29. *The Rearrangement of 2-Benzenesulphenamidothiazoles. Part II. Thiazole Compounds Substituted in Position 4.*

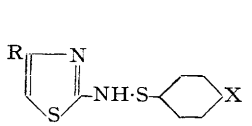
By Eric Hoggarth.

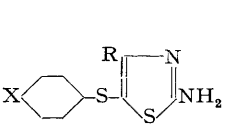
The course of the reactions discussed in Part I (preceding paper) is shown to be greatly modified by the substituent in position 4 of the thiazole ring.

It was shown in Part I that of the 2-benzenesulphenamidothiazoles (I; X = NO_2, Me, or Cl, R = H) only the *p*-nitro-compound is converted into the acetyl derivative of the isomeric phenyl 2-amino-5-thiazyl sulphide (II) by acetic anhydride. However, when the thiazole ring carries a methyl group in position 4, all three *sulphenamides* (I; X = NO_2, Me, or Cl, R = Me) have been found to rearrange to the corresponding compounds (II) by the same treatment. Like compounds lacking the 4-methyl group, 2-acetamido-4-methylthiazole was attacked by all three benzenesulphenyl chlorides to give acetyl derivatives of compounds of type (II) directly. These acetyl derivatives were hydrolysed to the free 2-amino-compounds, identical with those obtained by condensing 5-bromo-2-amino-4-methylthiazole (Ochiai and Nagasawa, *Ber.*, 1939, **72**, 1470) with the corresponding thiophenols. Oxidation of the acetyl derivatives of the sulphides (II) followed by deacetylation gave *phenyl 2-amino-4-methyl-5-thiazyl sulphones*.

5-Bromo-2-amino-4-methylthiazole reacted very much more readily with thiophenols than did 5-bromo-2-acetamidothiazole. This implied the possibility that in the former bromo

compound the bromine atom was not in the thiazole ring as has been assumed but in the methyl group; if this were so the sulphides (II) would have the isomeric structure (III). A sulphone


(I.)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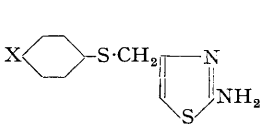
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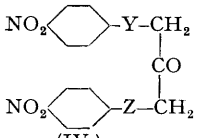
(IV.)

corresponding to (III) was synthesised as follows. *p*-Nitrophenylsulphonylacetone (Burton and Hoggarth, *J.*, 1945, 470) was monobrominated and the constitution of the product established as 3-*bromo*-1-p-*nitrophenylsulphonylacetone* by condensation with sodium *p*-nitrothiophenoxide to give a *sulphide-sulphone* (IV; Y = S, Z = SO_2) which was oxidised to a disulphone (IV; Y = Z = SO_2) identical with 1 : 3-*bis*-p-*nitrophenylsulphonylacetone* prepared by condensation of *s*-dichloroacetone with 2 mols. of sodium *p*-nitrothiophenoxide and oxidation of the resulting 1 : 3-*bis*-p-*nitrophenylthioacetone* (IV; Y = Z = S). 3-Bromo-1-*p*-nitrophenylsulphonylacetone reacted with thiourea to give 2-*amino*-4-(p-*nitrophenylsulphonylmethyl*)-*thiazole* (II; X = NO_2); this was reduced to the *diamine* (III; X = NH_2).

When the sulphenamides (I; R = Me, X = NO_2, Me, or Cl) were treated with acid under conditions suitable for the scission of the corresponding sulphenamides lacking the methyl group (see Part I) the isomeric phenyl 2-amino-4-methyl-5-thiazyl sulphides were obtained in excellent yield. It appears therefore that the presence of the 4-methyl group activates position 5 sufficiently to make attack possible by the (assumed) intermediate sulphenic acid. It was shown that this rearrangement, like that caused by the action of acetic anhydride, is intermolecular, for in the presence of resorcinol some 4-nitro-2′ : 4′-dihydroxydiphenyl sulphide was formed. However, unlike the reaction of 2-*p*-nitrobenzenesulphenamidothiazole with acetic anhydride in the presence of resorcinyl diacetate (Part I), much of the phenyl 5-thiazyl sulphide was also isolated. The action of acids on sulphenamides of 2-amino-4-methylthiazole is very similar to the rearrangement of some *o*-nitrobenzenesulphenylphenyl esters to *o*-nitro-*p*′-hydroxydiphenyl sulphides observed by Smiles and Learmonth (*J.*, 1936, 327). Both reactions are effected by acid and are not truly intramolecular.

