458. 1,2,3-*Benzothiadiazole. Part I. Nitro-, Amino-, and Hydroxy-derivatives.*

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4- and 6-Nitro-1,2,3-benzothiadiazoles are prepared from the corresponding nitrobenzothiazoles by ring opening, followed by tetrazotisation (and decomposition) of the derived diaminodiphenyl disulphide, thus providing a convenient route to 4- and 6-derivatives of 1,2,3-benzothiadiazole. The method fails with 5- and 7-nitrobenzothiazole.

By Fries and Reitz's method 1,2,3-benzothiadiazole yields 5- and 7-mononitro-derivatives, and not 4- and 7-isomers as previously believed.

The four nitrobenzothiadiazoles are orientated for the first time, by relating elution behaviour to dipole moments. The structures of the amino-benzothiadiazoles follow.

Diazotised 6-amino-1,2,3-benzothiadiazole yields the corresponding 6-hydroxy-compound but similar decompositions of the diazotised 4- and 7-amino-derivatives gave azo-dyes.

The only significant method for preparing 1,2,3-benzothiadiazoles is by diazotisation of *o*-aminothiophenols,[1] and a useful route to the latter is by ring opening of benzothiazoles. We recently described a method making all four nitrobenzothiazoles readily available [2] and have now investigated the conversion of these into the corresponding nitrobenzothiadiazoles. Boggust and Cocker [3] described an improved method for the ring fission, using refluxing ethanolic hydrazine hydrate and employed it to prepare di-(*o*-amino-5-nitrophenyl) disulphide from 6-nitrobenzothiazole. We converted this disulphide into 6-nitro-1,2,3-benzothiadiazole by Burawoy and Turner's procedure [4] (used to prepare the

[1] Hodgson and Dodgson, *J. Soc. Dyers and Colourists*, 1948, **64**, 65.
[2] Ward and Poesche, *J.*, 1961, 2825.
[3] Boggust and Cocker, *J.*, 1949, 355.
[4] Burawoy and Turner, *J.*, 1950, 469.

parent compound), and similarly obtained 4-nitro-1,2,3-benzothiadiazole from 4-nitrobenzothiazole. Ring fission of 5- or 7-nitrobenzothiazole appears to proceed in a different manner and we were unable to isolate the corresponding aminonitrothiophenols or di(aminophenyl) disulphides: the end products were insoluble red substances with the appearance of azo-compounds but which were not identified. Utilising this finding we were able to employ directly the mixtures of nitrobenzothiazoles obtained by steam-distillation of the mononitration product of benzothiazole [2] for the synthesis of either 4- or 6-nitrobenzothiadiazole, although expected overall yields were slightly reduced.

Jacobson [5] prepared 1,2,3-benzothiadiazole by boiling diazotised di-(*o*-aminophenyl) disulphide in water, and Hodgson [6] obtained a 50% yield by diazotisation in dilute mineral acid. Burawoy and Turner [4] claimed a 75% yield on tetrazotisation in nitrosylsulphuric acid followed by pouring on ice, and an 84% yield of the cuprous chloride complex of benzothiodiazole on addition of the diazo-solution to a solution of cuprous chloride in hydrochloric acid. Our yield of 6-nitrobenzothiadiazole was only 60% and many variations in procedure (*e.g.*, pH, addition of reducing agents) failed to raise this. Addition to the Sandmeyer reagent gave no cuprous chloride complex.

Similar reactions with 4-nitrobenzothiazole gave di-(2-amino-3-nitrophenyl) disulphide in 90% yield and from this a 45% yield of 4-nitro-1,2,3-benzothiadiazole was obtained. This compound showed a peak in its infrared spectrum at 814 cm.$^{-1}$ (hydrogen pattern 1,2,3) which is absent from the spectra of the 5- and the 6-isomer but present (820 cm.$^{-1}$) in that of the 7-isomer (which also has hydrogen pattern 1,2,3).

4-Nitro-1,2,3-benzothiadiazole has been claimed by Fries and Reitz [7] to be the predominant product, along with the 7-isomer, of the nitration of 1,2,3-benzothiadiazole in sulphuric acid with potassium nitrate at 100°. They isolated two mononitration products, of m. p.s 95° and 104°, and failing to synthesise 4-nitro-1,2,3-benzothiadiazole by an independent route suggested that, since the electrophilic substitution was more likely to occur in an *ortho*-position to the nitrogen atom than to the sulphur atom, the predominant lower-melting substance was the 4-isomer; and they made no comment on the other product. Hodgson and Dodgson [8] found the higher-melting isomer to be 7-nitro-1,2,3-benzothiadiazole, which they had synthesised by an independent route. Since the m. p. of the supposed 4-isomer was different also from that of the 6-isomer (136°) synthesised by Jacobson *et al.*[9] and of the 5-isomer (135°) synthesised by Fries *et al.*,[10] Hodgson and Dodgson [8] concluded that this confirmed the orientation allocated by Fries and Reitz.

