr^n_2S,HgCl_2$ into $Pr^n_2S,2HgCl_2$. These compounds are interconvertible by means of suitable solvents (Faragher, Morrell, and Comay, *J. Amer. Chem. Soc.*, 1929, **51**, 2774).

Attempted Regeneration of the Sulphide from Diallylsulphinetoluene-p-*sulphonylimine.*—The freshly prepared sulphilimine (2 g.) was heated with tin and hydrochloric acid (50 c.c.) under reflux. The issuing gases were aspirated through a series of absorption tubes, the first two containing 10% sodium hydroxide, the others 10% aqueous chloramine-T. In a small-scale reduction, hydrogen sulphide was detected. After an hour the first tube of chloramine-T contained only a trace of precipitate, which gradually formed an oil. There was therefore no appreciable evolution of allyl sulphide. Addition of 4% mercuric cyanide solution to the sodium hydroxide gave a white solid (0·15 g.; m. p. 69—72°). After two recrystallisations from ethyl acetate, this had m. p. 73° alone or mixed with the mercury derivative of prop-2-enethiol (Challenger and Greenwood, *Biochem. J.*, 1948, **44**, 87). Traces of an oil containing the same thiol were washed out from the condenser and characterised as before. The filtered reaction mixture deposited 0·8 g. of toluene-*p*-sulphonamide which on crystallisation from aqueous alcohol had m. p. and mixed m. p. 137°.

Reduction of Allyl Sulphide.—Allyl sulphide (0·5 g.) was warmed for 2 hours under reflux with hydrochloric acid (50 c.c.) and tin (20 g.). The volatile products were aspirated through absorption tubes containing (1) 5% cadmium sulphate solution in N-sulphuric acid to absorb hydrogen sulphide (Mapstone, *J. Proc. Australian Chem. Inst.*, 1946, **13**, 375), (2) 10% sodium hydroxide solution (2 tubes), (3) 4% mercuric cyanide solution, and (4) 3% mercuric chloride solution (3 tubes). A trap separated tubes (1) and (2). The precipitate in the mercuric chloride had the properties of the mercurichloride of allyl sulphide (see p. 1882). Formation of cadmium sulphide in tube (1) indicated hydrogen sulphide. Addition of 4% mercuric cyanide solution to the sodium hydroxide produced in the first tube a buff precipitate of m. p. 72° (0·3 g.), raised by recrystallisation from alcohol to 73° (alone or mixed with the mercury derivative of prop-2-enethiol).

Preparation of Reference Compounds.— p-*Sulphamylbenzoic acid and its methyl ester.* Toluene-*p*-sulphonamide (4 g.) was refluxed for 30 minutes with 6% aqueous potassium permanganate (200 c.c.). After decolorisation and acidification, excess of sodium hydrogen carbonate was added and the solution filtered from unchanged sulphonamide. Acidification of the filtrate gave the acid (3·7 g.), m. p. 283° (decomp.).

The *methyl* ester, prepared by means of diazomethane, had m. p. 181—182° (Found: C, 44·7; H, 4·0; N, 6·6. $C_8H_9O_4NS$ requires C, 44·7; H, 4·2; N, 6·5%).

N-*Allyltoluene*-p-*sulphonamide.* When prepared by Wedekind's method (*Ber.*, 1909, **42**, 3939) and crystallised twice from dilute alcohol this had m. p. 64—65°.

N-*Allylnaphthalene*-α-*sulphonamide.* Naphthalene-α-sulphonyl chloride (2 g.), freed from the β-isomer by recrystallisation from light petroleum, was shaken for 8 hours with allylamine (0·5 g.) in 2N-sodium hydroxide (50 c.c.). The product (0·8 g.) was precipitated with 6N-hydrochloric acid and after two recrystallisations from aqueous alcohol had m. p. 81° (Found: C, 63·0; H, 5·00; N, 5·78; S, 13·6. Calc. for $C_{13}H_{13}O_2NS$: C, 63·2; H, 5·24; N, 5·68; S, 13·0%).

N-Allyl-4-methyl-3-nitrobenzenesulphonamide. Prepared as was the α-naphthalene compound, by using the appropriate acid chloride, and recrystallised twice from aqueous alcohol, this amide had m. p. 70° (Found : C, 46·5; H, 4·45; N, 10·6; S, 12·7. Calc. for $C_{10}H_{12}O_4N_2S$: C, 46·8; H, 4·7; N, 10·9; S, 12·5%).

Diallyl sulphide mercurichloride. The sulphide (3 g.) was shaken for 3 hours with saturated aqueous mercuric chloride (500 c.c.). The precipitated *salt* was separated, washed with water and alcohol, and dried. It blackened at 170° without melting. Extraction with hot benzene removed mercuric chloride and traces of a sulphur compound. The insoluble residue sintered at 125° and blackened at 180° (Found : C, 8·85, 8·7; H, 1·65, 1·8; S, 4·2, 3·8; Cl, 16·1. $[ClHg{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2]_2S{\cdot}HgCl_2$ requires C, 8·05; H, 1·35; S, 3·6; Cl, 15·9%). Treatment of the derivative with sodium hydroxide gave mercuric oxide but no odour. Addition of hydrochloric acid to the resulting mixture gave a strong odour of a sulphur compound. This is in accordance with the structure given.

Addition of sodium hydroxide to the complex, separation of the mercuric oxide, and treatment of the alkaline solution with carbon dioxide precipitated a white solid. This sintered at 186° and blackened at 200°. It was crystallised from boiling xylene but could not be purified. The content of C, H, S, and Cl approximated to that required by $[ClHg{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2]_2S$. For the production of analogous compounds from ethylene and propylene see Hofmann and Sand, *Ber.*, 1900, **33**, 1340, 2692; Sand and Hofmann, *ibid.*, p. 1353; and Sand and Genssler, *ibid.*, 1903, **36**, 3699.

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