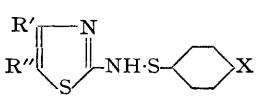
28. *The Rearrangement of 2-Benzenesulphenamidothiazoles. Part I. Thiazole Compounds not Substituted in Position 4.*

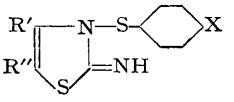
By Eric Hoggarth.

It is shown that a 2-benzenesulphenamidothiazole is rearranged by acetic anhyride to give a phenyl 5-thiazyl sulphide. The mechanism of the reaction and its limitations are discussed.

It has been assumed that benzenesulphenyl halides react with 2-aminothiazoles to give as a rule the 2-benzenesulphenamides (I) and that when two isomeric compounds are formed as in the particular case of *p*-nitrobenzenesulphenyl chloride and 2-amino-4-methylthiazole, the second is a 3-sulphenamido-2-iminothiazole (II) (Wheeler, Bann, Krug, Taylor, and Gladding, B.PP. 551,681, 559,384, 559,385). Further, acetyl derivatives, presumed to correspond to these structures, have been described, and that corresponding to (II) (*i.e.* III; X = NO_2, R′ = Me, R″ = H) was obtained by the acetylation of (I) or (II) with hot acetic anhydride and by condensation of *p*-nitrobenzenesulphenyl chloride with 2-acetamido-4-methylthiazole. This formul-

ation has been challenged by Bambas (*J. Amer. Chem. Soc.*, 1945, **67**, 671) on the grounds that the sulphenamide from *p*-nitrobenzenesulphenyl chloride and 2-methylamino-4-methylthiazole (IV) undergoes an apparently similar reaction with acetic anhydride, which it is impossible to account for in terms of structure (III). He suggested that the effect of acetic anhydride on sulphenamides of type (I) is to give 2-acetamido-derivatives of phenyl 5-thiazyl sulphides (V). Certain sulphenamides are known to undergo a similar rearrangement on heating with aromatic amines (Moore and Johnson, *J. Amer. Chem. Soc.*, 1935, **57**, 2234; 1936, **58**, 1091, 1960).


(I.)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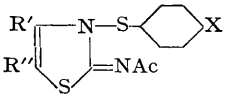
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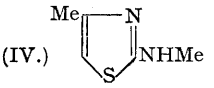
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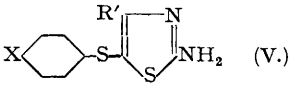
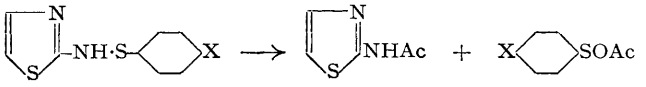

(V.)

We had arrived at the same conclusion by another route. With the information contained in the patents cited above, it seemed that in order to prepare phenyl 5-thiazyl sulphides (V) it would be necessary to protect both hydrogen atoms of the 2-aminothiazole before bringing it into reaction with a sulphenyl chloride. By the intereaction of *p*-nitrobenzenesulphenyl chloride with 2-benzylideneaminothiazole followed by scission of benzaldehyde, a compound analysing correctly for (V; X = NO_2, R′ = H) was obtained. This compound on acetylation gave an acetyl derivative which proved to be identical with that obtained by the action of acetic anhydride on 2-*p*-nitrobenzenesulphenamidothiazole (I; X = NO_2, R′ = R″ = H) and by condensation of *p*-nitrobenzenesulphenyl chloride with 2-acetamidothiazole. The constitution of this compound as p-*nitrophenyl 2-acetamido-5-thiazyl sulphide* was confirmed by hydrolysis experiments. 2-*p*-Nitrobenzenesulphenamidothiazole is rapidly hydrolysed by acid to 2-aminothiazole and 4 : 4′-dinitrodiphenyl disulphide, the latter presumably arising by decomposition of the sulphenic acid first formed (cf. Zincke and Farr, *Annalen*, 1912, **391**, 57; Moore and Johnson, *loc. cit.*). Hydrolysis of the compound to which structure (III; X = NO_2, R′ = R″ = H) would be assigned by the patents cited gives a compound isomeric with the sulphenamide (I) and stable to further hydrolysis. This is of course the amino-sulphide (V; X = NO_2, R′ = H), and it is clear that a compound of formula (III) would not retain the *p*-nitrophenylthio-group on such treatment. Final proof was afforded by alternative synthesis by condensation of *p*-nitrothiophenol with 5-bromo-2-acetamidothiazole (Backer and Buisman, *Rec. Trav. chim.*, 1944, **63**, 227). The bromothiazole is not very reactive and was recovered unchanged after boiling with an alcoholic solution of *p*-nitrothiophenoxide. However, it reacted instantly with the fused thiophenol.

