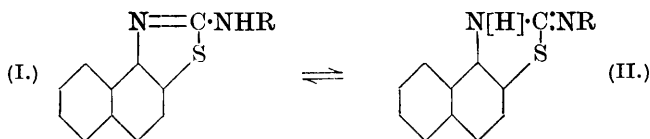


CCCXCVII.—*Aminobenzthiazoles. Part VII. The
2-Alkylamino- β -naphthathiazole System.*

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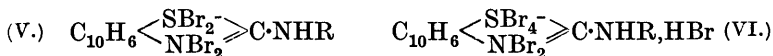
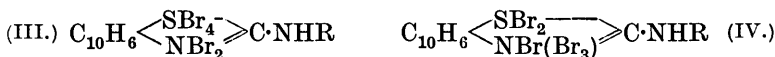
IN the investigation of the relation between unsaturation and mobility in tautomeric systems of the aminobenzthiazole type (preceding papers) it seemed desirable, for the purpose of comparison, to examine a system consisting almost entirely of the aminothiazole phase. The 2-alkylamino- β -naphthathiazole system ($I \rightleftharpoons II$)

should be in this state if the alkyl group R is sufficiently large and therefore the bromination of the *s*- α -naphthylalkylthiocarbamides under the usual conditions (Hunter, J., 1925, 127, 2023, 2270, and later papers) was studied. Unfortunately, however, owing to the



tendency of the thiazole nucleus in naphthathiazoles of this type to add on more than two bromine atoms (*loc. cit.*) and owing to the instability of some of the bromo-addition compounds (which partly decomposed with loss of bromine on dissolving in acetic acid), it was impossible to obtain a stability curve for the bromo-addition compounds of the alkylaminonaphthathiazole series.

On bromination in chloroform under the usual conditions, *s*-methyl- and *n*-propyl- α -naphthylthiocarbamides gave unstable *hexabromo*-addition compounds of the 2-alkylamino- β -naphthathiazoles, to which the formula III or IV (R = Me or Prⁿ) must be assigned,* whereas *s*-ethyl- and *n*-butyl- α -naphthylthiocarbamides were converted into *tetrabromides* (V; R = Et or *n*-C₄H₉) similar to the 1-arylaminobenzthiazole tetrabromides previously described. The



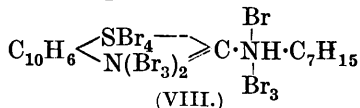
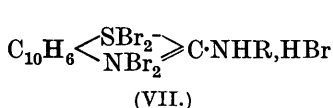
alternation of hexabromides and tetrabromides in the ascending homologous series is striking, particularly in view of the fact that α -naphthylthiocarbamide on bromination yields 2-amino- β -naphthathiazole tetrabromide (Hunter, this vol., p. 1390).

Bromination of *s*-isobutyl- and *iso*amyl- α -naphthylthiocarbamides yielded *heptabromo*-addition compounds of the 2-*iso*alkylamino- β -naphthathiazoles similar to the heptabromides of 1-*m*-toluidino-4-methylbenzthiazole (J., 1925, 127, 2025), 2- α -naphthylamino- β -naphthathiazole (*ibid.*, p. 2270), and 1-*m*-xylylidino-3:5-dimethylbenzthiazole (this vol., p. 1402), being doubtless the hydrobromides of the hexabromo-addition compounds (VI; R = *iso*-C₄H₉ or *iso*-C₅H₁₁).

The fact that the two branched-chain alkylaminonaphthathiazoles gave rise to heptabromides is noteworthy, since the large atomic volumes of such alkyl groups would be expected to enhance the aminothiazole phase of the triad system.

* The choice between these two formulæ will be discussed in a future paper.

s-n-Amyl- and *n*-hexyl- α -naphthylthiocarbamides yielded *penta*-*bromo*-addition compounds of the 2-alkylamino- β -naphthathiazoles (VII; R = *n*-C₅H₁₁ or *n*-C₆H₁₃). The former compound is the first hydrobromide of a tetrabromo-addition compound to be isolated.



