413. *The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part VI. The Mobility of 5-Substituted 1-Hydroxybenzthiazoles, and the Ultra-violet Absorption of Mobile and Static Derivatives of 1-Hydroxybenzthiazole.*

By Robert F. Hunter and Edwin R. Parken.

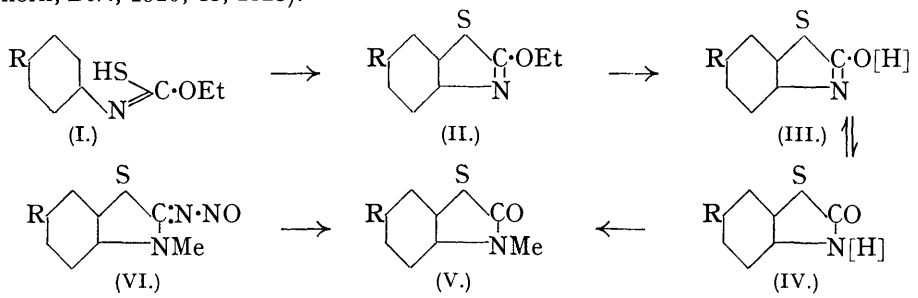
The unsymmetrical triad system [H]N·C:O ⇌ N:C·O[H] in 5-substituted 1-hydroxybenzthiazoles provides a striking contrast to the semicyclic amidine system in 5-substituted 1-aminobenzthiazoles (Hunter and Jones, J., 1930, 2190). Thus, although 5-bromo-1-hydroxybenzthiazole cannot be methylated with methyl iodide at 100° (Hunter, J., 1930, 136), an alkaline solution of the compound reacts readily with methyl sulphate at laboratory temperature, yielding 5-bromo-1-keto-2-methyl-1 : 2-dihydrobenzthiazole.

Attempts to accomplish methylation by heating with methyl sulphate alone, or in the presence of acetonitrile, were also abortive, but ethyl-alcoholic sodium ethoxide and *iso*propyl-alcoholic sodium *iso*propoxide proved highly effective catalysts in methylation (cf. Kon and Linstead, J., 1929, 1269). The covalent form of the molecule is therefore clearly inert, and it is only after the removal of the proton (or of a complex of this with the catalyst) that the system becomes reactive towards alkylating agents.

1-*Hydroxy*-5-*methylbenzthiazole* (III ⇌ IV; R = Me),* which was studied in greater detail than the other members of the series, was synthesised from *p*-tolylthiourethane (I, R = Me) by way of 1-*ethoxy*-5-*methylbenzthiazole* (II, R = Me) (cf. Jacobson, *Ber.*, 1886, **19**, 1069). On methylation with methyl sulphate in the presence of alkali, it yielded

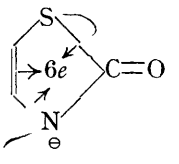
* Although the absorption spectra of the substances indicate that they have the ketodihydrothiazole structure, the names based on " reaction formula " have been retained for historical reasons.

solely 1-*keto*-2 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole* (V, R = Me), the constitution of which follows from its synthesis from the 1-*nitrosoimino*-1 : 2-*dihydro*-derivative (VI, R = Me) (Besthorn, *Ber.*, 1910, **43**, 1523).



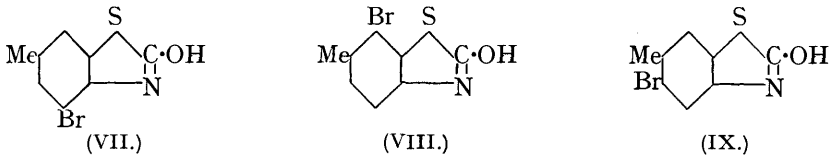
A similar result was obtained on methylation both of the sodium and of the silver salt of the hydroxybenzthiazole with methyl iodide.

