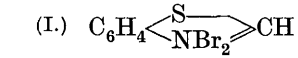
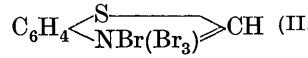
XXI.—*The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part I. Benzthiazole and Dihydrobenzthiazole Derivatives.*

By ROBERT FERGUS HUNTER.

THE objects of this series of investigations are: to study the chemistry of the azole bromides, to compare the mobility of symmetrical and unsymmetrical semicyclic triad systems, and to correlate the additive properties of such heterocyclic derivatives with their behaviour as tautomeric substances.

Benzthiazole was chosen as the starting point of the investigation. According to the conditions of bromination it gave rise either to a well-defined *dibromide* or to an unstable *tetrabromide*, to which the formulæ (I) and (II) respectively are assigned on the following grounds.

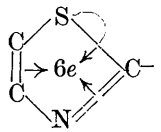
(I.)   (II.)

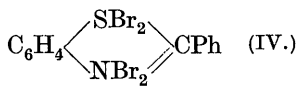
(i) The colour, thermal dissociation, and the ease with which the compounds regenerate the original base on treatment with sulphurous acid, hydriodic acid, ammonia, and similar reagents show that they are additive compounds. (ii) The inability of thiophen to give rise to anything in the nature of an additive complex with bromine under the mildest conditions, the existence of pyridine tetrabromide (Trowbridge, *J. Amer. Chem. Soc.*, 1897, **19**, 558), and the preparation of quinoline tetrabromide (Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124) in a condition of reasonable purity (p. 132) indicate that the nuclear nitrogen atom is the seat of unsaturation in the thiazole ring.

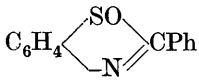
Regarding the electronic formulation of such compounds, it is suggested, since the fifth nitrogen valency is always an electrovalency, that the labile bromine atoms in the dibromide (I) are held by the nuclear nitrogen atom by means of semipolar single bonds, after the manner in which the labile chlorine atoms in phosphorus pentachloride are supposed to be held by the phosphorus atom (Prideaux, *Chem. and Ind.*, 1923, **42**, 672; Ingold and Ingold, J., 1926, 1315; Sugden, J., 1927, 1176). On such a basis, the elimination of Br_2 in preference to $\bar{B}r$ ion from the higher compounds and the facility with which many of the compounds, such as 1-aminobenzthiazole dibromide, pass into the hydrobromides of the corresponding 5-bromo-substituted bases (reversion to ammonium-ion structure) are readily accounted for. The inhibitory effect of the nitro-group on the formation of such compounds (Hunter, J., 1926, 538) also becomes explicable, since the positive end of the semi-

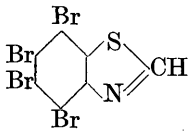
polar double bond, $\overset{-}{O}=\overset{+}{N}\cdot C\curvearrowright$, would tend to attract electrons from all parts of the molecule.

The formation of a tetrabromide (II) by a repetition of the process of singlet sharing is not difficult to visualise, but there is, however, the possibility that the second pair of labile electrons of the nuclear sulphur atom which are not required for the formation of the sextuple group (III) (Armit and Robinson, J., 1925, **127**, 1605; Goss and Ingold, J., 1928, 1268) might become sufficiently activated, under certain conditions, to give rise to a tetrabromide of the type (IV). On the other hand, the inability of stable tetrabromides, such as 1-phenylbenzthiazole tetrabromide, to yield sulphoxides of the type (V) is strong evidence in favour of the formula (II).

(III.) 


(IV.)

(V.) 


(VI.)

The bromides of benzthiazole present a direct anomaly to all the other compounds of the series in their conversion into a *tetrabromobenzthiazole* under the influence of hydroxylic solvents.

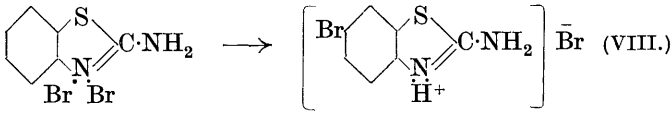
The lack of reactivity of the halogen atoms in this tetrabromo-compound in contrast to the behaviour of 1-chlorobenzthiazole towards hydroxylic and reducing agents (Hofmann, *Ber.*, 1879, **12**, 1126; 1880, **13**, 11) appears sufficient evidence for assigning the formula (VI) to the compound. The formation of a similar compound by quinoline (Claus and Istel, *Ber.*, 1882, **15**, 820) emphasises the close relationship existing between benzthiazole and quinoline derivatives.

The tautomeric mobility and the behaviour towards bromine of benzthiazole derivatives containing the triad systems [H]N·C:N $\rightleftharpoons$ N:C·N[H],[H]N·C:O $\rightleftharpoons$ N:C·O[H], and [H]N·C:S $\rightleftharpoons$ N:C·S[H] were next studied.

1-*Aminobenzthiazole.*—The mobility of the symmetrical triad system in 1-aminobenzthiazole has already been established by evidence of the symmetry and substitution type (Hunter, J., 1926, 1385; Hunter and Styles, J., 1928, 3019).

On treatment with a molecular equivalent of bromine at a low temperature, 1-aminobenzthiazole yielded a labile *dibromide* (VII), which, on exposure to air, or when the temperature of the solution

was allowed to rise, was quantitatively converted into the *hydrobromide* of 5-bromo-1-aminobenzthiazole (VIII).



The facility with which the transformation takes place suggests that the mechanism may involve a para-bridged form of 1-aminobenzthiazole, analogous to the formula which Shearer (*Proc. Physical Soc.*, 1923, **35**, ii, 81) has suggested for naphthalene on the basis of *X*-ray analysis (compare Hunter, J., 1926, 1390; Ingold, J., 1923, **123**, 2081).

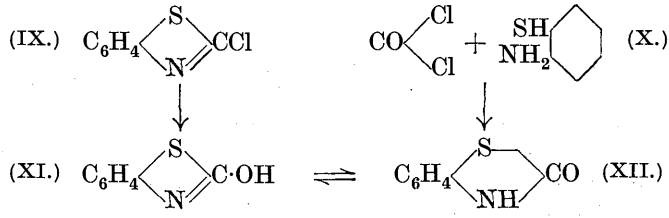
In the presence of excess of bromine, 1-aminobenzthiazole gave rise to an unstable *tetrabromide*, which resembled the dibromide in the ease with which it was converted into 5-bromo-1-aminobenzthiazole hydrobromide.

In the course of these experiments, the bromination of phenylthiocarbamide in chloroform was reinvestigated. The " dibromide of 1-aminobenzthiazole " obtained in this reaction (Hunter, J., 1926, 1389) and described by Hugershoff (*Ber.*, 1901, **34**, 3130) as a bromocarbaminophenylbromoaminodisulphide is actually a *hydrodibromide* of 1-aminobenzthiazole, which can readily be obtained from solutions of the hydrobromide of the amino-base and bromine in inert solvents.

The constitution of this hydrodibromide is a question of considerable importance. In the first place, it is desired to emphasise that the substance is a definite compound and that it is not a eutectic mixture of the hydrobromide of 1-aminobenzthiazole and a hypothetical hydrotribromide. It crystallises from solutions of different concentrations of the components (above a certain minimum concentration of bromine) in inert solvents, and all attempts to prepare the hypothetical hydrotribromide by employing a considerable excess of bromine have failed. Moreover, the remarkable stability of the substance (p. 134) does not appear to be capable of interpretation on the basis of the " physical mixture " type of explanation. It is therefore suggested that the compound may have a structure of the type (Base, $\overset{+}{\mathrm{H}})\overset{-}{\mathrm{Br}}_2$, containing the hitherto unknown $\overset{-}{\mathrm{Br}}_2$ ion, and involving the operation of a lone singlet linkage.*

* Similar corrections must be applied to all the even-numbered bromides obtained from arylthiocarbamides described in earlier papers (Hunter, J., 1925, **127**, 2023, 2270; 1926, 1385, 1401, 2951; Hunter and Soyka, *ibid.*, p. 2958; Dyson, Hunter, and Soyka, *ibid.*, p. 2964; Dyson, Hunter, and

Mobility and Bromination of 1-*Hydroxybenzthiazole*.—The mobility of 1-hydroxybenzthiazole was investigated in a manner similar to that of 1-aminobenzthiazole (*loc. cit.*). 1-Hydroxybenzthiazole (XI), prepared by hydrolysis of 1-chlorobenzthiazole (Hofmann, *Ber.*, 1879, **12**, 1126) (IX), was shown to be identical with the keto-dihydrobenzthiazole (XII) obtained by treating *o*-aminophenyl-mercaptan with carbonyl chloride. The low-melting ketodihydro-benzthiazole described by Claasz (*Ber.*, 1912, **45**, 1029; compare also Mills and Whitworth, J., 1927, 2752) was shown to be impure 1-hydroxybenzthiazole.