It was found that the rearrangement of 2-benzenesulphenamidothiazoles with acetic anhydride was by no means general. 2-p-*Chlorobenzenesulphenamido-* and 2-p-*toluenesulphenamidothiazole* (VI; X = Cl or Me) were converted by acetic anhydride even under very mild conditions into 2-acetamidothiazole and the corresponding 4 : 4′-disubstituted diphenyl disulphide. The latter possibly arises by decomposition of a mixed sulphenic-carboxylic anhydride (VII) on contact with water. Verification of the constitution of these sulphenamides was obtained by hydrolysis with acids to give 2-aminothiazole and the corresponding disulphide. The *sulphides* (V; X = Cl or Me, R′ = H) were obtained both by the action of the corresponding arylsulphenyl chloride on 2-acetamidothiazole and by condensation of 5-bromo-2-acetamidothiazole with the corresponding fused thiophenols. They were oxidised to *sulphones* by mild oxidising agents.


(VI.) (VII.)

It has been shown that the reaction of 2-*p*-nitrobenzenesulphenamidothiazole with acetic anhydride is an intermolecular rearrangement. In the presence of resorcinyl diacetate the *p*-nitrophenylthio-group substitutes almost exclusively the resorcinol molecule and no appreciable amount of thiazyl sulphide is obtained. This implies that the preliminary reaction is to split the sulphenamide linkage with subsequent attack of the 5-position of the thiazole nucleus

if the intermediate compound, perhaps (VII), is reactive enough (this depending on the aryl substituent X). Rearrangement of a 2-*p*-nitrobenzenesulphenamidothiazole will not take place if position 5 is occupied, *i.e.*, there is no tendency to attack position 4, not can compounds corresponding to the formulation (III) be isolated. 2-p-*Nitrobenzenesulphenamido-5-methylthiazole* (I; X = NO_2, R′ = H, R″ = Me) and 2-p-*nitrobenzenesulphenamido-4 : 5-dimethylthiazole* (I; X = NO_2, R′ = R″ = Me) are converted by acetic anhydride into the corresponding 2-acetamidothiazole and 4 : 4′-dinitrodiphenyl disulphide. These sulphenamides are readily hydrolysed by acid to the corresponding aminothiazole and dinitrodiphenyl disulphide.

Experimental.

p-*Nitrophenyl 2-Amino-5-thiazyl Sulphide*—(A) 2-Benzylideneaminothiazole (6·3 g.) was dissolved in hot benzene (500 c.c.), cooled to 30°, and a solution of *p*-nitrobenzenesulphenyl chloride (6·4 g.) in benzene (50 c.c.) added with stirring. After 3 hours the precipitate was collected, washed with a little light petroleum, and distilled in steam with concentrated hydrochloric acid (20 c.c.) until no more benzaldehyde was removed. The residue was diluted to 500 c.c. with hot water, filtered (charcoal), made just alkaline with sodium carbonate solution, and the solid collected and crystallised from xylene giving yellow prisms (0·8 g.), m. p. 177—178° (Found: C, 42·5; H, 2·7; S, 25·5. $C_9H_7O_2N_3S_2$ requires C, 42·7; H, 2·8; S, 25·3%). The *compound* with acetic anhydride gave an acetyl derivative which crystallised from β-ethoxyethanol in colourless prisms, m. p. 261—262° (Bambas, *loc. cit.*, gives m. p. 258—260°) (Found: C, 45·1; H, 3·05; N, 14·5. Calc. for $C_{11}H_9O_3N_3S_2$: C, 44·7; H, 3·05; N, 14·2%).

