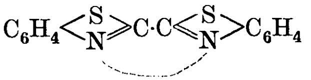
LXXI.—*Halogenation of* 2 : 6-*Dimethylbenzbisthiazole and of* 3 : 5-*Diphenylimino*-2 : 4-*diphenyltetrahydro*-1 : 2 : 4-*thiodiazole.*

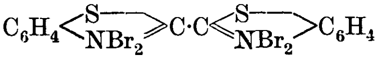
By ROBERT FERGUS HUNTER.

THE slight unsaturation of the nitrogen atoms of the heterocyclic nuclei in 1 : 1-bisbenzthiazole (I) and the consequent great lability of the tetrabromide (II), which is so unstable that it decomposes appreciably into the original bisthiazole (I) and bromine on exposure to air for a few minutes (J., 1925, **127**, 1319), must, in view of the stability of 1-substituted benzthiazole bromides such as 1-phenylbenzthiazole tetrabromide (*loc. cit.*), clearly be due to the presence of the second thiazole nucleus.



$C_6H_4{<}\genfrac{}{}{0pt}{}{S}{N}{\geqslant}C{\cdot}C{\leqslant}\genfrac{}{}{0pt}{}{S}{N}{>}C_6H_4$

(I.)



$C_6H_4{<}\genfrac{}{}{0pt}{}{S}{NBr_2}{\geqslant}C{\cdot}C{\leqslant}\genfrac{}{}{0pt}{}{S}{NBr_2}{>}C_6H_4$

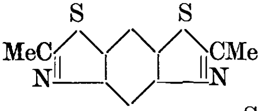
(II.)

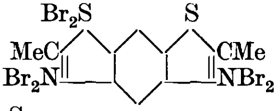
That is to say that the two thiazole nuclei joined as in (I) by way of their μ-carbon atoms, mutually " saturate " each other.

Regarding this effect, it seems reasonable to suggest that the phenomenon is due to partial self-neutralisation of the valencies of the nitrogen atoms after the manner in which the central pairs of partial valencies in conjugated systems neutralise each other according to Thiele's theory (*Annalen*, 1899, **306**, 87). This supposition can be represented by means of a dotted line as in (I).

In view of this, it was clearly desirable to examine the unsaturation of the benzbisthiazole system in which the thiazole nuclei are separated from each other by a benzene ring which should inhibit or prevent the self-saturation effect displayed by 1 : 1-bisbenzthiazole. The example chosen was 2 : 6-dimethylbenzbisthiazole (III) (Edge, J., 1922, **121**, 772).

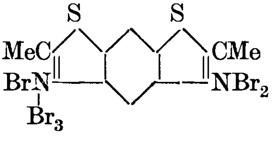
(III.)





(IV.)

(V.)



The reactive nitrogen atoms in this case are not linked by way of the ·N⋮C·C⋮N· system, but this is immaterial, since the supposed double bonds in the thiazole nucleus are aromatic in character, and the usual formula for the thiazole ring really can represent only *one* of the transient phases of the intra-annular semi-aromatic heterocyclic nucleus.

2 : 6-Dimethylbenzbisthiazole in presence of excess of bromine readily passes into a bright yellowish-orange, relatively stable *hexabromide*, the most probable constitution of which is (IV). This bromo-additive compound is quite devoid of the properties of 1 : 1-bisbenzthiazole tetrabromide; for instance, it only loses appreciable halogen on exposure to the atmosphere for several days and is in many ways similar to the stable tribromo-additive compounds of the arylaminobenzthiazoles (J., 1925, **127**, 2024). The self-saturation effect of the thiazole nuclei is therefore removed by the intervention of the common aromatic nucleus. There is, however, another effect which arises in connexion with the unsaturation of the benzbisthiazole complex, namely, the alternation of the affinity effect of carbon chains (Flürscheim, *J. pr. Chem.*, 1902, **66**, 321; J., 1909, **95**, 718; 1910, **97**, 84; Ingold, J., 1925, **127**, 513), which operates in the manner described hereunder.