On methylation with methyl sulphate in the presence of potassium hydroxide, however, 1-hydroxybenzthiazole yielded exclusively 1-keto-2-methyl-1 : 2-dihydrobenzthiazole (Besthorn, *Ber.*, 1910, **43**, 1523), no trace of the isomeric *O*-methyl derivative being isolable.

On bromination in chloroform at a low temperature, 1-hydroxy-benzthiazole yielded a highly unstable bromo-addition compound which immediately lost hydrogen bromide with the production of 5-*bromo*-1-*hydroxybenzthiazole* (XVI), whose constitution was established by its synthesis from p-*bromophenylthiourethane* (XIII) by

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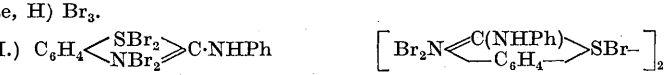
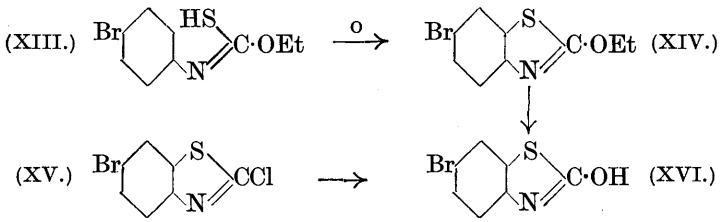
Morris, J., 1927, 1186; Hunter and Styles, *ibid.*, p. 1209; J., 1928, 3019; Hunter and Pride, J., 1929, 943). These compounds are all *hydroperbromides* and are quite distinct from the *true* bromides obtained from the bases themselves, from which they frequently differ in composition only by a hydrogen atom which cannot be detected by analysis. The formula (I) assigned to Hugershoff's 1-anilinobenzthiazole tetrabromide (*Ber.*, 1903, **36**, 3121) and to similar compounds (Hunter, J., 1925, **127**, 2024) is incorrect. The supposed bimeric tribromides (II) (*loc. cit.*) are hydrotribromides of the type $(\text{Base}, \overset{+}{\text{H}})\ \overset{-}{\text{Br}}_3$.



Similar remarks apply to the supposed hexabromides (J., 1925, **127**, 2024, 2270, etc.).

The increase of stability in a homologous series of 1-alkylaminobenzthiazole bromides (J., 1926, 2951) can no longer be regarded as due to an enhancement of tautomeric equilibrium in favour of the alkylamino-phase with increase in the atomic volume of the alkyl group.

way of 5-*bromo*-1-*ethoxybenzthiazole* (XIV), and also by its formation in the hydrolysis of 1-chloro-5-bromobenzthiazole (XV).



Mobility and Bromination of 1-*Thiolbenzthiazole.*—1-Thio-1 : 2-dihydrobenzthiazole (XVIII) obtained from thiocarbonyl chloride and *o*-aminophenylmercaptan proved to be identical with 1-thiolbenzthiazole (XVII), prepared from carbon disulphide and *o*-aminophenylmercaptan, whose identity with the mercaptan obtained from 1-chlorobenzthiazole and potassium hydrosulphide was established by Hofmann in 1887 (*Ber.*, **20**, 1788) (XVII and XVIII are XI and XII respectively with S in place of O).

Methylation of 1-thiolbenzthiazole, however, yielded the *S*-methyl derivative (XIX), unaccompanied by the isomeric thiomethyldihydrobenzthiazole (XX).

Bromination of 1-thiolbenzthiazole gave rise to a *tetrabromo*-addition compound, which yielded solely benzthiazolyl 1 : 1-disulphide on reduction with sulphurous acid.

Bromination of 1-*Phenylbenz-thiazole, -selenazole, and -oxazole.*

The bromination of 1-phenylbenzthiazole and of its selenium analogue gave rise to closely similar tetrabromides * (compare Fromm and Martin, *Annalen*, 1913, **401**, 178).

On the other hand, 1-phenylbenzoxazole yielded an unstable hexabromide, which rapidly lost bromine, giving a stable *hydrotribromide* of 5(?)-bromo-1-phenylbenzoxazole.

1 : 2-*Dihydrobenzthiazole Derivatives.*—Reduction of the double

* Some years ago, 1-phenylbenzthiazole tetrabromide was accidentally isolated in two forms, m. p. 126° and 153° respectively (J., 1926, 538). We have been unable to repeat this observation, using pure phenylbenzthiazole, only one tetrabromide (m. p. 134—136°) being isolated. Since benzthiazole prepared by Mohlau's method (*Ber.*, 1888, **21**, 59) and not specially purified (p. 131) yields a bromo-addition compound quite distinct from the dibromide and the tetrabromide obtained from the pure base, the original observation was probably due to the presence of an impurity introduced in the thionation process which was used in preparing the original specimen of phenylbenzthiazole from benzylideneaniline.

bond (1 : 2) of benzthiazole would be expected to lead to a decrease in the aromatic characteristics of the heterocyclic nucleus, and the bromination of certain 2-alkyl-1 : 2-dihydrobenzthiazoles was therefore undertaken.

The 1-imino-2-alkyl-1 : 2-dihydrobenzthiazoles (XXI) passed directly into the *hydrotribromides* of the corresponding 5-bromo-derivatives on bromination under the usual conditions. On the other hand, the 1-keto-2-alkyl-1 : 2-dihydrobenzthiazoles (XXII) yielded unstable *tetrabromides*, which were rapidly converted into the corresponding 5-bromo-1-keto-derivatives by loss of bromine and hydrogen bromide.

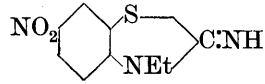
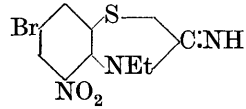
The order of stability of the bromo-addition compounds is therefore the reverse of that observed in the case of the mobile 1-amino- and 1-hydroxy-benzthiazoles.

(XXI.)   (XXII.)

1-Thio-2-methyl-1 : 2-dihydrobenzthiazole (XX) yielded a *tetrabromide*, which regenerated the original thioketone on reduction, and could not be converted into a bromo-substitution derivative.

Regarding the Hugershoff reaction, *as*-phenylmethylthiocarbamide gave rise to an unstable *hydropentabromide* of 1-imino-2-methyl-1 : 2-dihydrobenzthiazole, which lost bromine on exposure to air, giving a *hydrodibromide*. The ethyl homologue, however, yielded a stable *hydrotribromide*, which is of interest on account of its behaviour on nitration.

Under conditions of mononitration, the hydrotribromide yielded, approximately in the proportion of 2 : 5, 5-*nitro*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* (XXIII) and a bromonitro-derivative, which was also obtained from the mononitration of 5-*bromo*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* and its *hydrotribromide* and is presumably 5-*bromo*-3-*nitro*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* (XXIV).

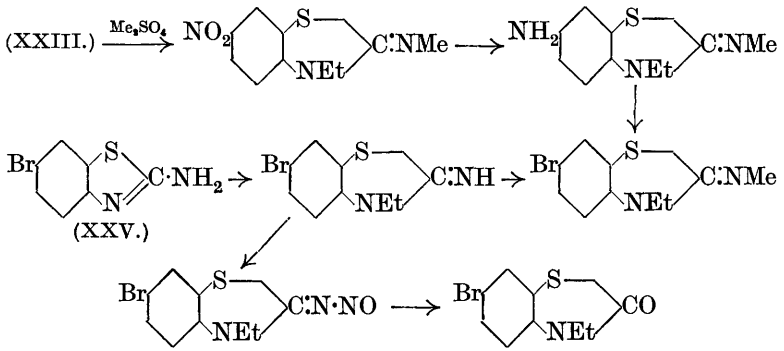
(XXIII.)   (XXIV.)

