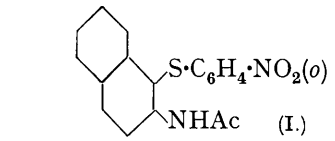
42. *A Rearrangement of* o-*Acetamido-sulphones and -sulphides.*

By WILFRID J. EVANS and SAMUEL SMILES.

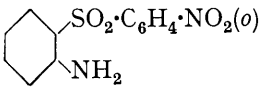
DURING a study of the rearrangement of *o*-amino-sulphones it was shown (J., 1932, 2774) that the acetamido-derivatives of one of these (I, S replaced by SO_2) suffered rearrangement without deacetylation. In this case the process evidently consists in a displacement of sulphonyl by the acetamido-group and is analogous with that observed (J., 1933, 1490) with *o*-acetamido-sulphoxides in which the thionyl group is similarly displaced. Two further examples of this rearrangement have been examined. The sulphone (II) with aqueous sodium hydroxide easily gave the sulphinic acid (III). This was characterised as a sulphinic acid by conversion into a disulphide and the methyl-sulphone (IV); further proof of its structure was obtained by removal of the sulphinic group. With sulphinic acids derived from diphenyl ether the degradation has been effected (J., 1931, 3267) by oxidation, followed by hydrolysis of the sulphonic acid in acid media; but with the diphenylamine derivatives now in question this process was unsuccessful. A better method and one which is recommended for general use in the degradation of aromatic sulphinic acids was found in their reaction with mercuric chloride, which removed sulphur dioxide and yielded the mercurichloride, Ar·HgCl (Peters, *Ber.*, 1905, **38**, 2567; Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1921, **43**, 607); the metal was then removed from the latter by hydrochloric acid. By this treatment the sulphinic acid (III) yielded 2-nitrodiphenylamine.

The acetyl derivative of (II) with one molecular proportion of alkali hydroxide gave the acetyl derivative of (III); this was characterised by methylation, which yielded the acetyl derivative of (IV), the relationship of this to (IV) being established by hydrolysis.

Similarly, the sulphone (V) with excess of alkali hydroxide yielded a sulphinic acid (compare III), which gave a methyl-sulphone (VI) and a disulphide and was converted into (VII) by the method of degradation described. The same sulphone (V) with one molecular proportion of alkali hydroxide was converted into the acetyl derivative of a sulphinic acid (compare III) and thence into the acetylated methyl-sulphone (compare VI), which yielded (VI) on hydrolysis. The methyl-sulphones (IV) and (VI) have served as standards in determining the structure of the products obtained by rearrangement of *o*-acetamido-sulphoxides (J., 1933, 1490).



(I.)



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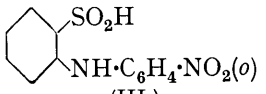

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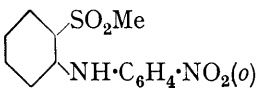

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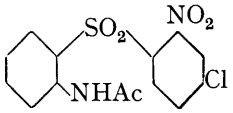

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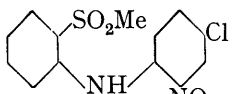

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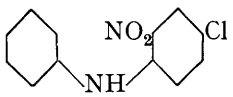
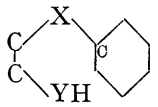


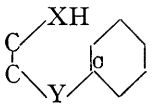
(VII.)

The results of these experiments and others preceding them (J., 1932, 2774; 1933, 1490) have now given several examples in each case of the rearrangement of *o*-amino-sulphones, *o*-acetamido-sulphones, and *o*-acetamido-sulphoxides; it is now evident in substances of this type, which contain the sulphur group attached to positive carbon, that sulphonyl may be displaced by aromatic amino- and acetamido-groups, and thionyl by the acetamido-group. A survey of the rearrangements which have been encountered (summary on p. 184) in the experiments arising from the conversion of *iso*-2-naphthol sulphide into 2-naphthol 1-sulphide shows not only that they may be referred to the same general type (VIII ⟶ IX), but also that the conditions controlling them are similar.

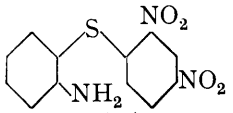
In the case of the 2-hydroxy-sulphones (VIII; X = SO_2, YH = OH) it has been shown (J., 1934, 422) that, apart from the stereochemical relationship of X and Y to C, the chief factors to be considered are (1) the positive character of C, (2) the capacity of Y to meet the electron demand at C, and (3) the tendency of YH to lose a proton in the medium employed. Comparing the behaviour of a series in which C was provided by an *o*-nitro-group, it was found that, when YH was aromatic hydroxyl, rearrangement took place when X was SO_2 but not with X as SO or S; and when YH was aliphatic hydroxyl, that X might be SO_2 or SO, but with S as X rearrangement did not take place. These relations indicate that the character of X must be regarded as a fourth condition determining this type of rearrangement and, as might be expected, that with a given YH and C a decrease in the positive



(VIII.)



