# CCCCIV.—*The Dicarbazyls. Part I. Synthesis of 3 : 3'-Dicarbazyl.*

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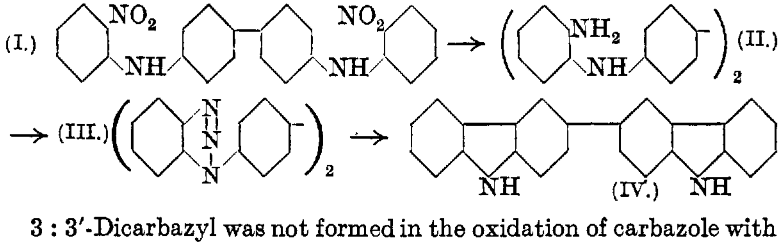
OXIDATION of carbazole gives rise to two dicarbazyls, m. p. 220° and 265°, respectively, and an amorphous substance (Perkin and Tucker, J., 1921, **119**, 216). Neither of these dicarbazyls is 3 : 3'-*dicarbazyl*, the synthesis of which has been achieved according to the scheme:



3 : 3'-Dicarbazyl was not formed in the oxidation of carbazole with potassium permanganate in acetone solution; and the amorphous substance obtained in 75% yield was not the product of oxidation of any 3 : 3'-dicarbazyl that might have been formed (compare the conversion of diphenylbenzidine into amorphous bisdiphenyldibiphenylenehydrazine; Wieland and Wecker, *Ber.*, 1922, **55**, 1804),

for 3 : 3′-dicarb zyl, on oxidation under similar conditions, gives a different amorphous substance.

3 : 3′-Dicarbazyl has also been prepared by the direct oxidation of carbazole in acid solution—a process that will be described in a future paper.

## EXPERIMENTAL.

NN′-*Di*-o-*nitrophenylbenzidine* (I).—(Method A.) A mixture of benzidine (16 g.) and *o*-chloronitrobenzene (72 g.) was stirred for 3 hours in an oil-bath at 245° (compare Schöpff, *Ber.*, 1889, **22**, 904), the hot melt poured into benzene, and, when cold, the insoluble portion extracted with cold benzene. The dark brown, powdery residue (10—15 g.) was extracted thrice with boiling xylene (200 c.c. each time). The xylene extract was boiled with animal charcoal for ½ hour and concentrated to a very small bulk; the brick-red crystals which separated on cooling recrystallised from acetic anhydride in scarlet crystals (5 g.), m. p. 240° (Found : N, 13·0. $C_{24}H_{18}O_4N_4$ requires N, 13·1%).

(Method B.) A mixture of *o*-nitrodiphenylamine (3 g.), glacial acetic acid (200 c.c.), and concentrated sulphuric acid (50 c.c.) was cooled and slowly treated with a solution of sodium dichromate (3 g.) in water (5 c.c.) and glacial acetic acid (20 c.c.) (compare Wieland, *Ber.*, 1913, **46**, 3300). After ½ hour, the reddish-purple solution was poured into excess of sulphurous acid, the brown precipitate was extracted several times with boiling xylene (residue, 1 g.), and the extracts were concentrated, filtered from a brown impurity which separated, and evaporated almost to dryness. The red crystals thus obtained melted at 240° after recrystallisation from acetic anhydride. The yield (1 g.) was slightly reduced when the quantities of acetic and sulphuric acids were halved.

The identity of the products obtained by methods A and B was established by the m. p. of a mixture of the two and also by the preparation of *NN*′-diacetyldi-*o*-nitrophenylbenzidine (see below) from each.

*o*-Nitrodiphenylamine and *NN*′-di-*o*-nitrophenylbenzidine were unattacked by sodium dichromate in cold glacial acetic acid, but were completely destroyed in the boiling solution. They were recovered unchanged from boiling acetone containing potassium permanganate.

NN′-*Di*-o-*nitrophenylbenzidine* is very sparingly soluble in glacial acetic acid or alcohol, more soluble in acetone, and very soluble in pyridine or benzaldehyde. It crystallises best from xylene or acetic anhydride.

N-o-*Nitrophenylbenzidine*.—The benzene extract mentioned above (method A) was steam-distilled, and the black residue boiled with alcohol. The solution, after being filtered from a small quantity of *NN′*-di-*o*-nitrophenylbenzidine, deposited orange crystals which, after several recrystallisations, became dark crimson and finally reddish-orange, pointed laminæ of N-*o-nitrophenylbenzidine* (Found : N, 13·7. $C_{18}H_{15}O_2N_3$ requires N, 13·8%). The yield was considerably increased by carrying out the experiment at 235°, less *NN′*-di-*o*-nitrophenylbenzidine being formed.

