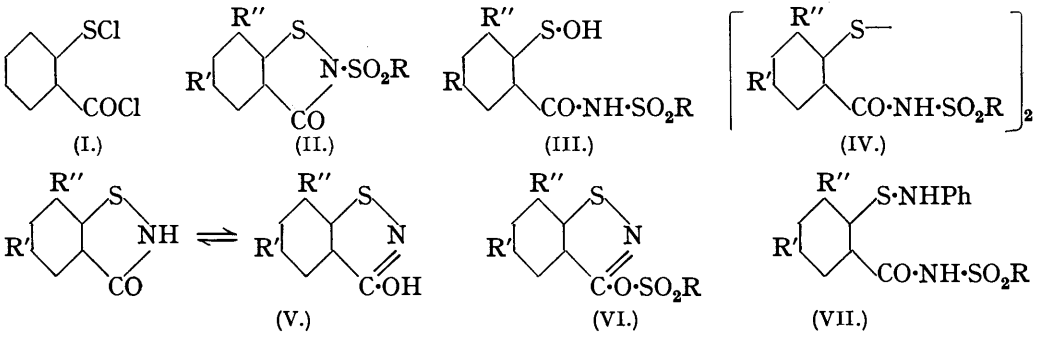
156. *The Preparation and Reactions of Some Arylsulphonylbenziso*thiazolones.

By R. G. Bartlett, L. E. Hart, and E. W. McClelland.

The preparation of 1-arylsulphonylbenz*iso*thiazolones by condensation of the chlorination product of 2 : 2′-dithiobenzoyl chloride with arylsulphonamides and the formation of the same substances and of 2-arylsulphonyloxybenz*iso*thiazoles by the action of arylsulphonyl chlorides on the unsubstituted benz*iso*thiazolone are described. The ring fission of the 1-arylsulphonylbenz*iso*thiazolones has been investigated.

1-Arylsulphonylbenzisothiazolones of the type (II; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me) may be obtained readily by chlorinating 2 : 2′-dithiobenzoyl chloride and condensing the product (I) with the requisite sulphonamide in presence of pyridine (compare McClelland and Gait, J., 1926, 921). When 2-thiolbenzoic acid is chlorinated in presence of ferric chloride (compare Hart, McClelland, and Fowkes, J., 1938, 2114), and the product condensed with an arylsulphonamide, the 4-chloro-1-arylsulphonylbenz*iso*thiazolone (II; $R' = Cl$, $R'' = H$, $R = C_6H_5$ or p-C_6H_4Me) and the 4 : 6-dichloro-1-arylsulphonylbenz*iso*thiazolone (II; $R' = R'' = Cl$, $R = C_6H_5$) result.



The 1-arylsulphonylbenz*iso*thiazolones (II; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me and $R' = Cl$, $R'' = H$, $R = C_6H_5$) appear to be less stable to alkaline reagents than the 1-alkyl or 1-aryl derivatives; they undergo hydrolytic ring fission with sodium hydroxide, yielding the corresponding disulphides (IV), evidently formed by way of the unstable sulphenic acid (III), and with aniline they give compounds to which the formula (VII) is assigned. 1-Phenylbenz*iso*thiazolone is unaffected by similar treatment with aniline.

Acid hydrolysis of the 1-arylsulphonylbenz*iso*thiazolones (II; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me and $R' = Cl$, $R'' = H$, $R = C_6H_5$) eliminates the arylsulphonyl group, giving the corresponding benz*iso*thiazolones (II, with H in place of SO_2R).

The disulphides (IV; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me and $R' = Cl$, $R'' = H$; $R = C_6H_5$) were also obtained by reduction of the appropriate benz*iso*thiazolones. Oxidation of the 1-arylsulphonylbenz*iso*thiazolones (II; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me) gives the corresponding *o*-benzoicsulphinides (II; with SO_2 in place of S).