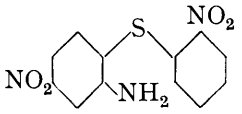
(IX.)



(X.)

character or increase in the negative character of X is less favourable to the displacement of the latter. This view is confirmed by the behaviour of the corresponding amino-derivatives. Whilst the amino-sulphones of this series (VIII; X = SO_2, YH = NH_2) readily undergo rearrangement in presence of warm alkali hydroxide, the relevant *o*-amino-sulphides (I, NHAc replaced by NH_2), (II, SO_2 replaced by S), (V, NHAc replaced by NH_2, and SO_2 by S), (X), and (XI) are unattacked even by alcoholic sodium hydroxide. The acetyl derivative of (XI) was obtained together with oxidation products by nitrating the acetyl derivative of (II); the given structure is assigned to it because after deamination 2 : 4′-dinitrodiphenyl sulphide was obtained, and the corresponding acetylated sulphone, after rearrangement and degradation of the sulphinic acid formed, yielded 2 : 3′-dinitro-diphenylamine. The method used (J., 1934, 422) with the *o*-hydroxy-sulphones for investi-

gating the influence of changes in the character of YH (VIII) cannot be applied to the *o*-amino-sulphones; nevertheless, interesting results have been obtained by a qualitative examination of suitable derivatives. For the present purpose the character of the amino-group (YH) was more effectively varied by substitution in the group itself than by substitution in the aromatic nucleus bearing it.



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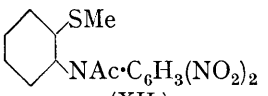

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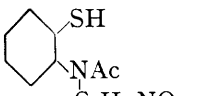

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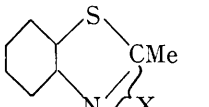


(XIV.)

The derivatives of the sulphone (II) in which YH is NHMe, NH_2, NHAc, or $NH{\cdot}SO_2Ph$ form a series in which the donor capacity of the nitrogen diminishes (condition 2) and its tendency to lose a proton increases (condition 3). All these derivatives undergo rearrangement, yielding the corresponding diphenylamine-2-sulphinates. Attention is directed to the requirement of concentrated alkali to effect the rapid change of the methylamino-sulphone (J., 1932, 2774) and to the incomplete conversion of the benzenesulphonyl derivative under usual conditions. The former circumstance may be regarded as due to the reluctance of the methylamino-group to lose a proton, and the latter to the feebler electron supply offered by the nitrogen.

Turning to the *o*-amino-sulphides, it was found, in contrast with the inactivity of the parent amines, that the acetyl derivatives of all these suffered rearrangement in alcoholic sodium hydroxide. The products, evidently the *N*-acetylthiols (compare XIII), were not in all cases isolated, but were obtained after methylation as the methylthiols (*e.g.*, XII); these gave methyl mercaptan with hydriodic acid and in the cases of the sulphides (I), (II, SO_2 replaced by S, and NH_2 by NHAc), (V, SO_2 replaced by S), and (XI, NH_2 replaced by NHAc) were identified after oxidation by comparison with the corresponding derivatives (*e.g.*, IV) obtained from the sulphones through the sulphinic acids. The methylthiol (XII), obtained from the acetyl derivative of (X), was hydrolysed; the product was identical with that furnished by synthesis from 2-aminothioanisole and 1-chloro-2 : 4-dinitrobenzene.

The *N*-acetylthiols (*e.g.*, XIII) behave as pseudo-bases (compare Mills, Clark, and Aeschliman, J., 1923, 2353) and are converted by acids into salts to which the structure (XIV) may be provisionally assigned; the investigation of the latter substances is being continued. The salts in question are also formed by reduction of the *N*-acetyl-sulphinic acids (compare III, where NH is NAc) with hydriodic acid. This noteworthy difference in behaviour of the 2-amino-sulphides and their acetyl derivatives is ascribed to the amino-group acquiring by acetylation an increased tendency to lose a proton; at the same time it is evident that acetylation has not depressed the donor function of the nitrogen sufficiently to prevent that element meeting the demand of the positive carbon atom concerned. It is worth notice that the conversion of the nitro-derivative (XI, NH_2 replaced by NHAc) was remarkably quicker than that of the parent sulphide (II; SO_2 replaced by S, and NH_2 by NHAc); this may be attributed mainly to weakening of the negative character of the thio-group by nitration in the para-position.