(B) 2-Aminothiazole (7·0 g.) in dry benzene (70 c.c.) was treated with a solution of *p*-nitrobenzenesulphenyl chloride (6·3 g.) in benzene (20 c.c.). After 3 hours, water (50 c.c.) was added, and the solid collected, washed with hot water, and crystallised from alcohol, giving sulphur-yellow flat needles (5·5 g.), m. p. 164° (B.P. 551,681 gives m. p. 155—160°) (Found: C, 42·4; H, 2·7; S, 25·1. Calc. for $C_9H_7O_2N_3S_2$: C, 42·7; H, 2·8; S, 25·3%). This 2-*p*-nitrobenzenesulphenamidothiazole (1·0 g.) was refluxed with concentrated hydrochloric acid (5 c.c.), alcohol (25 c.c.), and β-ethoxyethanol (10 c.c.) for 3 hours, and the solvents were evaporated under reduced pressure. The residue was treated with hot water (50 c.c.), and the insoluble powder collected and crystallised from β-ethoxyethanol giving pale yellow prisms (0·4 g.), m. p. 178—180° not depressed by 4 : 4′-dinitrodiphenyl disulphide. The aqueous filtrate was evaporated under reduced pressure, and the base liberated by concentrated sodium hydroxide solution, extracted with ether, dried (NaOH), and sublimed in a vacuum giving crystals (0·35 g.), m. p. 92—93°, not depressed by 2-aminothiazole.

2-*p*-Nitrobenzenesulphenamidothiazole (2·5 g.) was heated at 100° with acetic anhydride (15 c.c.) for 1 hour, poured into water, and the solid collected, washed with water, and crystallised from β-ethoxyethanol giving colourless prisms (1·9 g.), m. p. 260—262° not depressed by *p*-nitrophenyl 2-acetamido-5-thiazyl sulphide as prepared by the previous route (Found: C, 44·9; H, 3·5%). On hydrolysis with alcoholic hydrochloric acid this acetamido-compound (1·1 g.) gave *p*-nitrophenyl 2-amino-5-thiazyl sulphide (0·7 g.), m. p. 176—177° (Found: C, 42·4; H, 2·6%).

(C) 2-Acetamidothiazole (57·0 g.) was refluxed in dry benzene (500 c.c.) whilst a solution of *p*-nitrobenzenesulphenyl chloride (38·0 g.) in benzene (200 c.c.) was added over 10 minutes; heating was continued for 10 minutes and the solvent removed then under reduced pressure. The residue was extracted twice with boiling alcohol (1 l.) (to remove excess of 2-acetamidothiazole and small amounts of 4 : 4′-dinitrodiphenyl disulphide) and the insoluble *p*-nitrophenyl 2-acetamido-5-thiazyl sulphide crystallised from β-ethoxyethanol giving colourless prisms (33·0 g.), m. p. 260—261° (Found: C, 45·0; H, 3·4%). This compound was also obtained in excellent yield using only 1 mol. of 2-acetamidothiazole (instead of 2 as above) but it was then necessary to treat the residue, left on evaporation of the benzene, with acetic anhydride, as much deacetylation took place under these conditions. This acetamido compound was hydrolysed to *p*-nitrophenyl 2-amino-5-thiazyl sulphide, m. p. 178—179°.

(D) Dry *p*-nitrothiophenol (3·1 g.) was fused under nitrogen in an oil-bath at 160° and powdered 5-bromo-2-acetamidothiazole (4·5 g.) added with stirring. The temperature quickly rose to 210°. The reaction vessel was cooled, and the residue powdered, extracted with boiling β-ethoxyethanol (100 c.c.), filtered hot (charcoal), concentrated to 50 c.c. and allowed to crystallise. The buff powder (2·8 g.), m. p. 242—246°, was crystallised from β-ethoxyethanol giving colourless prisms, m. p. 261—262°, not depressed by *p*-nitrophenyl 2-acetamido-5-thiazyl sulphide as prepared above (Found: C, 44·9; H, 3·2%). This acetamido-compound (1·5 g.) was refluxed for 3 hours with alcohol (15 c.c.), β-ethoxyethanol (15 c.c.), and concentrated hydrochloric acid (5 c.c.), and the solvents were removed under reduced pressure. The residue was dissolved in hot water (100 c.c.), made just alkaline with sodium carbonate, and the solid collected and crystallised from xylene giving *p*-nitrophenyl 2-amino-5-thiazyl sulphide (1·1 g.), m. p. 178—179° (Found: C, 42·3; H, 3·1; S, 24·8%).