Nitration of the *hydrobromide* of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole under similar conditions also gave rise to the same products in the approximate proportion of 2 : 1 in favour of the 5-nitro-1-imino-derivative.

The first action of nitric acid (*d* 1·5) is evidently one of decomposition, possibly with the production of nitrosyl bromide, which may act as a brominating agent on the portion of the base initially escaping nitration.

Mononitration of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole and its *acetyl* derivative lead to exclusive nitration in the 5-position of the benzthiazole system, and 1-keto-2-ethyl-1 : 2-dihydrobenzthiazole behaves similarly.

The 5-bromo and 5-nitro-derivatives described in this paper were oriented by means of the following scheme [the constitution of 5-bromo-1-aminobenzthiazole (XXV) follows from its synthesis from *p*-bromophenylthiocarbamide (Hunter, J., 1926, 1397)].



EXPERIMENTAL.

Benzthiazole Derivatives.

Benzthiazole was prepared by the thionation of dimethylaniline (Mohlau, *Ber.*, 1888, **21**, 59), purified by means of the crystalline nitrate (Mills, J., 1922, **121**, 460), and redistilled over copper turnings. The pure base was a colourless, highly refractive oil, indistinguishable from quinoline in odour, b. p. 227—228°/765 mm., $d_4^{14°}$ 1·244. Specimens (b. p. 226—228°) of the base which had not been redistilled over copper, when kept for some months, darkened and acquired the unpleasant odour of the crude thionation product. Such specimens behaved abnormally on bromination (p. 132).

Benzthiazole Dibromide.—(i) A solution of the pure base (1·1 c.c.) in chloroform (12 c.c.) was treated at 0—3° with bromine (0·7 c.c. in 2 c.c. of chloroform). After a short time, the *dibromide* crystallised in glistening yellow needles, which were collected on porous earthenware and dried in a vacuum; m. p. 88—90° (decomp.) [Found : N, 4·9; Br (total), 54·5; Br (labile), iodometrically in chloroform containing a few drops of purified acetic acid, 54·4; S, 10·9. $C_7H_5NBr_2S$ requires N, 4·7; Br (total and labile), 54·3; S, 10·8%].

(ii) The compound was prepared in a similar manner from benzthiazole (1·2 g.), glacial acetic acid (7 c.c.), and a solution of bromine

(0·7 c.c.) in acetic acid (1 c.c.); m. p. 87—88° (decomp.) [Found : Br (total), 54·1; Br (labile), 54·0%].

The yellow crystals of the dibromide were stable in a vacuum, but rapidly reddened at the edges in moist air. The compound was quantitatively reduced by sulphurous acid, giving a colourless solution from which the original base was recovered by basification and extraction with ether; a similar decomposition, accompanied by evolution of nitrogen, took place when the dibromide was treated with aqueous ammonia (*d* 0·880). It was also decomposed by sulphuric acid at a low temperature (0—3°; 20 c.c. of 99% acid per g. of dibromide) with evolution of hydrogen bromide and regeneration of benzthiazole. *Thermal decomposition.* The dibromide was heated from 60° to 140°/18 mm. in the course of 10 minutes : fusion commenced at 100—105° and was complete at 115°. Reduction of the product by sulphurous acid yielded benzthiazole unaccompanied by the tetrabromo-substitution derivative.

Benzthiazole Tetrabromide.—Experiment (i) was repeated, 1·8 c.c. of bromine being used. A *tetrabromide* separated in small scarlet crystals, which were dried on porous earthenware in a vacuum for 5—10 minutes and then analysed; m. p. 67—68° (Found : Br, 70·0. $C_7H_5NBr_4S$ requires Br, 70·3%). This compound decomposed appreciably on being exposed to the atmosphere for a few minutes; in its reactions, it behaved similarly to the dibromide.*

When an experiment similar to (i) was performed with benzthiazole which had not been purified by redistillation over copper and had been kept for some months (2 g. of base, 24 c.c. of chloroform, and 1·3 c.c. of bromine), orange crystals of a *bromo*-addition compound separated, which had m. p. 100—103° (decomp.) after drying in a vacuum [Found : Br (total), 63·2; Br (labile), 63·0. $(C_7H_5NBr_3S)_2$ requires Br, 64·0%]. The substance dissolved in sulphurous acid, yielding a colourless solution from which, on basification and extraction with ether, benzthiazole was obtained; this was identified by its properties and by the analysis of its chloroplatinite (Found : Pt, 28·5. Calc. : Pt, 29·1%).

3 : 4 : 5 : 6-*Tetrabromobenzthiazole.*—When solutions of any of the preceding bromo-addition compounds in 70% alcohol were boiled for a short time and allowed to cool, the *tetrabromobenzthiazole* crystallised in glistening hair-like needles, m. p. 122° (Found : Br, 70·9; S, 6·9. C_7HNBr_4S requires Br, 70·9; S, 7·1%). This com-

* Quinoline tetrabromide (Grimaux, *loc. cit.*) was best prepared by treating a solution of quinoline (1 c.c.) in chloroform (12 c.c.) at 25—30° with bromine (2 c.c. in 3 c.c. of chloroform) and shaking the mixture : the temperature rose some 10° and the tetrabromide crystallised in glistening red plates, m. p. 95—97° [Found : Br (total), 70·4; Br (labile), 69·2. Calc. : Br, 71·3%].

pound was recovered unchanged after being heated under reflux in alcoholic solution containing about 10% of hydrochloric acid for 40 hours, and also after being heated (0·5 g.) with tin (1 g.) and concentrated hydrochloric acid (20 c.c.) for ½ hour. An attempt to reduce it (0·5 g.) in absolute alcohol (20 c.c.) with sodium (0·4 g.) also proved unsuccessful. The tetrabromobenzthiazole has no basic properties in the ordinary sense; although it dissolves in 98—99% sulphuric acid, it is reprecipitated by dilution with water. All attempts to prepare a bromo-addition compound of the tetrabromobenzthiazole proved unsuccessful.

1-*Aminobenzthiazole Dibromide.*—When a solution of 1·5 g. of 1-aminobenzthiazole in 50 c.c. of chloroform at 0° was gradually treated with a solution of bromine (0·7 c.c.) in the same solvent (3 c.c.), a yellow precipitate was produced which redissolved, giving a clear solution; the *dibromide* then separated in small, soft, orange-pink crystals, which were rapidly dried in a vacuum. This compound became pale yellow at 160—170° and had m. p. 265° (decomp.) (Found: Br, 51·8. $C_7H_6N_2Br_2S$ requires Br, 51·5%).

A solution of the compound in purified acetic acid liberated iodine from potassium iodide, but the iodometric titre was always low (*ca.* 30%) on account of partial isomerisation into the hydrobromide of 5-bromo-1-aminobenzthiazole.

The dibromide was converted into 5-bromo-1-aminobenzthiazole hydrobromide by exposure to air; the change, which was accompanied by loss of colour, was appreciable in ¼ hour and complete in less than 20 hours. The product was identified by its m. p. (265°), by the m. p. of the base liberated by alkali (210°), and by the m. p. of the acetyl derivative of the latter (222°). The dibromide was also isomerised by cold acetic anhydride.

1-*Aminobenzthiazole tetrabromide*, obtained by employing an excess of bromine, formed small, soft, dark reddish-brown plates, m. p. 266° (decomp.; sintering with loss of bromine at 170°) (Found: Br, 67·6. $C_7H_6N_2Br_4S$ requires Br, 68·1%).

1-*Aminobenzthiazole Hydrodibromide* (*Hugershoff's Dibromide*).—(i) A suspension of 1·5 g. of finely ground phenylthiocarbamide in 15 c.c. of chloroform was rapidly treated with bromine (1·4 c.c. in 1·4 c.c. of chloroform), and the mixture heated under reflux for 2—3 minutes. The *hydrodibromide* separated from the hot solution in glistening, orange-coloured, rhombic crystals, which were crushed on porous earthenware and dried in a vacuum; m. p. 127—128° (decomp. with efferv. at 131°) [Found: Br (total), 51·4; Br (labile), 24·9; S, 10·3. $C_7H_6N_2S$,HBr(Br) requires Br (total), 51·5; Br (labile), 25·6; S, 10·3%].

