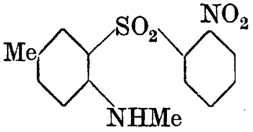
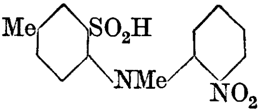
419. *A Rearrangement of* ortho-*Amino-sulphones.*

By LEONARD A. WARREN and SAMUEL SMILES.

THE displacement of benzenesulphonyl from 2-nitrodiphenylsulphone by aniline suggested (this vol., p. 1489) that a corresponding intramolecular displacement should be realisable with *o*-amino-sulphones of suitable constitution (*e.g.*, V). Experiments have now been made in accordance with this suggestion. The behaviour of the *methylamino-sulphone* (I) was first examined. This substance was obtained from the 2-*nitrobenzenesulphonyl* derivative of monomethyl-*p*-toluidine by the rearrangement recorded by Witt and Truttwin (*Ber.*, 1914, **47**, 2786) in the case of the 3-nitro-derivative. No evidence of the rearrangement of this sulphone could be found by the action of heat; with alcoholic sodium ethoxide (2*N*) the conversion was slow, but with warm concentrated alkali the sulphinate (II) was rapidly formed. The unstable acid was characterised by conversion into the *disulphide* and the *methylsulphone.* In hot acetic acid the sulphinate (II) yields the cyclic *sulphone* (III) and nitrous acid, and only a small amount of this product is formed in alkaline media.

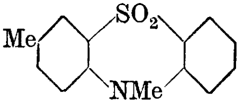
(I.)





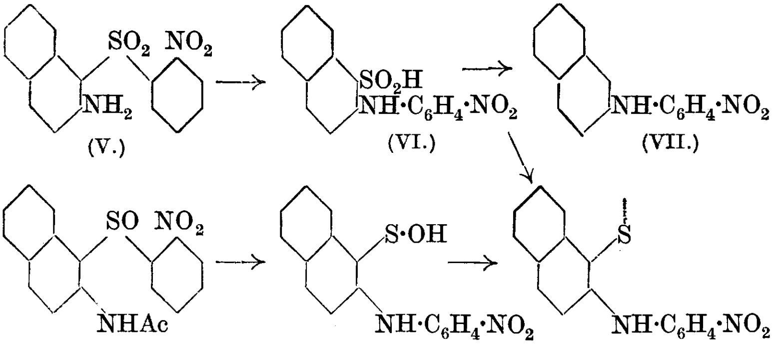
(II.)

(III.)



$[O_2N\cdot C_6H_4\cdot NH\cdot C_{10}H_6]_2SO$
(IV.)

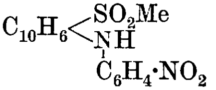
The acetyl derivative of the sulphide generated from 2-naphthylamine and 2-nitrophenylchlorothiol yielded the corresponding *sulphone* by oxidation; after hydrolysis of the latter in acid media the *amino-sulphone* (V) was obtained. Rearrangement of this sulphone took place more easily than that of (I), warm dilute alkali (2*N*) being sufficient. The *sulphinic acid* formed (VI) was further characterised by the *methyl-sulphone* (XI) and by conversion into a *disulphide* (VIII); moreover, it exhibited the instability of other sulphinic acids of this type and easily lost sulphur dioxide, forming the nitro-amine (VII). In the latter process the *sulphoxide* (IV) was usually formed also, presumably by condensation of the amine (VII) with the sulphinic acid according to the general behaviour of these reagents observed by Hinsberg (*Ber.*, 1903, **36**, 107) under similar conditions. Rearrangement of the acetyl derivative of (V) was effected in a similar manner; the product was the acetylated sulphinic acid (XII), which was characterised as the methyl-sulphone, the relationship of the latter to (XI) being established by hydrolysis.



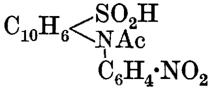
(V.) (VI.) (VII.)

(IX.) (X.) (VIII.)