In methyl-alcoholic solution, 1-hydroxy-5-methylbenzthiazole showed an ultra-violet absorption which was almost identical with that of the static ketodimethyldihydro-derivative (V, R = Me), and quite different from that of 1-*methoxy*-5-*methylbenzthiazole* (Fig. 1). It therefore follows that in the non-ionised condition the hydroxybenzthiazole has the ketodihydro-structure (IV). The general lowering of the absorption curve of 1-hydroxy-5-methylbenzthiazole in aqueous sodium hydroxide solution is evidently attributable to the decrease in concentration of absorbing molecules, due to the production of the ion $C_6H_3Me\langle^{S}_{N^{\ominus}}\rangle C{=}O$, which rapidly comes into equilibrium with the isomeric ion $C_6H_3Me\langle^{S}_{N}\rangle C{-}\overset{\ominus}{O}$. The first maximum at 2900 Å. is characteristic of the carbonyl group, and the curve therefore indicates a definite preponderance of the former ion. This may be interpreted on the basis of the sextuple group theory (Armit and Robinson, J., 1925, **127**, 1605; Goss and Ingold, J., 1928, 1268) by the annexed formula, but the preferential distribution of the electric charge on nitrogen is worthy of note.



The absorption spectrum of the hydroxythiazole in ethyl-alcoholic sodium ethoxide and in aqueous potassium hydroxide was also examined. The curve of the former (Fig. 2) suggests greater deformation in the Fajans sense, but the extinction coefficient is the same as in methyl-alcoholic solution. The first maximum in aqueous potassium hydroxide (at 3000 Å.) proved identical with that of the aqueous sodium hydroxide curve, but the second was raised to that of the curve for the hydroxythiazole in alcoholic sodium ethoxide (2600 Å.).

1-Hydroxy-5-methylbenzthiazole also exhibited a striking contrast to 1-amino-5-methylbenzthiazole as regards its behaviour towards bromine. Whereas the amidine undergoes substitution in the *o*-position to the nuclear nitrogen atom (Hunter and Jones, *loc. cit.*), the hydroxy-derivative gave rise to a *monobromo*-substitution product which differed from 3-*bromo*-1-*hydroxy*-5-*methylbenzthiazole* (VII) synthesised from o-*bromo*-p-*tolylthiourethane* by way of 3-*bromo*-1-*ethoxy*-5-*methylbenzthiazole*. Of the possible alternatives for the formula of this bromo-derivative, that of the 6-bromobenzthiazole structure (VIII) is



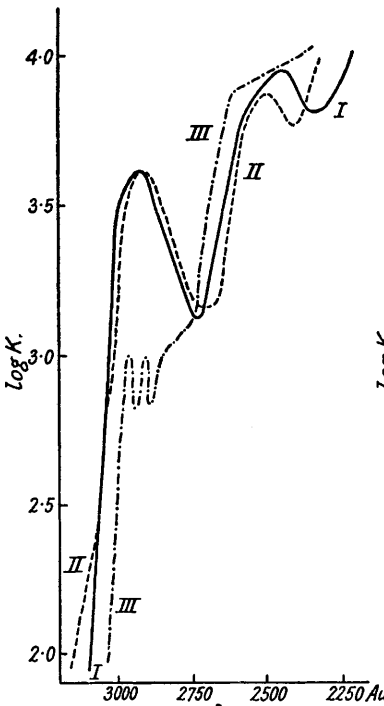
suggested by the naphthalene characteristics of the benzthiazole system (Fries, *Annalen*, 1927, **454**, 260). The synthesis of the compound from 2-*bromo*-p-*tolylthiocarbimide*, which

definitely establishes the *m*-position of the halogen substituent, however, appears to be in better agreement with the 4-bromo-structure (IX).

5-*Iodo*-, 5-*chloro*-, and 5-*ethoxy*-1-*hydroxybenzthiazoles* (III $\rightleftharpoons$ IV; R = I, Cl, or OEt), in all of which the direction of polarisation is in the sense opposite to that produced by a methyl group when attached to a benzene ring, behaved similarly to 1-hydroxy-5-methylbenzthiazole on methylation and gave rise to 5-*substituted* 1-*keto*-2-*methyl* derivatives (V; R = I, Cl, or OEt).

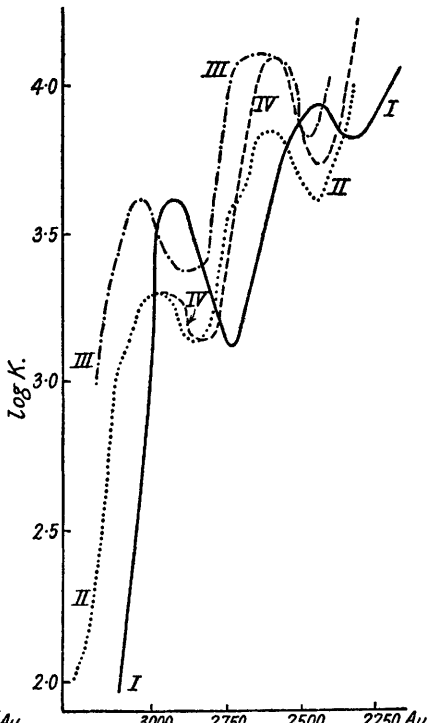
5-*Nitro*-1-*hydroxybenzthiazole*, obtained by nitration of 1-hydroxybenzthiazole (cf. Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826; Hunter, J., 1930, 125),

FIG. 1.