(ii) Bromine (1·6 c.c.) was added to a boiling solution of 1-amino-

benzthiazole (1 g.) in glacial acetic acid (24 c.c.) containing 4 g. of hydrogen bromide. The hydrodibromide crystallised in large orange-red prisms, m. p. 128—130° after drying in a vacuum [Found: Br (total), 51·2; Br (labile), 24·6; S, 10·6%]. A mixture of the two specimens melted at 128—130°.

This compound remained unchanged in a vacuum, or over potassium hydroxide in a desiccator. On prolonged exposure to the atmosphere (8—9 months), it lost bromine, yielding 1-aminobenzthiazole hydrobromide, m. p. 231—232°.

When the compound (3 g.) was heated with acetic anhydride (7 c.c.), the solution developed a pink colour and a white precipitate (2·2 g.) separated, containing impure 5-bromo-1-acetamidobenzthiazole (0·25 g.), which was identified by mixed m. p. and by hydrolysis to 5-bromo-1-aminobenzthiazole by 60% sulphuric acid, and 1-aminobenzthiazole hydrobromide (1·8 g.).

Thermal decomposition. A flask containing the hydrodibromide (1·7 g.) was exhausted to 11 mm., placed in an oil-bath at 125°, and heated to 210° in the course of ¼ hour; decomposition was then complete. The greyish-white granular residue (1·25 g.) consisted of 1-aminobenzthiazole hydrobromide, m. p. 228°. *Dissociation experiments.* (i) Three experiments were made with specimens of the hydrodibromide of different surface areas: the specimens were heated at 90—100°/10 mm. for 10 minutes, and the residues analysed for labile bromine. The results [Found: Br (labile), 20·8, 19·6, 19·9%] indicate that this factor has only a slight effect on the dissociation. (ii) Two similar experiments were performed at 97—98°/12 mm. for 2 minutes [Found: Br (labile), 24·1, 23·8%]. The degree of dissociation in these circumstances is about 5%.

1-*Anilinobenzthiazole Tetrabromide.*—Hugershoff's tetrabromide (*Ber.*, 1903, **36**, 3121) crystallised in red needles, m. p. 127° (decomp.) (previously given, J., 1925, **127**, 2025, as 117°) [Found: Br (total), 58·8; Br (labile), 40·1. Calc. for $C_{13}H_{10}N_2S,HBr(Br_3)$: Br (total), 58·6; Br (labile), 43·9%]. The *hydrotribromide* had m. p. 130° (decomp.) (previously given as 125°) [Found: Br (total), 51·5; Br (labile), 32·5. Calc. for $C_{13}H_{10}N_2S,HBr(Br_2)$: Br (total), 51·7; Br (labile), 34·4%]. The hydrotetrabromide was also prepared from a solution of the anilino-base (0·5 g.) and hydrogen bromide (0·5 g.) in glacial acetic acid (5·5 c.c.) and bromine (0·5 c.c.), and identified by m. p., mixed m. p., and analysis [Found: Br (total), 58·4; Br (labile), 39·8%].

1-p-*Toluidino-5-methylbenzthiazole hydrotetrabromide,* prepared from *s*-di-*p*-tolylthiocarbamide (J., 1925, **127**, 2027), formed red needles, m. p. 130—132° (decomp.) (previously given as 145°) [Found:

Br (total), 55·2; Br (labile), 36·6. Calc. for $C_{15}H_{14}N_2S,HBr(Br_3)$: Br (total), 55·6; Br (labile), 41·7%]. Its composition was not appreciably affected by keeping over potassium hydroxide in a desiccator for 2 days [Found: Br (labile), 36·4%]. It was also prepared from the toluidinobenzthiazole and hydrogen bromide in acetic acid and excess of bromine, and identified by m. p., mixed m. p., and analysis [Found: Br (labile), 36·4%]. The *hydrotribromide* had m. p. 145—147° (previously given as 148°) [Found: Br (total), 48·8; Br (labile), 31·5. Calc. for $C_{15}H_{14}N_2S,HBr(Br_2)$: Br (total), 48·5; Br (labile), 32·3%]. 3 : 2′-Dibromo-1-anilino-5 : 4′-dimethylbenzthiazole, prepared by heating a mixture of *s*-di-*o*-bromo-*p*-tolylthiocarbamide (0·5 g.), chloroform (6 c.c.), and bromine (0·6 c.c.) under reflux for 15 minutes and reducing the product with sulphurous acid, separated from alcohol in small prisms, m. p. 159—160°, which did not depress the m. p. of a specimen of the dibromotoluidinobenzthiazole described in 1925 (J., **127**, 2027).

5 : 4′-*Dibromo*-1-*anilino*-3 : 2′-*dimethylbenzthiazole*.—(i) The dibromo-base obtained from the hydrohexabromide of 1-*o*-toluidino-3-methylbenzthiazole (J., 1925, **127**, 2026) separated from alcohol–ethyl acetate in small needles, m. p. 210—211° (Found: Br, 38·6. Calc.: Br, 38·9%).

(ii) The *bromo*-addition compound obtained by heating a mixture of *s*-di-*p*-bromo-*o*-tolylthiocarbamide (1 g.), chloroform (17 c.c.), and bromine (1·3 c.c.) under reflux for 15 minutes formed dark crimson crystals, which became colourless at 180—190° and charred at 270° (Found: Br, 60·0. $C_{15}H_{12}N_2Br_2S,HBr(Br_2)$ requires Br, 61·3%). 5 : 4′-Dibromo-1-anilino-3 : 2′-dimethylbenzthiazole obtained by reduction of this bromo-addition compound proved identical with that described under (i).

The Mobility of 1-*Hydroxybenzthiazole. Synthesis from* 1-*Chlorobenzthiazole and from* o-*Aminophenylmercaptan and Carbonyl Chloride.*—(i) 1-Hydroxybenzthiazole was prepared by heating an alcoholic solution of 1-chlorobenzthiazole containing hydrochloric acid for 25 hours; on recrystallisation from alcohol, it formed glistening prisms, m. p. 138°.

(ii) *Claasz's experiment.* 25 G. of a 12% solution of carbonyl chloride in toluene were added to an ethereal solution of *o*-aminophenylmercaptan (2·5 g. in 40 c.c.) and the mixed liquids were decanted from the precipitate of *o*-aminophenylmercaptan hydrochloride and evaporated on a steam-bath. Extraction of the resulting oil with alkali, acidification of the extract, extraction with chloroform, and recrystallisation of the product from methyl alcohol yielded 1-hydroxybenzthiazole, which melted at 128—130° and at 134° when mixed with a genuine specimen prepared by Hofmann's

method. The identity was confirmed by conversion of the product into 5-bromo-1-hydroxybenzthiazole, identical with that prepared by other methods.

(iii) A solution of *o*-aminophenylmercaptan (1·2 c.c.) in chloroform (10 c.c.) was treated with carbonyl chloride from a cylinder for ½ hour, the mixture evaporated on a steam-bath, and the product extracted with ether. After removal of the ether, the crystalline residue separated from methyl alcohol in prisms (0·9 g.), m. p. 135°, and 135—136° when mixed with the specimen prepared under (i).

Methylation of 1-*Hydroxybenzthiazole and the Isolation of* 1-*Keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole.*—1-Hydroxybenzthiazole was recovered unchanged after it had been heated with methyl sulphate (1·5 c.c. for 1 g.) at 100° for ½ hour, the solution diluted with water (8 c.c.), and the heating continued for another hour.

4 C.c. of methyl sulphate were added to a mixture of 0·5 g. of 1-hydroxybenzthiazole and 1 c.c. of chloroform in 10 c.c. of 25% potassium hydroxide solution and the whole was shaken and kept for an hour. Extraction with chloroform and slow removal of the solvent yielded a gum which set to a crystalline mass of 1-keto-2-methyl-1 : 2-dihydrobenzthiazole, m. p. 74°, and 76° when mixed with an authentic specimen prepared from the 1-nitrosoimino-derivative (Besthorn, *Ber.*, 1910, **43**, 1523). The identity was further established by conversion of the product into 5-bromo-1-keto-2-methyl-1 : 2-dihydrobenzthiazole, which melted at 126—127° alone and when mixed with the specimen described on p. 140.

