231. *The Reactions of* N-*Benzenesulphonylbenz*isoth*iazolone with Aromatic Amines.*

By (the late) Ernest W. McClelland and Raymond H. Peters.

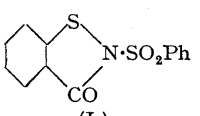
N-Benzenesulphonylbenz*iso*thiazolone (I) reacts readily with aromatic amines, the hetero-ring being opened and the sulphur atom becoming attached to the *p*-position of the amine to give substances of type (II). Hydrolysis of (II) yields the 4-amino-2′-carboxydiphenyl sulphide, which by the action of sulphuric acid undergoes ring closure to give a 2-aminothioxanthone (V). When the *p*-position of the aromatic amine is occupied by a substituent R (Me, OMe, or Cl) the sulphur atom becomes attached in the ortho-position relative to the amino-group of the amine and the product isolated is the lactam of the 2-amino-5-R-2′-carboxydiphenyl sulphide (XI), benzenesulphonamide having been eliminated. The lactam yields the free amino-acid on hydrolysis. Sulphuric acid converts these acids into 4-aminothioxanthones (XIII). 2-Amino-2′-carboxydiphenyl sulphide yields a similar lactam when boiled in xylene with phosphoric oxide.

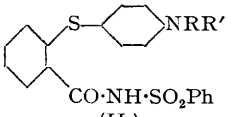
The reaction of *N*-benzenesulphonylbenz*iso*thiazolone (I) with aniline had been observed by McClelland and Hart (*J.*, 1939, 760), and preliminary experiments had also been made with dimethylaniline (Barton and McClelland, unpublished observations). In the present

investigation the reactions with a number of aromatic amines have been studied and the nature of the products established.

The benz*iso*thiazolone condenses with one molecular proportion of the amine and several possible formulæ were considered for the products, such as (II), (III), and (IV).

The compound from dimethylaniline is converted by heating with sulphuric acid into a dimethylaminothioxanthone. The formation of an aminothioxanthone is compatible with either formula (II) or (III) which would, however, give rise, respectively, to the 2- and 3-dimethylaminothioxanthones (V) and (VI).


(I.)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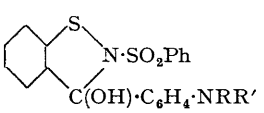
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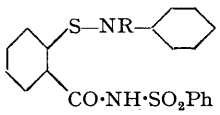
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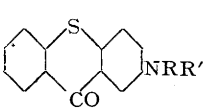
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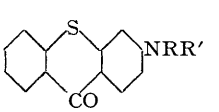
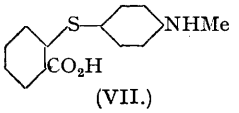

(VI.)

2-*Dimethylaminothioxanthone* (V, R = R′ = Me) was synthesised by a variation of Mayer's method (*Ber.*, 1909, **42**, 3046) as follows. The action of *p*-dimethylaminothiophenol on diazotised anthranilic acid yielded 4-dimethylamino-2′-carboxydiphenyl sulphide, which was converted by sulphuric acid into the required 2-dimethylaminothioxanthone found to be identical with the substance under discussion above. The condensation product from dimethylaniline is therefore of type (II) and not (III).

Similar results were obtained on using methylethylaniline and benzylmethylaniline, the aminothioxanthone being independently synthesised in the former case.

The product of reaction with monomethylaniline was hydrolysed to an acid which must be (VII) since it gives an acetyl derivative. This excludes formula (IV) for this condensation product, and points to formula (II, R = H, R′ = Me). The substance also yields a thioxanthone, which by analogy must be 2-*methylaminothioxanthone*.

The substance formed by condensation of the benz*iso*thiazolone with aniline is now found to contain a free primary amino-group and is converted by sulphuric acid into 2-aminothioxanthone. This compound therefore has the structure (II, R = R′ = H). In the production of the thioxanthones, sulphonic acids of the type (VIII) are also obtained. With *o*-toluidine an analogous condensation occurred.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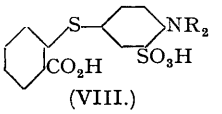

(VIII.)

Benzylamine and phenylhydrazine do not condense with the benz*iso*thiazolone in boiling alcohol, but cause opening of the ring and yield di-*N*-benzenesulphonyl-2 : 2′-dithiobenzamide.