I = 1-*Hydroxy*-5-*methylbenzthiazole*.
II = 1-*Keto*-2 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole*.
III = 1-*Methoxy*-5-*methylbenzthiazole*.

FIG. 2.



I = 1-*Hydroxy*-5-*methylbenzthiazole in* MeOH.
II = 1-*Hydroxy*-5-*methylbenzthiazole in* NaOH.
III = 1-*Hydroxy*-5-*methylbenzthiazole in* NaOEt.
IV = 1-*Hydroxy*-5-*methylbenzthiazole in* KOH.

behaved similarly on methylation and gave rise to 5-*nitro*-1-*keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, the synthesis of which from 5-nitro-1-imino-2-methyl-1 : 2-dihydrobenzthiazole establishes the position of the nitro-group in the hydroxybenzthiazole derivative.

McClelland and Warren (J., 1930, 1099) have pictured the Jacobson synthesis of benzthiazoles as a reversible dismutation of an intermediate disulphide :

$$C_6H_5\cdot N{:}C(SH)R \longrightarrow \left[C_6H_5\cdot N{:}C(S-)R\right]_2 \rightleftharpoons C_6H_4\langle{}^{S}_{N}\rangle CR + C_6H_5\cdot N{:}C(SH)R$$

The inherent improbability of this (implying a similar ease of oxidation for mobile hydrogen of a thioamide triad and hydrogen attached to a benzene nucleus) appears evident from the higher temperature required for conversion of arylthiourethanes into ethoxybenzthiazoles as compared with their oxidation to disulphides (Jacobson, *loc. cit.*). Confirmation of this is furnished by the fact that phenylthiourethane disulphide was unaffected by being maintained at its melting point for half an hour, and by the fact that no trace of this

substance could be obtained by heating an equimolecular mixture of phenylthiourethane and 1-ethoxybenzthiazole slightly above the melting point of the disulphide for a similar period of time.

Experimental.

1-*Hydroxy-5-methylbenzthiazole* (III $\rightleftharpoons$ IV; R = Me). *Synthesis from* p-*Tolylthiourethane by Way of* 1-*Ethoxy-5-methylbenzthiazole.*—The following experiments are typical of the series. (i) *p*-Tolylthiourethane, prepared in 80—85% yield by heating a solution of *p*-tolylthiocarbimide (60 g.) in absolute alcohol (200 c.c.), containing a few drops of quinoline, for 12 hours under reflux, formed triclinic crystals, m. p. 85—86° (Found: S, 16·6. Calc.: S, 16·4%). (ii) The thiourethane (20 g.) was ground with a little alcohol and dissolved in 30% aqueous sodium hydroxide (150 c.c.) and the solution was diluted with water (350 c.c.) and added in 20 c.c. portions at 5-minute intervals to a mechanically stirred solution of potassium ferricyanide (120 g.) in water (550 c.c.) at 80—90°. The *ethoxybenzthiazole* extracted by ether, on distillation in steam, formed a yellow oil, which solidified and then crystallised from alcohol in pale yellow plates (12 g.), m. p. 35—36° (Found: S, 16·3. $C_{10}H_{11}ONS$ requires S, 16·6%). (iii) 1-Ethoxy-5-methylbenzthiazole (5 g.) was hydrolysed by heating with concentrated hydrochloric acid (20 c.c.) for 20 minutes. On recrystallisation from alcohol, 1-*hydroxy-5-methylbenzthiazole* was obtained in needles (4 g.), m. p. 168—169° (Found: C, 58·1; H, 4·15; S, 19·7. C_8H_7ONS requires C, 58·2; H, 4·2; S, 19·4%). The *silver* salt, obtained from aqueous silver nitrate (1·5 g. in 4 c.c.) and the hydroxythiazole (1 g. in 40 c.c. of absolute alcohol), formed a cream-coloured precipitate, which decomposed at 180° after drying in a vacuum (Found: Ag, 39·3. C_8H_6ONSAg requires Ag, 39·7%). The *sodium* salt was prepared by heating the hydroxythiazole (1 g.) with sodamide (0·3 g.) in xylene (5 c.c.) at 130° for ½ hour under reflux, ammonia being evolved. It darkened at 233°, sintered, and finally decomposed at 260—261° (Found: S, 16·4. C_8H_6ONSNa requires S, 17·1%). This salt was partly hydrolysed by water, its aqueous solution being definitely alkaline.

