310. *The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part XII.* The Methylation of 6 : 4′-Disubstituted and 4′-Substituted 2-Anilinobenzothiazoles.*

By R. F. Hunter, E. R. Parken, and Eileen M. Short.

The effect of *para*-substituents to the nitrogen atoms of the semicyclic amidine system in 2-anilinobenzothiazoles on the proportion of methyl isomers derived from the tautomeric forms on methylation with methyl iodide alone has been examined. The formation of a strong preponderance of 2-phenyliminobenzothiazoline derivatives which occurs in all cases is attributed, on the basis of the ammonium mechanism of methylation, to the stability of the amino-aromatic form. It is concluded that a *p*-methyl group activates the unshared electrons of the nitrogen atom relative to hydrogen while halogen deactivates them, and the effect of the same substituent is greater when in the benzene ring of the benzothiazole system than in the side-chain benzene ring. In the presence of ethoxide ions there is a profound shift in the direction of methylation towards the production of 2-*N*-methylanilino-isomers, which is interpreted on the basis of operation of an amide mechanism of methylation of the amino-aromatic form, which is probably the main reaction in the presence of excess of sodium ethoxide.

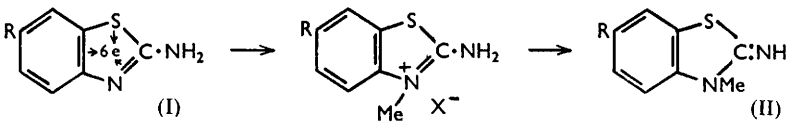
It was observed earlier [1] that 6-substituted 2-aminobenzothiazoles (I) are methylated exclusively on the nuclear nitrogen atom of the amidine system, irrespective of the nature of the *para*-substituent to this (I; R = Me, OEt, I, Br, Cl, F, or NO_2), yielding 2-imino-3-methylbenzothiazolines (II). This was attributed to the stability of the amino-aromatic form in which the formation of the sextet [2] can be pictured without calling on the unshared

* Part XI, *J.*, 1938, 321.

[1] Hunter and Jones, *J.*, 1930, 2190; Dyson, Hunter, Jones, and Styles, *J. Indian Chem. Soc.*, 1931, **8**, 147.

[2] Armit and Robinson, *J.*, 1925, **127**, 1605; Goss and Ingold, *J.*, 1928, 1268.

electrons of the nuclear nitrogen atom. The inertness of sulphur of the thiazole ring provides an example of an atom which, while it cannot provide unshared electrons for purposes such as salt formation or addition of bromine, can contribute these to another process such as the formation of the " aromatic " sextet.



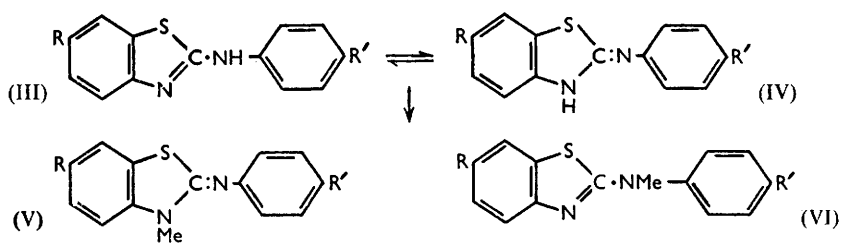
(I) (II)

The conjugating effect of the phenyl group in the anilino-substituent in 2-anilinobenzothiazole (III ⇌ IV; R = R′ = H), however, enables the nitrogen atom to which it is attached to compete with the thiazole-nitrogen atom in methylation, leading to substantial formation of the second methyl isomer (VI; R = R′ = H) and similar results were observed for the oxazole and selenazole analogues.[3] In accordance with this, we have found that 2-*cyclo*hexylaminobenzothiazole reacts apparently wholly in the amino-aromatic form, yielding 2-*cyclo*hexylimino-3-methylbenzothiazoline.

The effect of substituents on the proportion of isomeric methyl derivatives obtained by methylation of 6 : 4′-disubstituted (III ⇌ IV; R = R′) and 4′-substituted 2-anilinobenzothiazoles (III ⇌ IV; R = H) has now been examined.