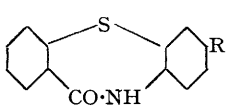
On the other hand when the *N*-benzenesulphonylbenz*iso*thiazolone was condensed with para-substituted amines a different reaction occurred, benzenesulphonamide being eliminated. The thiazolone reacted in this manner with *p*-toluidine, *p*-anisidine, and *p*-chloroaniline, but did not react with weaker bases such as the nitroanilines or anthranilic acid. The products were of high melting point and inert to bromine; they gave no colour with ferric chloride, were neither acidic nor basic, and gave no reaction for a keto-group. Their composition corresponded with that of the respective aryl*iso*thiazolone (I, C_6H_4X in place of SO_2Ph) or an isomer of it.

N-*p*-Tolylbenz*iso*thiazolone, however, prepared by the action of 2-chlorothiobenzoyl chloride on *p*-toluidine, was found to be an entirely different substance from the condensation product from *p*-toluidine.

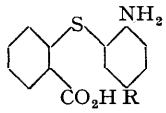
In view of the mode of reaction of benzylamine and phenylhydrazine with the benz*iso*thiazolone, mentioned above, the possibility was considered that a disulphide $\left(C_6H_4\!<\!\begin{matrix}S-\\CO\cdot NHR\end{matrix}\right)_2$ had been formed, the difference in composition being negligible. But, again, the disulphide prepared by the action of *p*-toluidine on 2 : 2′-dithiobenzoyl chloride was entirely different from the product under discussion: moreover the molecular weight of the corresponding substance

resulting from the reaction of *p*-anisidine with the benz*iso*thiazolone was not double as would be required for the disulphide.

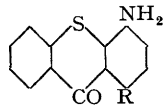
The condensation product yielded a *dioxide* soluble in aqueous sodium hydroxide and reprecipitated unchanged on acidification. Both the condensation product and its dioxide yielded monoacetyl derivatives. These were finally identified as lactams of the structure (XI) since hydrolysis with 55—65% sulphuric acid yielded in each case an aminocarboxylic acid. A thioxanthone is formed at the same time, which is evidently the result of further action of the sulphuric acid on the amino-acid. The acids must have the structure (XII) which should give 4-aminothioxanthones (XIII). This was confirmed by preparing 4-amino-1-methylthioxanthone from *o*-mercaptobenzoic acid and *p*-toluenesulphon-*p*-toluidide in sulphuric acid (cf. Ullmann and Glenck, *Ber.*, 1916, **49**, 2499); the product was identical with the thioxanthone from the amino-acid derived from the condensation product of *p*-toluidine and the benzenesulphonylbenz*iso*thiazolone.



(XI.)



(XII.)

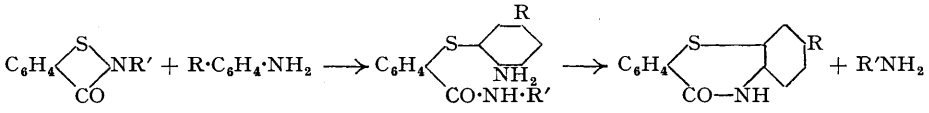


(XIII.)

The condensation products in question are thus lactams of the amino-acids of type (XII). These acids when heated with alcoholic hydrochloric acid were partly converted into the lactam. Acetic anhydride or phosphoric oxide also regenerated the lactam (XI) together with some of the thioxanthone in the latter case.

The seven-membered ring here present is not unusual in view of the presence of two *o*-phenylene groups, but it was thought desirable to provide the following confirmatory evidence. The parent sulphide, 2-amino-2′-carboxydiphenyl sulphide (Mayer, *loc. cit.*) with phosphoric oxide yielded a corresponding cyclic lactam together with some 4-aminothioxanthone. This was entirely similar in behaviour to the condensation products from *N*-benzenesulphonylbenz-*iso*thiazolone with para-substituted amines. Oxidation also gave a sulphone of similar properties, and this too was prepared independently from the sulphone of 2-nitro-2′-carboxydiphenyl sulphide.

The reaction of the benz*iso*thiazolone with para-substituted amines therefore proceeds thus :



and it follows that the products should be independent of the particular radical R′ present. This was confirmed by causing the *N*-*p*-toluenesulphonylbenz*iso*thiazolone to react with *p*-anisidine; the product was identical with that from *N*-benzenesulphonylbenz*iso*thiazolone.