A small amount of *p*-nitrophenyl 2-amino-4-methyl-5-thiazyl sulphide was found as a by-product in the preparation of 2-*p*-nitrobenzenesulphenamido-4-methylthiazole, and, when the thiazole ring carried a phenyl group in place of the methyl, reaction with *p*-nitrobenzenesulphenyl chloride gave only the phenyl 5-thiazyl sulphide (II; R = Ph, X = NO_2), no sulphenamide being isolable under the usual conditions. The structure of the product was established by stability to hydrolysis with acid and recovery unchanged after acetylation followed by hydrolysis. Furthermore, oxidation of the acetyl derivative gave an *acetamidosulphone* which was hydrolysed to p-*nitrophenyl* 2-*amino*-4-*phenyl*-5-*thiazyl sulphone*, whereas 2-*p*-nitrobenzenesulphonamido-4-phenylthiazole would result from this sequence of reactions if a very stable sulphenamide were assumed to be the product of the initial reaction. An alternative synthesis has been achieved as follows. 2-Amino-4-phenylthiazole under conditions suitable for the bromination of the 4-methyl compound gave a monobromo-derivative which must be 5-*bromo*-2-*amino*-4-*phenylthiazole*, and this was condensed with sodium-*p*-nitrothiophenoxide. These results bring the reactions of benzenesulphenyl chlorides with 2-aminothiazoles into line with the corresponding reactions with simple aromatic amines. 2-Aminothiazole itself resembles aniline and *p*-toluidine in giving no appreciable amount of sulphide under the usual conditions, 2-amino-4-phenylthiazole resembles the naphthylamines in giving nuclear substitution product almost exclusively, and 2-amino-4-methylthiazole is intermediate, both sulphide and sulphenamide being formed (cf. Zincke and Lenhardt, *Annalen*, 1913, **400**, 2).

Experimental.

2-p-*Nitrobenzenesulphenamido*-4-*methylthiazole*.—A solution of *p*-nitrobenzenesulphenyl chloride (11·4 g.) in benzene (100 c.c.) was added with stirring to a solution of 2-amino-4-methylthiazole (7·0 g.) in benzene (100 c.c.) during 1 hour, and the solid collected and crystallised from xylene to give faintly yellow plates (6·8 g.), m. p. 181° (B.P. 551,681 gives m. p. 183°) (Found: C, 45·0; H, 3·6. Calc. for $C_{10}H_9O_2N_3S_2$: C, 44·9; H, 3·4%). Evaporation of the benzene mother liquors gave a sticky solid which was ground with water and extracted with hot benzene–light petroleum (b. p. 60—80°). On cooling, the extract deposited a yellow powder (0·3 g.), m. p. 160—166°, which was recrystallised from the same solvents giving a mixture of the two dimorphs of p-*nitrophenyl* 2-*amino*-4-*methyl*-5-*thiazyl sulphide* (see below), m. p. 172°, 172—173° Found: S, 24·1, 24·25. $C_{10}H_9O_2N_3S_2$ requires S, 24·0%).

