

CLXXX.—*Aminobenzthiazoles. Part IV. The Stability of the Bromides of the 1-Xylidinodimethylbenzthiazoles.*

By ROBERT FERGUS HUNTER.

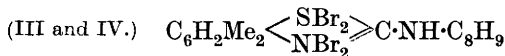
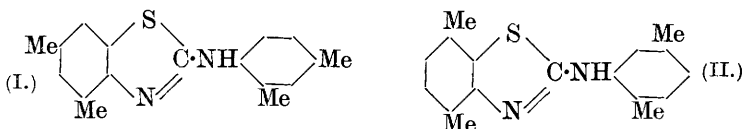
THE remarkable instability of 1-amino-3 : 5-dimethylbenzthiazole tetrabromide (this vol., p. 1389) must be attributed to the combined effects of the *o*- and *p*-methyl groups, since the stability of the bromo-addition compounds of 1-amino-5-methylbenzthiazole, 1-amino-3-methylbenzthiazole, and 1-amino-3 : 5-dimethylbenzthiazole decreases in the order given. The *o*-methyl group is mainly responsible for the instability, a fact which is further exemplified by the relative stabilities of the bromides of 1-*o*-toluidino-3-methylbenzthiazole and 1-*p*-toluidino-5-methylbenzthiazole (Hunter, J., 1925, 127, 2023).

It was therefore of interest to examine the effect of replacing the amino-group in 1-amino-3 : 5-dimethylbenzthiazole by an arylamino-group. In the first place, it might be expected on *a priori* grounds that the residual affinity of the aromatic nucleus of the arylamino-group would exert a stabilising influence on the bromo-addition compound of such a base, and secondly, on the basis of Ingold's modified strain theory (J., 1921, 119, 305 and later papers),* the bulky substituent might be expected to enhance the arylamino-

* The theoretical basis of this theory will be discussed in a paper dealing with the mobility of the 5-bromo-1-alkylaminobenzthiazole system and the addition of bromine to tautomeric systems of this type. The unsaturation of the ring nitrogen atom of the mobile triad system $N:C:N[H] X \rightleftharpoons N[H]:C:NX$ is profoundly affected by the mobility or potential mobility of the tautomeric hydrogen atom. For instance, there is a striking increase in the stability of the 5-bromo-1-alkylaminobenzthiazole 2 : 2-dibromide towards hydriodic acid as the alkyl group is in turn ethyl, *n*-propyl, *n*-butyl, and *isobutyl*. In this connexion it is hoped to obtain some information on the deflexion of the carbon tetrahedral angle (Deshapande and Thorpe, J., 1922, 121, 1430, and later papers) produced by the hitherto unstudied butyl, amyl, and hexyl groups.

phase of the mobile aminothiazole system (this vol., p. 1385) the ring nitrogen atom in which is more unsaturated than that in the 1-imino-1:2-dihydrothiazole form. The second effect also, owing to the nitrogen atom being the centre of unsaturation in a thiazole ring (this vol., p. 538), would increase considerably the stability of the bromo-addition compound.

The bromides of the 1-xylylidinodimethylbenzthiazoles (I and II) were therefore studied and it was found that the 1-xylylidino-group had a most striking stabilising effect on the aminobenzthiazole bromide complex.



Under the usual conditions of bromination in chloroform (*loc. cit.*), *s*-di-*m*-xylylthiocarbamide readily passed into the *tetrabromide* of 1-*m*-xylylidino-3:5-dimethylbenzthiazole (III), which is one of the most stable compounds of this type so far isolated, its stability in air being of the same order as that of the 2- β -naphthylamino- α -naphthathiazole bromides (J., 1925, 127, 2270). The formation, in the presence of an excess of halogen, of a labile *heptabromo*-addition compound of the dimethylbenzthiazole was also observed, this compound being doubtless the hydrobromide of the hexabromo-addition compound, which was on one occasion isolated in an impure condition. These compounds were all reduced in the usual manner by sulphurous acid, yielding the xylylidinodimethylbenzthiazole (I).

While these experiments were in progress, a paper by Levi (*Atti Cong. Naz. Chim. Ind.*, 1924, 400) appeared, in which 1-*m*-xylylidino-3:5-dimethylbenzthiazole (I) was described as being formed by the thionation of a mixture of *m*-xylylidine and phenyl-*m*-xylylthiocarbamide. Levi's product, however, although it gave the pure acetyl derivative, must have been very impure, because the melting point recorded is nearly 20° too low. This is not so surprising in view of the difficulties involved in such preparations (Hunter, *J. Soc. Chem. Ind.*, 1923, 42, 302 π).

Under the usual conditions of bromination, *s*-di-*p*-xylylthiocarbamide readily passed into the *tetrabromide* of 1-*p*-xylylidino-3:6-dimethylbenzthiazole (IV), a bright red compound resembling the *m*-xylylidino-isomeride in stability and other properties.