Attempts to bring about reaction between dimethylaniline and *N*-methyl-, *N*-phenyl-, *N*-*p*-tolyl-, *N*-*p*-nitrophenyl-, or *N*-benzoyl-benz*iso*thiazolone gave negative results, and it appears that this type of reaction of the arylsulphonylbenz*iso*thiazolones depends on the joint action of the SO_2 and CO groups attached to the same nitrogen atom, the simultaneous presence of which facilitates the rupture of the heterocyclic ring.

Experimental.

Reaction of N-*Benzenesulphonylbenz*iso*thiazolone with Tertiary Aromatic Amines.*—The benz*iso*-thiazolone (5 g.) was boiled in alcohol (20 ml.) with the amine (5 g.) until all the former had dissolved (3 hrs.). The product crystallised on cooling. *4-Dimethylamino-2′-*N*-benzenesulphonylcarbamyldiphenyl sulphide* was thus obtained from dimethylaniline, as yellow needles from alcohol, m. p. 172° (Found : C, 61·6; H, 4·7. $C_{21}H_{20}O_3N_2S_2$ requires C, 61·1; H, 4·9%). In his examination of this substance Dr. A. W. H. Barton isolated a *sodium* salt sparingly soluble in water crystallising from alcohol in white needles, m. p. 308° (Found : Na, 5·4. $C_{21}H_{19}O_3N_2S_3Na$ requires Na, 5·3%), and by methylation with methyl sulphate a *methyl* derivative, white needles from methyl alcohol, m. p. 144° (Found : C, 62·0; H, 5·2. $C_{22}H_{22}O_3N_2S_2$ requires C, 62·0; H, 5·2%), which on hydrolysis with acid yielded benzenesulphonmethylamide, m. p. 31°. The original condensation product was hydrolysed by boiling for 2 hours with concentrated hydrochloric acid, and the mixture poured into water, made alkaline with sodium hydroxide, and finally acidified with acetic acid. The greenish precipitate was purified by crystallisation of the sodium salt, reconversion into the acid and crystallisation from alcohol; it formed small greenish needles, m. p. 250—260° (decomp.). *4-Dimethylamino-2′-carboxydiphenyl sulphide* so obtained was identical with that prepared synthetically as follows. *pp′*-Bisdimethylaminodiphenyl disulphide (10 g.) prepared by the method of Merz and Weith (*Ber.*, 1889, **22**, 1571) was reduced by

warming with tin (3 g.) and concentrated hydrochloric acid (30 c.c.), the solution made alkaline (100 c.c. of 35% aqueous sodium hydroxide) and heated while a stream of nitrogen was passed through the flask, and a diazotised solution of anthranilic acid (8·8 g.) slowly added. After 5 minutes' boiling and cooling the grey-green sodium salt which separated was collected and dissolved in water, and the free acid precipitated by adding acetic acid. It was apparently identical with the hydrolysis product described above (Found on a sample from alcohol, dried in a vacuum: C, 64·9; H, 5·7. After drying at 110°: C, 66·4; H, 5·9. $C_{15}H_{15}O_2NS,C_2H_6O$ requires C, 64·0; H, 6·6%. $C_{15}H_{15}O_2NS$ requires C, 66·0; H, 5·5%). The presence of alcohol in the former specimen was confirmed by an iodoform test.