Methylation of 6-methyl-2-*p*-toluidinobenzothiazole (III ⇌ IV; R = R′ = Me) with methyl iodide contrasted with the original experiment with 2-anilinobenzothiazole in that the proportion of isomer (VI; R = R′ = Me) isolable (as picrate obtained by fractional crystallisation) was only of the order of 3%. 6-Chloro-2-*p*-chloroanilinobenzothiazole (III ⇌ IV; R = R′ = Cl), however, gave a mixture of isomers (V and VI; R = R′ = Cl) (isolated as picrate) in which the former predominated in the ratio of approximately 3 : 1.

2-*p*-Toluidinobenzothiazole (III ⇌ IV; R = H, R = Me) gave a mixture of 2-*p*-tolylimino-3-methyl- and 2-*N*-methyl-*p*-toluidino-isomers in the proportion of approximately 4 : 1 in favour of the former, very close to the result obtained for 2-anilinobenzothiazole itself. 2-*p*-Chloroanilinobenzothiazole (III ⇌ IV; R = H, R′ = Cl) reacted apparently exclusively in the amino-aromatic form, yielding 2-*p*-chlorophenylimino-3-methylbenzothiazoline and no detectable quantity of the isomer. This led us to



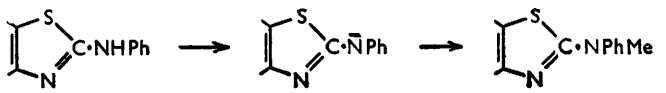
re-examine the methylation of 2-*p*-bromoanilinobenzothiazole (III ⇌ IV; R = H, R′ = Br), which had been reported to be methylated exclusively on the non-nuclear nitrogen atom. Some confusion appears to have crept into the original experiments[1] and we have now found that, in the absence of alkaline catalysts, methylation by methyl iodide proceeds entirely in the opposite direction, with the production of 2-*p*-bromophenylimino-3-methylbenzothiazoline.

It is therefore concluded that a *p*-methyl group activates the unshared electrons of

[3] Desai, Hunter, and Khalidi, *J.*, 1934, 1186; Chiragh Hasan and Hunter, *J.*, 1935, 1762.

the nitrogen atom relative to hydrogen, while halogens deactivate them, and that the effect of the same substituent is greater when in the benzene ring of the benzothiazole system than in the side-chain benzene ring.

The effect of alkoxide ions on the direction of methylation was also examined and in all cases caused a profound shift towards the production of the 2-*N*-methylarylamino-isomer.[4] On treatment in ethanolic sodium ethoxide with methyl sulphate, 6-methyl-2-*p*-toluidinobenzothiazole gave a mixture in which the 2-*N*-methyl-*p*-toluidino-derivative predominated, and 2-*p*-chloroanilinobenzothiazole gave roughly equal proportions of methyl isomers. 6-Chloro-2-*p*-chloroanilinobenzothiazole, which could not be methylated under similar conditions with methyl sulphate, gave with methyl iodide in the presence of ethanolic sodium ethoxide apparently exclusive methylation on the non-nuclear nitrogen atom. These results are interpreted on the basis of the operation of an amide mechanism of methylation of the amino-aromatic form, analogous to that for methylation of 2-hydroxybenzothiazoles in alkaline solution,[5] which is probably the main reaction in the presence of excess of sodium ethoxide:



The 3-methyl-2-phenyliminobenzothiazolines required for identification of methylation products were synthesised by cyclisation of the corresponding *NN'*-diaryl-*N*-methyl(thioureas) with bromine, the methyl group directing cyclisation on to the aromatic nucleus of the nitrogen atom to which it is attached in the intermediate bromothiol derivative through which thiazole cyclisation is presumed to take place.[6] Attempts to prepare 2-arylimino-3-methylbenzothiazolines by heating 2-thio-3-methylbenzothiazoline with arylamines were unsuccessful, as were similar experiments with 3-methylbenzothiazolin-2-one, even in the presence of dehydrating agents such as phosphorus oxychloride.