Methylation of 1-*Hydroxy-5-methylbenzthiazole and the Synthesis of* 1-*Keto-2*: 5-*dimethyl-1*: 2-*dihydrobenzthiazole.*—(i) A solution of 1-hydroxy-5-methylbenzthiazole (1 g.) in chloroform (2 c.c.) and 25% aqueous sodium hydroxide (20 c.c.) was treated with methyl sulphate (2 c.c.) and heated under reflux for 10 minutes. After an hour, the mixture was extracted with chloroform, and the extract allowed to evaporate spontaneously; 1-*keto-2*: 5-*dimethyl-1*: 2-*dihydrobenzthiazole* separated, which crystallised from alcohol in needles (1 g.), m. p. 76—77° (Found: C, 60·4; H, 5·0; S, 17·9. C_9H_9ONS requires C, 60·4; H, 5·0; S, 17·9%). Methylation of the sodium salt of the hydroxythiazole (1 g.) with methyl iodide (1·5 c.c.) in a sealed tube at 100° for 5 hours also gave the ketodimethyldihydro-derivative, unaccompanied by any detectable quantity of the *O*-methyl derivative.

(ii) A mixture of the silver salt of the hydroxythiazole (0·5 g.) and methyl iodide (1·5 c.c.) was heated in a sealed tube at 100°, and the product was extracted with alcohol. Concentration of the extract yielded a brown oil, which, on being kept in a vacuum for some days, deposited 0·2 g. of the ketodimethyldihydro-derivative.

(iii) A mixture of 1-amino-5-methylbenzthiazole (5 g.), methyl alcohol (50 c.c.), and methyl sulphate (5 c.c.) was heated under reflux for 15 minutes and kept over-night, the crystallised methosulphate was dissolved in water and decomposed with alkali, and the oily iminodimethyl base (cf. Hunter and Jones, J., 1930, 2198) was extracted with chloroform. A solution of the base in glacial acetic acid (25 c.c.) was treated at 5° with sodium nitrite (2 g. in 10 c.c. of water); 1-*nitrosoimino-2*: 5-*dimethyl-1*: 2-*dihydrobenzthiazole* separated after some time in dark red-brown crystals (3·5 g.), which exploded at 144° (Found: S, 15·5. $C_9H_9ON_3S$ requires S, 15·4%). When the nitroso-derivative (1 g.) was heated in xylene (30 c.c.) on a sand-bath, nitrogen was evolved; the solution was concentrated to 1—2 c.c., and the product recrystallised from methyl alcohol (animal charcoal), 1-keto-2: 5-dimethyl-1: 2-dihydrobenzthiazole being obtained, m. p. and mixed m. p. 75—76°.

Synthesis of 1-*Methoxy-5-methylbenzthiazole and Proof of its Absence from the Methylation Product of* 1-*Hydroxy-5-methylbenzthiazole.*—(i) *Methyl* p-*tolylthioncarbamate*, prepared from *p*-tolylthiocarbimide (20 g.), methyl alcohol (80 c.c.), and a trace of quinoline, formed triclinic crystals (20 g.), m. p. 79—80° (Found: S, 17·3. $C_9H_{11}ONS$ requires S, 17·6%). 1-*Methoxy-5-methylbenzthiazole*, obtained by oxidation of the tolylthioncarbamate (15 g.) with potassium ferricyanide, formed a red-brown oil, which solidified and then separated from methyl alcohol in needles (6 g.), m. p. 32—33° (Found: S, 17·8. C_9H_9ONS requires S, 17·9%). On hydrolysis

with concentrated hydrochloric acid, the methoxythiazole yielded 1-hydroxy-5-methylbenzthiazole.

(ii) The methylation product (m. p. 75°) obtained from 1-hydroxy-5-methylbenzthiazole (1 g.) and methyl sulphate was heated with concentrated hydrochloric acid (20 c.c.) for ½ hour and the mixture was diluted with water and thrice extracted with chloroform. Fractional crystallisation of the product from methyl alcohol yielded four fractions consisting of 1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole, unaccompanied by any trace of 1-hydroxy-5-methylbenzthiazole.