We have now examined the nitration product obtained by this method by column chromatography on alumina. Over half of it appears to consist of by-products and the remainder we find to be a mixture of 5- and 7-nitrobenzothiadiazole, the former predominating. The yield of isolated nitrobenzothiadiazoles was about 25%, from which some 5- or 7-isomer could be isolated, but we failed to devise a method of separating these in any appreciable amounts. However, infrared spectroscopy of several mixed fractions, obtained at different stages of the separation, confirmed the presence of both the 5- and the 7-isomer. We failed to find either the 4- or the 6-isomer by infrared spectroscopy. Further, if any 4-isomer had been present we should have expected it to be eluted last, since theoretical calculations indicate that it is likely to have the highest dipole moment of the four mononitrobenzothiadiazoles, and, amongst isomeric molecules which contain the same number and kind of functional groups, the sequence of elution is usually the inverse sequence of the dipole moments.[2,11,12] Ward and Poesche [2] have shown that

[5] Jacobson, *Ber.*, 1887, **20**, 1902.
[6] Hodgson, *J. Soc. Dyers and Colourists*, 1924, **40**, 330.
[7] Fries and Reitz, *Annalen*, 1936, **527**, 38.
[8] Hodgson and Dodgson, *J.*, 1948, 1005.
[9] Jacobson and Kwaysser, *Annalen*, 1893, **277**, 209.
[10] Fries, Vorbrodt, and Siebert, *Annalen*, 1927, **454**, 172.
[11] Johnson and Telesz, *J. Soc. Dyers and Colourists*, in the press.
[12] Franc and Latinak, *Chem. Listy*, 1955, **49**, 872.

the dipole moment in benzothiazole bisects the C–N–C angle. In 1,2,3-benzothiadiazole the 2-CH group is formally substituted by the more electronegative nitrogen atom, thus probably shifting the directions of both the σ- and the π-moment towards the 2-position. Hence the dipole vector in 1,2,3-benzothiadiazole will point in a direction somewhere between the two nitrogen atoms and 4-nitro-1,2,3-benzothiadiazole would be expected to have the highest dipole moment of the four isomers.

We do not wish, at this stage, to comment in detail on the qualitative or quantitative aspects of this nitration. We feel that the nitration method is not particularly satisfactory and the yield of mononitrobenzothiadiazoles is rather low; the absence of the 4- or 6-isomer might in fact be due to their more rapid destruction by oxidation under the conditions used. Our attempts to devise an alternative, more satisfactory, nitration procedure have failed but we are continuing this work, since beside our wish to obtain more exact information for theoretical consideration, this nitration potentially provides a very convenient route to 5- and 7-derivatives. Combined with the procedure already described for 4- and 6-derivatives, routes would be available to all types of 1,2,3-benzothiadiazole derivatives, so largely eliminating the tedious procedure often required to synthesise specific compounds through *o*-aminothiophenols.

That Fries and Reitz's 4-nitro-1,2,3-benzothiadiazole was a mixture invalidates their preparations from it (*e.g.*, 4-amino-, 4-hydroxy-, 4-amino-7-phenylazo-1,2,3-benzothiadiazole). We have now prepared authentic 4-amino-1,2,3-benzothiadiazole by reduction of the 4-nitro-compound. We found stannous chloride in hydrochloric acid was the most satisfactory of many methods tried and in the same way obtained the three other isomers (7-amino-1,2,3-benzothiadiazole is also new). Amongst the acyl derivatives we prepared from these amines were the *p*-acetamidobenzenesulphonamido-derivatives of 4- and 6-amino-1,2,3-benzothiadiazoles; whilst the latter was readily hydrolysed to the free sulphonamide we were unable to achieve this with the 4-isomer.