Experimental

6-Methyl-2-p-toluidinobenzothiazole.—This base was prepared [7] from *NN'*-di-*p*-tolyl(thiourea) and bromine, crystallised from alcohol–ethyl acetate in needles, m. p. 162°. The *picrate*, prepared in acetone, crystallised from ethyl acetate in pale yellow needles, m. p. 252° (Found: S, 6·7. $C_{15}H_{14}N_2S,C_6H_3O_7N_3$ requires S, 6·6%).

Methylation by methyl iodide. The base (5 g.) was heated with methyl iodide in sealed tubes at 100° for the times indicated and the product digested with 30% aqueous potassium hydroxide on a water-bath for 1—2 hr., then extracted with chloroform, and the gummy base stirred with cold absolute ethanol. The colourless residue was collected and the recovered uncrystallisable gum was treated in acetone with the calculated amount of picric acid. The picrate was fractionally recrystallised from ethyl acetate. Fractions of similar m. p. were united and recrystallised after mixed m. p. determinations. The final picrate fractions were very gummy and yielded sufficient solid for m. p. determinations only with difficulty. Results are tabulated.

MeI (ml.)	Time (hr.)	Residue, m. p. 118° (g.)	Gum (g.)	Yield (g.) (and m. p.) of picrate fractions I	II	III (gum)
7·5	1	3·4	2	0·56 (242°)	1·5 (162°)	1
7·5	2·5	3·7	1·9	0·07 (242°)	1·65 (144°)	0·6
15	2·5	3·87	1·35	0·05 (240°)	1·2 (146°)	0·6
7·5	4·5	3·84	1·57	0·05 (240°)	1·4 (145°)	0·5
15	4·5	3·8	1·38	0·06 (240°)	1·42 (147°)	0·6

[4] Hunter and Wali, *J.*, 1937, 1513.
[5] Hunter and Parken, *J.*, 1935, 1755.
[6] Hunter, *Sir P. C. Ray Commemoration Vol., J. Indian Chem. Soc.*, 1933, p. 73.
[7] Hunter, *J.*, 1925, **127**, 2023.

The picrate fractions of m. p. 240—242°, on recrystallisation, had m. p. 250—251° alone and when mixed with 6-methyl-2-*p*-toluidinobenzothiazole picrate. The residues of m. p. 118° consisted of 3 : 6-*dimethyl*-2-p-*tolyliminobenzothiazoline*, which on recrystallisation formed needles, m. p. 121° (Found: C, 71·8; H, 6·0; N, 10·3; S, 11·8. $C_{16}H_{16}N_2S$ requires C, 71·6; H, 6·0; N, 10·4; S, 11·8%). Its *picrate* formed needles (from ethyl acetate), m. p. 175—176° (Found: S, 6·5. $C_{16}H_{16}N_2S,C_6H_3O_7N_3$ requires S, 6·4%). The picrate of m. p. 162° obtained in the first experiment gave solely the picrate of m. p. 176° on recrystallisation. Fractional crystallisation of the picrates of m. p. 144—147° from ethyl acetate furnished mainly the 3 : 6-dimethyl-2-*p*-tolyliminobenzothiazoline picrate, m. p. 176°, accompanied by small amounts of 6-methyl-2-*N*-methyl-*p*-toluidinobenzothiazole picrate, m. p. 165°, the united yield of which from the four experiments was 0·8 g.

Methylation by dimethyl sulphate in ethanolic sodium ethoxide. The base (2 g.) in ethanolic sodium ethoxide (prepared from 1 g. of sodium in 100 ml. of ethanol) was heated with dimethyl sulphate (6 ml.) under reflux for 4 hr., treated with excess of ammonia (*d* 0·880) after removal of the bulk of the alcohol, and extracted with chloroform. An alcoholic solution of the resulting gum deposited 3 : 6-dimethyl-2-*p*-tolyliminobenzthiazoline (0·35 g.), m. p. 121° alone and when mixed with the previous specimen, after recrystallisation (Found: S, 11·8%). The recovered gum was separated by light petroleum into a residue of unmethylated base (0·7 g.; m. p. 162°) and a gum (0·6 g.) which in acetone gave a picrate which on recrystallisation from ethyl acetate had m. p. 165° alone and m. p. 165—166° when mixed with authentic 6-methyl-2-*N*-methyl-*p*-toluidinobenzothiazole picrate.