p-*Nitrophenyl 2-Amino-5-thiazyl Sulphone.*—*p*-Nitrophenyl 2-acetamido-5-thiazyl sulphide (36·0 g.) in glacial acetic acid (1 l.) was treated with a solution of potassium permanganate (60·0 g.) in water (1 l.), the temperature being allowed to rise to 30—35° but not higher. The mixture was stirred overnight, the manganese dioxide removed with sulphur dioxide, and the solid collected and crystallised from β-ethoxyethanol giving colourless prisms (28·2 g.), m. p. 275° (Bambas, *loc. cit.*, gives m. p. 274—276°) (Found: C, 40·9; H, 2·8; N, 13·4; S, 19·8. Calc. for $C_{11}H_9O_5N_3S_2$: C, 40·4; H, 2·8; N, 12·8; S, 19·6%). This acetamido-compound (22·0 g.) was hydrolysed by boiling with a saturated solution of hydrogen chloride in methyl alcohol (1 l.) for 3 hours. The solvent was removed under reduced pressure, the residue neutralised with sodium carbonate solution, and the solid collected and crystallised from alcohol giving golden yellow plates (13·5 g.), m. p. 228° (Bambas, *loc. cit.*, gives m. p. 230—232°) (Found: C, 38·3; H, 2·6; S, 22·7. Calc. for $C_9H_7O_4N_3S_2$: C, 37·9; H, 2·5; S, 22·45%).

p-*Aminophenyl 2-Amino-5-thiazyl Sulphone.*—*p*-Nitrophenyl 2-acetamido-5-thiazyl sulphone (10·0 g.) was reduced in a mixture of methyl alcohol (150 c.c.) and β-ethoxyethanol (350 c.c.) with Raney nickel catalyst at ordinary pressure and temperature. The liquid was filtered hot, saturated with hydrogen chloride, refluxed for 3 hours, and evaporated under reduced pressure. The residue was dissolved in water, neutralised with sodium carbonate, and the solid collected and crystallised from aqueous methyl alcohol giving colourless needles (7·7 g.), m. p. 218—219° (Bambas, *loc. cit.*, gives m p. 219—221°) (Found: C, 42·1; H, 3·45; N, 16·65; S, 24·7. Calc. for $C_9H_9O_2N_3S_2$: C, 42·4; H, 3·5; N, 16·5; S, 25·1%). The diamine was also obtained by direct catalytic reduction of *p*-nitrophenyl 2-amino-5-thiazyl sulphone.

2-p-*Toluenesulphenamidothiazole.*—*p*-Toluenesulphenyl chloride (7·9 g.) in dry benzene (100 c.c.) was added to a solution of 2-aminothiazole (10·0 g.) in benzene (300 c.c.) with stirring, water (200 c.c.) was added, and the benzene layer separated, washed twice with small amounts of water, and the solvent evaporated under reduced pressure. The residual brown oil was crystallised from light petroleum (b. p. 60—80°) giving large colourless needles (5·9 g.), m. p. 120°, discoloured by a few minutes' heating at 100° (Found: C, 54·35; H, 4·4. $C_{10}H_{10}N_2S_2$ requires C, 54·0; H, 4·5%). This *compound* (1·5 g.), concentrated hydrochloric acid (5 c.c.), and alcohol (15 c.c.) were refluxed for 2 hours, water (50 c.c.) added, and the oil extracted with benzene. The residual aqueous solution was evaporated, made alkaline with sodium hydroxide solution, and the liberated base extracted with ether, dried (NaOH), and sublimed in a vacuum giving colourless prisms (0·5 g.), m. p. 92—93°, not depressed by 2-aminothiazole. The benzene solution was evaporated and the residue distilled giving a yellow oil, b. p. 230—235°/35 mm., setting to a crystalline solid (0·55 g.), m. p. 46—47°, not depressed by 4 : 4′-ditolyl disulphide.

