527. *The Isomerisation of Sulphilimines. Part II.**

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(with an Addendum by THOMAS S. STEVENS and JOHN L. DUNN).

The migration of an allyl group from sulphur to nitrogen in diallyl sulphilimines, $(CH_2{:}CH{\cdot}CH_2)_2S{\rightarrow}N{\cdot}SO_2{\cdot}Ar$, giving *N*-allyl-*N*-allylthioarylsulphonamides $CH_2{:}CH{\cdot}CH_2{\cdot}N(S{\cdot}CH_2{\cdot}CH{:}CH_2){\cdot}SO_2{\cdot}Ar$, as described in Part I,* has now been observed with the sulphilimines derived from allyl benzyl sulphide and diallyl sulphide by using chloramine-T and *p*-acetamido-*N*-chloro-*N*-sodiobenzenesulphonamide respectively. Isomerisation occurs at room temperature or at the melting point, giving with allyl benzyl sulphilimine a crystalline isomer and, in the second case, an oil. Alkaline hydrolysis yields *N*-allyltoluene-*p*-sulphonamide in the first case, and *p*-acetamido-*N*-allylbenzenesulphonamide and N^1-allyl-*p*-aminobenzenesulphonamide in the second. Here also the acraldehyde resulting from the decomposition of the prop-2-enesulphenic acid $C_3H_5{\cdot}S{\cdot}OH$ formed during hydrolysis has been detected. Dibenzyl sulphilimine $(PhCH_2)_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ at 180—200° gives several products, including *N*-benzyltoluene-*p*-sulphonamide.

IN Part I * of this series Ash, Challenger, and Greenwood showed that the sulphilimines prepared from diallyl sulphide and *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide (chloramine-T) and *N*-chloro-4-methyl-3-nitro-*N*-sodiobenzenesulphonamide undergo a spontaneous isomeric change at room temperature, an allyl group migrating to nitrogen. The isomers are oils but alkaline hydrolysis (giving $R{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$, diallyl disulphide, hydrogen sulphide, and a resin arising from acraldehyde) shows that they have the structure $CH_2{:}CH{\cdot}CH_2{\cdot}N(S{\cdot}CH_2{\cdot}CH{:}CH_2){\cdot}SO_2{\cdot}R$. The last three products arise from the decomposition of prop-2-enesulphenic acid $C_3H_5{\cdot}S{\cdot}OH$, a primary product of hydrolysis. With *N*-chloro-*N*-sodionaphthalene-1-sulphonamide, the isomer is at once obtained. Further examples of this migration have now been observed. Allyl benzyl sulphide and chloramine-T give a sulphilimine $(CH_2Ph)(CH_2{:}CH{\cdot}CH_2)S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ which changes at its melting point or in a few days at room temperature, giving, by migration of the allyl group, the solid isomer $CH_2{:}CH{\cdot}CH_2{\cdot}N(S{\cdot}CH_2Ph){\cdot}SO_2{\cdot}C_6H_4Me$. On alkaline hydrolysis *N*-allyltoluene-*p*-sulphonamide, dibenzyl disulphide, hydrogen sulphide, and benzoic acid are obtained. The last two compounds no doubt arise from the decomposition of the intermediate toluene-ω-sulphenic acid: $CH_2Ph{\cdot}S{\cdot}OH = Ph{\cdot}CHO + H_2S$. A Cannizzaro reaction then follows. No benzyl alcohol was isolated. Diallyl sulphide and *p*-acetamido-*N*-chloro-*N*-sodiobenzenesulphonamide give diallyl sulphine *p*-acetamidobenzenesulphonylimine. This slowly isomerises at room temperature, and readily at its melting point, giving a semi-solid product and an oil respectively, from both of which *p*-acetamido-*N*-allylbenzenesulphonamide was isolated by crystallisation from alcohol, indicating that hydrolysis or alcoholysis had occurred. In boiling water the oil was slowly hydrolysed and acraldehyde was detected in the volatile products as the dimedone derivative. Alkaline hydrolysis yielded N^1-allyl-*p*-aminobenzenesulphonamide and hydrogen sulphide, the acetyl group being lost.