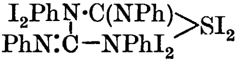
In the bromination of 2 : 6-dimethylbenzbisthiazole, the first reaction must necessarily consist in the addition of bromine to *one* of the ring nitrogen atoms. The consequent formation of the $\vdots NBr_2$ group at once causes an alternation in affinity along the carbon chain connected to the second nitrogen atom, which therefore becomes partly saturated. Now there can be very little doubt, from the facts already described in connexion with the bromo-additive compounds of the benzthiazoles (*loc. cit.*), that the *centre* of unsaturation in a thiazole ring is the *nitrogen* atom. The obvious result is that in the bromination of the benzbisthiazole system one thiazole nucleus is much more *reactive* than the other, and hence one ring is responsible for the addition of four bromine atoms, whilst the other is fully satisfied by the addition of two. In this connexion, it does not matter whether the hexabromide has the constitution (IV) or the less probable formula (V).

The above is well borne out by the behaviour of 2 : 6-dimethylbenzbisthiazole towards other reagents such as methyl iodide; even in the presence of a large excess of methyl iodide, it will form only a monomethiodide (Edge, *loc. cit.*).

Since benzbisthiazole is in a sense a dithio-di-azo-heterocyclic compound, it was of interest to examine the thiodiazole complex. The example chosen was 3 : 5-diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole (Hector, *Ber.*, 1890, **23**, 357), which would be expected to pass under suitable conditions into the octabromide (VI).

(VI.)

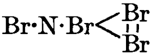
$$\left.\begin{array}{l}Br_2PhN\text{–}C(NPh)\\ PhN{:}C\cdot NPhBr_2\end{array}\right>SBr_4$$



$$\left.\begin{array}{l}I_2PhN\cdot C(NPh)\\ PhN{:}C\text{–}NPhI_2\end{array}\right>SI_2$$

(VII.)

Actually an *octabromide* having the expected properties was readily isolated as a bright red, crystalline compound, which gradually lost bromine on exposure to the atmosphere and was reduced by sulphurous acid (Hunter, *loc. cit.*) with regeneration of the original thiodiazole.

There are, however, alternative formulæ for this compound involving the  $\mathrm{Br{\cdot}N{\cdot}Br}<\begin{array}{c}\mathrm{Br}\\ \vdots\\ \mathrm{Br}\end{array}$ group. In view of the lesser affinity of iodine as compared with bromine for sulphur (compare Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826) and the facility iodine atoms have for combining with one another, which is greater even than that of bromine atoms, if the octabromide is indeed (VI), it might be expected that the thiodiazole on treatment with iodine would yield an additive compound of a *lower* order; whilst if the existence of the octabromide were due to the presence of the $\mathrm{Br{\cdot}N{\cdot}Br_3}$ group, an octaiodide would be formed. Actually the only iodo-additive compound isolated was a *hexaiodide*, which is best represented by the formula (VII). Its formation is by no means a crucial test, but is in favour of the formulæ suggested for these additive compounds.

EXPERIMENTAL.

Dithioacetyl-*m*-phenylenediamine was prepared from diacetyl-*m*-phenylenediamine (20 g.) and oxidised with potassium ferricyanide according to Edge's directions (*loc. cit.*). The product isolated from the ethereal extract was allowed to crystallise spontaneously from light petroleum–alcohol and recrystallised (without distillation) from light petroleum, 2 : 6-dimethylbenzbisthiazole being thus obtained in shining prisms, m. p. 105°.