2-*p*-Toluenesulphenamidothiazole (3·0 g.) and acetic anhydride (10 c.c.) were heated for 5 minutes at 50° and warm water (25 c.c.) was added. The aqueous liquor was decanted from the viscous gum, heated to 80°, neutralised with solid sodium carbonate, and filtered hot with a little charcoal. On standing, colourless needles (0·9 g.), m. p. 201—202°, not depressed by 2-acetamidothiazole, separated. The residual gum was extracted hot with light petroleum (b. p. 40—60°, 50 c.c.), the extract filtered with charcoal, evaporated, and the residue distilled, giving a yellow oil, b. p. 230—238°/40 mm. (1·0 g.), setting to a crystalline solid, m. p. 45—46°, not depressed by 4 : 4′-ditolyl disulphide. This experiment was repeated using the sulphenamide (1·5 g.) and acetic anhydride (5 c.c.), but heating at 95—100° for 1 hour. Much darkening took place, but there were isolated 2-acetamidothiazole (0·35 g., m. p. 202°) and the disulphide (0·55 g., m. p. 41—42°).

2-p-*Chlorobenzenesulphenamidothiazole.*—This compound was prepared from *p*-chlorobenzenesulphenyl chloride (6·0 g.) and 2-aminothiazole (6·8 g.) as described for the *p*-toluene compound and crystallised from benzene–light petroleum (b. p. 60—80°) giving colourless glistening needles (6·2 g.), m. p. 139° (Found: Cl, 14·6; S, 26·7. $C_9H_7N_2ClS_2$ requires Cl, 14·6; S, 26·4%). This *sulphenamide* (1·5 g.) was hydrolysed as described for the *p*-toluene compound giving 2-aminothiazole (0·5 g., m. p. 90—92°) and 4 : 4′-dichlorodiphenyl disulphide (0·6 g., m. p. 74°).

2-*p*-Chlorobenzenesulphenamidothiazole (2·0 g.) and acetic anhydride (10 c.c.) were heated at 50° for 10 minutes giving 2-acetamidothiazole (0·65 g., m. p. 202°) and 4 : 4′-dichlorodiphenyl disulphide (0·8 g., m. p. 74°) isolated as described for the *p*-toluene compound. Heated at 95—100°, the sulphenamide (1·5 g.) gave 2-acetamidothiazole (0·4 g., m. p. 203°) and the disulphide (0·3 g., m. p. 74°).

Reaction of 2-p-*Nitrobenzenesulphenamidothiazole with Acetic Anhydride in the Presence of Resorcinyl Diacetate.*—The sulphenamide (2·5 g.) was added to a solution of resorcinol (2·2 g. = 2 mols.) in acetic anhydride (20 c.c.) at 90° over ½ hour, heated for ½ hour longer, and diluted with water. The solid was collected, refluxed for 3 hours with alcohol (50 c.c.) and concentrated hydrochloric acid (5·0 c.c.), poured into water, and the precipitate again collected. The yellow solid was dissolved in 10% sodium carbonate solution (100 c.c.), filtered, precipitated with acetic acid, collected, and crystallised from dilute acetic acid giving yellow needles (1·8 g.), m. p. 184°, identical with 4-nitro-2′ : 4′-dihydroxydiphenyl sulphide (Burton and Hoggarth, *J.*, 1945, 469).