Dibenzyl sulphilimine (dibenzyl sulphine toluene-*p*-sulphonylimine; Mann and Pope, *J.*, 1922, 1052) has the normal structure as it gives toluene-*p*-sulphonamide on hydrolysis with dilute hydrochloric acid. It is stable at room temperature for several months but when heated in nitrogen at 180—200° for 16 hours undergoes a complex decomposition involving the migration of a benzyl group giving (*a*) *N*-benzyltoluene-*p*-sulphonamide, (*b*) toluene-*p*-sulphonamide, (*c*) dibenzyl disulphide, (*d*) stilbene, and (*e*) traces of benzaldehyde. The formation of stilbene suggests that this reaction may involve free radicals, *e.g.*, $Ph{\cdot}CH_2{\cdot}$, $Ph{\cdot}CH_2{\cdot}S{\cdot}$, and $C_6H_4Me{\cdot}SO_2{\cdot}\ddot{N}$ (Clarke, Kenyon, and Phillips, *J.*, 1927, 188;

* Part I, *J.*, 1951, 1877.

1930, 1225), which might arise from the primary isomerisation product (II) which was not, however, isolated from the reaction mixture. Dr. J. W. Baker (personal communication)

(I) $(CH_2Ph)_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ $CH_2Ph{\cdot}S{\cdot}N(CH_2Ph){\cdot}SO_2{\cdot}C_6H_4Me$ (II)

pointed out that the homolytic fission of the semipolar bond in (I) is unlikely. It is possible that (*a*) and (*c*) might be formed from (II) by the action of the cold aqueous sodium hydroxide used in the isolation of the reaction products, though this seems unlikely as hot alkali was employed for this purpose (see p. 2794 and *J.*, 1951, 1877). The isomerisation of sulphilimines is under further investigation.

When the experiments here described were almost complete, Dr. T. S. Stevens kindly informed us that he and Dunn (J. L. Dunn, Thesis, Univ. Glasgow, 1934) had already observed the migration of a benzyl group from benzyl phenyl sulphine toluene-*p*-sulphonylimine $(CH_2Ph)(Ph)S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ in boiling cymene, *N*-benzyltoluene-*p*-sulphonamide being isolated from the mixture. No migration occurred with benzyl methyl sulphine toluene-*p*-sulphonylimine at 165—170°.

Experimental

The diallyl sulphilimine derived from p-*acetamidobenzenesulphonic acid.*

p-Acetamido-*N*-chloro-*N*-sodiobenzenesulphonamide was prepared by the method of Todd, Fletcher, and Tarbell (*J. Amer. Chem. Soc.*, **1943**, **65**, 350) (Found: available Cl, 11·0. Calc. for $C_8H_8O_3N_2SClNa$: available Cl, 13·3%). The temperature must not drop below 10° while the hypochlorite solution is being added, as very little introduction of chlorine occurs below this temperature. In one experiment at 0°, the bulk of the sulphonamide was recovered unchanged.

Diallyl Sulphine p-*Acetamidobenzenesulphonylimine and its Isomer.*—Diallyl sulphide (7 g.) was added to an ice-cold aqueous 10% solution of the foregoing reagent, and the mixture shaken for an hour. A pale yellow precipitate separated which, after being washed first with water, then with 1% sodium hydroxide (to remove any sulphonamide), and finally with water, was dried (14 g.; m. p. 94—95°). After recrystallisation of this *sulphilimine* by addition of light petroleum (b. p. 60—80°) to a cold solution in much chloroform, the m. p. was 95°, unchanged on recrystallisation (Found: C, 51·3; H, 5·3; N, 8·4. $C_{14}H_{18}O_3N_2S_2$ requires C, 51·5; H, 5·5; N, 8·6%). After 4—5 weeks at room temperature this compound, without changing in weight, became pasty and gradually formed a wax. After 5 weeks, one sample had m. p. 46·5—49·5° whilst another was viscous. The sulphilimine was converted into a clear oil (A), without change in weight, when warmed on the steam-bath. The change seems incomplete at room temperature. The oily *isomer* (A) did not solidify below 0° (Found: C, 51·4; H, 5·7; N, 8·95%).

The wax, formed from the sulphilimine, was very soluble in acetone and methyl and ethyl alcohol, less so in benzene and chloroform, and insoluble in light petroleum. Attempts to crystallise it from mixtures of solvents at 0° failed. The solution in warm aqueous alcohol became deep yellow and there was a slight odour of an allyl-sulphur compound; some solid, m. p. 152—153°, separated on cooling. Similar treatment of the oil (A) yielded a further small quantity of this solid, m. p. 153° alone or on admixture with the above sample. The combined solids were recrystallised from chloroform and a mixture of chloroform and ethyl acetate, and the m. p. was raised to 154° alone or on admixture with authentic p-*acetamido*-N-*allylbenzenesulphonamide* (Found: C, 52·2; H, 5·6; N, 10·8. $C_{11}H_{14}O_3N_2S$ requires C, 52·0; H, 5·5; N, 11·1%).

