CLXV.—*Aminobenzthiazoles. Part IX. The Unsaturation of Aminobenzthiazoles containing a Static Triad System, and the Synthesis of some* 1*-Dimethylaminobenzthiazoles.*

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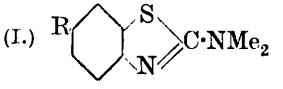
It has been suggested (Hunter, J., 1926, 1385; Hunter and Soyka, *ibid.*, p. 2959) that the production of isomeric bromides from aminothiazoles containing a mobile amidine system [H]N·C:N ⇌ N:C·N[H] is due to the addition of bromine to the tautomeric forms of the triad system. It being obviously desirable, therefore, to examine static derivatives (I) in which both mobile hydrogen atoms have been alkylated, the bromination of certain *s*-aryldimethylthiocarbamides and 1-dimethylaminobenzthiazoles was undertaken.

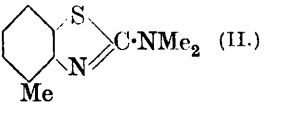
On bromination in chloroform, *s*-phenyldimethylthiocarbamide readily gave a *dibromide* of 1-dimethylaminobenzthiazole, which yielded the dimethylaminobenzthiazole (I; R = H) on reduction in the usual way (*loc. cit.*). A well-defined *pentabromide* of the dimethylamino-base was sometimes isolated, which was probably the hydrobromide of the tetrabromo-addition compound of the base. The bromination of *s*-phenyldimethylthiocarbamide, however, proceeded less readily than that of phenylthiocarbamide and of *s*-phenylmethylthiocarbamide (J., 1926, 1385), and this is probably due to the fact that in phenylthiocarbamide the mobile triad system [H]N·C:S ⇌ N:C·S[H] is duplicated in such a way as to favour the production of the thioamide phase of the thiocarbamide, through which thiazole ring formation takes place by way of a labile ·CBr–SBr derivative (Hunter and Soyka, *loc. cit.*). In any case, some *s*-phenyldimethylthiocarbamide was recovered un-

changed under conditions in which phenylthiocarbamide was completely transformed into 1-aminobenzthiazole dibromide.

On bromination in chloroform with excess of bromine, 1-*dimethylaminobenzthiazole* readily yielded a well-defined *hexabromide* (compare Hunter, J., 1925, **127**, 2271, and later papers).

The bromination of s-o-*tolyldimethylthiocarbamide*, however, gave rise to a well-defined, stable *tetrabromide* of 1-dimethylamino-3-methylbenzthiazole, which yielded the 3-methyl base (II) on





reduction in the usual way. This tetrabromide only lost bromine on exposure to moist air for several weeks, and it must be assumed that the instability produced in the NBr_2 complex by the *o*-methyl group (Hunter, J., 1926, 1401) is more than neutralised in the presence of the μ-NMe_2 group. This suggested that the bromides of the 5-substituted 1-aminobenzthiazole bases prepared by Dyson, Hunter, and Morris (preceding paper) might be greatly stabilised, and thereby rendered more readily comparable, by dimethylation of the amino-group, and the bromides of the 5-substituted 1-dimethylaminobenzthiazole bases (I) were therefore studied. In every case, bromination of the *s-p*-substituted phenyldimethylthiocarbamide gave rise to the bromide of the corresponding dimethylaminobenzthiazole, and these compounds differed strikingly from the bromo-addition compounds described in the preceding paper as regards their stability to moist air; on reduction, they all yielded the corresponding 5-substituted bases (I) in the usual way.

s-p-*Methoxy-* and s-p-*ethoxy-phenyldimethylthiocarbamide* yielded the tetrabromides of 5-methoxy- and 5-ethoxy-1-dimethylaminobenzthiazole, respectively. p-*Tolyldimethylthiocarbamide* resembled phenyldimethylthiocarbamide and gave rise to a *pentabromide* of 1-dimethylamino-5-methylbenzthiazole, which was very probably the hydrobromide of the tetrabromide. Bromination of 1-dimethylamino-5-methylbenzthiazole (I; R = Me) gave rise to a *hexabromide* of this base. p-*Chlorophenylthiocarbamide*, however, on bromination under the usual conditions yielded a *tribromide* of 5-chloro-1-dimethylaminobenzthiazole which was probably the hydrobromide of the dibromo-addition compound of the 5-chloro-base.

In view of the alternation of hexabromides and tetrabromides in the ascending homologous series of 2-alkylamino-β-naphthathiazole bromides (Dyson, Hunter, and Soyka, J., 1926, 2965), the bromination of s-α-*naphthyldimethylthiocarbamide* was also

studied. As might have been anticipated, this thiocarbamide gave rise to the tetrabromo-addition compound of the naphthathiazole, which yielded 2-*dimethylamino*-β-*naphthathiazole* on reduction.

