BIS-SEMIDINE INVERSION IN AROMATIC DIHYDRAZO-COMPOUNDS.

By Praphulla Chandra Guha and Hirendra Kumar Banerjee.

Benzidine inversion has hitherto been studied directly or indirectly only in the aromatic monohydrazo-compounds, and it is well known that if the para-position with respect to the hydrazo-grouping in any compound be unsubstituted, inversion generally takes place in the para-position, the para-inversion being always accompanied in a small measure by ortho-inversion (Schultz, *Ber.*, 1874, **7**, 52 ; 1882, **15**, 1539 ; 1884, **17**, 463 ; *Annalen*, 1881, **207**, 311. Andrea, *J. pr. Chem.*, 1880, **21**, 318. Jacobson, *Ber.*, 1892, **25**, 992, 1012 ; 1893, **26**, 688 ; 1894, **27**, 2700. Tauber, *Ber.*, 1892, **25**, 1025. Witt, *Ber.*, 1892, **25**, 1013, 1030 ; 1894, **27**, 2351. Stern, *Ber.*, 1884, **17**, 379. Brandraski, *Ber.*, 1884, **17**, 118. Graeff, *Annalen*, 1885, **229**, 340). The first object of undertaking the present investigation was to study the nature of inversion in the aromatic dihydrazo-compounds, the second being to ascertain whether this particular method can be utilised for the preparation of bisazo-compounds as benzidine is utilised for the preparation of congo-colours.

Symmetrical diphenylthiocarbohydrazide and symmetrical diphenylcarbohydrazide have been found to undergo bis-semidine inversion when heated at 60–65° with 3 per cent. hydrochloric acid solution. The resulting diaminodiphenylthiocarbamide (I), the carbamide (VIII) and their hydrochlorides are very rapidly oxidised by air to brownish black tarry products.

Diaminodiphenylthiocarbamide has been diazotised and coupled with β-naphthol, dimethylaniline and resorcinol to yield thiocarbamidobisbenzeneazo-β-napthol, (II), thiocarbamidobisbenzeneazodimethyaniline (III), and thiocarbamidobisbenzeneazoresorcinol (IV) respectively :

$CS(NH{\cdot}C_6H_4{\cdot}NH_2)_2$

I

$CS(NH{\cdot}C_6H_4{\cdot}N : N{\cdot}C_{10}H_6{\cdot}ONa)_2$

II

$CS(NH.C_6H_4{\cdot}N : N{\cdot}C_6H_4{\cdot}N(CH_3)_2)_2$

III

$CS(NH{\cdot}C_6H_4{\cdot}N : N{\cdot}C_6H_3(OH)_2)_2$

IV

Diaminodiphenylthiocarbamide reacts with phenyl mustard oil, phenyl *iso*cyanate and formaldehyde to yield diphenylthiocarbamidodiphenylthiocarbamide (V), diphenylcarbamidodiphenylthiocarbamide (VI) and dimethyleneaminodiphenylthiocarbamide (VII) respectively:

$\mathrm{CS(NH{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHPh)_2}$
V

$\mathrm{CS(NH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh)_2}$
VI

$\mathrm{CS(NH{\cdot}C_6H_4{\cdot}N : CH_2)_2}$
VII

Diaminodiphenylcarbamide (VIII) obtained by inversion similarly gives carbamidobisbenzeneazo-β-naphthol (IX), carbamidobisbenzeneazo-dimethylaniline (X), carbamidobisbenzeneazoresorcinol (XI) on diazotisation and coupling with β-naphthol, dimethylaniline and resorcinol respectively on the one hand and diphenylcarbamidodiphenylcarbamide (XII) and dimethyleneaminodiphenylcarbamide (XIII) with phenyl *iso*cyanate and formaldehyde respectively, on the other:

$\mathrm{CO(NH{\cdot}C_6H_4{\cdot}NH_2)_2}$
VIII

$\mathrm{CO(NH{\cdot}C_6H_4{\cdot}N : N{\cdot}C_{10}H_6{\cdot}ONa)_2}$
IX

$\mathrm{CO(NH{\cdot}C_6H_4{\cdot}N : N{\cdot}C_6H_4{\cdot}NMe_2)_2}$
X

$\mathrm{CO(NH{\cdot}C_6H_4{\cdot}N : N{\cdot}C_6H_3(OH)_2)_2}$
XI

$\mathrm{CO(NH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh)_3}$
XII

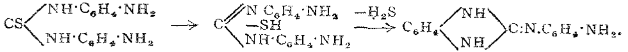
$\mathrm{CO(NH{\cdot}C_6H_4{\cdot}N : CH_2)_2}$
XIII