Bromination of 1-*Hydroxybenzthiazole and the Synthesis of* 5-*Bromo*-1-*hydroxybenzthiazole from* 1-*Chloro*-5-*bromobenzthiazole and from* p-*Bromophenylthiourethane by Way of* 5-*Bromo*-1-*ethoxybenzthiazole.*—(i) When a solution of 0·5 g. of 1-hydroxybenzthiazole in chloroform (6 c.c.) was treated with 0·5 c.c. of bromine at 0—3°, hydrogen bromide was evolved; the solution was concentrated under reduced pressure at laboratory temperature, and 5-*bromo*-1-*hydroxybenzthiazole* obtained. On recrystallisation from methyl alcohol, this formed needles, m. p. 225—226° (Found : Br, 35·1. C_7H_4ONBrS requires Br, 34·8%). It dissolved in alkalis and was reprecipitated by mineral acids. It was recovered unchanged after being heated with methyl iodide (more than 3 equivs.) at 100° for 25 hours.

(ii) 0·5 G. of 1-chloro-5-bromobenzthiazole (b. p. 158—159°/18 mm.; Dyson, Hunter, and Soyka, J., 1929, 461) was heated with alcohol, containing hydrochloric acid, for 40—45 hours. The resulting solution was made alkaline, filtered, and acidified with 20% acetic acid. The precipitate of 5-bromo-1-hydroxybenzthiazole was recrystallised from alcohol and identified by m. p. and mixed m. p. determination with the specimen prepared in (i).

(iii) p-*Bromophenylthiourethane*, prepared in 80—90% yield by heating a solution of *p*-bromophenylthiocarbimide (15 g.) in absolute alcohol (100 c.c.) under reflux for 30 hours, separated from methyl alcohol in prisms, m. p. 106—107° (Found : S, 12·5. $C_9H_{10}ONBrS$ requires S, 12·3%).

5-*Bromo*-1-*ethoxybenzthiazole*. 10 G. of *p*-bromophenylthiourethane, previously ground with a little alcohol, were dissolved in 75 c.c. of 30% aqueous sodium hydroxide; the solution was diluted to 200 c.c. with water and added in 20 c.c. portions at 5-minute intervals to a well-stirred solution of potassium ferricyanide (60 g.) in water (300 c.c.) which was maintained at 80—90°. Extraction with ether yielded a brown oil, which was distilled in steam; the *bromoethoxybenzthiazole* obtained (yield, 35%) separated from 90% methyl alcohol in pale yellow plates, m. p. 75—76° (Found : Br, 31·4. C_9H_8ONBrS requires Br, 31·0%). *Hydrolysis*. A solution of the bromoethoxythiazole in 40% hydrobromic acid was heated under reflux for 20 minutes and cooled; crystals then separated. The mixture was diluted with water and extracted with chloroform and the chloroform was removed on a steam-bath; the 5-bromo-1-hydroxybenzthiazole obtained crystallised from methyl alcohol in needles, m. p. 222—223°, 223° when mixed with the specimen prepared in (i).

The Mobility of 1-*Thiolbenzthiazole. Synthesis by Hofmann's Method and from* o-*Aminophenylmercaptan and Thiocarbonyl Chloride*. —(i) 1-Thiolbenzthiazole was prepared by heating a solution of *o*-aminophenylmercaptan (3 g.) in alcohol (10 c.c.) and carbon disulphide (15 c.c.) under reflux for 8 hours. After two recrystallisations from methyl alcohol (animal charcoal), it formed colourless needles, m. p. 179° (Hofmann, *Ber.*, 1887, **20**, 1879; Jacobson and Frankenbacher, *Ber.*, 1891, **24**, 1403, recorded m. p. 174°).

(ii) Thiocarbonyl chloride (1 c.c.) in chloroform (2 c.c.) was gradually added to *o*-aminophenylmercaptan (2 c.c.) in chloroform (10 c.c.) at 5°, the mixture being shaken after each addition. A vigorous reaction took place with the separation of yellow crystals; the chloroform and the excess of thiocarbonyl chloride were removed on a steam-bath, the product was extracted with ether (8 extractions), and the united extracts were filtered from the hydrochloride of *o*-aminophenylmercaptan. On removal of the ether and subsequent recrystallisation from methyl alcohol, 1-thiolbenzthiazole (0·7 g.) was obtained in pale yellow needles, m. p. 176—177°, and 177—179° when mixed with the specimen prepared by Hofmann's method.

Methylation. A mixture of 1-thiolbenzthiazole (1 g.), methyl sulphate (3 c.c.), and methyl alcohol (3 c.c.) was heated under reflux

for an hour. The solution was cooled, the excess of methyl sulphate decomposed with aqueous ammonia (*d* 0·880), and the mixture extracted while still warm with chloroform. A clear gum was obtained which on crystallisation from methyl alcohol yielded 0·9—1 g. of 1-methylthiolbenzthiazole in colourless prisms, m. p. 47—49°.

Bromination of 1-*Thiolbenzthiazole.*—A solution of the thiol (1 g.) in chloroform (50 c.c.) was treated with bromine (1·5 c.c. in an equal volume of the same solvent) at 10°; the *tetrabromide* formed orange plates, m. p. 147° (decomp. with efferv. after previous shrinking) (Found: Br, 65·6. $C_7H_5NBr_4S_2$ requires Br, 65·7%). On reduction with sulphurous acid, the tetrabromide yielded benzthiazolyl 1 : 1-disulphide, which crystallised from acetic acid in silvery plates, m. p. 180°, and 180—181° when mixed with a genuine specimen. (A mixture of this product with 1-thiolbenzthiazole melted at about 140°.)

1-*Phenylbenzthiazole Tetrabromide.*—1 G. of the base, purified by distillation under reduced pressure, was brominated as previously described (Hunter, J., 1926, 539); the *tetrabromide* crystallised in orange-red plates, m. p. 134—136° [Found: Br (total), 60·0; Br (labile), 45·3. Calc. for $C_{13}H_9NBr_4S$: Br, 60·25%]. Further crops of crystals, m. p. 130—132°, of the same tetrabromide were obtained from the mother-liquor by concentration under reduced pressure at laboratory temperature [Found: Br (labile), 45·0%].

Action of mercuric oxide. (i) When a mixture of precipitated mercuric oxide (1 g.) and the tetrabromide (0·6 g.) in chloroform (50 c.c.) was shaken, the colour was discharged. Evaporation of the filtered solution on a steam-bath yielded 1-phenylbenzthiazole unaccompanied by any trace of the 5-bromo-derivative (Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826).

(ii) A similar result was obtained with " dry " materials, excepting that the discharge of colour was somewhat retarded.

By treating a solution of 1-phenylbenzthiazole (1 g.) in chloroform (11 c.c.) with bromine (1·4 c.c.) at 0°, a red oil was obtained which sometimes crystallised in red needles; the *hexabromide* was unstable, m. p. 156° (decomp. with efferv. after sintering with loss of bromine over a range of about 40°) (Found: Br, 67·2. $C_{13}H_9NBr_6S$ requires Br, 69·5%).

Benzoxazole and Benzselenazole Derivatives.

Bromination of 1-*Phenylbenzoxazole.*—A solution of the phenylbenzoxazole (Ladenburg, *Ber.*, 1876, **9**, 1524) (0·5 g.) in chloroform (4 c.c.) was treated with bromine (0·9 c.c. in 1 c.c. of chloroform) at 0°. After an hour, the *hexabromo*-addition compound separated in small, soft, red crystals, m. p. 153—155° after rapid drying on

porous earthenware in a vacuum [Found: Br (total), 73·8; Br (labile), 54·9. $C_{13}H_9ONBr_6$ requires Br, 71·1%]. This substance lost bromine when kept over potassium hydroxide in a vacuum for 2 hours, giving a stable, yellow, microcrystalline *hydrotribromide* of 5(?)-bromo-1-phenylbenzoxazole, m. p. 154—155° (with previous shrinking) [Found: Br (total), 61·8; Br (labile), 31·5. $C_{13}H_8ONBr,HBr(Br_2)$ requires Br (total), 62·1; Br (labile), 31·1%]. A specimen of this compound prepared from the bromo-substituted benzoxazole, hydrogen bromide, and bromine in acetic acid had a higher m. p. (164—166° after previous shrinking) [Found: Br (labile), 31·3%], but lacked the stability in moist air of the specimen obtained from the hexabromide.