p-*Nitrophenyl 2-Amino-4-methyl-5-thiazyl Sulphide.*—(A) The above sulphenamide (2·7 g.) and acetic anhydride (5 c.c.) were heated at 95° for 5 minutes, water (200 c.c.) was added, and the precipitate collected and crystallised from aqueous alcohol to give faintly yellow needles of *p*-nitrophenyl 2-acetamido-4-methyl-5-thiazyl sulphide (2·2 g.), m. p. 178—179° (B.P. 559,384 gives m. p. 183°) (Found: C, 46·5; H, 3·7; S, 20·9. Calc. for $C_{12}H_{11}O_3N_3S_2$: C, 46·6; H, 3·55; S, 20·7%). This acetamido-compound (2·0 g.) was refluxed for 3 hours with alcohol (50 c.c.) and concentrated hydrochloric acid (5 c.c.), the solvents were evaporated under reduced pressure, and the residue was treated with water (50 c.c.) and made just alkaline with sodium carbonate. The solid was collected and crystallised from benzene–light petroleum (b. p. 60—80°) giving a yellow crystalline powder (1·5 g.), m. p. 172°, which on slow recrystallisation from the same solvents gave a mixture of two *dimorphs* of the amino-sulphide; (*a*) large deep golden yellow prisms, m. p. 172—173° (Found: C, 45·25; H, 3·5%), and (*b*) clusters of pale yellow needles, m. p. 172—173° (Found: C, 45·0; H, 3·7%). There was no depression of m. p. when (*a*) and (*b*) were mixed, and crystallisation of hand-picked samples always gave mixtures.

(B) 2-Acetamido-4-methylthiazole (31·0 g.) in benzene (200 c.c.) was treated with *p*-nitrobenzenesulphenyl chloride (19·0 g.) in benzene (100 c.c.) at 40—50°, the solvent evaporated, and the residue treated with acetic anhydride (100 c.c. at 100°), poured into water, and crystallised from aqueous alcohol giving colourless needles of the acetyl derivative (29·2 g.), m. p. 178—179°, identical with that prepared in (A) (Found: C, 46·4; H, 3·8%).

(C) 5-Bromo-2-amino-4-methylthiazole (3·8 g.) and sodium *p*-nitrothiophenoxide (3·6 g.) were refluxed in alcohol for 3 hours, water (200 c.c.) was added, and the solid collected and crystallised from benzene–light petroleum (b. p. 60—80°) giving the amino-sulphide (3·2 g.), m. p. 172—173°. On slow recrystallisation two dimorphs were formed identical with those described under (A) (Found: C, 44·7, 45·1; H, 3·7, 3·4%). Acetylation with acetic anhydride of hand-picked specimens of either dimorph gave the same acetyl derivative, m. p. 179° (Found: C, 46·4; H, 3·3; S, 20·6%).

(D) 2-*p*-Nitrobenzenesulphenamido-4-methylthiazole (2·0 g.), concentrated hydrochloric acid (10 c.c.), alcohol (50 c.c.), and β-ethoxyethanol (20 c.c.) were refluxed for 3 hours and then evaporated under reduced pressure. The residue was ground in a mortar with 10% sodium carbonate solution (50 c.c.), and the solid collected and crystallised from benzene–light petroleum (b. p. 60—80°) giving a mixture of the two dimorphic forms of the amino-sulphide (1·4 g.), m. p. 172—173°, 173° (Found: S, 24·3, 23·8%).

2-p-*Toluenesulphenamido-4-methylthiazole.*—2-Amino-4-methylthiazole (11·4 g.) in dry benzene (150 c.c.) was treated with a solution of *p*-toluenesulphenyl chloride (15·8 g.) in dry benzene (150 c.c.), added with stirring during ½ hour; the solid was collected, ground with warm water, again collected, and crystallised from ethyl acetate–alcohol giving colourless plates of 2-p-*toluenesulphenamido-4-methylthiazole dihydrate* (5·8 g.), m. p. 224° (Found: C, 48·3, 48·75; H, 5·5, 5·9; S, 23·9, 23·4. $C_{11}H_{12}N_2S_2,2H_2O$ requires C, 48·5; H, 5·9; S, 23·6%).

p-*Tolyl 2-Amino-4-methyl-5-thiazyl Sulphide.*—(A) The above sulphenamide (5·0 g.) and acetic anhydride (15 c.c.) were heated for 1 hour at 90°, poured into water (500 c.c.), and the solid collected and crystallised from light petroleum (b. p. 60—80°) giving colourless needles (3·1 g.), m. p. 149° (Found: C, 56·25; H, 4·65; S, 22·6. $C_{12}H_{14}ON_2S_2$ requires C, 56·2; H, 5·0; S, 22·9%). This *acetamido*-compound was hydrolysed by acid to the *amino-sulphide*, which crystallised from light petroleum (b. p. 60—80°) in fine colourless needles, m. p. 141° (Found: C, 55·6; H, 5·05. $C_{11}H_{12}N_2S_2$ requires C, 55·9; H, 5·1%).

