CXCIV.—*The Dicarbazyls. Part III. The Oxidation of Carbazole and* N-*Alkylcarbazoles in Acid Solution.*

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PERKIN and TUCKER (J., 1921, **119**, 216) have described three products of the oxidation of carbazole by potassium permanganate in acetone solution. Two of these were crystalline, A, m. p. 220°, and B, m. p. 265°, and the third amorphous, m. p. about 175°. A and B were proved to be dicarbazyls, the constitutions, however, being unknown; neither is 3 : 3′-dicarbazyl, since synthesised by Tucker (J., 1926, 3033). McLintock and Tucker (this vol., p. 1214) have shown that A is 9 : 9′-dicarbazyl.

In the present research, by oxidising 9-methylcarbazole, we made sure that, in any dicarbazyl produced, the two carbazole nuclei would be united by a bond between two carbon atoms. 9-Methylcarbazole was unaffected in acetone solution by potassium permanganate. Oxidation by Wieland's method (*Ber.*, 1913, **46**, 3296), however, gave 9 : 9′-dimethyl-3 : 3′-dicarbazyl, the constitution of which was proved by its preparation from 3 : 3′-dicarbazyl by direct methylation. These results were confirmed by analogous experiments on 9-ethylcarbazole, 9 : 9′-diethyl-3 : 3′-dicarbazyl being obtained. In both these oxidations there was no evidence of the formation of any isomeric 1 : 1′- or 1 : 3′-dicarbazyl.

The fact that no 3 : 3′-dicarbazyl was formed in Perkin and Tucker's oxidation of carbazole led us to attempt the oxidation by other methods. Carbazole, when oxidised in boiling acetic acid with sodium dichromate, gave a product which contained chromium. When, however, the :NH group was protected by sulphuric acid,

no chromium-containing products were obtained. Although no sulphate of carbazole has been isolated, it appears to exist under the experimental conditions employed, since oxidation by Wieland's method gave 3 : 3′-dicarbazyl, uncontaminated with any 9 : 9′-dicarbazyl.

The mechanism of the acid oxidation of carbazole was thought to be closely allied to that of the corresponding oxidation of diphenylamine to diphenylbenzidine (Wieland, *Ber.*, 1913, **46**, 3296. *o*-Nitrodiphenylamine gives, correspondingly, *NN′*-di-*o*-nitrophenylbenzidine; Tucker, *loc. cit.*, 3034). Two theories of the mechanism of this oxidation have been put forward : (1) That the benzene nuclei unite directly, without the formation of an intermediate product (Wieland); (2) that the primary attack occurs at the :NH group with the formation of an intermediate compound which subsequently undergoes transformation (Marqueyrol and Muraour, *Bull. Soc. chim.*, 1914, **15**, 191).

(1) In support of this assumption, Wieland has shown that tetraphenylbenzidine is formed by the oxidation of triphenylamine. This evidence is not conclusive, because the oxidation is effected in acetic acid solution, whereas in the case of diphenylamine the presence of sulphuric acid is necessary, and also because of the introduction of the acidic phenyl group. We have, however, been able to oxidise *N*-methyldiphenylamine in sulphuric acid solution to *NN′*-dimethyldiphenylbenzidine, $NMePh{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMePh$. The intermediate formation of an N—N-compound is here excluded; oxidation brings about direct C—C-linking. This is in complete agreement with Wieland's view.

(2) The investigations of Marqueyrol and Muraour have led them to the conclusion that the sulphuric acid is only necessary, in that it causes the transformation of an intermediate product. (The constitution of this intermediate product is unknown, but it has been shown that it cannot be tetraphenylhydrazine.) They base their conclusions on oxidation experiments in which they protected the NH group by varying quantities of concentrated sulphuric acid, and found that the amount of recovered diphenylamine increased with increase in the amount of concentrated sulphuric acid used. We have repeated their experiments, and have found that the amount of unchanged diphenylamine is negligible. There seems, therefore, to be no valid experimental work against the view of Wieland. Furthermore, in the analogous acid oxidation of carbazole to give 3 : 3′-dicarbazyl, the evidence is against the intermediate formation of 9 : 9′-dicarbazyl, since the transformation of 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl cannot be brought about (McLintock and Tucker, *loc. cit.*). Again, the oxidation of 9-methyl-

and of 9-ethyl-carbazole to the corresponding 3 : 3′-dicarbazyl derivatives cannot take place through the intermediate formation of a 9 : 9′-dicarbazyl.