5(?)-*Bromo*-1-*phenylbenzoxazole*, obtained by reduction of the hydrotribromide with sulphurous acid, or by dissolution of the hexabromide in alcohol, crystallised from methyl alcohol in small needles, m. p. 106—107° (Found: Br, 28·3. $C_{13}H_8ONBr$ requires Br, 29·1%).

1-*Phenylbenzselenazole tetrabromide*, obtained from the selenazole, chloroform, and excess of bromine at 0°, and also at 18°, crystallised in orange-red needles, m. p. 148° [Found: Br (total), 55·1; Br (labile), 41·0. $C_{13}H_9NBr_4Se$ requires Br, 55·4%]. It regenerated the original phenylselenazole on treatment with sulphurous acid, but all attempts to prepare a 5-bromo-substitution derivative led only to brown gummy products, which could not be crystallised.

1 : 2-*Dihydrobenzthiazole Derivatives.*

1-*Imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole Hydropentabromide*.—A solution of *as*-phenylmethylthiocarbamide (1 g.) in chloroform (10 c.c.) was treated with bromine (2 c.c. in 3 c.c. of the same solvent) and heated under reflux for a few minutes. The *hydropentabromide* crystallised in red plates (or needles), m. p. 121—122° (decomp. with efferv.), which were rapidly dried in a vacuum and immediately analysed [Found: N, 5·25; Br (total), 71·0; Br (labile), 57·0; S, 5·7. $C_8H_8N_2S,HBr(Br_4)$ requires N, 4·95; Br (total), 70·8; Br (labile), 56·7; S, 5·6%]. On exposure to air for some weeks, it lost bromine, giving a stable, yellow, insoluble *hydrodibromide*, m. p. 194—196° (decomp.; sintering at 190°) [Found: Br, 49·3. $C_8H_8N_2S,HBr(Br)$ requires Br, 49·4%]. Both compounds yielded 1-imino-2-methyl-1 : 2-dihydrobenzthiazole, m. p. 123°, on reduction with sulphurous acid, but failed to undergo nuclear substitution when heated with alcohol, giving the *hydrobromide* of 1-imino-2-methyl-1 : 2-dihydrobenzthiazole (prepared also from the base and hydrogen bromide) in small needles, m. p. 275° (decomp.) (Found: Br, 32·5. $C_8H_8N_2S,HBr$ requires Br, 32·8%). The hydropenta-

bromide was also prepared by treating a solution of the hydrobromide in glacial acetic acid with excess of bromine.

1-*Acetimido*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, prepared by acetylation of the imino-base with acetic anhydride, crystallised from alcohol in needles, m. p. 141—142° (Found : S, 15·8. $C_{10}H_{10}ON_2S$ requires S, 15·5%).

Bromination of 1-*Imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*.—The *hydrotribromide* of 5-bromo-1-imino-2-methyl-1 : 2-dihydrobenzthiazole, obtained by treatment of the imino-base (0·5 g.) in chloroform (15 c.c.) with bromine (1 c.c. in 2 c.c. of the same solvent) at 0°, formed orange-yellow crystals which lost bromine at 100—110° and were unmelted at 280° [Found : N, 5·8; Br (total), 66·2; Br (labile), in acetic acid, 33·4; S, 6·6. $C_8H_7N_2BrS,HBr(Br_2)$ requires N, 5·8; Br (total), 66·1; Br (labile), 33·0; S, 6·6%]. The *hydrobromide* of 5-bromo-1-imino-2-methyl-1 : 2-dihydrobenzthiazole, obtained by boiling a solution of the hydrotribromide in alcohol, formed small needles, which were unmelted at 290° [Found : Br, 49·3. $C_8H_7N_2BrS,HBr$ requires Br, 49·3%]. The 5-*bromo-base* crystallised with difficulty from methyl alcohol in needles, m. p. 110° (Found : N, 11·8; Br, 32·9; S, 13·4. $C_8H_7N_2BrS$ requires N, 11·5; Br, 32·7; S, 13·2%). The *acetyl* derivative, prepared by means of acetic anhydride, crystallised from much ethyl acetate in feathery needles, m. p. 219—220° (Found : N, 9·8; Br, 28·2. $C_{10}H_9ON_2BrS$ requires N, 9·8; Br, 28·05%).

Bromination of 1-*Keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole and the Synthesis of* 5-*Bromo*-1-*keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole from* 5-*Bromo*-1-*imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole by Way of* 5-*Bromo*-1-*nitrosoimino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*.—When a solution of 1-keto-2-methyl-1 : 2-dihydrobenzthiazole (0·4 g.) in chloroform (4 c.c.) was treated with bromine (0·5 c.c. in 1 c.c. of chloroform) at 0°, traces of hydrogen bromide were evolved and a dark purple-brown *tetrabromide* separated, which was rapidly dried in a vacuum and immediately analysed (Found : Br, 67·8. $C_8H_7ONBr_4S$ requires Br, 65·9%). It softened at 100° and melted to a clear red liquid at 120°; in a vacuum, it lost bromine, yielding red crystals, m. p. 101—103°, of a substance having the composition of a *dibromide* (Found : Br, 48·6. $C_8H_7ONBr_2S$ requires Br, 49·2%). 5-*Bromo*-1-*keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole* crystallised in feathery tufts of silky needles, m. p. 126—127° (Found : N, 5·9; Br, 32·5; S, 13·2. C_8H_6ONBrS requires N, 5·7; Br, 32·6; S, 13·1%).

5-*Bromo*-1-*nitrosoimino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*.—A solution of 5-bromo-1-imino-2-methyl-1 : 2-dihydrobenzthiazole (2 g.) in glacial acetic acid (16 c.c.) was kept at 15° during the addition

of a solution of sodium nitrite (1 g.) in water (5 c.c.), the mixture being well shaken; the *nitroso*-derivative soon separated in orange crystals (2·1 g.), which exploded at 161° (Found: N, 15·5. $C_8H_6ON_3BrS$ requires N, 15·4%).

A solution of the nitroso-compound (1 g.) in xylene (6 c.c.), when heated, turned yellow and nitrogen was evolved; the solution was concentrated to about 2 c.c., diluted with methyl alcohol, boiled with animal charcoal, filtered, and concentrated; 5-bromo-1-keto-2-methyl-1 : 2-dihydrobenzthiazole (0·8 g.) was obtained in slender needles, m. p. 126—127°, alone and when mixed with the specimen already described.

1-*Thiol*-2-*methyl*-1 : 2-*dihydrobenzthiazole tetrabromide*, prepared from the thiol derivative and bromine in chloroform, formed small orange crystals, m. p. 124—126° (decomp.; reddening at 115—120°) (Found: Br, 63·7; S, 12·6. $C_8H_7NBr_4S_2$ requires Br, 63·9; S, 12·8%). When heated with absolute alcohol, it rapidly regenerated the original thiol derivative.

The bromination of 1-nitrosoimino-2-methyl-1 : 2-dihydrobenzthiazole yielded a brown *tetrabromide*, m. p. 280° (decomp.) (Found: Br, 61·9. $C_8H_7ON_3Br_4S$ requires Br, 62·4%).

1-Imino-2-ethyl-1 : 2-dihydrobenzthiazole is conveniently prepared in quantity by the following method, which is generally applicable to iminoalkyldihydrobenzthiazoles and alkylaminobenzthiazoles. A solution of *as*-phenylethylthiocarbamide (50 g.) in chloroform (250 c.c.) was treated with bromine (30 c.c. in 50 c.c. of the same solvent) with cooling. After being heated under reflux for 10 minutes, the mixture was treated with excess of sulphurous acid and basified, and the product obtained by removal of the chloroform was recrystallised from alcohol, the iminoethyldihydro-derivative forming large crystals, m. p. 84—85°. Yield, 49 g. (98%).