(XI.)



$$C_{10}H_6<\begin{array}{l}SO_2Me\\ NH\\ |\\ C_6H_4\cdot NO_2\end{array}$$



$$C_{10}H_6<\begin{array}{l}SO_2H\\ NAc\\ |\\ C_6H_4\cdot NO_2\end{array}$$

(XII.)

The economical preparation of the sulphone (V) required the isolation of the *acetamido-sulphoxide* (IX) at an intermediate stage. The behaviour of this material with alkali hydroxide was examined. Rearrangement, accompanied by removal of the acetyl group, was effected under conditions similar to those required by the sulphone. This result was hardly expected, since according to the usual formulation the character of sulphur would appear to be less positive in thionyl than in sulphonyl, but a strict comparison between the two cases was not possible owing to difficulty in controlling the conditions of rearrangement. It is evident that the first product from the acetamido-sulphoxide (IX) after deacetylation and rearrangement should be the sulphenic acid (X), but since substances of this class are rapidly decomposed in warm alkaline media, yielding disulphides (Zincke and Farr, *Annalen*, 1912, **391**, 67), the disulphide (VIII) must be expected as the chief characteristic product. This substance was isolated in good yield and it was identical with the disulphide obtained by reduction of the sulphinic acid (VI).

EXPERIMENTAL.

o-*Nitrobenzenesulpho*-p-*toluidide*, $NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4Me$, was obtained from *o*-nitrobenzenesulphonyl chloride and *p*-toluidine in the usual manner; recryst. from EtOH, it had m. p. 116° (Found: C, 53·4; H, 4·5. $C_{13}H_{12}O_4N_2S$ requires C, 53·4; H, 4·1%). Treatment of this in aq. alk. solution with Me_2SO_4 gave o-*nitrobenzenesulpho*-p-*methyltoluidide*,

$$NO_2\cdot C_6H_4\cdot SO_2\cdot NMe\cdot C_6H_4Me,$$

m. p. 84° after recrystn. from EtOH (Found : C, 54·9; H, 4·8. $C_{14}H_{14}O_4N_2S$ requires C, 54·9; H, 4·6%). A solution of this (2 g.) in conc. H_2SO_4 (4 c.c.) was warmed (100°; 5 min.) and then diluted. o-*Nitrophenyl*-4-*methylamino*-m-*tolylsulphone* (I) separated as a viscous mass; it was recrystallised from EtOH and AcOH successively and then formed yellow prisms, m. p. 122° (Found: C, 54·9; H, 4·6. $C_{14}H_{14}O_4N_2S$ requires C, 54·9; H, 4·6%). Attempts to demethylate the substance (HBr in AcOH) were unsuccessful.

The K salt of 4-*o*-nitrophenylmethylamino-*m*-tolylsulphinic acid (II) was obtained from (I) by trituration with 50% KOH aq. at 70—80° until the liquid product had solidified to an orange cryst. mass. From this, cold H_2O removed the sulphinate, leaving a small residue of the thiazine dioxide (III).

4-o-*Nitrophenylmethylamino*-m-*tolylmethylsulphone* (compare II) was readily formed when the K salt yielded by conversion of the sulphone (I) (4 g.) was treated (2 hr.) with boiling MeOH (40 c.c.) and H_2O (4 c.c.) which contained MeI (8 c.c.). The oil which remained after the MeOH had been removed solidified in contact with EtOH. Recryst. from EtOH, the product formed yellow prisms, m. p. 120° (Found: C, 56·2; H, 5·1; N, 8·7; S, 9·8. $C_{15}H_{16}O_4N_2S$ requires C, 56·2; H, 5·0; N, 8·7; S, 10·0%). 4-o-*Nitrophenylmethylamino*-m-*tolyl disulphide* (compare II) was formed when an EtOH solution of the acid containing SO_2 and a little HI was boiled. The product separated as an oil which finally solidified and was recryst. from EtOH and then from AcOH (charcoal); it formed yellow plates, m. p. 132—133° (Found: C, 61·4; H, 5·0; N, 10·1; S, 11·8. $C_{28}H_{26}O_4N_4S_2$ requires C, 61·5; H, 4·7; N, 10·2; S, 11·7%).