EXPERIMENTAL.

The *s*-aryldimethylthiocarbamides described below were prepared, in yields of 80—90%, by treating the arylthiocarbimides (preceding paper) (1 mol.) in alcohol (5 vols.) with a 20% excess of a 33% solution of dimethylamine in absolute alcohol; in each case the mixture was warmed, and then concentrated at 15°/20 mm. The thiocarbamides were usually recrystallised from absolute alcohol.

s-Phenyldimethylthiocarbamide crystallised in long prisms, m. p. 133° (compare Dixon, J., 1892, **61**, 539) (Found: S, 17·6. Calc.: S, 17·8%).

1-*Dimethylaminobenzthiazole Dibromide.*—A solution of phenyldimethylthiocarbamide (1 g.) in chloroform (10 c.c.) was slowly treated with 0·8 c.c. of bromine; a yellow precipitate (bromo-addition compound of the thiocarbamide?) formed, which redissolved with evolution of heat and hydrogen bromide. The mixture was refluxed for 5 minutes and concentrated. It could not be induced to crystallise * and therefore was evaporated in a vacuum at 15°. The red gum obtained, after remaining in an evacuated desiccator for 20 hours, solidified in small, hard, vermilion crystals of the *dibromide*; these, after being crushed on porous earthenware and dried in a vacuum over potassium hydroxide, melted at 91—93° (decomp.; reddening at 60—70°, softening at 75—80°) (Found: Br, 48·0. $C_9H_{10}N_2Br_2S$ requires Br, 47·3%). This compound had the usual properties and liberated iodine from dilute hydriodic acid (Found: Br, 40%).

1-*Dimethylaminobenzthiazole tetrabromide hydrobromide* (prepared from phenyldimethylthiocarbamide, 2 g.; chloroform, 20 c.c.; bromine, 2 c.c., in chloroform, 5 c.c.; time of refluxing, 15 minutes) separated, after the mixture had been concentrated in a vacuum at 15°/20 mm., in small, orange-red prisms, m. p. 101° (decomp.) after drying (Found: Br, 69·1. $C_9H_{10}N_2Br_4S,HBr$ requires Br, 69·1%).

1-*Dimethylaminobenzthiazole.*—Either of the preceding bromides was treated with a large volume of sulphurous acid (saturated with sulphur dioxide at 15°) and the filtrate therefrom was made strongly alkaline with ammonia (*d* 0·880); the base then crystallised in glistening flakes, m. p. 86°. After recrystallisation from alcohol

* After this bromide had once been obtained crystalline, there was no difficulty in inducing subsequent preparations, made in the same laboratory, to crystallise.

it formed small, glistening needles, m. p. 87° (Found : S, 17·7. $C_9H_{10}N_2S$ requires S, 18·0%).

1-*Dimethylaminobenzthiazole hexabromide* (prepared from dimethylaminobenzthiazole, 0·8 g.; chloroform, 15 c.c.; bromine, 1 c.c.) separated in orange-red, glistening plates, m. p. 211° (with efferv.) after being dried (Found : Br, 73·2. $C_9H_{10}N_2Br_6S$ requires Br, 73·0%).

s-o-*Tolyldimethylthiocarbamide* crystallises in shining prisms, m. p. 138° (Found : S, 16·3. $C_{10}H_{14}N_2S$ requires S, 16·5%).

1-*Dimethylamino*-3-*methylbenzthiazole tetrabromide* (prepared from *o*-tolyldimethylthiocarbamide, 2 g.; chloroform, 10 c.c.; bromine, 2 c.c., in 5 c.c. of chloroform; spontaneous boiling with evolution of hydrogen bromide; time of refluxing, 10 minutes) crystallised in orange-yellow, glistening prisms, which after drying had m. p. 160° (decomp.; softening at 125—130°, charring at 180°) (Found : Br, 62·3. $C_{10}H_{12}N_2Br_4S$ requires Br, 62·5%).

1-*Dimethylamino*-3-*methylbenzthiazole* was obtained by reduction of the tetrabromide with a large volume of sulphurous acid, and crystallised from alcohol in stellate clusters of glistening needles, m. p. 84° (Found : S, 16·4. $C_{10}H_{12}N_2S$ requires S, 16·7%).

s-p-*Methoxyphenyldimethylthiocarbamide* crystallised in glistening plates, m. p. 125° (Found : S, 15·3. $C_{10}H_{14}ON_2S$ requires S, 15·2%).