The explanation given to the behaviour of these *N*-acetyl derivatives leads to the conclusion that the rearrangement of the *N*-substituted 2-amino-sulphides of this type depends for its success on the proper balance of these two essential properties of the nitrogen group (VIII; YH = NRH, X = S). In an extreme case where the donor capacity of Y in YH is high, the tendency to proton release would be slight and the rearrangement might then fail under mildly alkaline conditions. On the other hand, when a proton is easily set free from YH, and Y may form an ion in the medium used, the rearrangement might fail owing to the diminished electron supply available from Y. The series of *N*-substituted sulphones gave, as already described, indication that these conditions might be attained in cases where X (VIII) is less positive than sulphonyl and therefore less easily displaced. Accordingly the following series of *N*-substituted derivatives of 2′-nitro-2-aminodiphenyl sulphide was

examined; the results agree with those anticipated: NMe_2, NHMe, NH_2, NHAc, $NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2(o)$, $NH{\cdot}C_6H_2(NO_2)_3$, $NH{\cdot}SO_2Ph$.

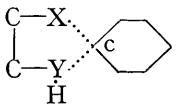
In hot alcoholic sodium hydroxide (1 mol., *N*/3), only the acetyl and the 2-nitrobenzoyl derivatives suffered rearrangement; the picryl and the benzenesulphonyl derivatives yielded sodium salts and were recovered from these. The case of the 2-nitrobenzoyl derivative is worth attention; rearrangement of this substance proceeds far less readily than that of the acetyl derivative; in fact under the usual conditions the greater part of the material was recovered and only a small amount of the product of rearrangement, about 20%, could be isolated as the *S*-methyl ether (compare XII). The accord of theory with this behaviour is evident.

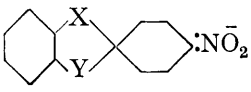
Further support is thus obtained for the views expressed concerning the general character of these rearrangements and the conditions which govern them.

Since the discovery of the conditions attending the conversion of *iso*-2-naphthol sulphide into 2-naphthol sulphide was made (J., 1931, 914) eight varieties of the general type of rearrangement (VIII ⟶ IX) have been encountered. These are summarised by the following list, which shows in the case of each YH the groups capable of playing the part of X in the rearrangements hitherto observed. All the rearrangements indicated have been observed with C (VIII) furnished by an *o*-nitro-group as well as in many other cases with C more, or less, positive than this. The list also shows the influence of varying YH and X on the occurrence of rearrangement: it is obviously capable of extension; *e.g.*, the rearrangement

If YH is	NHAc,	X may be	SO_2, SO, or S.
,,	,, OH (Al.),	,,	,, SO_2, SO, but not S.
,,	,, NH_2(Ar.),	,,	,, SO_2, (SO?), but not S.
,,	,, OH (Ar.),	,,	,, SO_2, but not SO or S.
,,	,, SH,	,,	,, O.

of *o*-thiol-sulphones may be expected, and this conclusion is supported by the recent observation of a corresponding intermolecular displacement (Cowie and Gibson, J., 1934, 47). At the present state of the investigation it may be stated in general terms that rearrangement of (VIII) may take place if Y in the substituent YH is able more fully to satisfy the demand at C than X and also is able under the conditions of experiment to lose a proton for the requirement of X. With regard to the mechanism of the process it is suggested, in accord with the view of Bennett and Chapman (*Ann. Reports*, 1930, 122), that the interaction of C and Y establishes a preliminary phase (compare also Baddeley and Bennett, J., 1933, 261), such as (XV), leading to the liberation of the proton from YH. The behaviour of the *o*-hydroxy-sulphones (J., 1931, 3266) indicates that, if C is ortho or para to a nitro-group, an unstable nitronic ion such as (XVI) is formed before final release of X from C takes place.

(XV.) 

 (XVI.)

Experimental.

Derivatives of 2-Aminodiphenyl Sulphide.—(a) 2-Nitro-2′-aminodiphenyl sulphide (J., 1933, 1492) gave an *acetyl* derivative, which formed yellow needles from alcohol, m. p. 138° (Found: C, 58·1; H, 4·4. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·2%), and a *benzenesulphonyl* derivative, forming needles from benzene, m. p. 172° (Found: C, 55·9; H, 3·8; N, 7·5. $C_{18}H_{14}O_4N_2S_2$ requires C, 56·0; H, 3·6; N, 7·3%). The *o-nitrobenzoyl* derivative was obtained from the amine by interaction with *o*-nitrobenzoyl chloride in acetone solution in presence of sodium carbonate; it had m. p. 150° and formed yellow needles from acetic acid (Found: C, 57·6; H, 3·5; N, 10·8. $C_{19}H_{13}O_5N_3S$ requires C, 57·7; H, 3·3; N, 10·6%). Picryl chloride and the amine in alcohol with sodium acetate gave the *picryl* derivative, which formed red prisms from acetic acid, m. p. 206—207° (Found: N, 15·6. $C_{18}H_{11}O_8N_5S$ requires N, 15·3%).