1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole hydrotribromide*, prepared from 1·5 g. of the ethylthiocarbamide in chloroform (12 c.c.) and bromine (2 c.c.), crystallised from the hot solution in orange-red plates, m. p. 160—161° (decomp.) [Found: N, 6·9; Br (total), 57·5; Br (labile), 38·5. $C_9H_{10}N_2S,HBr(Br_2)$ requires N, 6·7; Br (total), 57·3; Br (labile), 38·2%]. It was also prepared from the imino-base (0·5 g.) and hydrogen bromide (1 g.) in glacial acetic acid (9 c.c.) and bromine (1 c.c.). The alleged tetrabromide previously described (J., 1926, 1394) was a "wet" specimen of the hydrotribromide. An alcoholic solution of this compound, on being concentrated, yielded the *hydrobromide* of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole (which was also prepared from the base and hydrobromic acid) in plates, m. p. 247—248° (decomp.) (Found:

Br, 30·5. $C_9H_{10}N_2S,HBr$ requires Br, 30·9%). 1-*Acetimido*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* formed prisms, m. p. 127—128° (Found: N, 13·0; S, 14·6. $C_{11}H_{12}ON_2S$ requires N, 12·7; S. 14·55%).

Bromination of 1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole and the Ethylation of* 5-*Bromo*-1-*aminobenzthiazole.*—(i) The *hydrotribromide* of 5-bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, obtained by bromination of the imino-base, crystallised in orange needles, m. p. 182—184° (decomp.) [Found: Br (total), 64·2; Br (labile), iodometrically in acetic acid, 32·6. $C_9H_9N_2BrS,HBr(Br_2)$ requires Br (total), 64·2; Br (labile), 32·1%]. It was also prepared from the 5-bromo-base, hydrogen bromide, and bromine in acetic acid. Attempts to isolate an intermediate bromo-addition compound of the iminoethyl base by using dried materials were unsuccessful. The hydrotribromide was completely dissociated into the hydrobromide and bromine on being heated from 150° to 220°/16 mm. in the course of ½ hour. 5-*Bromo*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* formed a tenacious gum, which crystallised with difficulty from 80% methyl alcohol in small needles, m. p. 68—70° (Found: Br, 30·7. $C_9H_9N_2BrS$ requires Br, 31·1%). The *acetyl* derivative formed silvery needles, m. p. 187° (Found: Br, 26·7; S, 10·7. $C_{11}H_{11}ON_2BrS$ requires Br, 26·7; S, 10·7%). The *hydrobromide* crystallised from alcohol, containing a small quantity of hydrogen bromide, in small needles, m. p. 270—272° (Found: Br, 47·0. $C_9H_9N_2BrS,HBr$ requires Br, 47·3%).

(ii) A mixture of 5-bromo-1-aminobenzthiazole (0·5 g.) and ethyl iodide (1·5 c.c.) was heated at 100° for 18 hours, and the product basified and extracted with chloroform. After removal of the chloroform a gum remained which could not be crystallised. On acetylation, 5-bromo-1-acetimido-2-ethyl-1 : 2-dihydrobenzthiazole was obtained unaccompanied by other products; it was identified by m. p. and mixed m. p. determination. No trace of the isomeric 5-bromo-1-ethylaminobenzthiazole, m. p. 158° (previously misrecorded by Hunter and Soyka, J., 1926, 2962, as 256°), could be detected.

Nitration of 1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole and the Orientation of* 5-*Nitro*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole.*—(i) 10 G. of the imino-base were added to 50 c.c. of nitric acid (*d* 1·5) at 8° in the course of 40 minutes, the temperature not being allowed to rise above 10°. The solution was poured into 400 c.c. of water, the precipitated nitrate [small orange-pink crystals, m. p. 210—212° (decomp.), from alcohol] decomposed with 25% aqueous sodium hydroxide, and the nitro-base recrystallised from alcohol (yield, 9 g.). A further quantity (0·5—1 g.) was obtained by

basifying the filtrate from the nitrate and extracting it with chloroform. 5-*Nitro*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* forms small orange-yellow needles, m. p. 139—140° (Found : N, 19·3; S, 14·4. $C_9H_9O_2N_3S$ requires N, 18·9; S, 14·4%). The *acetyl* derivative crystallised from much ethyl acetate in soft, pale yellow needles, m. p. 242—243° (Found : N, 16·2; S, 12·2. $C_{11}H_{11}O_3N_3S$ requires N, 16·0; S, 12·1%).

(ii) *Methylation of* 5-*nitro*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole.* 6 C.c. of methyl sulphate were added to a suspension of 5 g. of the 5-nitro-1-imino-base in water (100 c.c.) and the mixture was boiled for 40 minutes and then basified with warm 20% sodium hydroxide solution. On recrystallisation from alcohol and thereafter from methyl alcohol, 1 g. of 5-nitro-1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole was obtained (m. p. 140°, depressed to 115—118° by admixture with 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole), which yielded the pure compound (see below) on further recrystallisation.

(iii) *Methylation of* 1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole and nitration of* 1-*methylimino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole.* A mixture of 20 g. of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, 100 c.c. of water, and 22 c.c. of methyl sulphate was boiled under reflux for 1½ hours. The product was made strongly alkaline with potassium hydroxide, boiled, and extracted with chloroform, and the chloroform removed through a fractionating column. The residual 1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole, a viscous oil which could not be crystallised, was added drop by drop with continuous shaking to 100 c.c. of nitric acid (*d* 1·5) at — 2° in the course of an hour, the temperature not being allowed to rise above 7°. The nitration mixture was poured into water (1000 c.c.) and basified; the *nitro*-base (23—24 g.), recrystallised from alcohol–ethyl acetate and thereafter from methyl alcohol (animal charcoal), formed yellow plates (10 g.), m. p. 154° (Found : N, 18·0; S, 13·6. $C_{10}H_{11}O_2N_3S$ requires N, 17·7; S, 13·5%).

(iv) 5-*Amino*-1-*methylimino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole.* The 5-nitro-compound (7 g.) was heated with tin (14 g.) and concentrated hydrochloric acid (100 c.c.) on a steam-bath for 20 minutes, and the mixture was diluted with 150 c.c. of water, filtered, and made strongly alkaline with 30% potassium hydroxide solution. The 5-*amino*-base, which was isolated by extraction with chloroform, crystallised from methyl alcohol in small plates (3·5—4 g.), m. p. 124—125° (Found : S, 15·2. $C_9H_{11}N_3S$ requires S, 15·5%). It dissolved in concentrated hydrochloric acid, giving a pink solution which became pale yellow and finally colourless on dilution with water; on diazotisation, it yielded a diazonium chloride which

coupled with alkaline β-naphthol, giving a red azo-dye. The amino-base slowly darkened and after some weeks the m. p. was 115°.

(v) *5-Bromo-1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole.* (A) A diazotised solution of the 5-amino-base (2·4 g.) in 20% hydrochloric acid (9 c.c.) was added to a cuprous bromide solution (prepared from 4·5 g. of copper sulphate crystals) at 0°. The mixture was heated on a steam-bath for ¼ hour and basified; the black oil obtained, isolated by means of chloroform, yielded yellowish needles of *5-bromo-1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole*, m. p. 89°, on crystallisation from methyl alcohol (animal charcoal) (Found: Br, 29·05. $C_{10}H_{11}N_2BrS$ requires Br, 29·1%). Yield, 60—70%. (B) A cleaner product was obtained by Gattermann's method. 0·8 G. of the amino-base was dissolved in 6 c.c. of hydrobromic acid (*d* 1·45) and water (3 c.c.) and diazotised; finely divided copper (prepared from 0·6 g. of zinc dust and 1·8 g. of copper sulphate crystals) having been added, the mixture was heated on a steam-bath for 10 minutes, diluted with 20 c.c. of water, basified, and extracted with chloroform. The 5-bromo-base obtained on recrystallisation from methyl alcohol was identical with that prepared in (A) and (C). (C) A mixture of 5-bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole (1 g.), water (10 c.c.), and methyl sulphate (1·5 c.c.) was heated under reflux for ½ hour, boiled with excess of 30% alkali solution, and extracted with chloroform. The oil obtained from the extract was dissolved in absolute methyl alcohol; when the solution was concentrated under reduced pressure at laboratory temperature, the methyl derivative sometimes crystallised in colourless needles which alone and when mixed with the specimens synthesised from 5-amino-1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole, melted at 88—89° (Found: Br, 29·1%).