2 : 6-*Dimethylbenzbisthiazole Hexabromide*.—The benzbisthiazole (0·25 g.) dissolved in chloroform (5 c.c.) was slowly treated with bromine (0·3 c.c.). The solution was then either warmed and rapidly treated with a further quantity of bromine (0·3 c.c.), when the *hexabromide* crystallised, or the addition was continued in the usual way and the resulting solution warmed, cooled, and scratched. The *hexabromide* crystallised in small, yellowish-orange prisms, which were dried in a vacuum over phosphorus pentoxide; m. p. 117—118° (decomp.) (Found : Br, 68·2. $C_{10}H_8N_2Br_6S_2$ requires Br, 68·6%). The yield was nearly quantitative. The hexabromide showed no change on exposure to air for several hours; on exposure for 5 days, the compound lost appreciable bromine, very slowly becoming red. It was reduced in the usual way by sulphurous acid (*loc. cit.*). It dissolved readily in warm alcohol; on dilution and warming, acetaldehyde was evolved. A pure bromo-substitution derivative could not be isolated.

3 : 5-*Diphenylimino*-2 : 4-*diphenyltetrahydro*-1 : 2 : 4-*thiodiazole.*—*s*-Diphenylthiocarbamide (15 g.) dissolved in absolute alcohol (300 c.c.) was gradually treated with bromine until a permanent yellow colour was obtained (Hugershoff, *Ber.*, 1903, **36**, 3121). The solution was filtered from coagulated sulphur into cold water (5 vols.), and the mixture made strongly alkaline with ammonia (*d* 0·880); the compound then separated in brittle, white granules. On crystallisation from ether, the thiodiazole separated in white plates, m. p. 136°, as recorded in the literature (yield, about 60%).

3 : 5-*Diphenylimino* - 2 : 4 - *diphenyltetrahydro* - 1 : 2 : 4 - *thiodiazole Octabromide.*—The thiodiazole (1 g.) dissolved in chloroform (10 c.c.) was gradually treated with bromine (1 c.c.), and the resulting solution warmed and kept ½ hour. On scratching, the *octabromide* separated in glistening, orange-red prisms, which were dried in a vacuum over potassium hydroxide; m. p. 103—105° (Found : Br, 66·2. $C_{26}H_{20}N_4Br_8S$ requires Br, 66·6%). The bromide dissolved in glacial acetic acid, giving a solution which became colourless and evolved bromine and hydrogen bromide on prolonged boiling. The solution, on being made alkaline, furnished a product which crystallised from alcohol, on persistent scratching, in minute prisms, m. p. 200° (decomp.; after sintering at 110°). The quantity was much too small for investigation, but the product was doubtless an impure bromo-substitution derivative (*loc. cit.*).

3 : 5-*Diphenylimino* - 2 : 4 - *diphenyltetrahydro* - 1 : 2 : 4 - *thiodiazole Hexaiodide.*—The thiodiazole (3·8 g.) dissolved in 20 c.c. of glacial acetic acid was gradually added to a warm solution of iodine (5 g.) in the same solvent (250 c.c.), and the resulting solution warmed and kept for 3 hours; a part of the *iodo*-additive compound then separated in small, black, glistening prisms, which were washed with a little acetic acid and dried in a vacuum; m. p. 120°. A second crop separated over-night in shining, black prisms having a dark green reflex, which were thoroughly washed with glacial acetic acid and dried in a vacuum as before; m. p. 122° (decomp.) (Found : I, 66·5. $C_{26}H_{20}N_4I_6S$ requires I, 66·8%).

The hexaiodide was practically unacted upon by sulphurous acid owing to its insolubility, but was readily reduced by sulphur dioxide in acetic acid solution. It was readily decolorised by sodium thiosulphate [0·1120 g. in glacial acetic acid (redistilled over potassium permanganate) required 27·5 c.c. of 1·97*N*/100-sodium thiosulphate. I, 57·4%]. The iodide was readily soluble in ether, ethyl acetate, and alcohol, but could not be recrystallised.

A number of experiments were also carried out on the halogenation of 3 : 5-di-*p*-tolylimino-2 : 4-di-*p*-tolyltetrahydro-1 : 2 : 4-thiodiazole, m. p. 138°, which was obtained in the same way as the phenyl derivative (Hugershoff, *loc. cit.*), but definite compounds could not be isolated; bromination and iodination in different solvents and under various conditions led to uncrystallisable gums or resins.

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