2-*Nitro*-2′-*methylaminodiphenyl sulphide* was obtained by boiling (2 hours) a solution of the above amino-sulphide (4 g.) in alcohol (10 c.c.) which contained methyl iodide (2 c.c.) and mag-

nesium oxide (0·6 g.). It formed orange prisms from alcohol, m. p. 110° (Found : C, 59·8; H, 4·7; N, 10·7; S, 12·0. $C_{13}H_{12}O_2N_2S$ requires C, 60·0; H, 4·6; N, 10·8; S, 12·3%), and was recovered from boiling (3 hours) alcohol containing sodium hydroxide (*N*/2). The *acetyl* derivative formed yellow plates from alcohol, m. p. 124° (Found : C, 59·8; H, 4·8; N, 9·3. $C_{15}H_{14}O_3N_2S$ requires C, 59·6; H, 4·6; N, 9·3%). The o-*nitrobenzoyl* derivative had m. p. 146° and formed yellow needles from alcohol (Found : C, 58·5; H, 3·9; N, 10·4. $C_{20}H_{15}O_5N_3S$ requires C, 58·7; H, 3·7; N, 10·3%).

2-*Nitro*-2′-*dimethylamino*-5′-*methyldiphenyl sulphide* separated when a solution of 2-nitrophenylchlorothiol (14 g.) and dimethyl-*p*-toluidine (28 g.) in ether was boiled (1·5 hours); it formed yellow prisms, m. p. 104° (Found : C, 62·5; H, 5·8; N, 10·0. $C_{15}H_{16}O_2N_2S$ requires C, 62·5; H, 5·5; N, 9·7%), which were unaltered by boiling *N*/2-alcoholic sodium hydroxide (3 hours).

(b) 2 : 4′-*Dinitro*-2′-*acetamidodiphenyl sulphide* (compare XI). When the acetyl derivative (5 g.) of the amino-sulphide (a) was added (15°) to stirred nitric acid (25 c.c., *d* 1·4), it dissolved and subsequently the required *product* separated in the crystalline state (35%). It formed yellow plates from acetic acid, m. p. 179—180° (Found : C, 50·4; H, 3·4; N, 12·9. $C_{14}H_{11}O_5N_3S$ requires C, 50·5; H, 3·3; N, 12·6%). When it was heated (100°, 1·5 hours) with sulphuric acid (60%), it was converted into 2 : 4′-*dinitro*-2′-*aminodiphenyl sulphide* (XI), which separated when the liquid was diluted. The amine formed yellow plates, m. p. 193° (Found : C, 49·3; H, 3·3. $C_{12}H_9O_4N_3S$ requires C, 49·5; H, 3·1%). The substance was recovered after its solution in *N*/2-alcoholic sodium hydroxide had been boiled (3 hours). It was deaminated by addition of cuprous oxide to a solution of the diazonium sulphate in alcohol. When decomposition was complete, cuprous oxide was removed; the required product separated from the cooled solution. It crystallised from alcohol in yellow plates, m. p. 158°, identical with a specimen of 2 : 4′-*dinitrodiphenyl sulphide* prepared by boiling (2 hours) a solution of *p*-chloronitrobenzene (13 g.) and sodium *o*-nitrophenyl mercaptide (20 g.) in alcohol (50 c.c.). The product contained *o*-nitrophenyl disulphide, which was removed by treatment in warm alcohol with glucose and sodium hydroxide; the residue (9 g.) was washed and purified from acetic acid; m. p. 158—159° (Found : C, 52·4; H, 2·8. $C_{12}H_8O_4N_2S$ requires C, 52·2; H, 2·9%).

(c) 4-Chloro-2-nitro-2′-aminodiphenyl sulphide and its acetyl derivative have been previously described (J., 1933, 1492).

(d) 2 : 4-*Dinitro*-2′-*aminodiphenyl sulphide* (X), obtained from sodium 2-aminophenyl mercaptide and 2 : 4-dinitrochlorobenzene by a process similar to that used in the cases of sulphides (a) and (c), separated from acetic acid in deep yellow needles, m. p. 148° (Found : C, 49·3; H, 3·1; N, 14·5. $C_{12}H_9O_4N_3S$ requires C, 49·5; H, 3·1; N, 14·4%). The *acetyl* derivative had m. p. 199° (Found : N, 12·8; S, 9·7. $C_{14}H_{11}O_5N_3S$ requires N, 12·6; S, 9·6%).