Acid Hydrolysis of the Sulphilimine.—Freshly prepared diallyl sulphine *p*-acetamidobenzenesulphonylimine (1 g.) dissolved in hydrochloric acid (5 c.c.) to form a clear solution. (A small amount, warmed with dilute hydrochloric acid, formed an oil, apparently the liquid isomer.) The mixture was heated under reflux for 15 minutes. The solution became cloudy at first but later cleared again, becoming slightly yellow, and a trace of oil was formed at the surface. The solution was cooled and a pale yellow precipitate separated (0·15 g.) which sintered from 200° to 214°. It contained chlorine and was soluble in water, being, apparently, sulphanilamide hydrochloride. The acid solution was therefore evaporated to dryness and the residue, with the above solid, treated with warm aqueous ammonia, buff-coloured platelets separating which had m. p. 158—160° (0·5 g.). After recrystallisation from water the m. p. and mixed m. p. with authentic sulphanilamide (m. p. 163°) was 162—163°.

Alkaline Hydrolysis of the Liquid Isomer (p-*Acetamido*-N-*allyl*-N-*allylthiobenzenesulphon-*

amide).—The oil (A) (9 g.) was warmed under reflux on the steam-bath for 30 minutes with aqueous 25% sodium hydroxide (50 c.c.). Some resinous material separated. The filtrate was acidified in a stream of nitrogen; hydrogen sulphide and diallyl disulphide were trapped in sulphuric acid–cadmium sulphate and in mercuric chloride respectively (cf. *J.*, 1951, 1879). More resin was removed and the acidified solution evaporated. The residue with warm aqueous ammonia yielded crystals (4 g.), m. p. 100—102°, on cooling. After two recrystallisations from chloroform and light petroleum, the m. p. was 103—103·5°; it was 104°, alone or on admixture with authentic N′-*allylsulphanilamide*, after two further recrystallisations from chloroform (Found: C, 50·8; H, 5·7; N, 12·9. $C_9H_{12}O_2N_2S$ requires C, 50·8; H, 5·7; N, 13·2%).

Aqueous Hydrolysis of p-*Acetamido*-N-*allyl*-N-*allylthiobenzenesulphonamide*.—This compound (5 g.) was boiled with water (100 c.c.) under reflux in a stream of nitrogen for 15 hours. The volatile products passed through absorption vessels containing (1) aqueous 0·4% "dimedone" solution, (2) 5% cadmium sulphate in N-sulphuric acid to absorb hydrogen sulphide (Mapstone, *J. Proc. Australian Chem. Inst.*, 1946, **13**, 375), and (3) 3% mercuric chloride solution. In a "trap" preceding the dimedone solution a pungent odour was detected. A precipitate formed in (1) with m. p. 192° (after recrystallisation from aqueous alcohol) alone or on admixture with the authentic condensation product of acraldehyde and dimedone. The precipitate in (3) had the properties of the mercurated fission product of diallyl disulphide (Ash, Challenger, and Greenwood, *J.*, 1951, 1877). Hydrogen sulphide was detected by lead acetate paper but the quantity was insufficient to give a precipitate in (2). When the main solution was cooled, some resin and a crystalline solid (1·3 g.), m. p. 153°, separated. After recrystallisation from hot water this had m. p. 154° alone or mixed with authentic *p*-acetamido-*N*-allylbenzenesulphonamide.

N[1]-*Allylsulphanilamide*.—*N*-Acetylsulphaniloyl chloride (Schroeter, *Ber.*, 1906, **39**, 1559) (2 g.) was shaken for 8 hours with allylamine (0·5 g.) in 2N-sodium hydroxide (50 c.c.). The solution was warmed at 100° for 30 minutes, to ensure hydrolysis of the acetyl group, evaporated to a small bulk, and neutralised with dilute hydrochloric acid. The solid (1·5 g.) which separated had m. p. 98—100°. Two recrystallisations from chloroform and light petroleum (b. p. 60—80°) and one from chloroform, raised the m. p. to 104° (Found: C, 50·7; H, 5·9; N, 13·5. Calc. for $C_9H_{12}O_2N_2S$: C, 50·8; H, 5·7; N, 13·2%).

