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ON INTERMEDIATES PRECEDING HUGERSHOFF'S BASE

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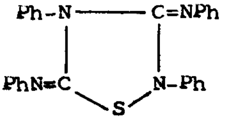
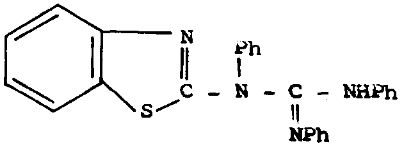
Hugershoff suggested[1] 2,4-diphenyl-3,5-diphenylimino-1,2,4- thiadiazolidine structure(I) for his base obtained from the oxidation of 1,3-diphenylthiocarbamide. No experimental evidence was furnished in support of this formulation. Suresh[2] reinvestigated the general chemistry and degradation products of Hugershoff's base and concluded that it could not be represented as (I) and suggested N-2-benzothiazolyl-N,N',N"-triphenylguanidine structure (II) for this base and it was later on confirmed by Verma and Sarkar[3] through unambiguous synthesis.



I



II

Apart from the above work there is no information in literature on the mechanism of the above changes. It has now been found possible to establish a series of stages in the oxidation of 1,3-diphenylthiocarbamide.

On careful oxidation with bromine in moist chloroform medium the bis-(diphenylformamidine)-disulphide dihydrobromide (III) m.p.146-47°C is formed in almost quantitative yield. This disulphide (III) on treatment with absolute ethanol extruded an atom of elemental sulphur and afforded yellow solution from which a pale yellow product identified as bis-(diphenylformamidine)-monosulphide hydrobromide[4] (IV),was isolated. It could not be crystallised without decomposition,m.p. 156°C.

The monosulphide (IV) on gentle warming in absolute ethanol was isomerised into yet another product (V) which could not be crystallised without decomposition; m.p.236-37°C. This compound(V) was formulated as tetraphenylformamidinothiocarbamide hydrobromide since on warming with water it rapidly decomposed into phenylisothiocyanate and triphenylguanidine hydrobromide. An ethanolic solution of (V) when further oxidised with bromine afforded Hugershoff's base,m.p.136°C in quantitative yields.The analytical values for elements in compounds III,IV and V corresponded with the formulae $C_{26}H_{22}N_4S_2$, 2HBr, $C_{26}H_{22}N_4S$,HBr and $C_{26}H_{22}N_4S$,HBr respectively.

From these results and other work in the related fields it appears that the sequence of oxidation and isomeric changes given in chart-1 represent the overall picture of the oxidation of 1,3-diphenylthiocarbamide in ionizing solvents in general. The process involved are undoubtedly "ionic" and further studies on these will be published elsewhere.

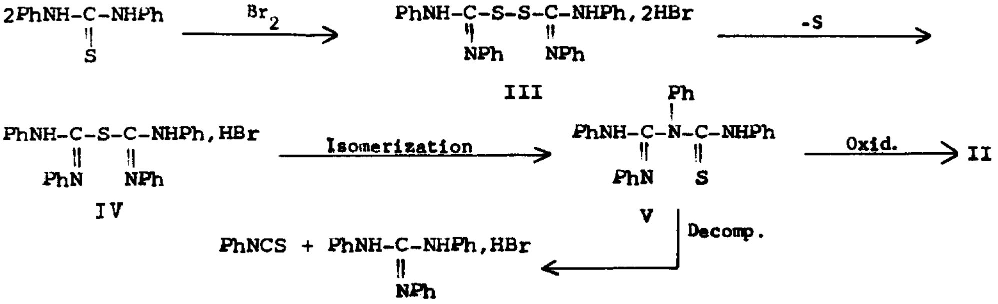


CHART-1

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