p-*Tolyl 2-Amino-5-thiazyl Sulphide.*—(A)—2-Acetamidothiazole (14·5 g.), *p*-toluenesulphenyl chloride (16·0 g.), and benzene (500 c.c.) were refluxed for 3 hours, the solvent evaporated, and the residue refluxed for 5 minutes with acetic anhydride (50 c.c.). Water (500 c.c.) was added, and the solid collected and crystallised from alcohol giving colourless needles of p-*tolyl 2-acetamido-5-thiazyl sulphide* (10·8 g.), m. p. 202° (Found: C, 54·85; H, 4·45; S, 24·6. $C_{12}H_{12}ON_2S_2$ requires C, 54·5; H, 4·5; S, 24·2%). This compound (2·0 g.) was refluxed with methyl alcoholic hydrogen chloride (100 c.c.) for 6 hours, water (50 c.c.) was added, and the solvents were removed under reduced pressure. The residue was dissolved in water, made just alkaline with sodium carbonate solution, and the solid collected and crystallised from methyl alcohol giving the *amino-sulphide* in fine colourless needles (1·6 g.), m. p. 146° (Found: C, 54·1; H, 4·3. $C_{10}H_{10}N_2S_2$ requires C, 54·0; H, 4·5%).

(B) 5-Bromo-2-acetamidothiazole (4·5 g.) and thio-*p*-cresol (5·0 g.) were heated for 4 hours at 130°, cooled, the excess of the thiophenol dissolved in ether, and the residual solid crystallised from alcohol giving colourless needles of *p*-tolyl 2-acetamido-5-thiazyl sulphide (2·2 g.), m. p. 202° (Found: C, 54·8; H, 4·6, S, 24·4%). Hydrolysis with acid gave the amino-sulphide, m. p. 146°, identical with the compound prepared by the first route (Found: C, 54·4; H, 4·6; S, 28·6).

p-*Chlorophenyl 2-Amino-5-thiazyl Sulphide.*—(A) *p*-Chlorobenzenesulphenyl chloride (6·0 g.) and 2-acetamidothiazole (4·8 g.) gave p-*chlorophenyl 2-acetamido-5-thiazyl sulphide*, which crystallised from benzene in colourless needles (5·0 g.), m. p. 196° (Found: C, 46·7; H, 3·4; Cl, 12·2. $C_{11}H_9ON_2ClS_2$ requires C, 46·5; H, 3·2; Cl, 12·5%). Deacetylation gave the *amino-sulphide* which crystallised from benzene giving colourless leaflets, m. p. 172° (Found: C, 44·5; H, 3·15. $C_9H_7N_2ClS_2$ requires C, 44·5; H, 2·9%).

(B) *p*-Chlorothiophenol (4·0 g.) and 5-bromo-2-acetamidothiazole (2·3 g.) were heated for 3 hours at 155—160° and gave *p*-chlorophenyl 2-acetamido-5-thiazyl sulphide, (1·1 g.), m. p. 195—196° (Found: Cl, 12·3; S, 22·6). This was deacetylated by acid to the amino-sulphide, m. p. 172° (Found: Cl, 15·1; S, 26·6).

p-*Tolyl* 2-*Amino*-5-*thiazyl Sulphone*.—*p*-Tolyl 2-acetamido-5-thiazyl sulphide (5·3 g.) in acetic acid (90 c.c.) was oxidised by a solution of potassium permanganate (6·6 g.) in water (100 c.c.), added with stirring at 30—35°. Sulphur dioxide was passed until the manganese dioxide had dissolved, the solid collected, and the p-*tolyl* 2-*acetamido*-5-*thiazyl sulphone* crystallised from alcohol giving lustrous needles (4·1 g.), m. p. 257—258° (Found: C, 48·55; H, 4·25; S, 21·9. $C_{12}H_{12}O_3N_2S_2$ requires C, 48·6; H, 4·1; S, 21·6%). This acetamido-compound (3·0 g.) was refluxed with concentrated hydrochloric acid (25 c.c.) and β-ethoxyethanol (25 c.c.) for 2 hours, evaporated under reduced pressure, the residue dissolved in strong ammonia solution, diluted with water, made just acid with acetic acid, and the solid collected and crystallised from alcohol giving colourless needles (2·1 g.) of the *amino-sulphone*, m. p. 234° (Found: C, 47·35; H, 3·7; S, 25·8. $C_{10}H_{10}O_2N_2S_2$ requires C, 47·2; H, 3·9; S, 25·2%).