4- and 6-Amino-1,2,3-benzothiadiazole were readily diazotised by adding solutions in nitrosylsulphuric acid to ice, and Sandmeyer reactions gave the chloro- and bromo-compounds in good yield. Boiling the diazonium solution from the 6-isomer afforded 6-hydroxy-1,2,3-benzothiadiazole in good yield, but the corresponding decompositions of the 4- or 7-isomers gave only azo-dyes. 5-Hydroxy-1,2,3-benzothiadiazole has been prepared by Hodgson and Dodgson [1] by decomposition of the 5-diazo-derivative, the latter being readily available through their very convenient route for 5-derivatives starting with bis-(2,4-dinitrophenyl) disulphide.

Experimental

Ultraviolet spectra were recorded with a Unicam S.P. 500 spectrophotometer for cyclohexane solutions. The infrared spectra were measured (for Nujol mulls) and interpreted by Dr. K. Morgan, and Dr. J. K. Brown, of the University of Birmingham.

6-*Nitro*-1,2,3-*benzothiadiazole*.—6-Nitrobenzothiazole (125 g.) was refluxed with ethanol (2·5 l.) and 100% hydrazine hydrate (250 ml.) for 2 hr. The mixture was treated, at *ca.* 30°, with stirring, with 20-vol. hydrogen peroxide (*ca.* 200 ml.) until the deep red colour faded. After 1 hr., the di-(2-amino-5-nitrophenyl) disulphide was collected and washed with water; it had m. p. 242° after crystallisation from ethanol (Jacobson and Kwaysser [9] give 236—237°; Boggust and Cocker [3] give 222°) (yield, 101 g., 86%). 2-Amino-5-nitrothiophenol was obtained from the original reaction mixture by adding 2N-hydrochloric acid until the red colour disappeared, keeping the whole overnight at *ca.* 5°, filtering off the solid under nitrogen, washing it with water, and drying it over sulphuric acid *in vacuo* (yield, 65%); the acid filtrate

yielded the disulphide on oxidation (*ca.* 20%). The disulphide (100 g.) was dissolved in sulphuric acid (*d* 1·84; 340 ml.), cooled to 0°, and treated slowly with sodium nitrite (47 g.) in sulphuric acid (*d* 1·84; 340 ml.) at *ca.* 10°. After 6 hr. the mixture was run into ice (5 kg.) and water (1 l.). The next day the solids were collected, washed with water, and dried at 60° *in vacuo*. The product was purified by chromatography on alumina in benzene, the impurities being strongly and the nitro-compound weakly absorbed. Evaporation of the benzene gave 6-nitro-1,2,3-benzothiadiazole, m. p. 131° (64 g., *ca.* 60%); from ethanol it formed pale yellow leaflets, m. p. 136° (Jacobson *et al.*[9] give 136—137°); it was volatile in steam and had $\lambda_{max.}$ 226, 270, 330 mμ (ε 19,990, 9670, 2650) and $\nu_{max.}$ 1611w, 1575m, 1628s, 1445w, 1416w, 1385m, 1356s, 1295s, 1288s, 1259w, 1225m, 1129m, 1049m, 1044m, 924m, 905m, 863m, 840m, 833m, 785s, 754s, 753s, 717m, 664w cm.$^{-1}$.

4-*Nitro*-1,2,3-*benzothiadiazole*.—4-Nitrobenzothiazole was converted, as described above for the 6-isomer, into *di*-(2-*amino*-3-*nitrophenyl*) *disulphide* (87%), orange needles (from ethanol), m. p. 210° (Found: C, 42·8; H, 2·6. $C_{12}H_{10}N_4O_4S_2$ requires C, 42·6; H, 3·0%). The disulphide was similarly converted into 4-*nitro*-1,2,3-*benzothiadiazole*. Chromatography gave a yellow band, followed by a dark brown and an ochre one. The first yielded a compound of m. p. 306°, not further investigated, and the second a red oil. The ochre band gave the nitro-compound (45%), yellow needles (from xylene), m. p. 122·5° (Found: C, 39·6; H, 1·6; N, 23·2. $C_6H_3N_3O_2S$ requires C, 39·7; H, 1·6; N, 23·2%), not volatile in steam, $\lambda_{max.}$ 218, 246sh, 276, 320 mμ (ε 17,300, 6830, 4870, 3260) $\nu_{max.}$ 1608m, 1525s, 1457m, 1418m, 1375s, 1347s, 1297m, 1294m, 1238m, 1208m, 1175w, 1122m, 927w, 878m, 825m, 814m, 779s, 745s, 722m, 664w cm.$^{-1}$.

