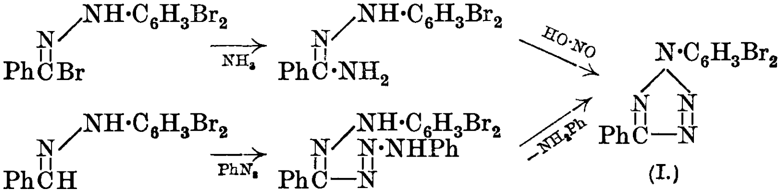
XIX.—*Substituted Dihydropentazines—A New Series of Cyclic Nitrogen Compounds.*

By Frederick Daniel Chattaway and George David Parkes.

It has recently been shown (J., 1925, **127**, 975, 1687) that when halogens react with benzaldehydephenylhydrazones substitution occurs in the hydrazine residue and in the so-called ω-position, that is, in the $\cdot CH{:}$ group. This affords an easy method of obtaining in quantity many substituted hydrazones, in which the ω-halogen is unusually reactive.

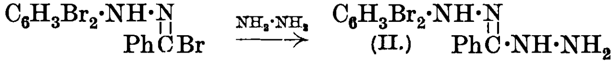
Such ω-bromo-substituted hydrazones, for example, react with ammonia to form hydrazidines which are converted by the action of nitrous acid into tetrazoles (compare Pinner, *Ber.*, 1894, **27**, 984).

Several tetrazoles, prepared by this method, which establishes their constitution, have been shown to be identical with the compounds produced by heating the corresponding hydrazone with phenyl azide (compare Dimroth, *Ber.*, 1910, **43**, 2899). For example, benzaldehyde-2 : 4-dibromophenylhydrazone yields 1-(2 : 4-*dibromophenyl*)-4-*phenyltetrazole* by either method, thus :



(I.)

These ω-halogen compounds react also with hydrazine, replacing by a hydrazino-group, the ω-halogen. For example, ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone yields *ω-hydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone* * (II) :



$$C_6H_3Br_2\cdot NH\cdot N{:}CPhBr \xrightarrow{NH_2\cdot NH_2} C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot NH\cdot NH_2 \quad \text{(II.)}$$

This compound behaves as a substituted hydrazine : it forms salts with halogen acids, yields an acetyl derivative when treated with acetyl chloride, and reacts with aldehydes, forming hydrazones. It also reacts with excess of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone, forming a compound having probably the constitution (III).

(III.) $C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot NH\cdot NH\cdot CPh{:}N\cdot NH\cdot C_6H_3Br_2$.

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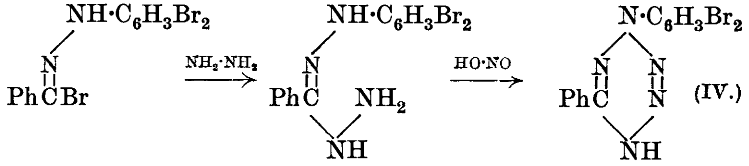
* This behaviour is in marked contrast to that of phenylhydrazine, which converts the hydrazone into a formazyl compound (compare Pechmann, *Ber.*, 1894, **27**, 322).

When treated with nitrous acid these ω-hydrazinobenzaldehydehydrazones are converted into dihydropentazines. Thus, for example, ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone yields 1-(2 : *4-dibromophenyl*)-5-*phenyl*-1 : *4-dihydropentazine* (IV) :


(IV.)

The 5-phenyldihydropentazines are crystalline, odourless, weakly basic compounds which on being rapidly heated decompose, yielding benzonitrile.

EXPERIMENTAL.

Preparation of 1-(2 : *4-Dibromophenyl*)-*4-phenyl*-1 : 2 : 3 : *5-tetrazole* (I).—(a) *From ω-bromobenzaldehyde*-2 : *4-dibromophenylhydrazone.* The hydrazone was prepared by the action of bromine upon benzaldehydephenylhydrazone and converted into the corresponding hydrazidine by boiling with an aqueous alcoholic solution of ammonia (compare Chattaway and Walker, *loc. cit.*).