Acetylation of 1-*Hydroxy-5-methylbenzthiazole.*—The solution obtained by heating the hydroxythiazole (1 g.) with acetic anhydride (4 c.c.) for ½ hour was diluted with alcohol and heated for a further hour. On recrystallisation, an *acetyl* derivative was obtained, which was also prepared from the sodium salt of the hydroxythiazole and acetyl chloride, m. p. 109° (Found : S, 15·2. $C_{10}H_9O_2NS$ requires S, 15·4%).

Bromination of 1-*Hydroxy-5-methylbenzthiazole and of its* N- *and* O-*Methyl Derivatives.*—(i) The solution obtained by treating 1-hydroxy-5-methylbenzthiazole in chloroform (1 g. in 10 c.c.) with bromine (1 c.c. in 1 c.c. of chloroform) at 0° was concentrated under reduced pressure at laboratory temperature, and the highly unstable perbromide was dissolved in alcohol. The solution was diluted with a little water and heated; the 4(or 6)-*bromo*-1-*hydroxy-5-methylbenzthiazole* obtained separated from methyl alcohol in needles (0·75 g.), m. p. 239—240° (Found : Br, 32·6; S, 12·8. C_8H_6ONBrS requires Br, 32·8; S, 13·1%). (ii) On methylation with methyl sulphate in 25% aqueous sodium hydroxide, and recrystallisation of the product from methyl alcohol, this yielded 4(or 6)-*bromo*-1-*keto*-2 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole*, m. p. 145° (Found : S, 12·8. C_9H_8ONBrS requires S, 12·4%). (iii) A solution of 1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole in chloroform (0·5 g. in 5 c.c.) was treated with bromine (0·6 c.c.) at laboratory temperature and the red hydroperbromide was dissolved in alcohol; the 4(or 6)-bromo-1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole obtained was identified by m. p. and mixed m. p. determination. (iv) A solution of 1-methoxy-5-methylbenzthiazole in chloroform (2 g. in 20 c.c.) was treated with bromine (2·4 c.c.), the bromo-addition compound dissolved in alcohol, and the solution concentrated after being diluted with water. The product had m. p. 204° after being crystallised from methyl alcohol and evidently consisted of a mixture of 4(or 6)-bromo-1-hydroxy-5-methylbenzthiazole and the bromomethoxybenzthiazole initially formed. Hydrolysis was therefore completed by heating with hydrochloric acid; the 4(or 6)-bromo-1-hydroxy-5-methylbenzthiazole obtained (Found : S, 12·95%) was identified by m. p. and mixed m. p. determinations and by conversion into 4(or 6)-bromo-1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole.

3-*Bromo*-1-*hydroxy-5-methylbenzthiazole.*—(i) o-*Bromo*-p-*tolylthiourethane* formed an oil, which deposited small crystals on being kept in a vacuum for some days; m. p. 32—33° (Found : S, 11·7. $C_{10}H_{12}ONBrS$ requires S, 11·7%). (ii) 3-Bromo-1-ethoxy-5-methylbenzthiazole formed a yellow oil, which, on being kept, furnished small needles, m. p. 36—37°. (iii) This ethoxythiazole (2·5 g.) was hydrolysed with hydrobromic acid (*d* 1·49); the 3-*bromo*-1-*hydroxy-5-methylbenzthiazole* obtained crystallised from methyl alcohol in needles (2 g.), m. p. 209° (Found : Br, 32·8. C_8H_6ONBrS requires Br, 32·8%). (iv) On methylation, this yielded 3-*bromo*-1-*keto*-2 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole*, which crystallised from methyl alcohol in snow-white needles, m. p. 116° (Found : Br, 31·3. C_9H_8ONBrS requires Br, 31·0%). A mixture of this with 4(or 6)-bromo-1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole melted at 93—94°.