Dinitration of 1-Imino-2-ethyl-1 : 2-dihydrobenzthiazole.—(i) The iminoethyl base (2 g.) was gradually added to 20 c.c. of nitric acid (*d* 1·5), the temperature rising to 55°. The mixture was poured into 100 c.c. of water; the precipitated nitrate, decomposed with 20% potassium hydroxide solution, gave *dinitroiminoethyldihydrobenzthiazole*, which crystallised from methyl alcohol–ethyl acetate in golden plates, m. p. 242—244° (Found: N, 21·2. $C_9H_8O_4N_4S$ requires N, 20·9%). The alkaline liquid on acidification yielded a substance which separated from methyl alcohol–ethyl acetate in yellow-brown needles, m. p. 200°.

(ii) 5-Nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole (0·5 g.) was gradually added to 10 c.c. of nitric acid (*d* 1·5), the solution was warmed, diluted with water, and basified, and the dinitro-compound was recrystallised; it formed golden plates, m. p. 242—244°, identical with the specimen already described.

1-*Nitrosoimino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*, prepared from 5 g. of iminoethyldihydrobenzthiazole in glacial acetic acid (35 c.c.) and sodium nitrite (2·6 g.) in water (13 c.c.), separated from alcohol in orange-red plates (4—4·5 g.), which exploded at 153° (Found : N, by slow combustion with twice the usual amount of fine CuO, 20·5; S, 15·2. $C_9H_9ON_3S$ requires N, 20·3; S, 15·5%).

1-*Keto*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*.—The nitrosoiminoethyldihydrobenzthiazole (3 g.) in xylene (20 c.c.) was heated until nitrogen was no longer evolved and the xylene was removed. The oily residue was distilled in steam, and the distillate extracted with chloroform; the *ketoethyldihydrobenzthiazole* was a colourless refractive oil (1·3 g.) which could not be crystallised (Found : S, 17·2. C_9H_9ONS requires S, 17·8%).

The *tetrabromide*, obtained as in the case of the methyl derivative, formed unstable purple-brown crystals, m. p. 80—82° (turning yellow at 60—70°) (Found : Br, 64·2. $C_9H_9ONBr_4S$ requires Br, 64·1%). 5-*Bromo*-1-*keto*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* crystallised from absolute methyl alcohol in needles, m. p. 96—97° (Found : N, 5·6; Br, 30·8; S, 12·8. C_9H_8ONBrS requires N, 5·4; Br, 31·0; S, 12·4%).

Synthesis of 5-*Bromo*-1-*keto*-2-*ethyl*-1 : 2-*dihydrobenzthiazole from* 5-*Bromo*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole by Way of* 5-*Bromo*-1-*nitrosoimino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*.—5-*Bromo*-1-*nitrosoimino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* crystallised in salmon-pink plates, which exploded at 157—158° on being fairly rapidly heated (Found : Br, 27·4; S, 11·4. $C_9H_8ON_3BrS$ requires Br, 27·6; S, 11·2%). The residue obtained by evaporation of a solution of the nitroso-derivative (4 g.) in xylene (25 c.c.), on recrystallisation from alcohol (animal charcoal), yielded 2·8 g. of 5-bromo-1-keto-2-ethyl-1 : 2-dihydrobenzthiazole, identical with that obtained above from the tetrabromide.

5-*Nitro*-1-*keto*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*. — (i) 5-*Nitro*-1-*nitrosoimino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*, prepared from 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, formed soft salmon-pink crystals, which exploded at 154° (Found : S, 12·5. $C_9H_8O_3N_4S$ requires S, 12·7%). 5-*Nitro*-1-*keto*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*, obtained by heating the nitrosoimino-compound (1 g.) in xylene (5 c.c.), separated from hot benzene in tufts of yellow needles, m. p. 198° (Found : S, 14·4. $C_9H_8O_3N_2S$ requires S, 14·3%).

(ii) The 5-nitro-1-keto-derivative was also obtained in 80—90% yield by adding the 1-keto-2-ethyldihydro-derivative to nitric acid (*d* 1·5) (10 vols.) at 0—5°.

1-*Thiol*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*.—A finely powdered, intimate mixture of 1-nitrosoimino-2-ethyl-1 : 2-dihydrobenzthiazole

(3 g.) and phosphorus pentasulphide (Kahlbaum) (3 g.) was heated in an oil-bath at 120°, a violent reaction taking place. The product was twice extracted with 50 c.c. of boiling benzene; the united extracts were boiled with copper turnings and filtered. The gum obtained by removal of the benzene crystallised from methyl alcohol in yellow plates, m. p. 75° (Found: S, 32·9. $C_9H_9NS_2$ requires S, 32·8%).

Nitration of 1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole Hydrotribromide*.—The hydrotribromide (7 g.) was added to 60 c.c. of nitric acid (*d* 1·5) at 3—6° in the course of 20 minutes; the solution was decanted from the liquid bromine which separated and poured into 250 c.c. of water. The filtrate from the precipitated nitrate, on basification, extraction with chloroform, and recrystallisation of the product from methyl alcohol, yielded 0·8 g. of 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole. The precipitated nitrate, on decomposition with 20% alkali solution, yielded 2 g. of 5-bromo-3-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, which was identified by its m. p. and mixed m. p. and by the m. p. and mixed m. p. of its acetyl derivative.

Decomposition of 1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole Hydrotribromide by Sulphuric Acid*.—3 G. of the hydrotribromide were gradually added to 25 c.c. of 99% sulphuric acid at 0—2°; hydrogen bromide was evolved and liquid bromine separated. The solution was poured on ice (200 g.), the mixture basified and extracted with chloroform, and the gum obtained by removal of the chloroform was acetylated with acetic anhydride (7 c.c.) and alcohol (15 c.c.). Fractional crystallisation of the product yielded 0·5 g. of 1-acetimido-2-ethyl-1 : 2-dihydrobenzthiazole and 0·7 g. of 5-bromo-1-acetimido-2-ethyl-1 : 2-dihydrobenzthiazole, which were identified by m. p. and mixed m. p. determinations.

Nitration of 1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole Hydrobromide*.—4 G. of the hydrobromide were gradually added to 50 c.c. of nitric acid (*d* 1·5) at 3—7°, and the solution poured into 200 c.c. of water. The mixture was cooled to 20°, and the precipitated nitrate collected; the filtrate, on basification and extraction with chloroform, yielded 2·2 g. of 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole. On decomposition with 20% alkali solution, the nitrate yielded 1·3 g. of 5-bromo-3-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, which was identified as in the previous case.

Nitration of 1-*Acetimido*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*.—4 G. of the acetyl derivative were gradually added to 40 c.c. of nitric acid (*d* 1·5) at 0—2°; the temperature was allowed to rise to 15°, the mixture poured into 250 c.c. of water, and the precipitated nitro-derivative collected and extracted with 35 c.c. of boiling alcohol.

The residue (2·1 g.) had m. p. 240—242° (241—242° when mixed with 5-nitro-1-acetimido-2-ethyl-1 : 2-dihydrobenzthiazole); the alcoholic extract on evaporation yielded a small quantity of what appeared to be impure nitrate of 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole. Basification of the original acid filtrate yielded a further 1·9—2 g. of the 5-nitro-1-acetyl derivative.

Nitration of 5-*Bromo*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole.*—This was carried out at 0—5° in the usual way. 5-*Bromo*-3-*nitro*-1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole* formed orange needles, m. p. 168—169° (Found : N, 14·0; Br, 26·3; S, 10·4. $C_9H_8O_2N_3BrS$ requires N, 13·9; Br, 26·4; S, 10·6%). The *acetyl* derivative crystallised from alcohol–ethyl acetate in pale yellow needles, m. p. 252—253° (Found : Br, 23·1. $C_{11}H_{10}O_3N_3BrS$ requires Br, 23·2%). The nitrate separated from alcohol in yellow needles, m. p. 230° (decomp.).

Nitration of 5-bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole hydrotribromide yielded solely 5-bromo-3-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole.

Nitration of 1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole in Sulphuric Acid Solution.*—The nitration of 5 g. of the base in 20 c.c. of 99% sulphuric acid at 70° with a mixture of nitric acid (*d* 1·4) (4 c.c.) and sulphuric acid (5 c.c.) gave 3·7 g. of impure 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, accompanied by a small quantity of the dinitro-derivative.

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