A suspension of finely ground benzaldehyde-2 : 4-dibromophenylhydrazidine (5 g.) in a mixture of 20 c.c. of concentrated hydrochloric acid and 10 c.c. of water was cooled in a freezing mixture and 1 g. of solid sodium nitrite was added very gradually with constant stirring. 1-(2 : *4-Dibromophenyl*)-*4-phenyltetrazole* separated as a slightly brown solid. It was filtered off, washed repeatedly with water, and recrystallised from boiling alcohol, in which it is moderately easily soluble and from which it separates in a felted mass of fine, white needles, m. p. 127° (Found : Br, 41·7. $C_{13}H_8N_4Br_2$ requires Br, 41·95%).

(b) *From benzaldehyde*-2 : *4-dibromophenylhydrazone and phenyl azide.* A mixture of 5 g. of benzaldehyde-2 : 4-dibromophenylhydrazone, 2 g. of phenyl azide, and a solution of 0·4 g. of sodium in 8 c.c. of alcohol was heated at 100° in a sealed tube for 15 hours. The tetrazole which separated was filtered off, washed with a little alcohol, and recrystallised several times from boiling alcohol, separating as a felted mass of fine, white needles, m. p. 127°.

This and the tetrazole prepared by method (a) were identical in every respect.

1 - (2 : 4 - *Dibromophenyl*) - 4 - m - *nitrophenyl* - 1 : 2 : 3 : 5 - *tetrazole* (formula corresponding with I) was prepared similarly from ω-bromo-*m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone. It separates from boiling alcohol, in which it is somewhat sparingly

soluble, in colourless needles, m. p. 215° (Found : C, 37·0; H, 1·7; N, 16·55; Br, 37·5. $C_{13}H_7O_2N_5Br_2$ requires C, 36·7; H, 1·6; N, 16·5; Br, 37·65%).

ω-*Hydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone* (II).—A suspension of 10 g. of finely divided ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone in 50 c.c. of alcohol was added to 10 c.c. of a 50% hydrazine hydrate solution, and the mixture shaken vigorously for 15 minutes. It was then kept for 12 hours, when the whole had become a semi-solid, light brown mass. The solid was filtered off and the ω-*hydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone* separated from the hydrazine hydrobromide with which it was mixed, by heating it with 40—50 c.c. of alcohol and filtering hot. On cooling the warm alcoholic solution, ω-hydrazinobenzaldehyde-2 - 4-dibromophenylhydrazone separated in almost colourless needles, m. p. 123° (decomp.) (Found : Br, 41·8. $C_{13}H_{12}N_4Br_2$ requires Br, 41·7%).

This compound can be preserved unchanged for a considerable time in a sealed tube, although it darkens somewhat when exposed to light. When exposed to the air, it undergoes slow decomposition.

On adding excess of strong hydrochloric acid to a warm alcoholic solution of ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone the hydrochloride of the base separates on cooling as a colourless, microcrystalline powder, m. p. 188° (decomp.). The sulphate, obtained similarly, separates in minute, colourless plates which on heating decompose without melting.

ω-*Benzylidenehydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, $C_6H_3Br_2{\cdot}NH{\cdot}N{:}CPh{\cdot}NH{\cdot}N{:}CHPh$, is obtained as a yellow, crystalline powder on warming together in alcoholic solution equivalent quantities of benzaldehyde and ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone. It separates from boiling alcohol, in which it is moderately easily soluble, in small, yellow needles, m. p. 126° (Found : Br, 33·8. $C_{20}H_{16}N_4Br_2$ requires Br, 33·9%).

This compound dissolves with a yellow colour in strong alcoholic potash, and in strong sulphuric acid with a brown colour which soon changes to red.

ω-p-*Nitrobenzylidenehydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, $C_6H_3Br_2{\cdot}NH{\cdot}N{:}CPh{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, was prepared similarly from *p*-nitrobenzaldehyde. It separates from boiling alcohol in small needles which appear dark violet by transmitted light and dark green by reflected light; m. p. 194° (Found : Br, 30·8. $C_{20}H_{15}O_2N_5Br_2$ requires Br, 31·0%).