Nitration of 1,2,3-*Benzothiadiazole*.—To a solution of 1,2,3-benzothiadiazole (13·6 g.) in sulphuric acid (*d* 1·84; 60 ml.) at 20° was added portionwise, with stirring, potassium nitrate (11 g.). The temperature rose to 31°, the mixture was then slowly heated in a bath, with continued stirring, and when the temperature of the mixture began to rise faster than that of the bath (at *ca.* 70°) the bath was removed. The temperature of the mixture eventually rose to *ca.* 100° and then fell again; it was kept at *ca.* 95° for 30 min. After cooling, the mixture was poured on ice, and the solid was collected, washed with water and dried over sulphuric acid *in vacuo* (yield 9·7 g.). The product was chromatographed in benzene (60 ml.) and on alumina (90 × 2·5 cm.), the column being protected against light. Elution was commenced with 2 : 3 v/v benzene–light petroleum (b. p. 40—60°) and when the yellowish front had nearly reached the bottom of the column the eluant was changed to a 1 : 1 v/v mixture and 25 ml. fractions were collected (before this only a small amount of oil was eluted). The fractions were allowed to evaporate in the dark and then dried for 3 min. at 80° *in vacuo*; 47 fractions were collected, the first 10 becoming grey on drying. The m. p. ranges were: fractions 1—5, 95—105°; 6—10, 91—101°; 11—26, 90—100°; 27—28, 99—115°; 29—35, 99—125°; 36—43, 129—135°; 44—47, 132—139°. Infrared spectroscopy showed that the fractions 1—10 were predominantly 7-nitro-1,2,3-benzothiadiazole (Hodgson and Dodgson [8] give m. p. 105°); fractions 11—25 mixtures of this with the 5-nitro-isomer, fractions 36—47 were predominantly 5-nitro-1,2,3-benzothiadiazole and crystallisation of these from ethanol, then xylene, gave the pure compound, m. p. 143° (Fries, Vorbrodt, and Siebert [10] give 144°). The chromatogram showed only one peak. The total recovery of nitro-compounds was 4·5 g. (25% for mononitration), 80% of this being distributed uniformly in fractions 1—25°.

5-Nitro-1,2,3-benzothiadiazole formed pale yellow needles, $\lambda_{max.}$ 240, 246, 259sh, 286 mμ (ε 22,290, 21,630, 10,600, 6410), $\nu_{max.}$ 1595s, 1565m, 1511s, 1437w, 1415w, 1382w, 1354s, 1340s, 1306s, 1297m, 1244w, 1207w, 1157m, 1078w, 1068m, 934m, 897m, 864m, 826m, 790s, 745s cm.$^{-1}$.

7-Nitro-1,2,3-benzothiadiazole formed yellow needles, m. p. 106° (obtained by deamination of 6-amino-7-nitro-1,2,3-benzothiadiazole [13]), $\lambda_{max.}$ 232, 254sh, 284, 332 mμ (ε 9790, 7390, 4280, 5760), $\nu_{max.}$ 1611s, 1552m, 1525s, 1503s, 1455m, 1360s, 1325s, 1291s, 1265m, 1240s, 1215m, 1151m, 1124m, 1100m, 1058m, 991m, 860s, 825s, 820s, 785s, 750m, 740s, 719m cm.$^{-1}$.

6-*Amino*-1,2,3-*benzothiadiazole*.—6-Nitro-1,2,3-benzothiadiazole (50 g.) was added to a warm solution of stannous chloride dihydrate (280 g.) in hydrochloric acid (*d* 1·2; 420 ml.) at such a rate that the temperature was maintained at *ca.* 55°. When addition was complete the mixture was heated for a short time at 65° and kept at *ca.* 5° for some hours. The solids were collected, dissolved in hot water (280 ml.), and added dropwise to 40% w/v aqueous sodium hydroxide (700 ml.) below 30°. The mixture was kept at *ca.* 5° for some hours, and the solids were collected, dried, and crystallised from hot benzene (800 ml.; charcoal). The yield of crude amine (m. p.

[13] Ward, Poesche, and Heard, unpublished work.