Bromination of *s*- α -naphthyl-*n*-heptylthiocarbamide in presence of a large excess of halogen gave rise to a *tetradecabromo*-addition compound of 2-*n*-heptylamino- β -naphthathiazole, which probably has the constitution (VIII). Notwithstanding its high halogen content, this compound is remarkably stable and is only slowly reduced to the heptylaminonaphthathiazole by sulphurous acid and sulphur dioxide.

The normal product of bromination of nascent 2-alkylamino- β -naphthathiazoles therefore appears to be a tetrabromide (V), which in certain circumstances is capable of adding on either bromine to give a hexabromide (III or IV), or hydrogen bromide to give a pentabromide (VII), or both of these to give a heptabromide (VI).

EXPERIMENTAL.

2-Methylamino- β -naphthathiazole Hexabromide (III or IV; R = Me).—*s*- α -Naphthylmethylthiocarbamide (Dyson and Hunter, *Rec. trav. chim.*, 1926, **45**, 421) (0.3 g.), dissolved in cooled chloroform (5 c.c.) was treated with bromine (0.5 c.c.) in the usual way (see previous papers), a precipitate of the bromo-addition compound being formed. The mixture was refluxed for 5 minutes, concentrated, and cooled, and the *hexabromide* was collected on porous earthenware and dried in a vacuum over potassium hydroxide for 12 hours. It formed silky, vermilion needles, m. p. 163° (decomp., blackening at 75–80°) (Found: Br, 68.2. C₁₂H₁₀N₂Br₆S requires Br, 69.0%). The compound had the usual properties, losing bromine gradually on exposure to moist air, liberating iodine from dilute hydriodic acid, and being reduced by sulphurous acid and sulphur dioxide to the methylaminonaphthathiazole in the usual way (Hunter, J., 1925, **127**, 2023, 2270).

2-Methylamino- β -naphthathiazole.—The product of the preceding reduction was dried, and boiled for a short time with 2*N*-sodium hydroxide. The free *base*, after being washed and dried, separated from alcohol-ethyl acetate (1 : 1) in small, soft crystals, m. p. 193° (Found: S, 13.4. C₁₂H₁₀N₂S requires S, 14.9%).

2-Ethylamino- β -naphthathiazole Tetrabromide (V; R = Et).—This was prepared from *s*- α -naphthylethylthiocarbamide (Dyson and Hunter, *loc. cit.*) (0.9 g.), chloroform (10 c.c.), and bromine (1 c.c.)

in the usual way. The *tetrabromide* separated in yellowish-brown, microscopic crystals which, after drying in a vacuum over potassium hydroxide, melted and charred at 203° (Found: Br, 57.9. $C_{13}H_{12}N_2Br_4S$ requires Br, 58.4%). It had the usual properties of these substances; on exposure to air for 12 hours, it became brown.

2-Ethylamino- β -naphthathiazole crystallised from alcohol-ethyl acetate in soft, silky needles, m. p. 218° (Found: S, 13.2. $C_{13}H_{12}N_2S$ requires S, 14.0%).

s- α -Naphthyl-n-propylthiocarbamide, prepared by condensing *n*-propylthiocarbimide (1 mol.) with α -naphthylamine (1 mol.) in alcoholic solution, crystallised in long, prismatic needles, m. p. 67° (Found: S, 12.8. $C_{14}H_{16}N_2S$ requires S, 13.2%).

2-n-Propylamino- β -naphthathiazole Hexabromide (III or IV; R = Pr^a).—This was prepared like the methyl compound (*s- α -naphthyl-n-propylthiocarbamide*, 1 g.; chloroform, 10 c.c.; bromine, 1 c.c.) and was obtained, by concentrating the solution, in microscopic, red crystals which sintered at 153° after drying in a vacuum (Found: Br, 66.5. $C_{14}H_{14}N_2Br_6S$ requires Br, 66.6%). The compound had the usual properties, and lost bromine on exposure to air, becoming reddish-brown. After a day, its m. p. fell to 147° (sintering).

