## 78. *The Reactions of Thiocarbonyl Chloride. Part III. Structure of the So-called "Thiocarbonyl Benzidine."*

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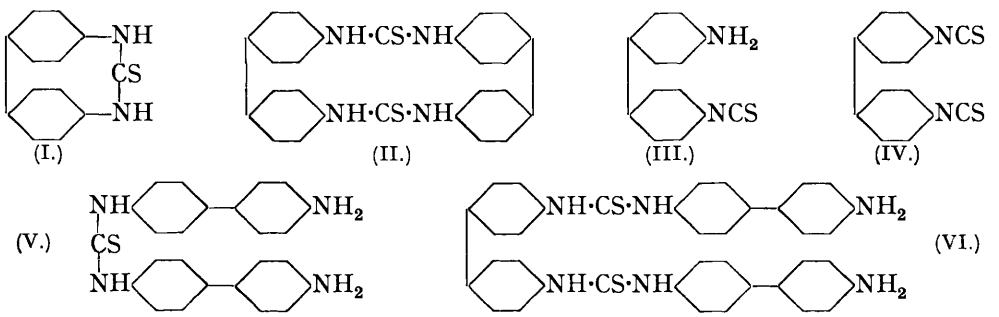
STRAKOSCH (*Ber.*, 1872, **5**, 240) prepared a compound, "thiocarbonyl benzidine," by the interaction of carbon disulphide and benzidine in alcoholic solution and suggested the formula (I) or (II) for it despite conflicting analytical evidence. Le Fèvre and Turner




(J., 1926, 2478) state that "thiocarbonyl benzidine has been found definitely to have the formula (III)." If this be correct, thiocarbonyl benzidine should have physical properties lying between those of benzidine and those of *diphenyl*-4 : 4′-*dithiocarbimide* (IV), prepared by the present authors by interaction of aqueous benzidine hydrochloride and thiocarbonyl chloride. This is emphatically not so: both benzidine and diphenyl-4 : 4′-dithiocarbimide are crystalline solids of definite m. p., distilling unchanged in a vacuum; both are soluble in benzene, ligroin, and glacial acetic acid; "thiocarbonyl benzidine," on the other hand, is an amorphous powder decomposing between 250° and 300° and insoluble in all the usual organic media. This apparent inconsistency suggested the present reinvestigation.

Formulæ (I), (II), and (III) are ruled out by analytical data; in addition, (III) is ruled out by the method of preparation, which involves prolonged boiling with alcohol, since it has been shown (Browne and Dyson, J., 1931, 3285) that compounds containing the *iso*thiocyano-group react rapidly with alcohol to form thiourethanes. This applies *a fortiori* to the purification of "thiocarbonyl benzidine" by Le Fèvre and Turner, by "repeated extraction with boiling methylated spirit."

The general properties of "thiocarbonyl benzidine" seemed to correspond to those of a substituted thiourea, and complete analysis pointed to compound (VI), 4 : 4′-*bis*-

(4''-*aminoxenyl*-4'''-*thiocarbamido*)*diphenyl*. Accordingly, this compound was synthesised by an alternative method, namely, the interaction of diphenyl-4 : 4'-dithiocarbimide and benzidine. It was identical in behaviour and appearance and properties with the " thiocarbonyl benzidine " of Strakosch.

*Analytical Data.*

| | Found. | | Calculated for formula | | |
|---|---|---|---|---|---|
| | Dyson and Browne. | Le Fèvre and Turner. | I, II, or III. | V. | VI. |
| C ..... | 72·0 | — | 69·0 | 73·2 | 71·7 |
| H ..... | 5·1 | — | 4·4 | 5·4 | 5·0 |
| N ..... | 13·0 | 13·0 | 12·4 | 13·6 | 13·2 |
| S ..... | 10·0 | — | 14·2 | 7·8 | 10·1 |

Further, when " thiocarbonyl benzidine " is heated with acetic anhydride, decomposition takes place (not acetylation as stated by Le Fèvre and Turner, *loc. cit.*), giving a product which can be separated into two fractions : (a) soluble in cold benzene, mainly 4-*acetyldiphenyl*-4'-*thiocarbimide* with a little diphenyl-4 : 4'-dithiocarbimide, and (b) monoacetylbenzidine, with a little diacetylbenzidine. In this, and in the absence of the characteristic properties of a thiocarbimide, " thiocarbonyl benzidine " conforms to the structure (VI).

## Experimental.

Thiocarbonyl benzidine was prepared by the method of Strakosch (*loc. cit.*) and purified by repeated extraction with warm ether.

4-*Acetyldiphenyl*-4'-*thiocarbimide*.—Thiocarbonyl benzidine (20 g.) was heated with acetic anhydride (175 ml.) over a small flame until it dissolved (10 hours) and was then poured into water. The cream-coloured solid obtained was washed, dried, and extracted with warm benzene. The benzene solution was concentrated and chilled to 5°; 4-*acetyldiphenyl*-4'-*thiocarbimide* then separated in needles, m. p. 224° (Found : S, 12·05. $C_{15}H_{12}ON_2S$ requires S, 11·9%). The concentrated benzene mother-liquor gave needles of *diphenyl*-4 : 4'-*dithiocarbimide*, m. p. 203° (Found : S, 23·9. $C_{14}H_8N_2S_2$ requires S, 23·8%). The benzene-insoluble portion was extracted with hot alcohol and gave monoacetylbenzidine, on cooling, in needles, m. p. 199°. The alcohol-insoluble portion proved to be diacetylbenzidine, m. p. 315° (decomp.).

*Diphenyl*-4 : 4'-*dithiocarbimide*.—Benzidine (15 g.), dissolved in 1200 ml. of 2*N*-hydrochloric acid, was agitated for 3 hours with thiocarbonyl chloride (10 g.). The thick white precipitate, having been dried, crystallised from ligroin in long needles, m. p. 203° (Found : S, 23·9%).

4 : 4'-*Dithiocarbimidodiphenylmethane*, prepared similarly from *pp'*-diaminodiphenylmethane, formed long needles, m. p. 196°, from benzene (Found : S, 22·5. $C_{15}H_{10}N_2S_2$ requires S, 22·7%).

4 : 4'''-*Diamino*-4' : 4''-*dixenylthiocarbamide* (V) was obtained as an insoluble by-product in the reaction of thiocarbonyl chloride and benzidine in acetic acid solution (cf. Jaffe, *Ber.*, 1894, **27**, 1557) giving diphenyl-4 : 4'-dithiocarbimide (Found : S, 7·8. $C_{25}H_{22}N_4S$ requires S, 7·8%).

4 : 4'-*Bis*-(4''-*aminoxenyl*-4'''-*thiocarbamido*)*diphenyl* (VI).—Benzidine (2 mols.) and diphenyl-4 : 4'-thiocarbimide in equimolecular proportion were warmed together in benzene solution. The precipitate which formed was insoluble in the usual organic media, but was purified by extraction with alcohol and ether. The final product was a cream-coloured powder, decomp. 260—280° (Found : S, 10·0. $C_{38}H_{32}N_6S_2$ requires S, 10·1%).

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