It dissolves in strong alcoholic potash with an intense blue colour, which fades almost immediately. With sulphuric acid a brown colour is produced which becomes violet on standing.

The action of a further quantity of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone upon ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone yields a compound, having in all probability the symmetrical constitution (III), *hydrazobenzaldehyde*-2 : 4-*dibromophenylhydrazone.*

This compound was obtained by boiling a solution of 2 g. of ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone and an equivalent quantity of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone in 20 c.c. of alcohol under reflux for 12 hours. A solid separated which was filtered off and recrystallised from boiling glacial acetic acid, in which it was fairly easily soluble and from which it separated in colourless needles, m. p. 237° (Found: Br, 43·2. $C_{26}H_{20}N_6Br_4$ requires Br, 43·4%).

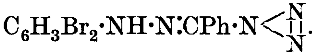
1-(2 : 4-*Dibromophenyl*)-5-*phenyl*-1 : 4-*dihydropentazine* (IV).—Five grams of finely divided ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone were added to a mixture of 25 c.c. of concentrated hydrochloric acid and 25 c.c. of water, and stirred vigorously. The hydrochloride of the base separated in the course of a few minutes as a finely divided, colourless, crystalline powder. The whole was then cooled in a freezing mixture and treated with 5 g. (a considerable excess) of sodium nitrite with constant stirring. The dihydropentazine separated as a pasty, slightly brown, semi-solid mass, which was filtered off and washed repeatedly with water. It was then washed with a little light petroleum (b. p. 40—60°) and recrystallised from boiling alcohol, in which it is fairly easily soluble and from which it separates as a colourless, microcrystalline powder, m. p. 172° (decomp.) (Found: Br, 40·4; N, 17·6. $C_{13}H_9N_5Br_2$ requires Br, 40·5; N, 17·7%).

When rapidly heated alone, the compound decomposes with a puff of black smoke and formation of benzonitrile. One g. of the substance was rapidly heated in a long glass tube sealed at one end. After decomposition drops of a yellow liquid condensed on the cool parts of the tube. The tube was washed out with ether, the ethereal solution filtered, and the ether evaporated. The residual drop of yellow oily liquid, which had a smell resembling that of benzonitrile, slowly dissolved when it was boiled with aqueous sodium hydroxide, ammonia being evolved; from the cooled, acidified solution, benzoic acid was obtained which separated from boiling water in white, shining flakes, m. p. 120°. The yellow oil was therefore benzonitrile.

1-(2 : 4-Dibromophenyl)-5-phenyldihydropentazine is a colourless, crystalline solid which exhibits slightly basic properties. It is without odour and is easily soluble in the common organic solvents. It is quite stable to air and light.

The action of nitrous acid on ω-hydrazinobenzaldehyde-2 : 4-

dibromophenylhydrazone might conceivably have yielded, not the dihydropentazine, but an azide of the structure



$$C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot N<\begin{matrix}N\\ \|\\ N\end{matrix}.$$

That the compound produced has not this structure is shown by the circumstance that when heated at 100° for 60 hours in a sealed tube with acetone saturated with acetylene at 0° the whole was recovered completely unchanged. Had it possessed the azide structure it should have reacted with the acetylene, yielding 1 : 2 : 3-triazole-1-(benzaldehyde-2 : 4-dibromophenylhydrazone) (compare Dimroth, *Ber.*, 1910, **43**, 2222). Further, as mentioned above, Pinner obtained phenyltetrazole and not benzenyliminoazide by the action of nitrous acid on benzenylhydrazidine, $NH{:}CPh\cdot NH\cdot NH_2$, which is an analogous compound to the ω-hydrazino-compound from which the new ring compound was prepared. Its behaviour, therefore, is inconsistent with an azide structure, whilst it possesses the properties which would be expected in a dihydropentazine.

The formation of this compound is of considerable interest, as it contains a type of nitrogen ring apparently hitherto undescribed.

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