Treatment of benz*iso*thiazolone (V; $R' = R'' = H$) with the appropriate sulphonyl chloride also gives the 1-arylsulphonyl derivatives (II; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me), but in poor yield. The main product of the reaction is the *O*-arylsulphonyl derivative (VI; $R' = R'' = H$, $R = C_6H_5$ or p-C_6H_4Me). The simultaneous formation of *N*- and *O*-arylsulphonyl derivatives from benz*iso*thiazolone is in accord with its tautomeric character (compare McClelland and Longwell, J., 1923, **123**, 3310; Reissert and Manns, *Ber.*, 1928, **61**, 1308; Reissert, *ibid.*, p. 1680) and is in contrast with its behaviour in acetylation, whereby only one acetyl derivative is formed. This acetyl derivative is evidently the *N*-acetyl derivative (II; $R' = R'' = H$, Ac in place of SO_2R), since it has now been obtained by condensation of 2-chlorothiolbenzoyl chloride (I) with

acetamide in pyridine. The *N*-acetyl derivative is also formed by the action of acetyl chloride on the sodium salt of benz*iso*thiazolone or on the substance itself in presence of pyridine. The formation of the *O*-acetyl derivative was not detected in these experiments.

Experimental.

1-p-*Toluenesulphonylbenziso thiazolone* (II; R′ = R″ = H, R = *p*-C_6H_4Me).—A chlorinated solution of 2 : 2′-dithiobenzoyl chloride (40 g.) in carbon tetrachloride (320 c.c.) was added with stirring to a solution of *p*-toluenesulphonamide (40 g.) in pyridine (75 c.c.). The mixture was poured into an excess of 2N-hydrochloric acid and the solid product was collected and boiled with water. It crystallised from acetic acid in colourless needles (35 g.), m. p. 207° (Found: C, 55·2; H, 3·6. $C_{14}H_{11}O_3NS_2$ requires C, 55·0; H, 3·6%). Refluxed for 1 hour with sulphuric acid (60%), it gave benz*iso*thiazolone.

1-p-*Toluenesulphonylbenziso thiazolone* (2 g.) in acetic acid (16 c.c.) and hydrogen peroxide (2·2 c.c., 90—100 vol.), after being heated at 100° for 45 minutes, on cooling and addition of water, gave N-p-*toluenesulphonyl*-o-*benzoicsulphinide*, which crystallised from alcohol in colourless needles, m. p. 214° [Found: C, 49·9; H, 3·3 (Schoeller). $C_{14}H_{11}O_5NS_2$ requires C, 49·8; H, 3·3%].

1-*Benzenesulphonylbenziso thiazolone* (II; R′ = R″ = H, R = C_6H_5), prepared in a similar way to the *p*-toluenesulphonyl derivative, crystallised from acetic acid in colourless prisms, m. p. 218° (Found: C, 53·5; H, 3·2. $C_{13}H_9O_3NS_2$ requires C, 53·6; H, 3·1%). On oxidation as in the previous experiment it gave a material which had m. p. 202° alone or mixed with authentic *N*-benzenesulphonyl-*o*-benzoicsulphinide (compare J., 1938, 2114). It gave benz*iso*thiazolone on refluxing with sulphuric acid (60%).

4-*Chloro*-1-*benzenesulphonylbenziso thiazolone* (II; R′ = Cl, R″ = H, R = C_6H_5).—Chlorine was passed through a suspension of 2-thiolbenzoic acid (25 g.) and anhydrous ferric chloride (1·25 g.) in carbon tetrachloride (200 c.c.) until solution was almost complete; the free chlorine was then removed by nitrogen. The solution was filtered, mixed with benzenesulphonamide (25 g.) in pyridine (45 c.c.), and poured into an excess of 2N-hydrochloric acid. The *product* crystallised from acetic acid in colourless needles (25 g.), m. p. 205° [Found: C, 47·9; H, 2·5; S, 19·7; Cl, 10·7 (Schoeller). $C_{13}H_8O_3NClS_2$ requires C, 47·9; H, 2·5; S, 19·7; Cl, 10·9%]. It gave 4-chlorobenz*iso*thiazolone (compare J., 1938, 2114) on hydrolysis with sulphuric acid (60%).