N-*Acetyl*-N′-o-*nitrophenylbenzidine* was prepared by boiling *o*-nitrophenylbenzidine with excess of acetic anhydride for ½ hour; the liquid, after being concentrated to a very small bulk, deposited the *acetyl* derivative. This crystallised from glacial acetic acid in orange laminæ (Found : N, 12·0. $C_{20}H_{17}O_3N_3$ requires N, 12·1%), from anisole in reddish-orange leaflets, from alcohol or xylene as a mixture of yellowish-orange and reddish-orange leaflets, and from ethyl acetate, in which it was sparingly soluble, in yellowish-orange leaflets with a bronze reflex; the ethyl acetate mother-liquor slowly deposited thick rods. All these varieties, alone or in admixture, melted at 222° and there was no evidence that solvent of crystallisation was present. The substance was almost insoluble in carbon tetrachloride or methyl alcohol but readily soluble in chloroform.

NN′-*Diacetyl*-NN′-*di*-o-*nitrophenylbenzidine* was prepared by boiling *NN′*-di-*o*-nitrophenylbenzidine with excess of acetic anhydride containing a trace of concentrated sulphuric acid (unless this catalyst was present, no reaction occurred). The solution, the colour of which changed in a few minutes from scarlet to brown, was poured into water and the precipitate was crystallised from benzene with the aid of animal charcoal, straw-yellow, diamond-shaped laminæ being obtained, m. p. 80—85° (Found : N, 8·8. $C_{28}H_{22}O_6N_4,2C_6H_6$ requires N, 8·4%). The compound separated with one molecule of solvent of crystallisation from ethyl alcohol (m. p. 120° with effervescence), glacial acetic acid (m. p. 100—105°), and methyl alcohol, in which it was sparingly soluble after the first crystallisation (m. p. 125—130°). It was very soluble in acetone, pyridine, acetic anhydride, or hot anisole, almost insoluble in carbon tetrachloride, and separated as an oil from xylene and toluene; it crystallised in minute, lemon-yellow rods from ethyl acetate.

The diacetyl derivative prepared from *NN′*-di-*o*-nitrophenylbenzidine which had been obtained from *o*-nitrodiphenylamine (method B) separated from methyl alcohol in orange crystals; successive crystallisations from ethyl acetate and methyl alcohol then gave yellow crystals.

NN′-*Di*-o-*aminophenylbenzidine* (II).—*NN′*-Di-*o*-nitrophenylbenzidine (10 g.), alcohol (250 c.c.), concentrated hydrochloric acid

(250 c.c.), and excess of tin were vigorously boiled together until the red colour changed to a faint brown (3—4 hours). The crystalline mixture obtained on cooling was separated and extracted with hot dilute hydrochloric acid and the hot extract was poured into a hot concentrated solution of caustic soda. The precipitate obtained, after being dried, crystallised from benzene, in which it was sparingly soluble, in nacreous, white plates of NN′-*di*-o-*aminophenylbenzidine*, which shrank at 205° and melted to a faintly brown liquid at 218° (yield, 60—70%) (Found: C, 78·4; H, 5·9; N, 15·3. $C_{24}H_{22}N_4$ requires C, 78·7; H, 6·0; N, 15·3%). The base is sparingly soluble in alcohol, and very soluble in acetone, *cyclo*hexanone, or pyridine, and is partly adsorbed from the solutions by animal charcoal; it is insoluble in carbon tetrachloride. It dissolves in cold glacial acetic acid and in acetic anhydride, and the solutions immediately deposit needles and prisms respectively; the reactions involved will be considered in a later paper.

The *dihydrochloride* crystallises from very dilute hydrochloric acid in cream-coloured needles arranged in fish-bone fashion and becomes green to blue at 230—260° (Found: Cl, 15·9. $C_{24}H_{22}N_4,2HCl$ requires Cl, 16·2%). It readily dissociates, even in boiling dilute hydrochloric acid, the base separating as a salmon-pink powder.

*NN*′-Di-*o*-nitrophenylbenzidine in boiling glacial acetic acid solution was readily reduced by zinc dust. This method was not adopted, however, because prolonged boiling with glacial acetic acid converted the diamino-compound produced into a benziminazole. The reaction is being studied.

4 : 4′-*Di*-1″ : 2″ : 3″-*benztriazolyldiphenyl* (III).—*NN*′-Di-*o*-aminophenylbenzidine (5 g.), dissolved in hot glacial acetic acid (100 c.c.), was added all at once to cold glacial acetic acid (100 c.c.) and solid sodium nitrite (10 g.). A pale brown, flocculent precipitate separated from the vigorously effervescing, red liquid. The mixture was boiled for a minute, and filtered while warm. The precipitate, after being washed with cold glacial acetic acid and with water, was boiled with acetic anhydride (about 1 l.) and animal charcoal for ½ hour; thereafter the product was obtained in cream-coloured micro-laminæ which shrank at 295° and melted at 299° with darkening but no effervescence (yield, 4·2 g.; 80%) (Found: N, 21·6. $C_{24}H_{16}N_6$ requires N, 21·6%). It is very soluble in hot benzaldehyde, pyridine, or nitrobenzene, sparingly soluble in anisole, and almost insoluble in glacial acetic acid, alcohol, acetone, carbon tetrachloride, amyl alcohol, xylene, or ethyl acetate. The colourless solution in concentrated sulphuric acid becomes mauve on the addition of a trace of nitric acid.