(B) A solution of *p*-toluenesulphenyl chloride (53·0 g.) in benzene (500 c.c.) was added to a solution of 2-acetamido-4-methylthiazole (52·0 g.) in benzene (1 l.) at 45—55°, the solvent evaporated under reduced pressure, the residue heated with acetic anhydride (200 c.c.) and poured into water, and the solid collected and crystallised from light petroleum (b. p. 60—80°) giving colourless flattened needles or plates of the acetyl derivative (56·5 g.), m. p. 149° (Found: C, 55·8; H, 4·8%).

(C) 5-Bromo-2-amino-4-methylthiazole (4·0 g.) and thio-*p*-cresol (5·0 g.) were heated by an oil-bath at 120° for 1 hour; the reaction mixture was cooled, treated with water (100 c.c.) and 40% sodium hydroxide solution (10 c.c.), and the solid precipitate collected and crystallised from light petroleum (b. p. 60—80°) giving 1·1 g., m. p. 141° (Found: C, 55·5; H, 5·0; S, 26·9%). The acetyl derivative, prepared with acetic anhydride, was crystallised from light petroleum (b. p. 60—80°); m. p. 149—150° (Found: C, 55·8; H, 4·5; S, 22·8%).

(D) 2-*p*-Toluenesulphenamido-4-methylthiazole (2·0 g.), concentrated hydrochloric acid (10 c.c.), and alcohol (50 c.c.) were refluxed for 3 hours to give the amino-sulphide (1·5 g.), m. p. 142° (Found: S, 27·3%).

2-p-*Chlorobenzenesulphenamido-4-methylthiazole.*—This *compound* was prepared as described for the *p*-toluene compound from 2-amino-4-methylthiazole and *p*-chlorobenzenesulphenyl chloride (71% yield). It crystallised from alcohol–ethyl acetate in colourless prisms, m. p. 221° (Found: Cl, 13·6; S, 24·8. $C_{10}H_9N_2ClS_2$ requires Cl, 13·8; S, 25·0%).

p-*Chlorophenyl 2-Amino-4-methyl-5-thiazyl Sulphide.*—(A) The above sulphenamide (2·5 g.) was heated with acetic anhydride (10 c.c.) to give p-*chlorophenyl 2-acetamido-4-methyl-5-thiazyl sulphide*, which crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms (1·9 g.), m. p. 152° (Found: Cl, 11·6; S, 21·5. $C_{12}H_{11}ON_2ClS_2$ requires Cl, 11·9; S, 21·4%). By hydrolysis with acid the *amino-sulphide* was obtained; this crystallised from light petroleum (b. p. 60—80°) in colourless needles (73%), m. p. 145° (Found: Cl, 13·8; S, 24·65. $C_{10}H_9N_2ClS_2$ requires Cl, 13·8; S, 25·0%).

(B) The acetyl derivative was prepared by interaction of *p*-chlorobenzenesulphenyl chloride and 2-acetamido-4-methylthiazole as described for the *p*-tolyl compound above (85% yield); m. p. 151—152° (Found: C, 48·4; H, 3·75%).

(C) 5-Bromo-2-amino-4-methylthiazole and *p*-chlorothiophenol reacted together as described for the corresponding *p*-tolyl compound to give the amino-sulphide, m. p. 144—145° (Found: C, 47·1; H, 3·75; S, 24·6%). The acetyl derivative was prepared with acetic anhydride; m. p. 151—152° (Found: C, 48·35; H, 3·7; S, 21·5%).