Synthesis of 4(or 6)-*Bromo*-1-*hydroxy-5-methylbenzthiazole.*—(i) 2-*Bromo*-p-*tolylthiocarbimide.* A solution of 2-bromo-*p*-toluidine (Scheufelen, *Annalen*, 1885, **231**, 171) (9·3 g.) in chloroform (20 c.c.) was gradually added to a mechanically stirred suspension of thiocarbonyl chloride (3 c.c.) in water (30 c.c.), and stirring was continued for a further 15 minutes. The *thiocarbimide* (9 g.) separated from alcohol in long needles, m. p. 44—45° (Found : Br, 29·9. C_8H_6NBrS requires 30·1%). (ii) 2-*Bromo*-p-*tolylthiourethane* crystallised in small prisms, m. p. 106° (Found : Br, 29·0. $C_{10}H_{12}ONBrS$ requires Br, 29·2%). (iii) 4(or 6)-*Bromo*-1-*ethoxy-5-methylbenzthiazole* formed a yellow oil, which solidified on keeping and separated from alcohol in silky needles, m. p. 50—51° (Found : Br, 29·2. $C_{10}H_{10}ONBrS$ requires Br, 29·4%). (iv) On hydrolysis this gave 4(or 6)-bromo-1-hydroxy-5-methylbenzthiazole, which separated from alcohol in needles, m. p. 226°, and 228—229° when mixed with the specimen obtained by bromination of 1-hydroxy-5-methylbenzthiazole. All attempts to raise the m. p. to that of the specimens previously described, by recrystallisation, were unsuccessful. On methylation of this product with methyl sulphate, however, 4(or 6)-bromo-1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole was obtained, m. p. and mixed m. p. 145—146°.

1-*Hydroxy*-5-*ethoxybenzthiazole*.—(i) p-*Phenetylthiourethane* formed prisms, m. p. 93—94° (Found: S, 14·2. $C_{11}H_{15}O_2NS$ requires S, 14·3%). (ii) 1 : 5-*Diethoxybenzthiazole* crystallised from alcohol in plates, m. p. 54° (Found: S, 14·4. $C_{11}H_{13}O_2NS$ requires S, 14·35%). (iii) 1-*Hydroxy*-5-*ethoxybenzthiazole*, obtained by hydrolysis of the diethoxy-derivative, separated from alcohol in needles, m. p. 147° (Found: C, 56·0; H, 4·7; S, 16·2. $C_9H_9O_2NS$ requires C, 55·4; H, 4·6; S, 16·4%).

1-*Keto*-5-*ethoxy*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, obtained by methylation of 1-hydroxy-5-ethoxybenzthiazole, crystallised from alcohol (animal charcoal) in long needles, m. p. 85° (Found: S, 15·4. $C_{10}H_{11}O_2NS$ requires S, 15·3%).

1-Nitrosoimino-5-ethoxy-2-methyl-1 : 2-dihydrobenzthiazole, obtained by treatment of a solution of 1-imino-5-ethoxy-2-methyl-1 : 2-dihydrobenzthiazole (Hunter and Jones, J., 1930, 2201) in glacial acetic acid with sodium nitrite, formed a red-brown microcrystalline powder, which decomposed at 139°. On being heated in xylene, it lost nitrogen and yielded 1-keto-5-ethoxy-2-methyl-1 : 2-dihydrobenzthiazole, m. p. 84—85°, and 85° when mixed with the specimen obtained above.

Methyl p-*phenetylthioncarbamate*, prepared from *p*-phenetylthiocarbimide and methyl alcohol (A.R.), formed crystals, m. p. 68—69° (Found: S, 14·9. $C_{10}H_{13}O_2NS$ requires S, 15·2%). On oxidation with alkaline potassium ferricyanide, it gave 1-*methoxy*-5-*ethoxybenzthiazole*, which crystallised from methyl alcohol in feathery needles, m. p. 75—76° (Found: S, 15·2. $C_{10}H_{11}O_2NS$ requires S, 15·3%). A mixture of this with the isomeric keto-ethoxymethyldihydrobenzthiazole melted at 64—67°. On hydrolysis with hydrobromic acid (*d* 1·49), it yielded 1-hydroxy-5-ethoxybenzthiazole.

5-*Iodo*-1-*hydroxybenzthiazole*.—(i) p-*Iodophenylthiourethane* formed needles, m. p. 106—107° (Found: S, 10·3. $C_9H_{10}ONIS$ requires S, 10·4%). (ii) 5-*Iodo*-1-*ethoxybenzthiazole* separated from alcohol in needles, m. p. 76—77° (Found: S, 10·7. C_9H_8ONIS requires S, 10·5%). (iii) 5-*Iodo*-1-*hydroxybenzthiazole* crystallised from alcohol in fine needles, m. p. 225—226° (Found: S, 12·1. C_7H_4ONIS requires S, 11·9%).