In view of the indefiniteness of the melting point of this substance the *ethyl* ester was prepared from both the hydrolysis product and the synthetic acid. In each case it formed white needles from alcohol, m. p. 143° (not depressed by mixture of the two). For analysis the substance was purified by molecular distillation (Found: C, 67·5, 67·5; H, 6·8, 6·4. $C_{17}H_{19}O_2NS$ requires C, 67·7; H, 6·4%). Other amines yielded the corresponding 4-aminodiphenyl sulphides. *4-Methylethylamino-2′-N-benzenesulphonylcarbamyldiphenyl sulphide* formed pale yellow plates from alcohol, m. p. 141° (Found: C, 61·1, 60·6; H, 5·6, 6·0. $C_{22}H_{22}O_3N_2S_2$ requires C, 61·7; H, 5·2. $C_{22}H_{22}O_3N_2S_2,C_2H_6O$ requires C, 61·0; H, 6·0%). On hydrolysis with concentrated hydrochloric acid it yielded *4-methylethylamino-2′-carboxydiphenyl sulphide* as a greenish microcrystalline powder, m. p. *ca.* 230° (decomp.) (Found: C, 66·8; H, 5·9. $C_{16}H_{17}O_2NS$ requires C, 66·8; H, 6·0%). This acid was also synthesised. 4 : 4′-Bismethylethylaminodiphenyl disulphide prepared by Merz and Weith's method (*loc. cit.*) formed an amorphous mass which did not crystallise and was used in the crude form. It was reduced to the thiol as described above, and with diazotised anthranilic acid gave the 4-methylethylamino-2′-carboxydiphenyl sulphide as a pale green microcrystalline powder, m. p. *ca.* 230° (decomp.) (Found: C, 66·8; H, 5·9%). *4-Benzylmethylamino-2′-N-benzenesulphonylcarbamyldiphenyl sulphide* crystallised in pale green needles from alcohol, m. p. 123°. The crystals contain alcohol of crystallisation as shown by direct test (Found: C, 65·1; H, 5·2. $C_{27}H_{24}O_3N_2S_2$ requires C, 66·4; H, 4·9. $C_{27}H_{24}O_3N_2S_2,C_2H_6O$ requires C, 65·1; H, 5·6%). Hydrolysis with 60% sulphuric acid yielded *4-benzylmethylamino-2′-carboxydiphenyl sulphide*, which crystallised from alcohol as a pale green microcrystalline powder, m. p. 194° (Found: C, 71·7; H, 5·0. $C_{21}H_{19}O_2NS$ requires C, 72·1; H, 5·5%).

4-Methylamino-2′-N-benzenesulphonylcarbamyldiphenyl sulphide separated from alcohol in white plates which turned green on exposure to air, m. p. 142° (Found: C, 60·5; H, 4·4. $C_{20}H_{18}O_3N_2S_2$ requires C, 60·3; H, 4·5%). The *nitroso*-derivative crystallised from alcohol in golden needles, m. p. 170° (Found: C, 56·0; H, 4·1. $C_{20}H_{17}O_4N_3S_2$ requires C, 56·1; H, 4·0%). Hydrolysis with 60% sulphuric acid yielded *4-methylamino-2′-carboxydiphenyl sulphide*, small needles from butyl alcohol, m. p. 215° (Found: C, 64·9; H, 5·5. $C_{14}H_{13}O_2NS$ requires C, 64·8; H, 5·1%). The *acetyl* derivative formed white plates, m. p. 209° (Found: C, 63·4; H, 5·3. $C_{16}H_{15}O_3NS$ requires C, 63·8; H, 5·0%).

4-Ethylamino-2′-N-benzenesulphonylcarbamyldiphenyl sulphide separated from aqueous alcohol in cream coloured crystals, m. p. 150° (Found: C, 61·0; H, 5·1. $C_{21}H_{20}O_3N_2S_2$ requires C, 61·1; H, 4·9%). The *nitroso*-derivative crystallised from alcohol in small red prisms which turned yellow on heating, m. p. 138° (Found: C, 56·7; H, 4·3. $C_{21}H_{19}O_4N_3S_2$ requires C, 57·1; H, 4·4%). Hydrolysis with 60% sulphuric acid yielded *4-ethylamino-2′-carboxydiphenyl sulphide*, which crystallised from butyl alcohol in buff needles, m. p. 224° (Found: C, 65·6; H, 5·4. $C_{15}H_{15}O_2NS$ requires C, 65·0; H, 5·5%). The *acetyl* derivative separated from aqueous alcohol in almost colourless needles, m. p. 184° (Found: C, 64·7; H, 5·4. $C_{17}H_{17}O_3NS$ requires C, 64·7; H, 5·4%).