Synthesis of 6-*methyl*-2-N-*methyl*-p-*toluidinobenzothiazole and* 3 : 6-*dimethyl*-2-p-*tolyliminobenzothiazoline.* (i) 2-Chloro-6-methylbenzothiazole (1·5 g.) and *N*-methyl-*p*-toluidine (1 g.) were heated until a vigorous reaction occurred. The basified product extracted with chloroform did not crystallise and was converted into the *picrate* of 6-methyl-2-*N*-methyl-*p*-toluidinobenzothiazole which after several recrystallisations from ethyl acetate formed yellow needles, m. p. 166° (Found: C, 53·15; H, 3·8; S, 6·5. $C_{16}H_{16}N_2S,C_6H_3O_7N_3$ requires C, 53·1; H, 3·8; S, 6·4%). (ii) N-*Methyl*-NN'-*di*-p-*tolyl*(*thiourea*), prepared from *p*-tolylthiocarbimide (3 g.) and *N*-methyl-*p*-toluidine (2·4 g.) in ethanol, formed needles, m. p. 103° (Found: S, 11·8. $C_{16}H_{18}N_2S$ requires S, 11·85%). A solution of the thiourea (2 g.) in chloroform (20 ml.) was heated with bromine (2 ml. in 2 ml. of chloroform) under reflux for 20 min. and the orange-red hydroperbromide obtained by concentration at laboratory temperature under reduced pressure was ground with aqueous sulphurous acid until colourless. The basified product on recrystallisation from ethanol had m. p. 110—116° but gave 3 : 6-dimethyl-2-*p*-tolyliminobenzothiazoline picrate, m. p. 176° alone and when mixed with a specimen obtained by methylation of 6-methyl-2-*p*-toluidinobenzothiazole (Found: S, 6·5%).

6-*Chloro*-2-p-*chloroanilinobenzothiazole.*[8]—This base, m. p. 224°, gave a *picrate* as needles (from ethyl acetate), m. p. 258° (Found: S, 6·3. $C_{13}H_8N_2Cl_2S,C_6H_3O_7N_3$ requires S, 6·1%).

The base (10 g.) and methyl iodide (10 ml.) were heated at 100° for 9—10 hr., and the product digested with hot 30% aqueous potassium hydroxide for several hours to ensure complete decomposition of hydriodides. The alcoholic solution of the gum isolated by chloroform deposited 6-chloro-2-*p*-chlorophenylimino-3-methylbenzothiazoline which after recrystallisation from methanol–ethyl acetate formed needles (3·3 g.), m. p. 119°, and m. p. 120° when mixed with a specimen synthesised from *NN'*-di-*p*-chlorophenyl-*N*-methyl(thiourea), and gave a *picrate*, needles, m. p. 158—159° (Found: Cl, 13·1. $C_{14}H_{10}N_2Cl_2S,C_6H_3O_7N_3$ requires Cl, 13·2%). Fractional crystallisation of the picrate from the gum obtained from the mother-liquors gave 0·8 g. of 6-chloro-2-*p*-chloroanilinobenzothiazole picrate (m. p. 259° and 251°), and 1·9 g. of 6-chloro-2-*p*-chloro-*N*-methylanilinobenzothiazole picrate (needles, m. p. 167—169°).

Attempted methylation of 6-chloro-2-*p*-chloroanilinobenzothiazole in ethanolic sodium ethoxide as in the previous case, but with a higher concentration of dimethyl sulphate, proved unsuccessful. A mixture of the base (2 g.), ethanolic sodium ethoxide (sodium, 0·5 g.; ethanol, 4 ml.), and methyl iodide (4 ml.) was heated in a sealed tube at 100° for 5—6 hr. The basified product gave 6-chloro-2-*p*-chloro-*N*-methylanilinobenzothiazole, which had m. p. 96° after recrystallisation and gave a picrate, m. p. 169°. The mother-liquors gave a further 0·9 g. of this base and the residual gum (0·4 g.) furnished its picrate. No evidence was obtained of the presence of 6-chloro-2-*p*-chlorophenylimino-3-methylbenzothiazoline.