Diazotisation of *NN*′-di-*o*-aminophenylbenzidine with amyl nitrite in glacial acetic acid gave an impure product; and treatment of the amine hydrochloride in excess of hydrochloric acid with sodium or potassium nitrite solution gave deep mauve products from which it was difficult to isolate any of the desired benztriazole.

3 : 3′-*Dicarbazyl* (IV).—The preceding benztriazole derivative (4 g.) in 2 g. lots was very carefully heated over a free flame for a few minutes until it had melted and the gentle effervescence that set in had ceased. (The liquid explodes if it is overheated.) The black residue dissolved completely in anisole * (about 500 c.c.). The solution was boiled for 5 minutes with animal charcoal and filtered; the pale yellow filtrate deposited 3 : 3′-*dicarbazyl* (1·7 g.; yield, about 50%) as a colourless, microcrystalline powder (Found : C, 86·4; H, 4·7; N, 8·7. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·8; N, 8·4%).

If the decomposition of the dibenztriazolyldiphenyl has been incomplete, the filtrate from the charcoal first deposits the unchanged material as feathery crystals.

3 : 3′-Dicarbazyl melts above 350° without decomposition. It crystallises from benzaldehyde with considerable loss and from nitrobenzene, aniline, or tetrahydronaphthalene in an impure condition. It is insoluble in alcohol, carbon tetrachloride, or trichloroethylene, slightly soluble in acetone, amyl alcohol, xylene, or acetic anhydride, more soluble in methyl ethyl ketone, and readily soluble in *cyclo*hexanone or pyridine; the concentrated solutions deposit amorphous material. Mixed solvents also are ineffectual for crystallisation. 3 : 3′ -Dicarbazyl is insoluble in camphor, acetic acid, bromoform, benzene, naphthalene, and other solvents used for determining molecular weights. It dissolves in cold concentrated sulphuric acid; the emerald-green solution becomes ink-blue on addition of a trace of nitric acid—a reaction characteristic of carbazoles. 3 : 3′-Dicarbazyl distils at a red heat, subliming in small quantity in long, rectangular laminæ, and the vapour has a carbazole-like odour. It also resembles carbazole in having a faint violet fluorescence when quite pure.

3 : 3′-Dicarbazyl can be separated from dibenztriazolyldiphenyl by means of much acetone, in which the latter is insoluble.

*Oxidation of* 3 : 3′-*Dicarbazyl.*—A solution of 3 : 3′-dicarbazyl in acetone was boiled with excess of potassium permanganate for one hour. The brown precipitate was separated and warmed with sulphurous acid, and the yellow precipitate thus formed was washed with water and dried. The acetone filtrate gave similarly what seemed to be the same substance. The united amorphous products

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* The anisole was washed with aqueous ammonia (*d* 0·880) to remove traces of sulphuric acid, which turn 3 : 3′-dicarbazyl green.

dried to a pale brown powder. This was boiled with acetic anhydride containing a trace of concentrated sulphuric acid to remove unchanged 3 : 3′-dicarbazyl, but it was completely insoluble. It was insoluble in benzene, xylene, acetone, acetic anhydride, acetic acid, alcohol, ether, or chloroform. It dissolved partly, leaving gelatinous residues, in nitrobenzene, anisole, tetrahydronaphthalene, pyridine, *cyclo*hexanone, and aniline. Solutions of the substance in the last three solvents were boiled with charcoal, filtered, and poured into acetone. The small amount of precipitate obtained was pale brown. It charred at a high temperature, contained a trace of sulphur, and left no residue when burnt in oxygen.

9 : 9′-*Diacetyl*-3 : 3′-*dicarbazyl*.—3 : 3′-Dicarbazyl dissolved gradually in excess of boiling acetic anhydride, but solution was effected at once by addition of a trace of concentrated sulphuric acid. The mixture was poured into water; the precipitate crystallised from glacial acetic acid in minute rosettes of colourless needles, m. p. 247—249° (Found : C, 80·6; H, 4·6; N, 6·7. *M*, by Rast's method, 425. $C_{28}H_{20}O_2N_2$ requires C, 80·8; H, 4·8; N, 6·7%; *M*, 416). It crystallised also from anisole and was readily soluble in acetic anhydride or cold pyridine, less soluble in acetone, xylene, toluene, or ethyl acetate, and insoluble in benzene, alcohol, or carbon tetrachloride. Hydrolysis was brought about in 1—2 hours by a boiling mixture of glacial acetic acid and dilute sulphuric or hydrochloric acid; 3 : 3′-dicarbazyl was slowly precipitated as a green or as a clean grey product according as sulphuric acid or hydrochloric acid was used.

I wish to thank Mr. James Cameron for repeating several of the analyses and preparing the initial nitro-compound in quantity.

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