(e) *o*-Nitrophenyl 2-acetamido-1-naphthyl sulphide (I) was prepared by Zincke's method (*Annalen*, 1912, **391**, 82).

Derivatives of 2-*Aminodiphenylsulphone.*—(a) 2-*Nitro*-2′-*acetamidodiphenylsulphone*. A solution of the corresponding sulphide (2 g.) in acetic acid (20 c.c.) containing hydrogen peroxide (3 c.c., 30%) was kept at 100° (1 hour). The required *sulphone* (1·9 g.) separated when the cooled mixture was diluted; it formed needles from alcohol, m. p. 107° (Found : C, 52·4; H, 3·9; N, 9·1. $C_{14}H_{12}O_5N_2S$ requires C, 52·5; H, 3·8; N, 8·8%). The use of a larger excess of hydrogen peroxide in this process gave 2 : 2′-dinitrodiphenyl sulphide, m. p. 183°, as the chief product.

(b) 2-*Nitro*-2′-*aminodiphenylsulphone* was formed by hydrolysis of the acetamido-sulphone (a) (10 g.) with sulphuric acid (60%) at 100° (1 hour) and was isolated (7·8 g.) by dilution of the cold mixture. It formed prisms from alcohol, m. p. 132—134° (Found : C, 51·7; H, 4·1; N, 10·4; S, 11·7. $C_{12}H_{10}O_4N_2S$ requires C, 51·8; H, 3·6; N, 10·1; S, 11·5%).

(c) 4-*Chloro*-2-*nitro*-2′-*acetamidodiphenylsulphone*. A solution of the corresponding sulphide (2 g.) in acetic acid (20 c.c.) containing hydrogen peroxide (2·3 c.c., 30%) was kept at 100° (1 hour). The product, isolated in the usual way, formed needles, m. p. 171°, from alcohol (Found : C, 47·2; H, 3·4. $C_{14}H_{11}O_5N_2ClS$ requires C, 47·4; H, 3·1%).

(d) 2-*Nitro*-2′-*benzenesulphonamidodiphenylsulphone*. The sulphide (5 g.) slowly dissolved in hot (100°) acetic acid (30 c.c.) when "hyperol" (5·2 g.) was gradually added to the mixture; the required *sulphone* (4·4 g.) separated when the solution was subsequently (1 hour) cooled. It formed needles from acetic acid, m. p. 144—145° (Found : C, 51·6; H, 3·5. $C_{18}H_{14}O_6N_2S_2$ requires C, 51·7; H, 3·3%).

(e) When the preceding sulphone was methylated with methyl sulphate in presence of aqueous alkali, 2-*nitro*-2′-*benzenesulphonylmethylaminodiphenylsulphone* separated as an oil,

which solidified in contact with alcohol and was purified from acetic acid; m. p. 189° (Found: C, 52·5; H, 3·5. $C_{18}H_{16}O_6N_2S_2$ requires C, 52·8; H, 3·7%).

(f) 2 : 4′-*Dinitro*-2′-*acetaminodiphenylsulphone*. A mixture of acetic acid (20 c.c.) containing hydrogen peroxide (2·5 c.c., 30%) and the acetamido-sulphide (b) (2 g.) was kept at 100° (1·5 hours) and then diluted. The impure material which separated was re-oxidised (1·2 c.c., 30% H_2O_2) under the same conditions. When the mixture was cooled, the required *sulphone* separated; it formed pale yellow prisms, m. p. 186—187° (Found: C, 45·7; H, 3·4. $C_{14}H_{11}O_7N_3S$ requires C, 46·0; H, 3·0%).

Attempts to convert the picryl derivative of sulphide (a) into the sulphone by the usual method yielded 2-*nitro*-2′-*picrylamidodiphenyl sulphoxide*, which formed pale yellow needles, m. p. 250—251° (decomp.) Found: N, 15·0. $C_{18}H_{11}O_9N_5S$ requires N, 14·8%).