p-*Chlorophenyl* 2-*Amino*-5-*thiazyl Sulphone*.—*p*-Chlorophenyl 2-acetamido-5-thiazyl sulphide (2·8 g.) was oxidised as described for the *p*-tolyl sulphide and gave p-*chlorophenyl* 2-*acetamido*-5-*thiazyl sulphone*, which crystallised from alcohol giving a mass of felted needles (1·9 g.), m. p. 275° (Found: C, 41·95; H, 3·1; Cl, 10·9; S, 20·2. $C_{11}H_9O_3N_2ClS_2$ requires C, 41·7; H, 2·8; Cl, 11·2; S, 20·2%). This acetamido-compound (1·6 g.) was hydrolysed to the *amino-sulphone*, which crystallised from alcohol giving large clumps of colourless needles (0·9 g.), m. p. 209° (Found: C, 39·3; H, 2·6; S, 23·7. $C_9H_7O_2N_2ClS_2$ requires C, 39·3; H, 2·55; S, 23·3%).

2-p-*Nitrobenzenesulphenamido*-5-*methylthiazole*.—2-Amino-5-methylthiazole reacted with *p*-nitrobenzenesulphenyl chloride as described for 2-aminothiazole giving the *sulphenamide*, which crystallised from xylene in golden yellow plates (58% of theory), m. p. 158° (Found: C, 45·05, H, 3·4; S, 23·7. $C_{10}H_9O_2N_3S_2$ requires C, 44·9; H, 3·4; S, 24·0%). This compound (2·7 g.) was hydrolysed by acid to 4 : 4′-dinitrodiphenyl disulphide (0·9 g., m. p. 180°) and 2-amino-5-methylthiazole (1·0 g., m. p. 96—98°).

2-*p*-Nitrobenzenesulphenamido-5-methylthiazole (13·3 g.) was heated for 1 hour with acetic anhydride (70 c.c.) at 100°, the solution poured into water, and the solid collected, dried, and crystallised from toluene (300 c.c.) giving 2-acetamido-5-methylthiazole (3·5 g., m. p. 221°). The mother liquor was evaporated under reduced pressure and the residue crystallised from β-ethoxyethanol (100 c.c.) giving 4 : 4′-dinitrodiphenyl disulphide (4·4 g., m. p. 180°). The filtrate was treated with concentrated hydrochloric acid (20 c.c.), refluxed for 3 hours, diluted with water (100 c.c.), and the solid collected and crystallised from β-ethoxyethanol giving a further quantity of dinitrodiphenyl disulphide (1·7 g., m. p. 179°). The acid filtrate was evaporated under reduced pressure and basified with concentrated sodium hydroxide solution, and 2-amino-5-methylthiazole (1·8 g., m. p. 96°) was isolated by ether extraction and sublimation in a vacuum.

2-p-*Nitrobenzenesulphenamido*-4 : 5-*dimethylthiazole*.—2-Amino-4 : 5-dimethylthiazole reacted with *p*-nitrobenzenesulphenyl chloride as described for 2-aminothiazole giving the *sulphenamide*, which crystallised from xylene in golden yellow prisms (62% of theory), m. p. 166° (Found: C, 47·15; H, 3·65. $C_{11}H_{11}O_3N_3S_2$ requires C, 47·0; H, 3·9%). Hydrolysis of this compound (1·5 g.) with hydrochloric acid gave 4 : 4′-dinitrodiphenyl disulphide (0·6 g., m. p. 180°) and 2-amino-4 : 5-dimethylthiazole (0·5 g., m. p. 82°).

2-*p*-Nitrobenzenesulphenamido-4 : 5-dimethylthiazole (4·0 g.) was heated for 2 hours with acetic anhydride at 90° and the excess removed under reduced pressure. The residue was stirred with a mixture of water (50 c.c.) and alcohol (50 c.c.), filtered, and the solid crystallised from β-ethoxyethanol giving 4 : 4′-dinitrodiphenyl disulphide (1·6 g., m. p. 180°). The filtrate was evaporated and the residue crystallised from water giving 2-acetamido-4 : 5-dimethylthiazole (1·8 g., m. p. 146°).

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