4 : 6-*Dichloro*-1-*benzenesulphonylbenziso thiazolone* (II; R′ = R″ = Cl, R = C_6H_5) was obtained by evaporation of the carbon tetrachloride solution from the above preparation. It separated from acetic acid as a white amorphous powder, m. p. 162° [Found: C, 43·3; H, 2·2; Cl, 19·6 (Schoeller). $C_{13}H_7O_3NCl_2S_2$ requires C, 43·3; H, 2·0; Cl, 19·7%].

4-*Chloro*-1-p-*toluenesulphonylbenziso thiazolone* (II; R′ = Cl, R″ = H, R = *p*-C_6H_4Me), prepared in a similar way to the benzenesulphonyl derivative, crystallised from acetic acid in colourless needles, m. p. 203° (Found: C, 49·5; H, 3·4. $C_{14}H_{10}O_3NClS_2$ requires C, 49·5; H, 3·0%).

Reaction of Benziso thiazolone with Arylsulphonyl Chlorides.—Benz*iso*thiazolone (2 g.) and benzenesulphonyl chloride (2·4 g.) in pyridine (6 c.c.) were heated for 30 minutes at 100°. The product was poured into 2N-hydrochloric acid and the precipitate was collected and dissolved in hot alcohol. On cooling, 1-benzenesulphonylbenz*iso*thiazolone was deposited, m. p. (after purification) and mixed m. p. 218—219°. The alcoholic mother-liquor was evaporated to dryness, and the residue washed with warm 2N-sodium hydroxide and water. The 2-*benzenesulphonyloxybenziso thiazole* (VI; R′ = R″ = H, R = C_6H_5) thus obtained crystallised from alcohol in colourless needles, m. p. 68° (Found: C, 53·3; H, 3·0. $C_{13}H_9O_3NS_2$ requires C, 53·6; H, 3·1%).

The toluenesulphonyl derivatives were obtained in a similar way. 2-p-*Toluenesulphonyloxybenziso thiazole* (VI; R′ = R″ = H, R = *p*-C_6H_4Me) crystallised from alcohol in colourless prisms, m. p. 96° (Found: C, 55·1; H, 3·8; N, 4·8. $C_{14}H_{11}O_3NS_2$ requires C, 55·0; H, 3·6; N, 4·6%).

A solution of 2-*p*-toluenesulphonyloxybenz*iso*thiazole (0·5 g.) in acetic acid (5 c.c.) and hydrogen peroxide (2 c.c., 90—100 vol.) was heated for 30 minutes at 100°; on dilution with water *o*-benzoicsulphinide separated. 2-*p*-Toluenesulphonyloxybenz*iso*thiazole (0·5 g.) was refluxed for 1 hour in sulphuric acid (10 c.c. of 60%) or heated with alcoholic sodium ethoxide; benz*iso*thiazolone was obtained in both cases.

2 : 2′-*Bis*-p-*toluenesulphonylcarbamyldiphenyl disulphide* (IV; R′ = R″ = H, R = *p*-

C_6H_4Me) was obtained by passing hydrogen sulphide through a boiling alcoholic solution of 1-*p*-toluenesulphonylbenz*iso*thiazolone. It crystallised from acetic acid in colourless needles, m. p. 218° (Found: C, 54·5; H, 3·9. $C_{28}H_{24}O_6N_2S_4$ requires C, 54·9; H, 3·9%).