p-*Acetamido*-N-*allylbenzenesulphonamide*.—Allylamine (0·5 g.) was slowly added to *N*-acetylsulphaniloyl chloride (1·8 g.) at 0°, giving an oily mass. The reaction was completed by warming for 10 minutes at 100°, and excess of allylamine removed with dilute hydrochloric acid. The resultant granular *amide* was filtered off and washed with water (2 g.; m. p. 117—119°). After recrystallisation from water the m. p. was 153·5—154·5° (needles), raised by recrystallisation from chloroform to 154—154·5° (Found: C, 52·3; H, 5·1; N, 11·0; S, 12·8. $C_{11}H_{14}O_3N_2S$ requires C, 52·0; H, 5·5; N, 11·1; S, 12·6%).

The dibenzyl sulphilimine derived from toluene-p-*sulphonic acid.*

The sulphilimine (dibenzyl sulphine toluene-*p*-sulphonylimine), prepared by Mann and Pope's method (*J.*, 1922, 1052), was shaken with 1% aqueous sodium hydroxide (100 c.c.). After two recrystallisations from benzene it had m. p. 192° (Found: C, 65·9; H, 5·6; N, 3·7. Calc. for $C_{21}H_{21}O_2NS_2$: C, 65·8; H, 5·5; N, 3·65%). Toluene-*p*-sulphonamide (0·25 g.), m. p. 136—137°, was recovered from the alkaline wash-liquors. A specimen kept for several months at room temperature had not altered in m. p.

The sulphilimine (0·5 g.) was boiled for 30 minutes with dilute hydrochloric acid, giving toluene-*p*-sulphonamide, m. p. and mixed m. p. 137°.

Pyrolysis.—The foregoing compound (25 g.) was heated under reflux in nitrogen for 16 hours at 180—200°, with protection by calcium chloride tubes. The melt gave, on cooling, an orange paste (P). A small amount of precipitate separated in a solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid through which the issuing nitrogen was passed. On crystallisation from alcohol the m. p. alone or on admixture with authentic benzaldehyde 2 : 4-dinitrophenylhydrazone was 235°.

The paste (P), when triturated with ether (20 c.c.), gave almost colourless crystals (7 g.) which after repeated washing with ether were treated with 2N-sodium hydroxide (30 c.c.) to remove sulphonamide. The residue, when washed with water and dried, sintered from 130—150°. Recrystallisation from chloroform and light petroleum (b. p. 60—80°) and then from benzene raised the m. p. to 190° alone and 190—191° on admixture with authentic dibenzyl sulphine toluene-*p*-sulphonylimine (m. p. 191—192°). Acidification of the alkaline wash-liquors gave a solid (1·5 g.), m. p. 115—120°. When recrystallised from chloroform and light

petroleum (b. p. 60—80°) this had m. p. 136—137° alone or mixed with authentic toluene-*p*-sulphonamide.

The ethereal washings from (P) were extracted with 2N-sodium hydroxide (15 c.c.). Acidification of the aqueous layer precipitated more toluene-*p*-sulphonamide (2·3 g.). Evaporation of the ether left an orange-coloured mass of m. p. 55—60° (2·5 g.). After three crystallisations from methyl alcohol the m. p. was 69—70° alone or on admixture with authentic dibenzyl disulphide (Found : C, 68·0; H, 5·7; S, 26·1. Calc. for $C_{14}H_{14}S_2$: C, 68·4; H, 5·7; S, 26·0%).

Evaporation of the mother-liquors from the disulphide left a waxy orange solid. Crystallised twice from chloroform and light petroleum (b. p. 60—80°) and then twice from ethyl alcohol this had m. p. 115° alone or mixed with authentic *N*-benzyltoluene-*p*-sulphonamide (Chattaway, *J.*, 1905, **87**, 159) (Found : C, 64·4; H, 6·0; N, 5·4; S, 12·7. Calc. for $C_{14}H_{15}O_2NS$: C, 64·4; H, 5·8; N, 5·4; S, 12·3%).

The mother-liquors from the orange wax were evaporated, leaving a red oil (4 g.) which did not crystallise. Distillation at 0·5 mm. yielded a red oil, b. p. 110—120°. This partly solidified and when crystallised from light petroleum (b. p. 60—80°) (yield, 2 g.) and then from ethyl alcohol had m. p. 124—125° alone or mixed with stilbene (Found : C, 93·3; H, 6·7. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). The mother-liquors yielded more stilbene and traces of an orange-red oil. The colour was not discharged by zinc dust in acetic acid, so an azo-compound was not present. The oil contained no component volatile in steam and was not identified.