Rearrangement of Sulphones.—The sulphone (a) gradually (30 mins.) dissolved in hot (100°) *N*-sodium hydroxide (2·5 mols.). When the red solution had been cooled and acidified with dilute sulphuric acid, 2-o-*nitrophenylaminobenzenesulphinic acid* (III) was liberated; it formed orange plates from acetic acid, m. p. 124° (Found: C, 51·7; H, 3·8. $C_{12}H_{10}O_4N_2S$ requires C, 51·8; H, 3·6%). Bis-2-*o*-nitrophenylaminophenyl disulphide separated when hydriodic acid (*d* 1·7) was added to a solution of this sulphinic acid in warm acetone containing sulphur dioxide; it formed orange plates from acetic acid, m. p. 149—150° (Found: C, 58·7; H, 3·4; N, 11·7. Calc.: C, 58·8; H, 3·7; N, 11·4%), and was identical with the disulphide (J., 1933, 1493) isolated from the product of rearrangement of the sulphoxide. Interaction of methyl iodide and the sodium sulphinate yielded 2-*o*-nitrophenylaminophenylmethylsulphone, m. p. 132° (Found: C, 53·3; H, 4·4. Calc.: C, 53·4; H, 4·1%), identical with the product obtained by oxidising the methyl sulphoxide (*loc. cit.*). When a boiling solution of the sulphinate, obtained as described from the sulphone (a) (2 g.) by rearrangement, was added to a hot solution of mercuric chloride (1·8 g.) in water (6 c.c.), sulphur dioxide was liberated. Subsequently (30 mins.) the impure mercurichloride was collected, washed with water, and treated (1·5 hours) with a boiling mixture of alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.). The oil which separated from the mixture solidified when it was cooled; the product after purification (0·6 g.) from alcohol had m. p. 76° and was identical with a synthetic sample of 2-nitrodiphenylamine. The acetamido-sulphone (a) was also submitted to the action of 1 mol. of aqueous-alcoholic sodium hydroxide (*N*/2). When the boiling solution had become neutral, methyl iodide was added; finally the solvent was evaporated and the product which separated from the residue was purified from alcohol, 2-*aceto*-o-*nitrophenylamidophenylmethylsulphone* (compare IV) being obtained, m. p. 135—136° (Found: C, 53·4; H, 4·4; S, 9·4. $C_{15}H_{14}O_5N_2S$ requires C, 53·8; H, 4·2; S, 9·6%): this was converted by hydrolysis with alcoholic sodium hydroxide into the methyl-sulphone (IV). The amino-sulphone (b) yielded in presence of boiling *N*-sodium hydroxide (1 mol.) a solution of the sodium sulphinate (III). This product was identified by conversion into the disulphide and the methyl-sulphone (IV) described above.

The acetamido-sulphone (c, V) rapidly dissolved (5 mins.) in boiling *N*-sodium hydroxide (2·5 mols.); the sulphinic acid, liberated from the cooled solution, was not purified, but converted into *bis*-2-p-*chloro*-o-*nitrophenylaminophenyl disulphide*, which formed orange plates from acetic acid, m. p. 174° (Found: C, 51·7; N, 10·0; S, 11·5. $C_{24}H_{16}O_4N_4Cl_2S_2$ requires C, 51·5; N, 10·0; S, 11·5%). Methylation of the sulphinic acid in alkaline solution yielded 2-p-*chloro*-o-*nitrophenylaminophenylmethylsulphone* (VI), which separated from propyl alcohol in orange plates, m. p. 190° (Found: C, 47·5; H, 3·5; S, 9·8; Cl, 10·8. $C_{13}H_{11}O_4N_2ClS$ requires C, 47·8; H, 3·4; S, 9·8; Cl, 10·9%). Degradation of the sulphinic acid by the usual method gave 4-chloro-2-nitrodiphenylamine (VII), which was identified by comparison with a synthetical specimen.

2-*Aceto*-p-*chloro*-o-*nitrophenylamidophenylmethylsulphone*. Alcohol containing sodium hydroxide (1 mol., *N*/4) and the acetamido-sulphone (c) was boiled (30 mins.) until the solution had become neutral. After addition of methyl iodide and further boiling, the solution was cooled; the required *methyl-sulphone* then separated, m. p. 172° (Found: C, 48·8; H, 3·2. $C_{15}H_{13}O_5N_2ClS$ requires C, 48·8; H, 3·5%), and was converted by alkaline hydrolysis into the methyl-sulphone (VI).

A solution of the sulphone (d) in aqueous alcohol (50%) containing sodium hydroxide (1·25 mols., 0·5*N*) was boiled (2 hours). Methylation of the solution thus obtained yielded 2-o-*nitrophenylbenzenesulphonamidophenylmethylsulphone*, which formed plates, m. p. 169° (Found: C, 52·7; H, 4·0. $C_{19}H_{16}O_6N_2S_2$ requires C, 52·8; H, 3·7%), and was different from the sulphone (e).