4-Amino-2′-*N*-benzenesulphonylcarbamyldiphenyl sulphide, obtained by using aniline, crystallised from aqueous alcohol in small white needles, m. p. 167° (analysed, but incorrectly formulated by McClelland and Hart, *J.*, 1939, 760). The *perchlorate* separated in minute needles from dilute perchloric acid, m. p. 221° (decomp.) (Found: C, 45·5, 45·7; H, 4·1, 4·0. Found after drying at 100°: C, 45·0; H, 3·4. $C_{19}H_{17}O_7N_2ClS_2,H_2O$ requires C, 45·4; H, 3·8%. $C_{19}H_{17}O_7N_2ClS_2$ requires C, 45·4; H, 3·8%). Diazotisation and coupling with alkaline β-naphthol gave the corresponding *azo-β-naphthol*, which crystallised in red prisms from ethyl acetate or acetone, m. p. 148° (Found: C, 64·0, 64·0; H, 4·1, 4·1. $C_{29}H_{21}O_4N_3S_2$ requires C, 64·5; H, 3·9%). The filtered diazo-solution after addition of urea and boiling yielded 4-hydroxy-2′-*N*-benzenesulphonylcarbamyldiphenyl sulphide, which separated from hot water in small white needles, m. p. 143°. Hydrolysis with 60% sulphuric acid yielded 4-amino-2′-carboxydiphenyl sulphide, which after crystallisation from aqueous alcohol had m. p. 193° not depressed by admixture of an authentic specimen prepared from the nitro-acid obtained from *p*-nitrothiophenol and anthranilic acid (cf. Mayer, *loc. cit.*).

Reaction with *o*-toluidine produced *4-amino-2′-N-benzenesulphonylcarbamyl-3-methyldiphenyl sulphide*, which after purification through the perchlorate crystallised from alcohol in white needles, m. p. 118° (Found: C, 59·7; H, 5·3. $C_{20}H_{18}O_3N_2S_2,C_2H_6O$ requires C, 59·4; H, 5·4%). The *perchlorate* formed cream coloured needles from dilute perchloric acid, m. p. 225° (decomp.) (Found: C, 48·6; H, 4·0. $C_{20}H_{19}O_7N_2ClS_2$ requires C, 48·2; H, 3·8%). The corresponding *azo-β-naphthol* crystallised from ethyl acetate in dark red prisms, m. p. 136° (Found: C, 65·0; H, 4·6. $C_{30}H_{23}O_4N_3S_2$ requires C, 65·1; H, 4·2%).

Action of Sulphuric Acid on the Foregoing Aminodiphenyl Sulphides.—The 4-substituted 2′-*N*-benzenesulphonylcarbamyldiphenyl sulphides were warmed at 50° for 1 hour with concentrated sulphuric acid (20 c.c. for 5 g.). The resulting solution on being poured into water gave a white precipitate of a sulphonic acid, and addition of alkali to the filtered solution yielded an aminoxanthone, a further yield of which was obtained by redissolving the sulphonic acid in alkali.

2-Dimethylaminothioxanthone crystallised from alcohol in orange needles, m. p. 122° (Found: C, 70·4; H, 5·3; N, 5·7. $C_{15}H_{13}ONS$ requires C, 70·5; H, 5·1; N, 5·5%). The substance gave a green fluorescence in sulphuric acid solution. It was found by m. p. and mixed m. p. to be identical with the xanthone produced by the action of concentrated sulphuric acid on synthetic 4-dimethylamino-2′-carboxydiphenyl sulphide (see above).

The sulphonic acid was purified by precipitation from alkaline solution, redissolved and boiled in

alkali with charcoal, reprecipitated, and finally boiled with water. It was a white microcrystalline powder, m. p. 318°, presumably 4-*dimethylamino*-2′-*carboxydiphenyl sulphide*-3-*sulphonic acid*, but the position of the sulphonic acid group was not proved (Found: C, 50·9; H, 4·1; N, 3·6. $C_{15}H_{15}O_5NS_2$ requires C, 51·0; H, 4·2; N, 3·9%). When this substance was heated in concentrated sulphuric acid (10 parts) for ½ hour at 150° a brown solution with green fluorescence was formed. The solution was diluted and made alkaline, the dark red mass deposited was dissolved in water, and the solution was acidified. The acid precipitated was crystallised from hot water and formed a light brown microcrystalline powder not melting at 310°. The substance was hygroscopic and analyses were unsatisfactory, but it was presumably 2-*dimethylaminothioxanthone*-3-*sulphonic acid* (Found: C, 49·8; H, 4·3. Found after drying at 100° in a vacuum: C, 51·9; H, 4·5. $C_{15}H_{13}O_4NS_2,H_2O$ requires C, 51·0; H, 4·3%. $C_{15}H_{13}O_4NS_2$ requires C, 53·7; H, 3·9%). The sodium salt had m. p. 310°; the *potassium* salt was a dihydrate (Found: H_2O, 6·8. $C_{15}H_{12}O_4NS_2K,2H_2O$ requires H_2O, 6·8%) and had m. p. 95° or, after heating at 100° in a vacuum, m. p. 230°.