*The allyl benzyl sulphilimine derived from toluene-*p*-sulphonic acid and its isomer.*

*Preparation of Allyl Benzyl Sulphine Toluene-*p*-sulphonylimine.*—Allyl benzyl sulphide (von Braun and Engelbertz, *Ber.*, 1923, **56**, 1573) (2 g.) was slowly added, with shaking, to ice-cold aqueous 10% chloramine-T solution (40 c.c.). The pasty precipitate which became granular after 1 hour's shaking was shaken with 1% sodium hydroxide solution (to remove sulphonamide). After filtration and washing with water it had m. p. 73—74°. Three crystallisations from chloroform–light petroleum (b. p. 60—80°) raised the m. p. to 84—85°. A sample of the *sulphilimine* was freshly prepared and immediately sent for analysis (Found : C, 61·0; H, 5·8; N, 4·2. $C_{17}H_{19}O_2NS_2$ requires C, 61·3; H, 5·7; N, 4·2%). After one week the sulphilimine was re-washed with water and recrystallised as before. The m. p. was then constant at 51° (Found : C, 61·4; H, 5·7; N, 4·2%). Two further preparations gave yields of sulphilimine of 92 and 88%. At first the m. p. of the pure product was 85°. After one week the weight was unchanged and the m. p. 50—51°. The m. p.s of samples 3, 5, and 7 days after preparation were 76—77°, 62—64°, and 50—51° respectively. At 100° the sulphilimine formed an oil which resolidified on cooling, without changing in weight, and melted at 50—51°.

Investigation of the Time required to Isomerise the Sulphilimine at its Melting Point.—Allyl benzyl sulphine toluene-*p*-sulphonylimine was prepared and purified as before. The m. p., after one hour, was 84—85°. Four flasks (*a*—*d*), each containing 0·2 g. of the sulphilimine, were immersed, in turn, in a bath at 90—100°. The duration of heating, timed from the onset of melting, was (*a*) 15 sec., (*b*) 5 min., (*c*) 10 min., (*d*) 15 min. The resultant solids, when washed with light petroleum, had m. p. 50—51°. It appears that isomerisation of the sulphilimine occurs practically instantaneously at its m. p.

Identical results were obtained when the sulphilimine (15 g.) within 12 hours of preparation was heated at 75—85° in dry nitrogen for 16 hours.

Acid Hydrolysis of the Sulphilimine.—Freshly prepared allyl benzyl sulphilimine (0·25 g.) was refluxed for 1 hour with hydrochloric acid. Traces of oil quickly formed. A solid, m. p. 112—115°, separated on cooling, and on crystallisation from dilute alcohol and then from chloroform and light petroleum (b. p. 60—80°) had m. p. 136·5—137·5° and mixed m. p. 136—137° with toluene-*p*-sulphonamide.

Alkaline Hydrolysis of "Altered Allyl Benzyl Sulphilimine" (The Solid Isomer, m. p. 50—51°, formed after seven days at room temperature).—The isomer (8 g.) was boiled under reflux for 1 hour with 25% aqueous sodium hydroxide (45 c.c.), giving an orange oil which gradually dissolved and a faint sulphide odour. The cold solution was acidified with hydrochloric acid and volatile products aspirated through tubes containing (i) 5% cadmium sulphate in N-sulphuric acid (Mapstone, *loc. cit.*), (ii) 4% mercuric cyanide solution, and (iii) 3% mercuric chloride solution. Cadmium sulphide was precipitated in (i). No precipitate formed in the mercuric cyanide or mercuric chloride, indicating the absence of volatile thiols or sulphides.

The acidified reaction mixture contained a colourless solid and a yellow oil. The first when crystallised from aqueous alcohol (2·5 g.) and then from chloroform and light petroleum (b. p.