3 : 6-*Dimethylthiodiphenylamine Dioxide* (III).—When the sulphinate (II) obtained from the sulphone (5 g.) was dissolved in warm AcOH, oxides of N were liberated. Addition of H_2O gave a viscous ppt. which, after treatment with aq.-alc. NaOH, crystallised from AcOH (charcoal) in prisms (1·8 g.), m. p. 153° (Found: C, 64·6; H, 5·3; N, 5·4; S, 12·3; *M*, 261. $C_{14}H_{13}O_2NS$ requires C, 64·8; H, 5·0; N, 5·4; S, 12·4%; *M*, 259). In hot conc. H_2SO_4 the cyclic *sulphone* gave the characteristic blue solution observed (Bernthsen, *Annalen*, 1885, **230**, 92) with 6-methylthiodiphenylamine dioxide.

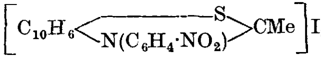
o-*Nitrophenyl* 2-*Acetamido*-1-*naphthyl Sulphoxide* (IX).—The corresponding amino-sulphide was obtained by Zincke's method (*Annalen*, 1912, **391**, 82). It had m. p. 188°, and the acetyl derivative m. p. 187°. Zincke records m. p. 183—184° for both substances. AcOH (10 c.c.) containing the acetamido-sulphide (3 g.) and H_2O_2 (4 c.c.; 30%) was kept at 100° (½ hr.). The required *sulphoxide* separated when the solution was agitated; recryst. from AcOH, it formed yellow plates, m. p. 198° (decomp.) (Found: C, 61·1; H, 4·2; N, 7·7; S, 9·0. $C_{18}H_{14}O_4N_2S$ requires C, 61·0; H, 4·0; N, 7·9; S, 9·0%).

o-*Nitrophenyl*-2-*acetamido*-1-*naphthylsulphone* (compare V).—The sulphoxide (IX) (3 g.) in AcOH (10 c.c.) with H_2O_2 (4 c.c.; 30%) was kept at 100° (1 hr.); the product separated when the mixture was cooled. Oxidation was repeated if the m. p. of the product was below 158—159°. Recryst. from AcOH, the *sulphone* formed orange plates, m. p. 160° (Found: C, 58·2; H, 4·0; S, 8·6. $C_{18}H_{14}O_5N_2S$ requires C, 58·4; H, 3·8; S, 8·6%). When EtOH (100 c.c.) containing this sulphone (6 g.) and conc. H_2SO_4 (20 c.c.) was boiled, the material dissolved. Half the solvent was then evaporated, and H_2O added to the cold mixture. o-*Nitrophenyl*-2-*amino*-1-*naphthylsulphone* (V), which separated, formed yellow-brown plates, m. p. 171°, from AcOH (Found :

C, 58·7; H, 4·0; N, 8·2; S, 9·8. $C_{16}H_{12}O_4N_2S$ requires C, 58·5; H, 3·7; N, 8·5; S, 9·8%).

2-o-*Nitrophenylaminonaphthyl*-1-*sulphinic Acid* (VI).—A boiling *N*-solution of NaOH in H_2O and EtOH (equal vols.) slowly (½ hr.) dissolved the sulphone (V) suspended in it. After EtOH had been removed, the *sulphinic acid* was liberated by dil. H_2SO_4. This was purified, first as the red Na salt from warm aq. 2*N*-NaOH, and finally from H_2O and acetone. The acid formed orange plates, m. p. 210° (decomp.), which were sol. in Na_2CO_3 aq. and gave a purple solution in conc. H_2SO_4 (Found: C, 58·6; H, 4·0; N, 8·6. $C_{16}H_{12}O_4N_2S$ requires C, 58·5; H, 3·7; N, 8·5%).