(D) 2-*p*-Chlorobenzenesulphenamido-4-methylthiazole (2·0 g.), concentrated hydrochloric acid (10 c.c.), and alcohol (50 c.c.) were refluxed for 3 hours to give the amino-sulphide (1·2 g.), m. p. 146° (Found : Cl, 11·7; S, 21·8%).

p-*Nitrophenyl* 2-*Amino*-4-*methyl*-5-*thiazyl Sulphone.*—*p*-Nitrophenyl 2-acetamido-4-methyl-5-thiazyl sulphide (13·0 g.) in acetic acid (150 c.c.) was oxidised with potassium permanganate (13·0 g.) in water (150 c.c.), sulphur dioxide passed until the brown colour was discharged, and the solid collected and crystallised from alcohol giving shining leaflets (8·8 g.), m. p. 232° (Found : C, 42·15; H, 3·05; S, 18·5. $C_{12}H_{11}O_5N_3S_2$ requires C, 42·2; H, 3·2; S, 18·8%). This *acetamido*-compound (6·5 g.) was hydrolysed by acid to the *amino-sulphone* which crystallised from β-ethoxyethanol in sulphur yellow prisms (5·2 g.), m. p. 204° (Found : C, 40·25; H, 3·1; S, 21·7. $C_{10}H_9O_4N_3S_2$ requires C, 40·1; H, 3·0; S, 21·4%).

p-*Aminophenyl* 2-*Amino*-4-*methyl*-5-*thiazyl Sulphone.*—This compound was obtained by catalytic reduction of the above amino-nitro-sulphone in alcohol with Raney nickel catalyst; it crystallised from water in shining leaflets, m. p. 173° (B.P. 559,385 gives m. p. 180°) (Found : C, 44·4; H, 3·9; S, 23·4. Calc. for $C_{10}H_{11}O_2N_3S_2$: C, 44·6; H, 4·1; S, 23·8%).

p-*Tolyl* 2-*Amino*-4-*methyl*-5-*thiazyl Sulphone.*—*p*-Tolyl 2-acetamido-4-methyl-5-thiazyl sulphide (20·0 g.) in acetic acid (250 c.c.) was oxidised with a solution of potassium permanganate (25·0 g.) in water (250 c.c.) added during 1 hour, sulphur dioxide was passed, and the solid collected and crystallised from alcohol giving colourless plates (12·0 g.), m. p. 238° (Found : C, 49·9, H, 4·3. $C_{13}H_{14}O_3N_2S_2$ requires C, 50·3; H, 4·5%). This *acetamido*-compound (10·1 g.) was hydrolysed by acid to the *amino-sulphone* which crystallised from benzene–light petroleum (b. p. 60—80°) in colourless needles (6·8 g.), m. p. 176° (Found : C, 49·0; H, 4·5. $C_{11}H_{12}O_2N_2S_2$ requires C, 49·1; H, 4·5%).

p-*Chlorophenyl* 2-*Amino*-4-*methyl*-5-*thiazyl Sulphone.*—The acetamido-sulphide was oxidised in the usual way with potassium permanganate; the p-*chlorophenyl* 2-*acetamido*-4-*methyl*-5-*thiazyl sulphone* crystallised from alcohol in colourless needles (53·3%), m. p. 266° (Found : C, 43·45; H, 3·55; S, 19·7. $C_{12}H_{11}O_3N_2ClS_2$ requires C, 43·6; H, 3·3; S, 19·4%). Hydrolysis with acid gave the *amino-sulphone*, which crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms, m. p. 160° (Found : Cl, 12·5; S, 22·0. $C_{10}H_9O_2N_2ClS_2$ requires Cl, 12·3; S, 22·2%).

3-*Bromo*-1-p-*nitrobenzenesulphonylacetone.*—*p*-Nitrobenzenesulphonylacetone (27·0 g.) in acetic acid (250 c.c.) at 40° was treated with bromine (18·0 g.) in acetic acid (100 c.c.) and shaken until the colour was (suddenly) discharged. The pale yellow solution was poured into water (1 l.), the solid collected, and crystallised from dilute acetic acid giving large colourless needles (32·5 g.), m. p. 149° (Found : Br, 25·0; S, 9·8. $C_9H_8O_5NBrS$ requires Br, 24·9; S, 9·9%). When this *compound* (3·2 g.) in alcohol (100 c.c.) was refluxed with sodium *p*-nitrothiophenoxide (1·8 g.) for 1 hour and the solution poured into water a solid *sulphide-sulphone* was obtained which crystallised from β-ethoxyethanol in yellow prisms (1·5 g.), m. p. 168° (Found : C, 45·35; H, 3·2; S, 16·3. $C_{15}H_{12}O_7N_2S_2$ requires C, 45·45; H, 3·0; S, 16·2%). On oxidation of this compound (1·0 g.) in boiling acetic acid (10 c.c.) by hydrogen peroxide (100-vol., 1·2 c.c.) a disulphone was precipitated on pouring into water; it crystallised from β-ethoxyethanol giving large golden yellow prisms (0·6 g.), m. p. 188—189°, identical with 1 : 3-*bis*-p-*nitrobenzenesulphonylacetone* prepared as below (Found : C, 42·4; H, 2·75; S, 15·0. $C_{15}H_{12}O_9N_2S_2$ requires C, 42·05; H, 2·8; S, 14·9%).