Similar azo-dyes were prepared by a somewhat indirect method from acetyl-*p*-phenylenediamine (D.R.P. 46737, 47902, 50852) thus:

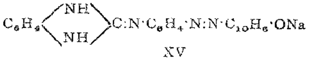
$$\mathrm{NHAc{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow NHAc{\cdot}C_6H_4{\cdot}N : N{\cdot}R \longrightarrow NH_2.C_6H_4{\cdot}N : N{\cdot}R \longrightarrow CO(NH{\cdot}C_6H_4{\cdot}N : N{\cdot}R)_3}$$

The instability of the inverted compound (I) is in direct contrast with the properties of *pp'*-diaminodiphenylthiocarbamide (a stable compound, m. p. 195°; D.R.P. 58204, 60152).

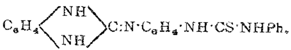
An attempt was made to prepare *pp'*-diaminodiphenylthiocarbamide by reducing *pp'*-dinitrodiphenylthiocarbamide, but the product was found to be quite different from the expected diaminodiphenylthiocarbamide and from the product obtained by inverting diphenylthiocarbohydrazide. The reduced compound is a stable base (XIV) possessing the composition $\mathrm{C_{13}H_{12}N_4}$; it contains one amino-group which gives a characteristic azo-compound (XV) and phenyl mustard oil derivative (XVI). The formation of the base may be explained on the assumption that as soon as *pp'*-diaminodiphenylthiocarbamide is formed it loses one molecule of hydrogen sulphide forming a *p*-phenyleneguanidine derivative thus :



XIV



XV



XVI

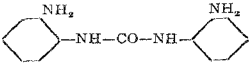
It was anticipated that if the diacetylaminodiphenylthiocarbamide could be hydrolysed by strong hydrochloric acid at ordinary temperature, elimination of hydrogen sulphide might be avoided ; but in this case also the deacetylated product was found to be free from sulphur and identical with compound XIV.

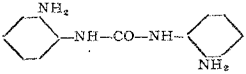
The diaminodiphenylcarbamide obtained by the inversion of diphenylcarbohydrazide is quite distinct from *pp'*-diaminodiphenylcarbamide (a stable compound, m.p 310° ; *Bull. Soc. Chim.*, 1899, **21**, 157), which has now been found to give a bis-azo compound (XVII) and a phenyl *iso*thiocyanate derivative (XVIII), different from the corresponding derivatives of the inverted compound :

$CO\,(NH{\cdot}C_6H_4{\cdot}N:N{\cdot}C_{10}H_6{\cdot}ONa)_2$ XVII

$CO\,(NH{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NHPh)^2$ XVIII

Though *oo'*-diaminodiphenylthiocarbamide is not known, its oxygen analogue, *oo'*-diaminodiphenylcarbamide is a stable compound (m.p. 243–245° ; *Bull. Soc. Chim.*, 1899, **21**, 157) and distinct from the inverted carbo-compound. Evidently, then diphenylcarbo- and thiocarbohydrazides have not undergone para-inversion. But *oo'*-diaminodiphenylcarbamide (or the thiourea) can exist in more than one possible isomeric form, e.g.,





and it is quite probable that the unstable diamino-compound obtained by inversion corresponds to the first formula and the stable one to the second formula.

EXPERIMENTAL.

IMPROVED METHOD OF PREPARING DIPHENYLTHIOCARBOHYDRAZIDE.

Phenylhydrazine phenyldithiocarbazinate (50 gms.) was placed on a shallow basin inside a steam oven at 80°. Hydrogen sulphide was evolved slowly during 3–4 hours when the mass assumed a greenish coloration; the temperature was then raised to 90°. The substance was powdered and washed several times with cold alcohol and dried in a desiccator. The yield was 30–40 gms., whereas by Fischer's method (*Annalen*, 1878, **190**, 118) scarcely 10 gms. could be obtained.