[8] Dyson, Hunter, and Soyka, *J.*, 1929, 458.

6-*Chloro*-2-p-*chloro*-N-*methylanilinobenzothiazole*, obtained by condensation of 2 : 6-dichlorobenzothiazole and *p*-chloro-*N*-methylaniline, formed needles (from alcohol), m. p. 95° (Found: Cl, 22·75; S, 10·2. $C_{14}H_{10}N_2Cl_2S$ requires Cl, 23·0; S, 10·4%). The picrate formed deep yellow needles (from ethyl acetate), m. p. 169—170° (Found: C, 44·4; H, 2·4; Cl, 13·1; S, 5·9. Calc. for $C_{14}H_{10}N_2Cl_2S,C_6H_3O_7N_3$: Cl, 44·4; H, 2·5; Cl, 13·1; S, 5·9%).

NN'-*Di*-p-*chlorophenyl*-N-*methyl*(*thiourea*) formed needles (from ethanol), m. p. 148° (Found: Cl, 22·9; S, 10·2. $C_{14}H_{12}N_2Cl_2S$ requires Cl, 22·8; S, 10·3%). 6-*Chloro*-2-p-*chlorophenylimino*-3-*methylbenzothiazoline*, prepared from this thiourea, formed needles (from alcohol), m. p. 121° (Found: C, 54·5; H, 3·6; N, 8·8; Cl, 22·8; S, 10·4. $C_{14}H_{10}N_2Cl_2S$ requires C, 54·4; H, 3·2; N, 9·1; Cl, 23·0; S, 10·6%), and gave a picrate, m. p. 158° (Found: Cl, 13·1%).

2-p-*Toluidinobenzothiazole*.—The alcoholic solution of the gum obtained by methylation of the base (5·4 g.) with methyl iodide (10 ml.) at 100° for 3—4 hr. deposited 3-*methyl*-2-p-*toluidinobenzothiazoline* (2 g.), m. p. 87°, and the recovered gum (2·6 g.) gave a further 1 g. (m. p. 88°) on washing with cold acetone; this had m. p. 89° after recrystallisation (Found: S, 12·3. $C_{15}H_{14}N_2S$ requires S, 12·6%). Fractional crystallisation of the picrate from the gum recovered from the acetone solution gave 3-*methyl*-2-p-*tolyliminobenzothiazoline picrate*, m. p. 180° alone and when mixed with an authentic specimen (Found: S, 6·45. $C_{15}H_{14}N_2S,C_6H_3O_7N_3$ requires S, 6·6%), a further fraction, m. p. 176° (total 0·6 g.), and impure 2-*N*-methyl-*p*-toluidinobenzothiazole picrate, m. p. 144° and 146°; total: 1·4 g.) which after recrystallisation had m. p. 170° alone, and 169—170° when mixed with a authentic specimen.

2-*N*-Methyl-*p*-toluidinobenzothiazole, obtained as a gum from 2-chlorobenzothiazole and *N*-methyl-*p*-toluidine, gave a *picrate* which formed deep yellow needles (from ethyl acetate), m. p. 170° (Found: C, 52·3; H, 3·8; N, 14·2; S, 6·4. $C_{15}H_{14}N_2S,C_6H_3O_7N_3$ requires C, 52·2; H, 3·5; N, 14·45; S, 6·6%).

N-*Methyl*-N-*phenyl*-N'-p-*tolyl*(*thiourea*) formed needles (from alcohol), m. p. 126° (Found: S, 12·7. $C_{15}H_{16}N_2S$ requires S, 12·8%). 3-Methyl-2-*p*-tolyliminobenzothiazoline, obtained by cyclization of the thiourea with bromine, was a gum and was converted into the *picrate* which formed needles (from alcohol), m. p. 180° (Found: C, 52·2; H, 3·7; N, 14·2; S, 6·4%).