1 : 3-*Bis*-p-*nitrobenzenesulphonylacetone.*—*s*-Dichloroacetone (12·7 g.) and sodium *p*-nitrothiophenoxide (35·0 g.) were refluxed in alcohol (500 c.c.) for 6 hours, poured into water, and the *disulphide* collected, washed with water and crystallised from β-ethoxyethanol giving golden yellow plates (12·8 g.), m. p. 156° (Found : C, 49·2; H, 3·1; S, 17·3. $C_{15}H_{12}O_5N_2S_2$ requires C, 49·45; H, 3·3; S, 17·6%). When this disulphide (3·6 g.) in boiling acetic acid (30 c.c.) was oxidised with hydrogen peroxide (100-vol., 9 c.c.) the disulphone was precipitated on pouring into water and crystallised from β-ethoxyethanol giving large golden yellow prisms (2·9 g.), m. p. 188—189° (Found : C, 42·2; H, 2·5; S, 15·4. Calc. for $C_{15}H_{12}O_9N_2S_2$: C, 42·05; H, 2·8; S, 14·9%).

2-*Amino*-4-(p-*nitrophenylsulphonylmethyl*)*thiazole.*—3-Bromo-1-*p*-nitrobenzenesulphonylacetone (32·0 g.) and thiourea (7·6 g.) were refluxed in alcohol (200 c.c.) for 2 hours, water (500 c.c.) added, the solution filtered (charcoal), the filtrate made just alkaline with ammonia, and the precipitate collected and crystallised from β-ethoxyethanol giving almost colourless prisms of the *compound* (23·0 g.), m. p. 238° (Found : C, 40·35; H, 3·1; S, 21·4. $C_{10}H_9O_4N_3S_2$ requires C, 40·1; H, 3·0; S, 21·4%). The *acetyl* derivative, prepared with acetic anhydride, crystallised from β-ethoxyethanol giving colourless prisms, m. p. 204° (Found : C, 42·5; H, 3·5; S, 18·4. $C_{12}H_{11}O_5N_3S_2$ requires C, 42·2; H, 3·2; S, 18·8%). The above nitro-sulphones were reduced in alcohol with Raney nickel catalyst.

2-*Amino*-4-(p-*aminophenylsulphonylmethyl*)*thiazole* formed long slender faintly buff-coloured needles from β-ethoxyethanol, m. p. 229° (Found : C, 44·3; H, 4·1; S, 24·0. $C_{10}H_{11}O_2N_3S_2$ requires C, 44·6; H, 4·1; S, 23·8%).

1 : 3-*Disulphanilylacetone* formed colourless plates from alcohol, m. p. 187—188° (Found : C, 49·0; H, 4·5. $C_{15}H_{16}O_5N_2S_2$ requires C, 48·9; H, 4·3%).

Reaction of 2-p-*Nitrobenzenesulphenamido*-4-*methylthiazole with Acid in the Presence of Resorcinol.*—The sulphenamide (2·7 g.) was added to a refluxing solution of resorcinol (2·2 g. = 2 mols.) in alcohol (50 c.c.) and concentrated hydrochloric acid (5 c.c.) during 10 minutes, and the solvents were evaporated under reduced pressure and the residue treated with water (50 c.c.) and concentrated hydrochloric acid (1 c.c.). The insoluble residue was dissolved in dilute sodium carbonate solution, filtered (charcoal), precipitated with acid, and crystallised from acetic acid giving 4-nitro-2′ : 4′-dihydroxydiphenyl sulphide (0·25 g., m. p. 184°). The acid filtrate was made alkaline with sodium carbonate, and the solid collected and crystallised from benzene–light petroleum (b. p. 60—80°) giving a mixture of the two dimorphs of *p*-nitrophenyl 2-amino-4-methyl-5-thiazyl sulphide (1·9 g., m. p. 173°).