2-n-Propylamino- β -naphthathiazole crystallised from alcohol-ethyl acetate in glistening, silky plates having a pink tinge; m. p. 242° (Found: S, 13.0. $C_{14}H_{14}N_2S$ requires S, 13.2%).

s- α -Naphthyl-n-butylthiocarbamide was obtained from *n*-butylthiocarbimide and α -naphthylamine in the usual way and crystallised from alcohol in small prisms, m. p. 98° (Found: S, 11.8. $C_{15}H_{18}N_2S$ requires S, 12.3%).

2-n-Butylamino- β -naphthathiazole Tetrabromide (V; R = *n*-C₄H₉).—*s- α -Naphthyl-n-butylthiocarbamide* (0.9 g.) in chloroform (10 c.c.) was treated with bromine (0.8 c.c.) as in the previous case. On concentration, the *tetrabromide* was obtained in tufts of glistening, golden needles having a pink tinge; m. p. 134° (decomp.) (Found: Br, 55.6. $C_{15}H_{16}N_2Br_4S$ requires Br, 55.5%). It had the usual properties, but showed no appreciable colour change after 48 hours' exposure to air.

2-n-Butylamino- β -naphthathiazole separated from alcohol-ethyl acetate in small, glistening prisms, m. p. 177° (Found: S, 12.0. $C_{15}H_{16}N_2S$ requires S, 12.5%).

s- α -Naphthylisobutylthiocarbamide was obtained by the condensation of *isobutylthiocarbimide* and α -naphthylamine in alcohol, the reaction being complete after 10 minutes' boiling. The thiocarbamide crystallised in aggregates of long needles, m. p. 106° (Found: S, 12.3. $C_{15}H_{18}N_2S$ requires S, 12.4%).

2-isoButylamino- β -naphthathiazole Hexabromide Hydrobromide (VI;

R = *iso*-C₄H₉).—This was prepared from *s*- α -naphthylisobutylthiocarbamide (0.75 g.), chloroform (10 c.c.), and bromine (0.8 c.c.), an orange-yellow precipitate forming. After the mixture had been refluxed, the *heptabromide* was obtained in brown, microscopic needles, m. p. 103° (decomp.) (Found: Br, 69.7. C₁₅H₁₆N₂Br₆S.HBr requires Br, 68.6%). After 2 days' exposure to air, the substance became brownish-grey and melted at 243° (decomp.).

2-*iso*Butylamino- β -naphthathiazole separated from alcohol-ethyl acetate in crystals contaminated with resinous material; these were triturated with ether and recrystallised, and were thus obtained in small, grey prisms with a purple tinge; m. p. 242° (Found: S, 12.5. C₁₅H₁₆N₂S requires S, 12.5%).

s- α -Naphthyl-*n*-amylthiocarbamide was prepared by boiling an alcoholic solution of *n*-amylthiocarbimide (Dyson and Hunter, *loc. cit.*) (1 mol.) and α -naphthylamine (1 mol.) for 3 hours; it crystallised in colourless prisms, m. p. 103° (Found: S, 11.2. C₁₆H₂₀N₂S requires S, 11.8%).

2-*n*-Amylamino- β -naphthathiazole *Tetrabromide Hydrobromide* (VII; R = *n*-C₅H₁₁).—The preceding thiocarbamide (1.1 g.) was brominated in chloroform (10 c.c.) in the usual way. There was no precipitation on addition of the halogen and the action was less vigorous than in the previous cases. The solution was concentrated to 7 c.c. and cooled; the *pentabromide* then crystallised in glistening, silky, yellow plates, m. p. 123° (decomp.) (Found: Br, 58.9. C₁₆H₁₈N₂Br₄S.HBr requires Br, 59.6%). The pentabromide had the usual properties.