2-*Methylethylaminothioxanthone* was similarly obtained and crystallised from alcohol in pale orange needles, m. p. 120° (Found: C, 70·9; H, 5·6. $C_{16}H_{15}ONS$ requires C, 71·3; H, 5·6%). This compound was identified by m. p. and mixed m. p. with that obtained by the action of sulphuric acid on synthetic 4-methylethylamino-2′-carboxydiphenyl sulphide (see above).

The accompanying sulphonic acid formed white needles from hot water, m. p. 314° (decomp.), and was 4-*methylethylamino*-2′-*carboxydiphenyl sulphide*-3-*sulphonic acid* (Found: C, 52·6; H, 4·6. $C_{16}H_{17}O_5NS_2$ requires C, 52·3; H, 4·6%). The sodium salt had m. p. 272°, the potassium salt m. p. 215°. 2-*Benzylmethylaminothioxanthone* crystallised from alcohol in yellow needles, m. p. 149·5° (Found: C, 76·2; H, 5·4. $C_{21}H_{17}ONS$ requires C, 76·1; H, 5·2%). 4-*Benzylmethylamino*-2′-*carboxydiphenyl sulphide* 3-*sulphonic acid* was a microcrystalline powder sparingly soluble in hot water, m. p. 286° (decomp.) (Found: C, 58·9; H, 4·6. $C_{21}H_{19}O_5NS_2$ requires C, 58·7; H, 4·5%).

2-*Methylaminothioxanthone* crystallised from aqueous alcohol in small yellow needles, m. p. 158°, or minute red crystals becoming yellow at *ca.* 144° (Found: C, 70·0; H, 4·5. $C_{14}H_{11}ONS$ requires C, 69·7; H, 4·6%). The accompanying 4-*methylamino*-2′-*carboxydiphenyl sulphide*-3-*sulphonic acid* formed white needles from hot water, m. p. 321° (decomp.) (Found: C, 46·3; H, 4·2. $C_{14}H_{13}O_5NS$ requires C, 49·6; H, 3·8. $C_{14}H_{13}O_5NS,H_2O$ requires C, 47·0; H, 4·2%).

2-*Ethylaminothioxanthone* was obtained as orange plates or needles from alcohol, m. p. 134° (Found: C, 70·3; H, 5·1. $C_{15}H_{13}ONS$ requires C, 70·5; H, 5·1%). No sulphonic acid was isolated in this case.

2-Aminothioxanthone formed yellow needles from alcohol or plates from nitrobenzene, m. p. 227° (Found: C, 69·3, 70·0; H, 3·7, 4·3. Calc.: C, 68·7; H, 4·0%. Cf. Mayer, *loc. cit.*, who also reports poor analyses). It was shown to be identical with the aminothioxanthone synthesised (in poor yield) by the method of Smiles (*J.*, 1911, 2046) or by that of Mayer (*loc. cit.*).

This substance, boiled with acetic anhydride in toluene solution for 4 hours, yielded a *diacetyl* derivative which crystallised from toluene in yellow crystals, m. p. 245° (Found: C, 65·3; H, 3·9. $C_{17}H_{13}O_3NS$ requires C, 65·6; H, 4·2%). On hydrolysis it furnished the parent aminoxanthone.

In its production from the condensation product from aniline it was accompanied by 4-*amino*-2′-*carboxydiphenyl sulphide*-3-*sulphonic acid*, which separated in small white crystals from water, m. p. > 320° (Found: C, 48·0; H, 3·5. $C_{13}H_{11}O_5NS_2$ requires C, 48·0; H, 3·4%).