2-o-*Nitrophenylamino*-1-*naphthylmethylsulphone* (XI) was obtained when a solution of the sulphinic acid (VI) (5 g.) in MeOH (60 c.c.) containing MeI (10 c.c.) and the necessary amount of MeONa was boiled (1½ hr.); it was isolated as a red oil by removal of the greater part of the solvent and addition of H_2O, and was purified (4 g.) successively from EtOH and AcOH; it then formed orange plates, m. p. 125° (Found: C, 59·8; H, 4·3; N, 8·2; S, 9·3. $C_{17}H_{14}O_4N_2S$ requires C, 59·6; H, 4·1; N, 8·2; S, 9·4%).

2-o-*Nitrophenylacetamido*-1-*naphthylmethylsulphone* (compare XII).—The acetamido-sulphone (compare V) readily dissolved in warm 2*N*-NaOH. The sodium sulphinate separated from the cooled liquid, but the acid (XII) could not be obtained pure; the former was therefore converted into the *methylsulphone* by reaction with MeI in hot MeOH and H_2O. The viscous mass which remained after the MeOH had been evaporated solidified in contact with EtOH; it was purified from AcOH and then had m. p. 195° (Found: C, 59·5; H, 4·5; N, 7·6. $C_{19}H_{16}O_5N_2S$ requires C, 59·4; H, 4·2; N, 7·3%). Hydrolysis of this acetyl derivative with excess NaOH in boiling EtOH and H_2O gave the methylsulphone (XI), m. p. 125°, which was identical with that obtained from the sulphinic acid (VI). Attempts to obtain the disulphide from the sulphinic acid (XII) by reducing it with HI were unsuccessful. From boiling AcOH containing HI and this acid, a *periodide* separated in brown needles, m. p. 183°. This substance,  $\left[C_{10}H_6<\begin{matrix}S\\N(C_6H_4\cdot NO_2)\end{matrix}>CMe\right]I_3$, is evidently derived from the naphthathiazole (Found: C, 30·8; H, 2·2; N, 3·9; I, 54·3. $C_{18}H_{13}O_3N_2I_3S$ requires C, 30·8; H, 1·9; N, 4·0; I, 54·3%) formed by reaction of the thiol and the acetyl group.

2-o-*Nitrophenylamino*-1-*naphthyl Disulphide* (VIII).—(a) When a solution of the sulphinic acid (VI) in acetone containing a little HI (*d* 1·7) was boiled, a red disulphide separated. (b) When the acetamido-sulphoxide (IX) (3 g.) was treated with excess of boiling 2*N*-NaOH, it was rapidly attacked, yielding a red solution of the sulphinate and the disulphide (VIII) (1·3 g.), which remained suspended. This was recryst. from PhCl or $C_2H_2Cl_4$ and formed orange needles, m. p. 235° (decomp.), identical with the disulphide obtained in (a) (Found: C, 65·0; N, 9·3; S, 10·6. $C_{32}H_{20}O_4N_4S_2$ requires C, 65·1; N, 9·5; S, 10·8%).

o-*Nitrophenyl*-2-*naphthylamine* (VII).—(a) When a solution of the sulphinic acid (VI) in AcOH was boiled, SO_2 was liberated and *bis*-2-o-*nitrophenylamino*-1-*naphthyl sulphoxide* (IV) separated as red needles, m. p. 225° (decomp.) (Found: C, 67·0; H, 4·1; N, 9·7; S, 5·6. $C_{32}H_{22}O_5N_4S$ requires C, 66·9; H, 3·8; N, 9·7; S, 5·6%), which were very sparingly sol. in most org. media. After removal of this sulphoxide the solution was diluted and the material which then separated was recrystallised from EtOH (charcoal). The *amine* formed orange needles, m. p. 110° (Found: C, 72·5; H, 4·6; N, 10·6. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·5; N, 10·6%). This amine was also obtained by reduction of (a) the sulphoxide (IV) or (b) the disulphide (VIII) in boiling AcOH with HI (*d* 1·7). In both cases H_2S was liberated.

KING'S COLLEGE, LONDON. [*Received, September* 29*th*, 1932.]