2-*n*-Amylamino- β -naphthathiazole separated from alcohol-ethyl acetate in small, glistening prisms, m. p. 107° (Found: S, 11.6. C₁₆H₁₈N₂S requires S, 11.8%).

s- α -Naphthylisomylthiocarbamide was obtained in the same way as the *n*-isomeride, but the reaction was complete after 10 minutes' boiling. The thiocarbamide crystallised from alcohol in white prisms, m. p. 92° (Found: S, 11.9. C₁₆H₂₀N₂S requires S, 11.8%).

2-*iso*Amylamino- β -naphthathiazole *Hexabromide Hydrobromide* (VI; R = *iso*-C₅H₁₁).—The thiocarbamide (1 g.), dissolved in warm chloroform (10 c.c.), was treated with bromine (1 c.c.), hydrogen bromide being copiously evolved and a precipitate forming. After drying in a vacuum, the *heptabromide* was obtained in small, yellow crystals having a green tinge; these sintered at 135°, blackened at 200°, and disintegrated at 222° (Found: Br, 67.5. C₁₆H₁₈N₂Br₆S.HBr requires Br, 67.5%). The compound had the usual properties.

2-*iso*Amylamino- β -naphthathiazole separated from alcohol-ethyl acetate in small, light grey, microscopic crystals having a pink tinge; m. p. 117° (Found: S, 11.0. C₁₆H₁₈N₂S requires S, 11.8%).

s- α -Naphthyl-*n*-hexylthiocarbamide crystallised from alcohol in rosettes of minute needles, m. p. 89° (Found : S, 11.2. $C_{17}H_{22}N_2S$ requires S, 11.2%).

2-*n*-Hexylamino- β -naphthathiazole Tetrabromide Hydrobromide (VII; R = *n*- C_6H_{13}).—This was obtained from the naphthylhexylthiocarbamide (0.3 g.), chloroform (3 c.c.), and bromine (0.4 c.c.), but no precipitate formed until the solution had been heated, concentrated, and cooled; then, on rubbing, the pentabromide separated in shining, yellow plates, m. p. 127° (decomp.) (Found : Br, 58.9. $C_{17}H_{20}N_2Br_4S$, HBr requires Br, 58.5%). The compound had the usual properties.

2-*n*-Hexylamino- β -naphthathiazole separated from alcohol-ethyl acetate in small plates having a pink tinge; m. p. 111° (Found : S, 11.0. $C_{17}H_{20}N_2S$ requires S, 11.3%).

s- α -Naphthyl-*n*-heptylthiocarbamide crystallised from alcohol in brilliant, flat needles, m. p. 62° (Found : S, 10.0. $C_{18}H_{24}N_2S$ requires S, 10.7%).

2-*n*-Heptylamino- β -naphthathiazole Tetradecabromide (VIII).—A solution of *s*- α -naphthyl-*n*-heptylthiocarbamide (0.9 g.) in chloroform (10 c.c.) was treated with bromine (0.8 c.c.) in the usual way; the shining, yellow, microscopic needles of the bromide thus obtained became green when washed with chloroform. The product was therefore suspended in chloroform and again treated with bromine; dark olive-green crystals of a tetradecabromide were then obtained which, after drying, charred and disintegrated at 220° (Found : Br, 79.5. $C_{18}H_{22}N_2Br_{14}S$ requires Br, 79.0%). This compound became mauve after exposure to air for 2 days.

2-*n*-Heptylamino- β -naphthathiazole.—The tetradecabromide was suspended in sulphurous acid and treated with sulphur dioxide for 2—3 hours. The product was collected after some time, boiled with 2*N*-sodium hydroxide, washed, dried, and crystallised from ethyl acetate-alcohol, from which the base separated in small, shining, purple needles, m. p. 97° (decomp.) (Found : S, 10.5. $C_{18}H_{22}N_2S$ requires S, 10.7%).

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