2 : 2′-*Bisbenzenesulphonylcarbamyldiphenyl disulphide* (IV; R′ = R″ = H, R = C_6H_5) was prepared in a similar way to the *p*-toluenesulphonyl derivative. It was also obtained as follows: 1-benzenesulphonylbenz*iso*thiazolone (4 g.) in acetic acid (100 c.c.) containing concentrated hydrochloric acid (2 c.c.) and zinc dust (2 g.) was refluxed for 2 hours. The solid was removed and to the warm filtrate ferric chloride (6 g.) was added; the product was washed with water and crystallised from acetic acid, forming colourless needles, m. p. 225—227° (Found: C, 53·1; H, 3·4. $C_{26}H_{20}O_6N_2S_4$ requires C, 53·4; H, 3·4%).

4 : 4′-*Dichloro*-2 : 2′-*bisbenzenesulphonylcarbamyldiphenyl disulphide* (IV; R′ = Cl, R″ = H, R = C_6H_5), obtained from 4-chloro-1-benzenesulphonylbenz*iso*thiazolone in a similar way to the foregoing disulphides or by treatment in acetic acid with hydriodic acid (*d* 1·7) at 100° for a few minutes, crystallised from acetic acid in colourless needles, m. p. 225° (Found: C, 47·5: H, 2·7; Cl, 11·0. $C_{26}H_{18}O_6N_2Cl_2S_4$ requires C, 47·8; H, 2·8; Cl, 10·9%).

These three disulphides were also obtained by boiling the corresponding benz*iso*thiazolones with 2N-sodium hydroxide and acidifying the product.

2-*Anilinothiobenzobenzenesulphonylamide* (VII; R′ = R″ = H, R = C_6H_5).—1-Benzenesulphonylbenz*iso*thiazolone (1 g.) was heated with aniline (3 c.c.) at 100° for 3 hours, and the mixture poured into an excess of 2N-hydrochloric acid. The *precipitate* crystallised from aqueous alcohol in colourless needles, m. p. 167° (Found: C, 59·2; H, 4·0. $C_{19}H_{16}O_3N_2S_2$ requires C, 59·3; H, 4·2%).

2-*Anilinothiobenzo*-p-*toluenesulphonylamide* (VII; R′ = R″ = H, R = *p*-C_6H_4Me), prepared in a similar way, crystallised from aqueous alcohol in colourless needles, m. p. 187° (Found: C, 60·4; H, 4·5. $C_{20}H_{18}O_3N_2S_2$ requires C, 60·3; H, 4·6%).

5-*Chloro*-2-*anilinothiobenzobenzenesulphonylamide* (VII; R′ = Cl, R″ = H, R = C_6H_5), prepared from 4-chloro-1-benzenesulphonylbenz*iso*thiazolone, crystallised from aqueous methyl alcohol in colourless needles, m. p. 167° (Found: C, 54·4; H, 4·0; S, 15·7. $C_{19}H_{15}O_3N_2ClS_2$ requires C, 54·5; H, 3·6; S, 15·3%).

1-Acetylbenz*iso*thiazolone identical with that obtained by acetylation of benz*iso*thiazolone with acetic anhydride was obtained in the following experiments: (i) 2 : 2′-Dithiobenzoyl chloride (5 g.) in carbon tetrachloride (40 c.c.), after chlorination in the usual way, was mixed with a solution of acetamide (1·8 g.) in pyridine (9 c.c.). The product was poured into 2N-hydrochloric acid, and the solid collected and purified; m. p. 139°. (ii) A suspension of the sodium salt of benz*iso*thiazolone in benzene and acetyl chloride (1·2 mols.) was refluxed for 4 hours. The solution was filtered and evaporated to dryness; the residue after purification had m. p. 139°. (iii) Benz*iso*thiazolone (1 g.) in pyridine was cooled in ice, and acetyl chloride (0·5 c.c.) added. After 15 minutes the product was treated as in (i). Mixtures of the three specimens showed no depression in m. p.

KING'S COLLEGE, LONDON. [*Received, February 16th,* 1939.]