107°; pure enough for further work) was 75—85%; recrystallisation from benzene gave material of m. p. 110° (Jacobson *et al.*[9] give 112°). Exploratory reductions with other reducing agents, on a 1 g. scale, gave inferior results

6-*Toluene*-p-*sulphonamide*-1,2,3-*benzothiadiazole* was prepared by refluxing the amine (6 g.) with toluene-*p*-sulphonyl chloride (9·5 g.) in pyridine (6 ml.) for 1 hr. The cooled solution was added to 3N-hydrochloric acid (500 ml.) with stirring. After 2 hours' stirring the tar had solidified and was collected, washed with water, and dried *in vacuo* at 80° (yield 12·3 g.). This was extracted with 3% warm aqueous sodium hydroxide (2 × 200 ml.), and the extract added dropwise with stirring to 15% w/v hydrochloric acid (100 ml.), and the precipitate was collected, washed with water, and dried (10·6 g., 87%; m. p. 181—182°). Crystallised from ethanol this had m. p. 182° (Found: C, 50·6; H, 3·9; N, 14·2. $C_{13}H_{11}N_3O_2S_2$ requires C, 51·1; H, 3·6; N, 13·8%). The alkali-insoluble material (1·34 g.) was crystallised twice from acetic acid (charcoal), giving 6-NN-*di*(*toluene*-p-*sulphonyl*)*amino*-1,2,3-*benzothiadiazole*, m. p. 213° (Found: C, 52·2; H, 3·5; S, 21·2. $C_{20}H_{17}N_3O_4S_3$ requires C, 52·3; H, 3·7; S, 20·9%).

6-p-*Aminobenzenesulphonamido*-1,2,3-*benzothiadiazole*.—The above amine (1 g.) was refluxed in pyridine (3 ml.) and acetone (20 ml.) with *p*-acetamidobenzenesulphonyl chloride (1·75 g.) for 1 hr., the mixture was cooled and poured into 2N-hydrochloric acid (300 ml.), and the solids were collected and washed with water (yield 85%); crystallised from ethanol the *product* had m. p. 250° (Found: C, 48·3; H, 3·5. $C_{14}H_{12}N_4O_3S_2$ requires C, 48·2; H, 3·5%). This (1·75 g.) was refluxed with ethanol (180 ml.) and hydrochloric acid (*d* 1·2; 75 ml.) for 1 hr. Most of the ethanol was distilled off, the remainder being removed on the water-bath. The residue was crystallised twice from 1 : 1 v/v ethanol–water, then having m. p. 207° (1·0 g., 60% overall yield from amine) (Found: C, 47·4; H, 3·1; N, 18·2; S, 20·6. $C_{12}H_{10}N_4O_2S_2$ requires C, 47·0; H, 3·3; N, 18·3; S, 20·9%).

Diazotisation and Decompositions of 6-*Amino*-1,2,3-*benzothiadiazole*.—To a solution of the amine (6 g.) in sulphuric acid (*d* 1·84; 80 ml.) at *ca.* 0° was added one of sodium nitrite (5 g.) in sulphuric acid (*d* 1·84; 50 ml.), the temperature not being allowed to rise above 5°; after 3 hours' stirring, the mixture was poured on ice (300 g.), giving a yellow solution. When this diazo-solution was refluxed for 1 hr. and left overnight a red product was obtained (2·7 g., 90% calc. as hydroxybenzothiadiazole). From chlorobenzene (charcoal) discoloured leaflets of 6-hydroxy-1,2,3-benzothiadiazole, m. p. 219° (decomp.), were obtained which could not be obtained white (Fries, Vorbrodt, and Siebert [10] give m. p. 211°), insoluble in water and chloroform, sparingly soluble in ether, soluble in acetic acid and ethanol.

From light petroleum (b. p. 100—120°) 6-*acetoxy*-1,2,3-*benzothiadiazole* formed white needles, m. p. 78° (Found: C, 49·5; H, 2·6. $C_8H_6N_2O_2S$ requires C, 49·5; H, 3·1%).

6-*Bromo*-1,2,3-*benzothiadiazole* was obtained by a Sandmeyer reaction; the product was steam-distilled from the reaction mixture and crystallised from methanol (yield *ca.* 45%); it formed white needles, m. p. 70° (Found: C, 33·9; H, 1·4; N, 13·1. $C_6H_3BrN_2S$ requires C, 33·5; H, 1·4; N, 13·0%). 6-*Chloro*-1,2,3-*benzothiadiazole* was obtained similarly (*ca.* 55%) as white needles, m. p. 80° (Found: C, 42·1; H, 1·8; N, 16·7; Cl, 21·2. $C_6H_3ClN_2S$ requires C, 42·2; H, 1·8; N, 16·5; Cl, 20·8%). Both compounds readily sublime.

