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ON HECTOR'S BASE

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THE new structure (VIII) is suggested for Hector's base from a consideration of its conversion into the isomer (IV) and synthesis from (VII).

Phenyl thiocarbamide by its oxidation in acidic aqueous or alcoholic solutions is known to form a base $C_{14}H_{12}N_4S$, m.p. 181°, first obtained by Hector[1] who assigned its structure (I): 3,5-diimino-2,4-diphenyl-1,2,4-thiadiazolidine. Dost[2] by heating Hector's base with (i) fuming hydrochloric acid and (ii) alcoholic ammonia obtained a non-basic compound $C_{14}H_{11}N_3SO$ and another base isomeric with Hector's base, respectively. He also obtained diphenylguanidine as one of its reduction products. Dost on his evidence favoured structure (II) while Lal and Krall[3] who carried out several unfruitful attempts towards its synthesis thought that structure (III) could not be precluded from consideration. Kurzer[4,5] has shown recently that the isomeric base obtained by Dost was really 3,5-diphenylimino-1,2,4-thiadiazolidine (IV) and opined that the structure (I) initially assigned

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[1] D.S. Hector, Ber.Dtsch.Chem.Ges. 22, 1176 (1889). For other references K.B. Lal and H. Krall, J.Indian.Chem.Soc. 16, 31 (1939); K.S. Suresh, J. Sci. Res. Banaras Hindu Univ. IX (2), 94 (1958/59); Ph. D. Thesis, Banaras Hindu University.

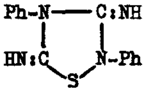
[2] K. Dost, Ber.Dtsch.Chem.Ges. 39, 863 (1906).

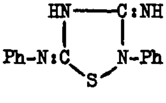
[3] K.B. Lal and H. Krall, J.Indian.Chem.Soc. 16, 31 (1939).

[4] F. Kurzer, Chem. & Ind. 526 (1956).

[5] F. Kurzer, J.Chem.Soc. 2345-52 (1956).

for the base probably represented it correctly.


I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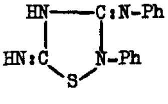
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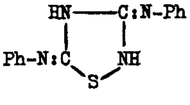
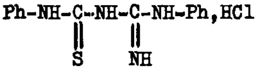

IV

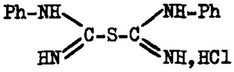
We have now found that when Hector's base is reduced with ammonium hydrogen sulphide diphenylguanidine and thiocyanic acid are produced almost quantitatively. This again favoured structure (I) but excluded (II). We have been able to synthesize Hector's base by the following sequence of changes.

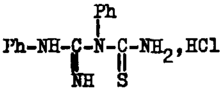
Phenylcyanamide was condensed with phenylthiocarbamide in ether acetone mixture in presence of hydrochloric acid when a colourless hydrochloride $C_{14}H_{14}N_4S$, HCl m.p. 158° of a base (VII) was obtained. This was found different from the other expected likely isomeric products (V) and (VI): The N-phenylformamidino-N'-phenylthiocarbamide (V)[5] was already known and as judged from its properties and absence of yellow colour it could also not be assigned the structure of isomeric diphenylformamidine monosulphide (VI).[6]



$\text{Ph-NH-}\underset{\underset{S}{\|}}{C}\text{-NH-}\underset{\underset{NH}{\|}}{C}\text{-NH-Ph,HCl}$

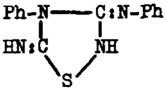
V


VI



$\text{Ph-NH-}\underset{\underset{NH}{\|}}{C}\text{-}\overset{\overset{Ph}{|}}{N}\text{-}\underset{\underset{S}{\|}}{C}\text{-NH}_2\text{,HCl}$

VII


VIII

On oxidation of VII with hydrogen peroxide (bromine and iodine also) Hector's base was obtained quantitatively.

This route of its formation, however, could lead to 3-phenylimino-4-

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[6] cf. K.S. Suresh, J.Indian.Chem.Soc. 37,483 (1960).

phenyl-5-imino-1,2,4-thiadiazolidine (VIII) or to Hector's originally suggested structure (I). Since (I) is not convertible into (IV) by a simple isomeric change as observed by Dost and Kurzer (loc.cit.) and confirmed by us now in the case of this and other Hector's bases also, we prefer structure (VIII) for this compound. A rupture of the C—N bond between positions 3 and 4 followed by an interchanging of positions of :NH and N-Ph in positions 5 and 4 respectively and reformation of C—N bond would convert (VIII) into (IV). This is supported by our observation that the corresponding C—N bond in (VII) and in 5-phenylimino-4-phenyl-3-thion-1,2,4-dithiazolidine and in 5-phenylimino-4-phenyl-3-imino-1,2,4-dithiazolidine is prone to easy disruption when heated with an amine or ammonia.

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