Inversion of Diphenylthiocarbohydrazide to Diaminodiphenylthiocarbamide (I).—Diphenylthiocarbohydrazide (2 gms.) was shaken with 200 c.c. of 3 per cent. hydrochloric acid in a conical flask provided with a Bunsen valve to prevent contact with air, for half an hour at 30°. The temperature was then raised to 60–65° with constant shaking and kept at that temperature for an hour. The solution became brown and was quickly filtered, being allowed to cool out of contact with air. The residue was washed several times with dilute alcohol, dried and weighed, when it was found that 0·8 gm. of the substance had passed into solution.

ATTEMPTS TO ISOLATE THE FREE BASE.

(i) The solution was evaporated to dryness on the water-bath, but as evaporation proceeded a brownish black tarry mass began to separate.

(ii) The solution was next evaporated in vacuum when a greyish solid substance was obtained which also very rapidly became brownish black in contact with air.

(iii) Even when kept in contact with air at room temperature the solution changes colour rapidly and deposits a brownish black sediment.

(iv) Sodium acetate in excess was added to the solution when a white solid appeared and in contact with air changed to a black tarry mass in 3 or 4 seconds.

From the results of the above experiments it was inferred that the free base cannot be isolated as it changes to a brownish black tarry mass in contact with air. So it was thought advisable to attempt the isolation of the hydrochloride which might possibly be more stable than the free base.

ATTEMPT TO ISOLATE THE HYDROCHLORIDE.

An excess of sodium acetate solution and 20 c.c. of ether were added to 100 c.c. of the inverted solution and shaken. The ethereal solution which turned reddish was separated and saturated with dry hydrogen chloride. The ethereal solution of the hydrochloride was then dried in a desiccator containing fused calcium chloride and dry caustic potash. Next day, the ether was allowed to evaporate, but the hydrochloride soon turned brownish black.

By adding iodine solution to the acid solution containing the diamine a brown disulphide was obtained which also became tarry very rapidly. With mercuric chloride a white precipitate was obtained, but this also soon turned black. A lead salt was also obtained by heating in a test tube an alcoholic solution of lead acetate with the inverted solution; this compound similarly turned black immediately.

Thus all attempts to isolate the diamine, its hydrochloride, disulphide or metallic derivatives proved futile.

COUPLING DIAZOTISED DIAMINODIPHENYLTHIOCARBAMIDE.

Thiocarbamidobisbenzeneazo-β-naphthol (II).—The inverted acid solution (200 c.c.) containing 0·8 gm. of the diamine was cooled to zero and treated with sodium nitrite solution drop by drop till a drop of the diazo-solution gave indication of excess of nitrous acid with iodised starch paper. A yellow precipitate of the diazonium salt separated and was gradually added to an alkaline solution of β-naphthol (1 gm.) at 0°. An orange-red azo-compound separated; it was filtered, dried and crystallised from glacial acetic acid in deep orange needles, highly soluble in alcohol, m.p. 131–132°. Yield 1·2 gms. (Found: N, 14·0; S, 4·83. $C_{33}H_{22}N_6O_2Na_2S$ requires N, 13·7; S, 5·23 per cent.).

Thiocarbamidobisbenzeneazodimethylaniline (III).—A similar solution was diazotised as before and added to 1 gm. of dimethylaniline dissolved in the least quantity of dilute hydrochloric acid with constant stirring, when a bright yellow azo-compound separated. It crystallised in deep yellow needles from absolute alcohol and melted at 164–166°. It is soluble in acetic acid. Yield 0·8 gm. (Found: N, 21·20. $C_{29}H_{30}N_8S$ requires N, 21.4 per cent.).

Thiocarbamidobisbenzeneazoresorcinol (IV).—A similarly diazotised solution was poured gradually into 1·5 gms. of resorcinol dissolved in a slight excess of alkali at 0° with constant stirring. On acidifying the product a brick red azo-compound separated; this was filtered, washed repeatedly with water and crystallised from acetic acid. It separated in plates melting explosively at 158° (Found: N, 16·41. $C_{25}H_{20}N_6O_4S$ requires N, 16·8 per cent.).

Diphenylthiocarbamidodiphenylthiocarbamide (V).—The inverted solution (200 c.c.) was neutralised with sodium carbonate and heated on the water-bath under reflux for 3 or 4 hours with phenyl mustard oil (1 gm.). The solution on concentration and cooling gave a brownish cake which was powdered and crystallised from glacial acetic acid, m.p. 182–183° ; yield 1 gm. (Found : N, 15·62. $C_{27}H_{24}N_6S_3$ requires N, 15·9 per cent.).