Reaction of N-*Benzenesulphonylbenz*iso*thiazolone with* p-*Substituted Aromatic Amines. Formation of the Lactams of the* 2-*Amino*-2′-*carboxydiphenyl Sulphides.*—The thiazolone was heated for 5 hours in boiling alcohol with an equal weight of *p*-toluidine, the solution evaporated to dryness, and the product recrystallised from alcohol or glacial acetic acid. The *lactam* of 2-*amino*-2′-*carboxy*-5-*methyldiphenyl sulphide* was thus isolated as glistening plates, m. p. 274° (Found: C, 69·2; H, 4·5. $C_{14}H_{11}ONS$ requires C, 69·7; H, 4·6%). Benzenesulphonamide was found in the mother liquors. The lactam was oxidised by hydrogen peroxide in acetic acid to its *sulphone*, a white microcrystalline powder, m. p. > 320° (Found: C, 61·5; H, 4·1. $C_{14}H_{11}O_3NS$ requires C, 61·4; H, 4·1%). The lactam was hydrolysed by boiling it for 4 hours with 65% sulphuric acid. On dilution a precipitate was formed containing the sulphate of the amino-acid, and a thioxanthone, separated by dissolving the former out in alkali. The residue was 4-amino-1-methylthioxanthone, yellow needles from alcohol, m. p. 183° not depressed by admixture of a specimen prepared by the method of Ullmann and Glenck (*Ber.*, 1916, **49**, 2499). The alkaline solution, on acidification with acetic acid, gave a 2-*amino*-2′-*carboxy*-5-*methyldiphenyl sulphide*, which crystallised from butyl alcohol in pale buff needles, m. p. 170° (Found: C, 65·2; H, 5·1. $C_{14}H_{13}O_2NS$ requires C, 64·9; H, 5·1%). The acid was re-converted by boiling in acetic anhydride for ½ hour or by standing overnight in sulphuric acid solution into the lactam, m. p. 271°. The lactam was also formed when the acid was heated for 3 hours in boiling ethyl alcohol containing 2—5% of hydrogen chloride, and the ethyl ester of the acid, m. p. 100°, was also produced. When the acid was heated in boiling xylene for ½ hour with phosphoric oxide it yielded the lactam together with 4-amino-1-methylthioxanthone.

The thiazolone with *p*-anisidine furnished the *lactam* of 2-*amino*-2′-*carboxy*-5-*methoxydiphenyl sulphide*, which crystallised from alcohol in white needles, m. p. 235° (Found: C, 64·9; H, 4·1; *M*, ebullioscopic in alcohol, 250. $C_{14}H_{11}O_2NS$ requires C, 65·3; H, 4·3%; *M*, 241). The *acetyl* derivative formed white needles from alcohol, m. p. 165° (Found: C, 63·7; H, 4·6. $C_{16}H_{13}O_3NS$ requires C, 64·2; H, 4·4%). The *sulphone* separated as a microcrystalline powder from acetic acid, m. p. 246° (Found: C, 58·3; H, 4·2. $C_{14}H_{11}O_4NS$ requires C, 58·1; H, 3·8%), which also yielded an *acetyl* derivative, m. p. 194° (Found: C, 58·5; H, 4·0. $C_{16}H_{13}O_5NS$ requires C, 58·0; H, 3·9%).

The same lactam was obtained when *N*-*p*-toluenesulphonylbenz*iso*thiazolone was used in place of the benzenesulphonyl derivative. Hydrolysed by acid it furnished the 2-*amino*-2′-*carboxy*-5-*methoxydiphenyl sulphide*, which crystallised from dilute acetic acid or butyl alcohol in buff needles, m. p. 168° (Found: C, 61·5; H, 4·9. $C_{14}H_{13}O_3NS$ requires C, 61·1; H, 4·8%), and formed a *perchlorate*, which separated from dilute perchloric acid as a white microcrystalline powder, m. p. 210° (decomp.) (Found: C, 43·3; H, 4·5. $C_{14}H_{14}O_3NClS,H_2O$ requires C, 42·9; H, 4·1%). As a by-product in the hydrolysis a

substance was isolated which crystallised from glacial acetic acid in red needles, m. p. 238°, and appeared to be 4-*amino*-1-*hydroxythioxanthone* (Found: C, 63·0; H, 3·8. $C_{13}H_9O_2NS$ requires C, 63·5; H, 3·8%). The acid kept overnight in sulphuric acid solution yielded 4-*amino*-1-*methoxythioxanthone*, yellow plates from alcohol, m. p. 168° (Found: C, 64·9; H, 4·4. $C_{14}H_{11}O_2NS$ requires C, 65·3; H, 4·3%).