5-*Iodo*-1-*keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, obtained by methylation of the hydroxythiazole, crystallised in fine needles, m. p. 135° (Found: S, 11·2. C_8H_6ONIS requires S, 11·0%).

The gum obtained by methylation of 5-iodo-1-aminobenzthiazole (0·8 g.) with methyl iodide (1 c.c.) at 100° (cf. Dyson, Hunter, Jones, and Styles, *J. Indian Chem. Soc.*, 1931, **8**, 147) was dissolved in glacial acetic acid (10 c.c.) and treated with sodium nitrite (1 g. in 5 c.c. of water); 5-*iodo*-1-*nitrosoimino*-2-*methyl*-1 : 2-*dihydrobenzthiazole* was obtained as a salmon-pink microcrystalline powder, which exploded at 160° (Found: S, 10·0. $C_8H_6ON_3IS$ requires S, 10·0%). When heated in xylene, this gave 5-iodo-1-keto-2-methyl-1 : 2-dihydrobenzthiazole.

5-*Bromo*-1-*hydroxybenzthiazole*.—(i) *Methyl* p-*bromophenylthioncarbamate* had m. p. 99—100° (Found: Br, 32·3; S, 13·3. C_8H_8ONBrS requires Br, 32·1; S, 13·0%). (ii) 5-*Bromo*-1-*methoxybenzthiazole* separated from methyl alcohol in needles, m. p. 82—83° (Found: Br, 32·9; S, 13·0. C_8H_6ONBrS requires Br, 32·8; S, 13·1%). On hydrolysis it yielded 5-bromo-1-hydroxybenzthiazole, m. p. 223—224°, undepressed by admixture with a specimen obtained by bromination of 1-hydroxybenzthiazole (Hunter, J., 1930, 125).

Methyl phenylthioncarbamate, m. p. 93°, obtained from phenylthiocarbimide (Found: S, 18·9. C_8H_9ONS requires S, 19·1%), was oxidised to give 1-*methoxybenzthiazole*, which separated from methyl alcohol in needles, m. p. 88—89° (Found: S, 19·6. C_8H_7ONS requires S, 19·4%). A solution of this in chloroform (1 g. in 10 c.c.) was treated with bromine (1·2 c.c.), and the hydroperbromide obtained by concentration in a vacuum was dissolved in alcohol. The solution was boiled, diluted with a little water, and concentrated; the 5-bromo-1-methoxybenzthiazole obtained had m. p. 83—84°, and 83° when mixed with the specimen described above.

Methylation of 5-*Bromo*-1-*hydroxybenzthiazole*.—(i) The hydroxythiazole was recovered unchanged after being heated under reflux for an hour with methyl sulphate (0·9 c.c. to 0·5 g.) on a water-bath or with methyl sulphate (1·5 c.c. to 1 g.) in acetonitrile (10 c.c.). (ii) On methylation with methyl sulphate in the presence of 25% aqueous sodium hydroxide, however, 5-bromo-1-keto-2-methyl-1 : 2-dihydrobenzthiazole was obtained, m. p. and mixed m. p. 125—126°; no trace of the isomeric 5-bromo-1-methoxybenzthiazole was detected.

5-*Chloro*-1-*hydroxybenzthiazole*.—(i) *p*-Chlorophenylthiourethane had m. p. 98° (Found: S, 15·0. Calc.: S, 14·9%). (ii) 5-*Chloro*-1-*ethoxybenzthiazole* separated from alcohol in plates, m. p. 60—61° (Found: Cl, 16·5; S, 14·5. C_9H_8ONClS requires Cl, 16·6; S, 14·9%). (iii) 5-*Chloro*-1-*hydroxybenzthiazole* crystallised in needles, m. p. 204° (Found: C, 45·6; H, 2·8; Cl, 19·2; S, 17·4. C_7H_4ONClS requires C, 45·3; H, 2·2; Cl, 19·1; S, 17·25%).

5-*Chloro*-1-*keto*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, obtained by methylation of the hydroxy-

thiazole, formed needles, m. p. 112° (Found : Cl, 17·9; S, 16·2. C_8H_6ONClS requires Cl, 17·8; S, 16·0%).