p-*Nitrophenyl* 2-*Amino*-4-*phenyl*-5-*thiazyl Sulphide.*—(A) 2-Amino-4-phenylthiazole (17·0 g.) was dissolved in hot benzene, cooled to 30°, and treated with a solution of *p*-nitrobenzenesulphenyl chloride (9·5 g.) in benzene (50 c.c.), water (300 c.c.) added, the solid collected, washed with hot water and crystallised from xylene giving golden-yellow plates (16·8 g.), m. p. 228° (Found : 54·85; H, 3·1; S,

19·4. $C_{15}H_{11}O_2N_3S_2$ requires C, 54·7; H, 3·3; S, 19·5%). This *compound* was recovered unchanged after boiling for 3 hours with concentrated hydrochloric acid and β-ethoxyethanol. With acetic anhydride (30 c.c.) at 100° the compound (5·0 g.) gave an *acetyl* derivative which crystallised from alcohol in colourless felted needles (3·8 g.), m. p. 208° (Found: C, 55·2; H, 2·4; S, 17·2. $C_{17}H_{13}O_3N_3S_2$ requires C, 55·0; H, 3·5; S, 17·3%), and was reconverted into the amino-sulphide, m. p. 228° (Found: S, 19·2%) by hydrolysis with concentrated hydrochloric acid and β-ethoxyethanol.

(B) 2-Amino-4-phenyl-thiazole (8·8 g.) was dissolved in hot chloroform (200 c.c.), cooled to 25°, and treated with bromine (8·0 g.) in chloroform (20 c.c.). After ½ hour the solvent was removed under reduced pressure, the residue dissolved in chloroform (100 c.c.), shaken with sodium carbonate solution, again evaporated under reduced pressure and the residue dissolved in hot *cyclo*hexane. On standing, *5-bromo-2-amino-4-phenylthiazole* separated in clumps of colourless needles (8·1 g.), m. p. 106° (Found: C, 43·1; H, 2·6; Br, 31·4; S, 12·7. $C_9H_7N_2BrS$ requires C, 42·4; H, 2·7; Br, 31·4; S, 12·5%).

The bromo-compound (2·6 g.) and sodium *p*-nitrothiophenoxide (1·9 g.) were refluxed in alcohol (50 c.c.) until the colour was discharged (½ hour), poured into water, and the solid collected and crystallised from xylene giving yellow plates (1·2 g.), m. p. 228° not depressed by *p*-nitrophenyl 2-amino-4-phenyl-5-thiazyl sulphide prepared by method (A) (Found: C, 54·5; H, 3·1; S, 19·7%).

p-*Nitrophenyl 2-Amino-4-phenyl-5-thiazyl Sulphone.*—The above acetamido-sulphide (3·7 g.) was stirred in acetic acid (120 c.c.) at 85°, hydrogen peroxide (100-vol., 5 c.c.) added during ½ hour, the solution boiled for 1 hour, poured into water (500 c.c.), and the p-*nitrophenyl 2-acetamido-4-phenyl-5-thiazyl sulphone* collected and crystallised from β-ethoxyethanol giving pale yellow needles (2·3 g.), m. p. 253—255° (Found: C, 50·7; H, 3·25; S, 15·9. $C_{17}H_{13}O_5N_3S_2$ requires C, 50·6; H, 3·2; S, 15·9%). This acetamido-sulphone (2·0 g.) was hydrolysed by concentrated hydrochloric acid and β-ethoxyethanol to the *amino-sulphone* which crystallised from alcohol in slender yellow needles (1·1 g.), m. p. 238° (Found: C, 49·8; H, 3·05; S, 17·6. $C_{15}H_{11}O_4N_3S_2$ requires C, 49·9; H, 3·0; S, 17·7%).

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