The action of *p*-chloroaniline on *N*-benzenesulphonylbenz*iso*thiazolone (12 hours' boiling) yielded the *lactam* of 5-*chloro*-2-*amino*-2′-*carboxydiphenyl sulphide*, which crystallised from glacial acetic acid in colourless plates, m. p. 321° (Found: C, 59·0; H, 3·4. $C_{13}H_8ONClS$ requires C, 59·6; H, 3·1%). Hydrolysis with 65% sulphuric acid gave the *acid*, which separated from dilute acetic acid as a microcrystalline powder, m. p. 183° (Found: C, 55·1; H, 3·8. $C_{13}H_{10}O_2NSCl$ requires C, 55·8; H, 3·6%).

Lactam of 2-Amino-2′-carboxydiphenyl Sulphide.—2-Amino-2′-carboxydiphenyl sulphide of m. p. 157° prepared Mayer's method (*loc. cit.*), when heated with phosphoric oxide in boiling xylene for ½ hour, gave the *lactam*, which crystallised from acetic acid in colourless plates, m. p. 256° (Found: C, 68·4; H, 4·2. $C_{13}H_9ONS$ requires C, 68·7; H, 4·4%). Oxidation with hydrogen peroxide in acetic acid yielded the *lactam sulphone*, which separated from dilute acetic acid in colourless needles, m. p. 290° (Found: C, 60·4; H, 3·8. $C_{13}H_9O_3NS$ requires C, 60·1; H, 3·5%). These lactams are soluble in warm aqueous sodium hydroxide. The same lactam sulphone was also obtained from 2-nitro-2′-carboxydiphenyl sulphone (Mayer, *loc. cit.*) by reduction to the amino-acid sulphone and heating the latter with phosphoric oxide in xylene.

p-*Toluidide and* p-*Nitroanilide of Dithiobenzoic Acid.*—2 : 2′-Dithiobenzoyl chloride reacted with *p*-toluidine or *p*-nitroaniline in carbon tetrachloride or toluene solution, yielding the p-*toluidide*, m. p. 233° (Found: C, 69·2; H, 5·1. $C_{28}H_{24}O_2N_2S_2$ requires C, 69·4; H, 5·0%), and the p-*nitroanilide*, which crystallised from aqueous pyridine in light brown needles, m. p. 263° (Found: C, 57·0; H, 3·5. $C_{26}H_{18}O_6N_4S_2$ requires C, 57·1; H, 3·3%).

N-*Arylbenz*iso*thiazolones.*—Chlorine was passed into 2 : 2′-dithiobenzoyl chloride (10 g.) covered with carbon tetrachloride (60 c.c.) until it had dissolved, the excess of chlorine removed by a current of nitrogen, and the resulting solution added to an ice-cooled solution of *p*-toluidine (20 g.) in carbon tetrachloride (200 c.c.). The dark solution was filtered and evaporated, and the product crystallised from methyl alcohol (charcoal). N-p-*Tolylbenz*iso*thiazolone* was thus obtained as colourless needles, m. p. 135° (Found: C, 69·3; H, 4·3. $C_{14}H_{11}ONS$ requires C, 69·7; H, 4·5%). A similar condensation with *p*-nitroaniline using pyridine as solvent yielded N-p-*nitrophenylbenz*iso*thiazolone*, a microcrystalline powder from acetic acid, m. p. 238° (Found: C, 57·1; H, 3·2. $C_{13}H_8O_3N_2S$ requires C, 57·3; H, 3·0%). This substance was also obtained by adding to the *p*-toluidide of dithiobenzoic acid (3 g.) covered with carbon tetrachloride (50 c.c.) a solution of bromine (2 g.) in carbon tetrachloride (10 c.c.). The dirty red precipitate of bromo-thiol was removed by filtration and boiled with acetic acid (100 c.c.). The thiazolone crystallised on cooling, m. p. 238°. Oxidation by hydrogen peroxide in hot acetic acid converted it into N-p-*nitrophenylsaccharin*, pale yellow plates from acetic acid, m. p. 229° (Found: C, 50·8; H, 2·4. $C_{13}H_8O_5N_2S$ requires C, 51·3; H, 2·6%).

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