1-*Dimethylamino*-5-*methoxybenzthiazole tetrabromide*, obtained from 0·9 g. of *p*-methoxyphenyldimethylthiocarbamide in chloroform (6 c.c.) and bromine (0·9 c.c.), formed small, yellowish-orange plates, m. p. 195° (with efferv.) (Found : Br, 61·1. $C_{10}H_{12}ON_2Br_4S$ requires Br, 60·6%).

1-*Dimethylamino*-5-*methoxybenzthiazole* crystallised from alcohol in small, white prisms, m. p. 144° (Found : S, 15·1. $C_{10}H_{12}ON_2S$ requires S, 15·4%).

s-p-*Ethoxyphenyldimethylthiocarbamide* formed small, shining prisms, m. p. 163° (Found : S, 14·2. $C_{11}H_{16}ON_2S$ requires S, 14·3%).

1-*Dimethylamino*-5-*ethoxybenzthiazole tetrabromide* (prepared from the ethoxyphenyldimethylthiocarbamide, 1 g.; chloroform, 10 c.c.; bromine, 1 c.c.; time of refluxing, 2 minutes) separated in orange, glistening plates, m. p. 190° (decomp.) (Found : Br, 59·0. $C_{11}H_{14}ON_2Br_4S$ requires Br, 59·1%).

1-*Dimethylamino*-5-*ethoxybenzthiazole* crystallised in small prisms, m. p. 118° (Found : S, 14·1. $C_{11}H_{14}ON_2S$ requires S, 14·4%).

s-p-*Tolyldimethylthiocarbamide* crystallised in glistening plates, m. p. 169° (Found : S, 16·1%).

1-*Dimethylamino*-5-*methylbenzthiazole tetrabromide hydrobromide* was obtained from *p*-tolyldimethylthiocarbamide (2 g.) in chloro-

form (15 c.c.) and bromine (2 c.c.). After the mixture had been refluxed, and then concentrated in a vacuum for 2 minutes, the product crystallised in glistening, orange-red needles, m. p. 95° (decomp.; efferv. at 125°) (Found: Br, 67·8. $C_{10}H_{12}N_2Br_4S$,HBr requires Br, 67·6%).

1-*Dimethylamino*-5-*methylbenzthiazole* separated from alcohol in small, glistening prisms, m. p. 86° (Found: S, 16·3%).

1-*Dimethylamino*-5-*methylbenzthiazole Hexabromide*.—One c.c. of bromine in chloroform (5 c.c.) was added to a solution of 0·9 g. of 1-dimethylamino-5-methylbenzthiazole in chloroform (15 c.c.); the hexabromide then separated in orange-red, glistening plates, m. p. 188° (decomp.) (Found: Br, 72·0. $C_{10}H_{12}N_2Br_6S$ requires Br, 71·4%).

s-p-*Chlorophenyldimethylthiocarbamide* formed small prisms, m. p. 152° (Found: S, 14·6. $C_9H_{11}N_2ClS$ requires S, 14·9%).

5-*Chloro*-1-*dimethylaminobenzthiazole dibromide hydrobromide*, obtained from 0·6 g. of *p*-chlorophenyldimethylthiocarbamide, suspended in chloroform (4 c.c.), and bromine (0·6 c.c.), crystallised in aggregates of orange-yellow needles, m. p. 264° (decomp.; sintering at 190°) (Found: Br, 54·6. $C_9H_9N_2ClBr_2S$,HBr requires Br, 52·9%).

5-*Chloro*-1-*dimethylaminobenzthiazole* crystallised from alcohol in long, colourless prisms, m. p. 99° (Found: S, 15·0. $C_9H_9N_2ClS$ requires S, 15·1%).

s-α-*Naphthyldimethylthiocarbamide* crystallised in long prisms, m. p. 162° (Found: S, 13·8. $C_{13}H_{14}N_2S$ requires S, 13·9%).

2-*Dimethylamino*-β-*naphthathiazole tetrabromide* was prepared from the naphthyldimethylthiocarbamide (0·3 g.) in chloroform (3 c.c.) and bromine (0·3 c.c.) and formed a bright yellow, crystalline powder which sintered at 185° and melted at 225° (decomp. with charring) (Found: Br, 58·3. $C_{13}H_{12}N_2Br_4S$ requires Br, 58·4%).

2-*Dimethylamino*-β-*naphthathiazole* crystallised from alcohol in large, flat prisms having a yellow tinge; m. p. 138° (Found: S, 13·9. $C_{13}H_{12}N_2S$ requires S, 14·0%).

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