Diphenylcarbamidodiphenylthiocarbamide (VI).—The acid solution (200 c.c.) was shaken with excess of sodium acetate and 1 gm. of phenyl *iso*cyanate. Instantaneously, a white solid separated and crystallised in colourless, rectangular plates from glacial acetic acid; yield 1·2 gms., m.p. 238–240° (Found : N, 17·2. $C_{27}H_{24}N_6O_2S$ requires N, 16.9 per cent.).

Dimethyleneaminodiphenylthiocarbamide (VII).—The inverted solution (200 c.c.) was shaken with 1 gm. of formaldehyde (5 c.c. of 20 per cent. solution) for two hours in the shaking machine, when a white crystalline powder separated. It was insoluble in alcohol, acetic acid, acetone, pyridine, benzene and nitrobenzene, and was therefore washed with all these solvents hot. It does not melt below 300° ; yield 1·2 gms. (Found: S, 10. 9; N, 19.7. $C_{15}H_{14}N_4S$ requires S, 11·3 ; N, 19·9 per cent.).

INVERSION OF DIPHENYLCARBOHYDRAZIDE TO DIAMINODIPHENYLCARBAMIDE.[1]

Diphenylcarbohydrazide (2 gms.) was treated with 200 c.c. of 3 per cent. hydrochloric acid as in the case of the diphenylsulphocarbohydrazide. The filtered solution was allowed to cool in the absence of air. All varieties of method for isolating the base or its hydrochloride in the pure state were tried as in the case of the sulpho-compound, but without success, though definite indications were obtained as to the presence of an unstable basic compound in the inverted solution.

COUPLING DIAZOTISED DIAMINODIPHENYLCARBAMIDE.

Carbamidobisbenzeneazo-β-naphthol (IX).—The inverted solution (200 c.c.) was diazotised in the usual way and poured gradually into a solution of 1 gm. of β-naphthol in excess of alkali at 0°. A deep red azo-compound was thus obtained and crystallised from glacial acetic acid in deep red needles, m.p. 131–132° ; yield 1 gm. (Found : N, 14·4 $C_{33}H_{22}N_6O_3Na_2$ requires N, 14·1 per cent).

Carbamidobisbenzeneazodimethylaniline (X).—The inverted solution (200 c.c.) was diazotised and poured into a hydrochloric acid solution of 1 gm. of dimethylaniline. A brownish yellow azo-compound was

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[1] The preparation of the diphenylcarbohydrazide was tried by the method of G. Heller (*Annalen*, 1891, **263**, 269), but the process was found to be tedious and the yield poor. The method of S. Skinner and Ruhemann (*Ber.*, 1887, **20**, 3372) was found preferable and gave a very good yield.

thus precipitated and crystallised from absolute alcohol in needles, m.p. 160–161° ; yield 1 gm. (Found : N, 22·00. $C_{29}H_{30}ON_8$ requires N, 22·13 per cent.).

Carbamidobisbenzeneazoresorcinol (XI).—The inverted solution (200 c.c.) containing 0·8 gm. of the diamine was diazotised and poured gradually with constant stirring into a solution of 1 gm. of resorcinol in excess of alkali at 0°. On acidifying the solution, a brick-red azo-compound separated and was crystallised from glacial acetic acid, m.p 157° (decomp.) ; yield 1 gm. (Found : N, 17·7. $C_{25}H_{20}N_6O_5$ requires N, 17·3 per cent.).

Diphenylcarbamidodiphenylcarbamide (XII).—The inverted solution (200 c.c.) was treated as in the case of the corresponding thio-compound with excess of sodium acetate and 1 gm. of phenyl *iso*cyanate. The white precipitate which came out on standing was crystallised from absolute alcohol in colourless needles, m.p. 236–238° ; yield 1·2 gm. (Found : N, 17·9. $C_{27}H_{24}N_6O_3$ requires N, 17·5 per cent.).