A hot aqueous solution of the sodium sulphinate formed by rearrangement of the sulphone (d) yielded with mercuric chloride sulphur dioxide and a mercurichloride which was not attacked

by hydrochloric acid under the usual conditions. This substance, evidently 2-o-*nitrophenylbenzenesulphonamidophenyl mercurichloride*, formed needles from acetone, m. p. 224—225° (Found : C, 36·7; H, 2·5. $C_{18}H_{13}O_4N_2ClSHg$ requires C, 36·7; H, 2·2%).

The sulphone (f) was rapidly attacked (10 mins.) by sodium hydroxide (1 mol.) in boiling alcohol. Methylation of the product yielded *5-nitro-2-aceto-o-nitrophenylamidophenylmethylsulphone*, m. p. 175—176° (Found : C, 47·1; H, 3·7; N, 11·2. $C_{15}H_{13}O_7N_3S$ requires C, 47·5; H, 3·4; N, 11·1%). With 2 mols. of sodium hydroxide the sulphone (f) yielded a sulphinic acid, from which by degradation 2 : 3′-*dinitrodiphenylamine* was obtained. This formed orange needles, m. p. 158° (Found : N, 16·1. $C_{12}H_9O_4N_3$ requires N, 16·2%), which were different from 2 : 4-dinitrodiphenylamine (m. p. 156°) and identical with the product obtained by heating (190°, 4 hours) a mixture of *m*-nitroaniline (3 g.), *o*-bromonitrobenzene (5 g.), sodium carbonate (1·5 g.), and cuprous bromide (0·1 g.).

Rearrangement of Sulphides.—A solution of the acetyl derivative of the sulphide (a) (2 g.) in a mixture (50%) of acetone and alcohol which contained sodium hydroxide (1·25 mols., *N*/2) was boiled (15 mins.); when excess of methyl iodide was added to the solution, the red colour faded and after most of the solvent had been evaporated the methylthiol (1·4 g.) separated. 2-*Aceto*-o-*nitrophenylamidophenyl methyl sulphide* formed yellow needles, m. p. 151° (Found : C, 59·6; H, 4·9; N, 9·4; S, 10·6. $C_{15}H_{14}O_3N_2S$ requires C, 59·6; H, 4·6; N, 9·3; S, 10·6%), which gave methyl mercaptan with hot hydriodic acid and on oxidation yielded the methyl-sulphone obtained by rearrangement of the acetamido-sulphone (a). Hydrolysis of the substance with alcoholic sodium hydroxide gave 2-o-*nitrophenylaminophenyl methyl sulphide*, which formed red needles from alcohol, m. p. 98° (Found : C, 59·9; H, 4·6; N, 10·9; S, 12·2. $C_{13}H_{12}O_2N_2S$ requires C, 60·0; H, 4·6; N, 10·8; S, 12·3%). Oxidation of this substance yielded the methyl-sulphone obtained by methylation of the sulphinic acid related to the sulphone (b) by rearrangement.

2-*Aceto*-o-*nitrophenylamidophenyl mercaptan* was isolated by rearrangement of the sulphide (a) in acetone as described. After the solvent had been removed, water was added and the clear solution of the sodium salt was acidified with dilute sulphuric acid. The product separated from alcohol in yellow needles, m. p. 114° (Found : C, 58·2; H, 4·5; *M*, 286. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·2%; *M*, 288).

2-o-*Nitrophenyl*-1-*methylbenzthiazolonium iodide* (XIV) was obtained from this thiol by addition of hydrogen iodide to an acetone solution; it formed yellow plates, m. p. 203° (decomp.) (Found : C, 42·0; N, 7·1. $C_{14}H_{11}O_2N_2IS$ requires C, 42·2; N, 7·0%). The same substance was obtained from the corresponding sulphinic acid by reduction with hydriodic and sulphurous acids; it was decomposed by warm water, yielding hydriodic acid and a red material which was not further investigated. The *perchlorate*, obtained from the thiol with perchloric acid, had m. p. 192° (Found : N, 7·7. $C_{14}H_{11}O_6N_2ClS$ requires N, 7·6%).

Rearrangement of the sulphide (c) was effected in boiling alcoholic sodium hydroxide (1·25 mols., *N*/2) as in the case of (a). After methylation, 2-*aceto*-p-*chloro*-o-*nitrophenylamidophenyl methyl sulphide* separated from the cooled mixture; it formed yellow plates, m. p. 142° (Found : C, 53·7; H, 4·1; S, 9·4. $C_{15}H_{13}O_3N_2ClS$ requires C, 53·5; H, 3·9; S, 9·5%), and on oxidation yielded the methyl-sulphone which had been obtained by rearrangement of the sulphone (c).