The gum obtained by methylation of 5-chloro-1-aminobenzthiazole (Hunter and Jones, *loc. cit.*) was acetylated with acetic anhydride. 1 G. of the acetyl derivative (m. p. 197°) was hydrolysed with hydrochloric acid, and the gum obtained by basification and extraction with chloroform was dissolved in glacial acetic acid and treated with sodium nitrite. The *5-chloro-1-nitrosoimino-2-methyl-1 : 2-dihydrobenzthiazole* obtained exploded at 138—139° (Found : Cl, 15·5; S, 14·4. $C_8H_6ON_3ClS$ requires Cl, 15·6; S, 14·15%). When heated in xylene, it yielded 5-chloro-1-keto-2-methyl-1 : 2-dihydrobenzthiazole, m. p. 110—111°, and 112° when mixed with the specimen obtained by methylation of 5-chloro-1-hydroxybenzthiazole.

5-Nitro-1-hydroxybenzthiazole, obtained by nitration of 1-hydroxybenzthiazole with nitric acid (*d* 1·5) (6 c.c. per g.) below 8°, separated from alcohol–ethyl acetate in almost colourless crystals, m. p. 251°.

5-Nitro-1-keto-2-methyl-1 : 2-dihydrobenzthiazole, obtained by methylation of 5-nitro-1-hydroxybenzthiazole, separated from alcohol–ethyl acetate in yellow needles, m. p. 162—163°, undepressed by admixture with the specimen described below.

5-Nitro-1-nitrosoimino-2-methyl-1 : 2-dihydrobenzthiazole formed a salmon-pink powder, which exploded at 152° (Found : S, 13·3. $C_8H_6O_3N_4S$ requires S, 13·2%). When heated in xylene, it yielded *5-nitro-1-keto-2-methyl-1 : 2-dihydrobenzthiazole*, which separated from alcohol–ethyl acetate (animal charcoal) in brilliant yellow needles, m. p. 162—163° (Found : S, 15·2. $C_8H_6O_3N_2S$ requires S, 15·2%). This compound, m. p. and mixed m. p. 162—163°, was also prepared by the nitration of 1-keto-2-methyl-1 : 2-dihydrobenzthiazole (Besthorn, *Ber.*, 1910, **43**, 1523) with fuming nitric acid at 0—8°.

Experiments on the Alleged Dismutation of Phenylthiourethane Disulphide.—Phenylthiourethane disulphide, prepared by oxidation of phenylthiourethane with alkaline potassium ferricyanide at laboratory temperature (Jacobson, *loc. cit.*), separated from alcohol in plates, m. p. 96—97°. (i) A specimen was fused on a water-bath for ½ hour, and the cooled product kept for 24 hours. No apparent change having occurred, the specimen was heated in an electric oven at 102—103° for 45 minutes. The m. p. of the resolidified product was unaltered, and was undepressed by admixture with the original disulphide. (ii) A mixture of phenylthiourethane and 1-ethoxybenzthiazole in molecular proportion was kept at 100° for ½ hour; after cooling, the mixture was dissolved in alcohol and fractionally crystallised under reduced pressure at laboratory temperature. Almost the whole of the phenylthiourethane was recovered unchanged, and identified by its properties and a mixed m. p. determination. The mother-liquors furnished 1-ethoxybenzthiazole unaccompanied by any detectable quantity of the disulphide of phenylthiourethane.

Absorption Spectra Measurement [with Abdul Aziz Firdaus].—1-Hydroxy-5-methylbenzthiazole, 1-keto-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole, and 1-methoxy-5-methylbenzthiazole were carefully recrystallised, and dried in a vacuum. The last compound was prepared by the condensation of 1-chloro-5-methylbenzthiazole and sodium methoxide in methyl alcohol and had m. p. 45° after drying in a vacuum. The measurements were made with a Carl Leiss Spectrograph (type C), quartz absorption cells and a Wellington anti-screen plate being used. An improved form of hydrogen tube which gave a constant intensity of light enabled constant comparison spectra to be inserted between successive exposures, with various cell thicknesses of solution. Juxtaposition was secured by means of a Hartman diaphragm, and from the density matchpoints, molecular extinction coefficients followed.

M/1000-Solutions of the three compounds in absolute methyl alcohol were first examined and the solutions were thereafter diluted with methyl alcohol to *M*/10,000 and then to *M*/100,000. *M*/1000-Solutions of 1-hydroxy-5-methylbenzthiazole in *N*/100-aqueous sodium hydroxide, *N*/100-ethyl-alcoholic sodium ethoxide, and *N*/100-aqueous potassium hydroxide were then examined, the solutions being subsequently diluted to *M*/10,000, with water in the cases of sodium and potassium hydroxide and with alcohol in the case of sodium ethoxide.

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