2-p-*Chloroanilinobenzothiazole*.—The *picrate* formed needles, m. p. 239° (Found: S, 6·4. $C_{13}H_9N_2ClS,C_6H_3O_7N_3$ requires S, 6·5%). (i) The ethanolic solution of basified product from methylation of this base (10 g.) with methyl iodide (15 ml.) at 100° for 6 hr. gave 5 g. of 2-p-*chlorophenylimino*-3-*methylbenzothiazoline*, m. p. 105° (108°) which rose to 109° on recrystallisation (Found: S, 11·55. $C_{14}H_{11}N_2ClS$ requires S, 11·6%), and gave a picrate which had m. p. 180° alone and when mixed with an authentic specimen. A further 2 g. of this methyl derivative were obtained from mother-liquors, and the residual gum (0·8 g.) gave the picrate of this [m. p. 179° (177°)] and of unchanged base (m. p. 235°). (ii) The picrate of the gum obtained by methylation of the base (5 g.) in ethanolic sodium ethoxide with dimethyl sulphate (15 ml.) for 4 hr. gave the picrate (1 g.; m. p. 233°) of unchanged base, and impure 2-*p*-chlorophenylimino-3-methylbenzothiazoline (m. p. 176—177°, 172—173° total: 1 g.; and 0·8 g. of m. p. 163—170°). The mother-liquors gave an obvious mixture of crystals which were collected separately and on recrystallisation gave the picrate (0·65 g.; m. p. 173—174°) of the 2-phenylimino-3-methyl derivative, and 2-p-*chloro*-N-*methylanilinobenzothiazole picrate*, m. p. 162—163° (1·75 g.) (Found: S, 6·2. $C_{14}H_{11}N_2ClS,C_6H_3O_7N_3$ requires S, 6·4%). The mother-liquors gave a further 1·1 g. of the latter, m. p. 153—159°.

2-p-*Chloro*-N-*methylanilinobenzothiazole*, prepared from 2-chlorobenzothiazole, formed a gum which crystallised from ethanol, then having m. p. 103—104° (Found: S, 11·4. $C_{14}H_{11}N_2ClS$ requires S, 11·65%), and gave a picrate, m. p. 162° (Found: C, 47·9; H, 3·1; S, 6·2. Calc. for $C_{14}H_{11}N_2ClS,C_6H_3O_7N_3$: C, 47·4; H, 2·8; S, 6·4%).

N'-p-*Chlorophenyl*-N-*methyl*-N-*phenyl*(*thiourea*) formed plates, m. p. 131—132° (Found: Cl, 12·6; S, 11·5. $C_{14}H_{13}N_2ClS$ requires Cl, 12·8; S, 11·6%). 2-*p*-Chlorophenylimino-3-methylbenzothiazoline, obtained by cyclisation of this with bromine, formed needles (from ethanol), m. p. 110° (Found: C, 61·3; H, 4·0; N, 9·9; Cl, 12·7; S, 11·5. Calc. for $C_{14}H_{11}N_2ClS$: C, 61·2; H, 4·0; N, 9·9; Cl, 12·9; S, 11·65%), whose *picrate* formed needles, m. p. 182° (Found: S, 6·1%). This base was also prepared by heating 2-imino-3-methylbenzothiazoline (1·6 g.) and *p*-chloroaniline (1·9 g.) at 220—230° for 3½ hr., then having m. p. and mixed m. p. 108—109° (picrate, m. p. and mixed m. p. 180°).

2-p-*Bromoanilinobenzothiazole*.—The picrate of the base formed needles (from ethyl acetate), m. p. 243° (Found: S, 6·0. $C_{13}H_9N_2BrS,C_6H_3O_7N_3$ requires S, 6·0%). (i) Crystallisation of