None of the 1-xylidinodimethylbenzthiazole bromides gave any evidence whatsoever of the existence of stable yellow tribromides (*loc. cit.*). Therefore, with regard to stability in the air, the 1-arylaminobenzthiazole bromides fall into two groups, the first of which includes the labile red bromo-addition compounds, such as those derived from 1-anilinobenzthiazole and its tolyl and α -naphthyl homologues, which on exposure to air evolve bromine and pass into stable yellow tribromides; and the second of which includes the stable red bromides of 2- β -naphthylamino- α -naphthathiazole and of the 1-xylidinodimethylbenzthiazoles described in this paper, which lose bromine appreciably only on prolonged exposure to moist air and do not appear to be capable of yielding yellow tribromides.

EXPERIMENTAL.

1-m-Xylidino-3 : 5-dimethylbenzthiazole Hexabromide Hydrobromide.—A solution of 1 g. of *s*-di-*m*-xylylthiocarbamide in chloroform (10 c.c.) was gradually treated with a solution of bromine (1 c.c., in chloroform, 3 c.c.) and then heated under reflux for 2 minutes, cooled, and a part of the solvent evaporated off in a vacuum at 15°. The red gum produced, which solidified, was triturated with an ethereal solution of bromine; the *heptabromide* was then obtained in small, red prisms which, after drying in a vacuum over potassium hydroxide, sintered at 153° and melted at 158° (decomp.) (Found : Br, 66·7. $C_{17}H_{18}N_2Br_6S, HBr$ requires Br, 66·7%).

1-m-Xylidino-3 : 5-dimethylbenzthiazole Tetrabromide (III).—The dixylylthiocarbamide (5 g. in chloroform, 10 c.c.) was treated as above (bromine, 4·8 c.c., in chloroform, 10 c.c.) and the cooled solution allowed to crystallise in a vacuum; the *tetrabromide* was then obtained in small, orange-red crystals which, after being washed with bromine in ether and dried in a vacuum, melted at 130° (decomp.) (Found : Br, 52·7. $C_{17}H_{18}N_2Br_4S$ requires Br, 53·3%). The tetrabromide had the usual properties of these compounds, being reduced by hydriodic acid with liberation of iodine, and evolving acetaldehyde on boiling with dilute alcohol.

Bromination in similar circumstances of 5 g. of the thiocarbamide with 5 c.c. of bromine produced on one occasion a red gum which, on trituration with bromine in ether, solidified to a mass of small, red crystals, m. p. 126° after drying in a vacuum (Found : Br, 61·3. $C_{17}H_{18}N_2Br_6S$ requires Br, 62·9%).

1-m-Xylidino-3 : 5-dimethylbenzthiazole obtained in the usual way by reducing any of the bromides with sulphurous acid and sulphur dioxide (*loc. cit.*) and liberating the base with ammonia, crystallised from alcohol-ethyl acetate (1 : 1) in large flakes and thereafter

from light petroleum (b. p. 40—60°) in small prisms, both forms melting at 175° (Found : S, 11.4. Calc. : S, 11.4%).

The acetyl derivative, obtained by heating a solution of the base in acetic anhydride for a few minutes and pouring it into alcohol, slowly crystallised in large prisms, m. p. 131—132° after recrystallisation from alcohol (Levi, *loc. cit.*, gives m. p. 131°).

s-Di-p-xylylthiocarbamide.—A mixture of technical *p*-xylydine (18 g.), alcohol (27 c.c.), carbon disulphide (33 c.c.), and potassium hydroxide (4 g.) was heated for 2—3 hours, and the product worked up in the usual way; on recrystallisation from alcohol the thio-carbamide was obtained in needles, m. p. 146—147° (Dyson and George, J., 1924, **125**, 1705, give the m. p. as 148.5°). The yield was about 50%.

1-p-Xylylidino-3 : 6-dimethylbenzthiazole Tetrabromide (IV).—Di-*p*-xylylthiocarbamide (1.25 g.) in chloroform was treated with bromine (1.2 c.c.) in chloroform (2.5 c.c.) in the usual way, the solution concentrated in a vacuum, and the product triturated with an ethereal solution of bromine. The red oil obtained, on partial evaporation of the ether, solidified to a mass of small, red crystals of the *tetrabromide* which were washed with chloroform and dried in a vacuum in the usual way. They had the usual properties and charred above 200° (Found : Br, 53.6. $C_{17}H_{18}N_2Br_4S$ requires Br, 53.2%).

1-p-Xylylidino-3 : 6-dimethylbenzthiazole, obtained by the reduction of the tetrabromide in the usual way, crystallised from ethyl acetate in small prisms, m. p. 200° (Found : S, 11.6. $C_{17}H_{18}N_2S$ requires S, 11.4%).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.

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