60—80°), had m. p. 63° alone or on admixture with authentic *N*-allyltoluene-*p*-sulphonamide (m. p. 63°). (Found: C, 57·1; H, 6·25; N, 6·5. Calc. for $C_{10}H_{13}O_2NS$: C, 56·9; H, 6·2; N, 6·6%). The combined filtrate and washings were extracted twice with ether. The aqueous solutions yielded sodium chloride. The ether was shaken with 2N-sodium hydroxide (5 c.c.). Acidification of the alkaline layer gave a precipitate (0·2 g.). After two recrystallisations from aqueous alcohol, the m. p. and mixed m. p. with *N*-allyltoluene-*p*-sulphonamide was 63—64°. A further small quantity separated from the alcoholic mother-liquors. Evaporation of these liquors left a residue with m. p. 100—102° (111—114° on recrystallisation from hot water). After sublimation the m. p. and mixed m. p. with benzoic acid was 120—121°. The ethereal layer yielded an orange-coloured oil and a solid. When crystallised from aqueous alcohol the latter had m. p. 62—63° alone or on admixture with *N*-allyltoluene-*p*-sulphonamide. The oil was therefore treated with 2N-sodium hydroxide and twice re-extracted with ether. Acidification of the alkali gave a further 0·1 g. of *N*-allyltoluene-*p*-sulphonamide. Evaporation of the ether gave a yellow wax which after trituration with methyl alcohol melted at 64—65°, and after three recrystallisations, from methyl alcohol, at 69—70° alone or mixed with dibenzyl disulphide.

Alkaline Hydrolysis of "Altered Allyl Benzyl Sulphilimine."—The solid isomer (0·5 g.; m. p. 50—51°) formed by heating the sulphilimine was boiled under reflux for 1·5 hours with 25% sodium hydroxide solution (3 c.c.). The orange-red solution had an odour of benzaldehyde. The cold solution was acidified and volatile products were aspirated as before. Hydrogen sulphide was evolved. The precipitate in the acidified reaction mixture was separated. The m. p. was indefinite. Extraction with hot benzene left a small residue of silica. The benzene yielded a yellow oil which was crystallised from water and then had m. p. 58—60°. On recrystallisation from light petroleum (b. p. 60—80°) and then aqueous alcohol, crystals, m. p. 62—63° alone or mixed with *N*-allyltoluene-*p*-sulphonamide, were obtained.

Attempted Acid Hydrolysis of N-*Allyl*-N-*benzylthiotoluene*-p-*sulphonamide.*—*N*-Allyl-*N*-benzylthiotoluene-*p*-sulphonamide (0·5 g.), formed from allyl benzyl sulphilimine in 7 days at room temperature, was boiled under reflux for 30 minutes with hydrochloric acid (10 c.c.). The resultant oil was extracted with ether, the aqueous layer separated, and the ethereal solution washed with water and evaporated leaving a colourless semi-solid product (0·5 g.). After three recrystallisations from alcohol the m. p. was constant at 76—77°. Chlorine was present but no precipitate was formed with silver nitrate. The *substance* is still under investigation (Found: N, 3·9; Cl, 9·7. $C_{17}H_{20}O_2NS_2Cl$ requires N, 3·7; Cl, 9·6%). It may arise by addition of hydrogen chloride to the double bond of the allyl group of the "altered sulphilimine."

ADDENDUM by THOMAS S. STEVENS and JOHN L. DUNN.

Benzyl Phenyl Sulphine Toluene-p-*sulphonylimine.*—Benzyl phenyl sulphide did not react with chloramine-T in hot aqueous acetone. The sulphide (10 g.) and chloramine-T (15 g.) were therefore boiled in alcohol for 2 hours during which sodium chloride separated. After removal of most of the solvent and dilution with water the mixture gave a solid *sulphilimine* which crystallised from alcohol in cubes, m. p. 145—146° (12 g.) (Found: S, 17·1. $C_{20}H_{19}O_2NS_2$ requires S, 17·3%). Boiling with aqueous sodium hydroxide for 3 hours and acidification gave toluene-*p*-sulphonamide.

The sulphilimine was boiled for 24 hours in *p*-cymene, the solvent removed in steam, and the residue extracted with dilute aqueous sodium hydroxide. Acidification gave *N*-benzyltoluene-*p*-sulphonamide, identified by its m. p. and mixed m. p. No trace of the intermediate product could be found.

Benzyl methyl sulphine toluene-p-*sulphonylimine* was prepared from the sulphide (3·2 g.) in acetone (20 c.c.) and chloramine-T (8 g.) in water (45 c.c.). Much heat was evolved and crystals separated. After 1 hour's shaking the acetone was removed and the sulphilimine filtered off; it recrystallised from alcohol in cubes, m. p. 161—162° (6 g.) (Found: N, 4·7. $C_{15}H_{17}O_2NS_2$ requires N, 4·6%). When this was heated to 165—170° for 4 hours, slight decomposition occurred but the major portion was recovered unchanged; at 200° complete decomposition took place.

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