the basified product obtained by treating the base (10 g.) with methyl iodide (15 ml.) at 100° for 8—10 hr. gave (from alcohol) 2-p-*bromophenylimino*-3-*methylbenzothiazoline* (7·3 g.), needles, m. p. 105° undepressed on admixture with an authentic specimen (Found: S, 9·95. $C_{14}H_{11}N_2BrS$ requires S, 10·0%). The gummy residue gave a further 1·2 g. (m. p. 103—105°) when washed with cold acetone, and the extract furnished 2-*p*-bromoanilinobenzothiazole picrate, m. p. 237°, accompanied by 2-p-*bromophenylimino*-3-*methylbenzothiazoline picrate*, m. p. 184° (Found: S, 5·8. $C_{14}H_{11}N_2BrS,C_6H_3O_7N_3$ requires S, 5·8%). (ii) The gum obtained by methylation of the base (4 g.) in ethanolic sodium ethoxide with dimethyl sulphate (16 ml.) gave on treatment with cold ethanol 1·8 g. of 2-*p*-bromo-*N*-methylanilinobenzothiazole, m. p. 117—118°, and microcrystalline fractions which yielded 2-*p*-bromophenylimino-3-methylbenzothiazoline picrate (2·9 g.) and the picrate (0·8 g.) of the isomer. From the uncrystallisable gum a further 0·1 g. and 0·25 g. respectively of these picrates were isolated, with 0·2 g. of the picrate of unchanged base. 2-p-*Bromo*-N-*methylanilinobenzothiazole*, prepared from 2-chlorobenzothiazole and *p*-bromo-*N*-methylaniline, had m. p. 115—116° (Found: C, 52·7; H, 3·5; Br, 24·8; S, 10·1. $C_{14}H_{11}N_2BrS$ requires C, 52·7; H, 3·4; Br, 25·1; S, 10·0%). The *picrate* obtained from this had m. p. 166° (Found: S, 5·9%). N′-p-*Bromophenyl*-N-*methyl*-N-*phenyl*(*thiourea*) formed plates, m. p. 147° (Found: Br, 25·1; S, 10·0. $C_{14}H_{13}N_2BrS$ requires Br, 24·9; S, 10·0%). 2-*p*-Bromophenylimino-3-methylbenzothiazoline, obtained by cyclisation with bromine, formed needles, m. p. 105° (Found: C, 52·7; H, 3·5; N, 8·4; Br, 24·9; S, 9·95%). The picrate from this had m. p. 184° (Found: S, 5·9%).

Methylation of 2-Anilinobenzothiazole.—(i) This base (4 g.) with methyl iodide (6 ml.) at 100° for 6—7 hr. gave 3-methyl-2-phenyliminobenzothiazoline (3 g.), m. p. 96° (after recrystallisation, undepressed by a specimen prepared from 2-imino-3-methylbenzothiazoline and aniline), and gum which yielded 0·5 g. of the picrate of this (m. p. 162°) and 1·1 g. of 2-*N*-methylanilinobenzothiazole picrate, m. p. 184° (after recrystallisation, undepressed by an authentic specimen). (ii) Methylation of the base (2 g.) in ethanolic sodium ethoxide with dimethyl sulphate (12 ml.) gave 2-*N*-methylanilinobenzothiazole picrate (2·7 g.) and the picrate (1·15 g.) of the isomer.

2-cyclo*Hexylaminobenzothiazole.*—The *base*, prepared from *N-cyclo*hexyl-*N′*-phenyl(thiourea) (m. p. 145—146°) and crystallised from methanol, had m. p. 103—104° (Found: C, 67·4; H, 6·7; N, 11·9; S, 13·7. $C_{13}H_{16}N_2S$ requires C, 67·2; H, 6·9; N, 12·1; S, 13·8%). The *picrate* formed needles (from ethyl acetate), m. p. 233—234° (Found: S, 7·1. $C_{13}H_{16}N_2S,C_6H_3O_7N_3$ requires S, 6·9%). The gum obtained by methylation of this base (2 g.) with methyl iodide (3 ml.) at 100° for 18 hr. gave solely 2-cyclo*hexylimino*-3-*methylbenzothiazoline picrate*, m. p. 145° (after recrystallisation) undepressed on admixture with a specimen obtained from the base prepared by heating 2-imino-3-methylbenzothiazoline and *cyclo*hexylamine at 185—190° (Found: C, 50·8; H, 4·5; S, 6·4. $C_{14}H_{18}N_2S,C_6H_3O_7N_3$ requires C, 50·5; H, 4·4; S, 6·7%).

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