Dimethyleneaminodiphenylcarbamide (XIII).—The inverted solution (200 c.c.) was treated with 1 gm. of formaldehyde as before, and the white crystalline powder purified by washing with hot glacial acetic acid, absolute alcohol and water. It was almost insoluble in all ordinary organic solvents and does not melt even at 300° ; yield 1 gm. (Found : N, 21·4. $C_{15}H_{14}ON_4$ requiries N, 21·0 per cent.).

p-AMINOPHENYL-p-PHENYLENEGUANIDINE HYDROCHLORIDE.

pp-Dinitrodiphenylthiocarbamide (10 gms.) was heated on the water bath for 2–3 hours with tin (50 gms.) and concentrated hydrochloric acid (125 c.c.) when the yellow colour of the mixture disappeared and hydrogen sulphide was evolved. The acid solution was then diluted to 600–700 c.c. with water, warmed and freed from tin by passing hydrogen sulphide repeatedly. The solution was then evaporated on a water bath until the appearance of crystals which recrystallised from very dilute alcohol in rectangular plates, not melting even at 300°. Absence of sulphur in this compound was proved (Found : N, 17·2. $C_{13}H_{12}N_4$, $2HCl$ $2H_2O$ requires N, 16·8 per cent.).

The base (XIV) was obtained in dark crystalline needles on adding ammonia to a cold concentrated aqueous solution of the hydrochloride, and crystallised from very dilute alcohol as long colourless needles, m.p. 295° with decomposition. In contact with air it gradually becomes black (Found : N, 24·8. $C_{13}H_{12}N_4$ requires N, 25·10 per cent.).

p-*Phenyleneguanidinobenzeneazo-β-naphthalate of sodium* (XV).—The hydrochloride (1 gm.) was diazotised and poured into an alkaline solution of β-napthol (1 gm.). The deep red azo-compound was very slightly soluble in alcohol, acetic acid and other organic solvents; m.p. above 300°.

Phenylthiocarbamidophenyl-p-*phenyleneguanidine* (XVI).—The hydrochloride (1 gm.) was heated with water (5 c.c.) and phenyl mustard oil (0·5 gm.) on the water bath under reflux for 3 to 4 hours, when a white solid separated. This was insoluble in all ordinary organic solvents and was therefore purified by repeated washing with alcohol and water. It does not melt even at 300° (Found: N, 19·1; S, 8·51. $C_{20}H_{17}N_5S$ requires N, 19·5; S, 8·91 per cent.).

pp′-DIACETYLAMINODIPHENYLTHIOCARBAMIDE.

Acetyl-*p*-phenylenediamine (10 gms.) was heated on the water bath with carbon bisulphide (10 gms.) and alcohol (10 gms.) for three hours under reflux. The white precipitate crystallised in needles from alcohol, m.p. 245°. Yield 10–11 gms. (Found: S, 9·0. $C_{17}H_{18}O_2N_4S$ requires S, 9·35 per cent.). A compound m.p. 239–40° obtained from acetyl-*p*-phenylenediamine and carbon bisulphide is described in D.R.P. 127446.

Aminophenyl-p-*phenyleneguanidine hydrochloride*.—The above compound (5 gms.) on hydrolysis with hydrochloric acid gave 2 gms. of a hydrochloride having the composition $C_{13}H_{12}N_4$, 2HCl, $2H_2O$; m.p. above 300° (Found: N, 17·0 Theory requires N, 16·9 per cent.). The base liberated by ammonia from the hydrochloride was identical with the compound (XIV) obtained from *pp*-dinitrodiphenylthiocarbamide by reduction (Found: N, 24·7. $C_{13}H_{12}N_4$ requires N, 25·1 per cent.). The acetyl derivative was obtained in the usual manner and crystallised from dilute alcohol; m.p. above 300°. Evidently, it is different from the original *pp′*-diacetylaminodiphenylthiocarbamide, m.p. 245°.

Carbamidobisbenzeneazo-β-naphthalate of sodium (XVII).—*pp′*-Diaminodiphenylcarbamide hydrochloride (1 gm.) was diazotised in the usual manner with sodium nitrite (1 gm.) and poured into an alkaline solution of β-naphthol (2 gms.). A red precipitate separated and was crystallised from glacial acetic acid, m.p. 263° (Found: N, 13·71. $C_{33}H_{22}N_6O_3Na_2$ requires N, 14·10 per cent.). Hence, it was quite different from the β-naphtholazo-compound of the inverted diphenylcarbohydrazide, which melts at 131–132° (compound IX).

Diphenylthiocarbamidodiphenylcarbamide (XVIII).—*pp′*-Diaminodiphenylcarbamide (1 gm.) was heated with alcohol (10 c.c.) and phenyl-mustard oil (0·8 gm.) under reflux for 2–3 hours, and the white precipitate crystallised from nitrobenzene; yield 0·8 gm. (Found: N, 16·8. $C_{27}H_{24}ON_6S_2$ requires N, 16·4 per cent.).

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