2-p-*Chloro*-o-*nitrophenylaminophenyl methyl sulphide*, obtained from the above acetyl derivative by hydrolysis in an alkaline medium, formed red needles from acetic acid, m. p. 126° (Found : C, 53·0; H, 4·0. $C_{13}H_{11}O_2N_2ClS$ requires C, 53·0; H, 3·1%). It yielded methyl mercaptan with hydrogen iodide and was converted by oxidation into the methyl-sulphone (VI).

Rearrangement of the sulphide (d) was effected as in the cases of (a) and (c). Since the product of rearrangement underwent further change in presence of warm alkali solution, it was isolated as the methylthiol. 2-*Aceto*-op-*dinitrophenylamidophenyl methyl sulphide* (XII) was obtained by the gradual addition of methyl iodide during the process (15 mins.). It separated from the cooled reaction mixture and formed yellow needles from acetic acid, m. p. 155—156° (Found : C, 51·5; H, 3·9; N, 12·3; S, 8·9. $C_{15}H_{13}O_5N_3S$ requires C, 51·9; H, 3·7; N, 12·1; S, 9·2%). By deacetylation with hot (100°) dilute sulphuric acid (60%) it was converted into 2-*op*-dinitrophenylaminophenyl methyl sulphide identical with a specimen prepared by Zincke's method (*Ber.*, 1915, **48**, 1242) from *o*-aminothioanisole and 2 : 4-dinitrochlorobenzene.

Rearrangement of the sulphide (e) was effected in a boiling acetone–alcohol solution of sodium hydroxide (1·25 mols., *N*/3), the alkaline reagent being gradually added as the change progressed. When methyl iodide was added to the boiling solution, the colour rapidly faded and after removal of most of the solvent and addition of water the required product separated.

2-*Aceto*-o-*nitrophenylamido*-1-*naphthyl methyl sulphide* formed yellow needles from alcohol,

m. p. 158° (Found: C, 64·8; H, 4·8. $C_{19}H_{16}O_3N_2S$ requires C, 64·8; H, 4·5%). The substance yielded methyl mercaptan with warm hydriodic acid and was converted by oxidation into the 2-aceto-*o*-nitrophenylamido-1-naphthylmethylsulphone (m. p. 195°) previously (J., 1932, 2777) obtained by rearrangement of the sulphone. Alkaline deacetylation of the substance gave 2-o-*nitrophenylamino*-1-*naphthyl methyl sulphide*, which formed bright red plates from alcohol, m. p. 110° (Found: C, 65·8; N, 9·3. $C_{17}H_{14}O_2N_2S$ requires C, 65·8; N, 9·0%). Rearrangement of the sulphide (e) in acetone without concurrent methylation gave a solution of the sodium salt of the thiol; this was isolated by acidification of the clear diluted solution and was converted by hydrogen iodide in acetic acid into 2-*o*-nitrophenyl-1-methylnaphthathiazolonium tri-iodide, m. p. 183°, which had been previously (*loc. cit.*) obtained by reduction of the sulphinic acid.

Rearrangement of the *N*-*o*-nitrobenzoyl derivative (8 g.) of the sulphide (a) was effected in acetone–alcohol (*N*/2-sodium hydroxide, 1·25 mols.) and required longer (1·5 hours) treatment than usual. Gradual methylation was begun during the latter part of the process; most of the required product separated when the liquid was cooled; a further quantity was subsequently obtained from the solution (yield, 1·8 g.). 2-o-*Nitrobenzo*-o-*nitrophenylamidophenyl methyl sulphide* formed pale yellow needles, m. p. 245° (Found: C, 58·7; N, 10·3. $C_{20}H_{15}O_5N_3S$ requires C, 58·7; N, 10·3%); it yielded methyl mercaptan with hydriodic acid and was different from the *N*-methyl derivative of the sulphide from which it was prepared.

Rearrangement of the sulphide (b) (1 g.) was rapidly effected (15 mins.) as usual (1 mol. sodium hydroxide, *N*/3) in boiling acetone–alcohol. After methylation of the product in the solution, most of the solvent was evaporated; the methylthiol (0·9 g.) then separated. Obtained in this way, 5-*nitro*-2-*aceto*-o-*nitrophenylamidophenyl methyl sulphide* formed prisms from acetic acid, m. p. 192—193° (Found: C, 51·7; N, 12·3. $C_{15}H_{13}O_5N_3S$ requires C, 51·9; N, 12·1%), which gave methyl mercaptan as usual and yielded after oxidation a methyl-sulphone (m. p. 176°) identical with that obtained by rearrangement of the sulphone (f).

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