4-*Amino*-1,2,3-*benzothiadiazole*.—This was prepared from 4-nitro-1,2,3-benzothiadiazole by reduction, as for the 6-isomer. The crude product was extracted with boiling light petroleum (b. p. 100—120°) and this extract afforded almost pure 4-*amino*-1,2,3-*benzothiadiazole* (75—85%), m. p. 85—87°. Further purified by chromatography on alumina in 6 : 1 v/v benzene–light petroleum (b. p. 40—60°) and crystallisation from 1 : 3 v/v benzene–light petroleum (b. p. 100—120°), this formed yellow needles, m. p. 88° (Found: C, 48·2; H, 3·8. $C_6H_5N_3S$ requires C, 47·7; H, 3·3%), readily soluble in benzene. 4-*Acetamido*-1,2,3-*benzothiadiazole* (from ethanol) had m. p. 187° (Found: C, 49·5; H, 3·5; N, 21·8. $C_8H_7N_3OS$ requires C, 49·7; H, 3·7; N, 21·8%). 4-*Toluene*-p-*sulphonamido*-1,2,3-*benzothiadiazole* was prepared similarly to the 6-isomer (but in this case affording no ditosyl derivative) in 90% yield with m. p. 151° (from ethanol) (Found: C, 50·9; H, 3·7; N, 13·5. $C_{13}H_{11}N_3O_2S_2$ requires C, 51·1; H, 3·6; N, 13·8%). 4-p-*Acetamidobenzenesulphonamido*-1,2,3-*benzothiadiazole* was prepared as for the 6-analogue (crude yield 40%) and had m. p. 228°; from ethanol (charcoal) it formed colourless prisms, m. p. 240° (Found: C, 48·3; H, 3·8; N, 15·5; S, 17·4. $C_{14}H_{12}N_4O_3S_2$ requires C, 48·2; H, 3·5; N, 16·1; S, 18·4%).

Diazotisation and Decompositions of 4-*Amino*-1,2,3-*benzothiadiazole*.—To a solution of the amine (3·8 g.) in sulphuric acid (*d* 1·84; 20 ml.) was added one of nitrosylsulphuric acid in

2M-sulphuric acid (12·5 ml.). After 1 hour's stirring, this was poured on ice. 4-*Chloro*-1,2,3-*benzothiadiazole* was obtained by steam-distillation after a Sandmeyer reaction. The distillate was cooled to *ca.* 5° and the solid collected; the residue in the flask appeared to be largely azo-dyes. The crude product (*ca.* 35%) was purified by crystallisation (twice) from methanol (charcoal), then having m. p. 101° (Found: C, 42·1; H, 1·85; N, 17·1; Cl, 21·0. $C_6H_3ClN_2S$ requires C, 42·2; H, 1·8; Cl, 20·8; N, 16·5%). The preparation of 4-*bromo*-1,2,3-*benzothiadiazole* proceeded similarly (yield *ca.* 40%); the product had m. p. 113° (Found: C, 33·5; H, 1·4; Br, 37·4; N, 12·9. $C_8H_3BrN_2S$ requires C, 33·5; H, 1·4; Br, 37·2; N, 13·0%). When the diazo-solution was boiled for 1 hr. a deep red-brown solid was precipitated. The mixture was cooled to 5°, the solid collected (0·8 g. from 1 g. of amine; m. p. 360°; azo-dye), and the filtrate extracted with ethyl acetate; removal of the solvent from the extract left an offensive-smelling oil (0·1 g. from 1 g. of amine).

7-*Amino*-1,2,3-*benzothiadiazole*.—This was prepared by reduction of 7-nitro-1,2,3-benzothiadiazole as for the 4- and 6-isomers. The yield was *ca.* 60%, the m. p. 136° (yellow needles) (Found: C, 47·7; H, 3·3. $C_6H_5N_3S$ requires C, 47·6; H, 3·3%. It gave an *acetyl derivative*, m. p. 190° (from ethanol) (Found: C, 49·3; H, 3·6. $C_6H_7N_3OS$ requires C, 49·8; H, 3·7%).

Ultraviolet Spectra of the Amino-1,2,3-*benzothiadiazoles*.—4-, $\lambda_{max.}$ 230, 250, 274sh, 362 mμ (ε 16,610 9,690, 5580, 4230); 5-, $\lambda_{max.}$ 230, 262, 292sh, 359 mμ (ε 25,160, 9820, 3020, 2346); 6-, $\lambda_{max.}$ 218, 264, 310, 318sh mμ (ε 23,400, 6040, 9480, 7490); 7-, $\lambda_{max.}$ 228, 250, 270, 349 mμ (ε 17,450, 7800, 5310, 2357).

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