In all the acid oxidations of carbazole and its derivatives, and also in the acid oxidation of *N*-methyldiphenylamine, brightly coloured substances are produced. We suggest that these substances possess quinonoid structures, and are similarly constituted to the analogously formed oxidation products of diphenylamine (Kehrmann and Micewicz, *Ber.*, 1912, **45**, 2641).

Experimental.

Oxidation of 9-Methylcarbazole by Wieland's Method (modified).—Methylcarbazole (5 g.) was dissolved in a mixture of glacial acetic acid (200 c.c.) and sulphuric acid (5 c.c.), and sodium dichromate (6·5 g.; $1\frac{1}{2}$ times the theoretical quantity) dissolved in the smallest quantity of water was added during 1 minute, the whole being cooled in ice. The solution turned bluish-green immediately, and a precipitate formed. After 10 minutes, the solution was poured into an equal bulk of a concentrated solution of sodium bisulphite, and heated on the water-bath until the blue colour disappeared. The green precipitate obtained was removed and extracted with benzene; the residue (0·5 g.) contained chromium. The concentrated, hot benzene solution was poured into twice its volume of hot alcohol to remove unchanged 9-methylcarbazole. The light brown, crystalline mass, deposited over-night, was dissolved in hot acetic anhydride, and glacial acetic acid added, followed by zinc dust. After boiling for 10 minutes, the dark brown solution lightened in colour; it was filtered, and the filtrate poured cautiously into ammonia solution (ammonia, *d* 0·88, diluted with its own bulk of water). The slightly coloured mass deposited was crystallised three times from benzene (charcoal). Slightly pink needles of 9 : 9′-*dimethyl*-3 : 3′-*dicarbazyl*, m. p. 200—202°, were obtained (Found: C, 86·4; H, 5·6; N, 7·8; *M*, cryoscopic in benzene, 380, 375. $C_{26}H_{20}N_2$ requires C, 86·7; H, 5·6; N, 7·8%; *M*, 360).

Oxidation of 9-Ethylcarbazole.—9-Ethylcarbazole (20 g.), glacial acetic acid (1 litre), sulphuric acid (25 c.c.), and sodium dichromate (12·8 g.) were used as in the preceding oxidation. The residue (2 g.) after the extraction with benzene contained chromium. The benzene solution was concentrated and poured into hot alcohol (400 c.c.). The brown, crystalline mass deposited over-night (16 g.) melted at 174—176°. It was purified as described above and cream-coloured prisms of 9 : 9′-*diethyl*-3 : 3′-*dicarbazyl*, m. p. 188—190°, were obtained (Found: C, 86·5; H, 6·4; N, 7·2; *M*, by Rast's method, 342, 391. $C_{28}H_{24}N_2$ requires C, 86·6; H, 6·2 N, 7·2%; *M*, 388).

Excellent yields of the crude alkylated dicarbazyls were obtained, but great difficulty was experienced in isolating the pure dicarbazyls. Fractional crystallisation from benzene, toluene, xylene, acetic anhydride, or pyridine, in which the dicarbazyls are very soluble, and also from acetic acid, alcohol, or acetone, in which they are sparingly soluble, was tried in the attempt to isolate an isomeride. Sublimation in a vacuum or treatment with potassium permanganate in acetone solution had little effect. There was no evidence of the presence of any 1 : 1′- or other isomeride.

Oxidation of Carbazole.—The procedure used in the oxidation of 9-methylcarbazole (above) was followed, pure carbazole (5 g.), glacial acetic acid (1250 c.c.), sulphuric acid (30 c.c.), and sodium dichromate (3·2 g.) being employed. After the heating following the addition of the bisulphite (1 litre), the solution was further diluted and left over-night. The light brown, flocculent precipitate was washed, dried, and extracted with anisole (500 c.c.); the green residue (1 g.) did not contain chromium. The dark brown filtrate was concentrated and boiled. with charcoal; 3 : 3′-dicarbazyl (1·7 g.), m. p. over 300°, was then obtained in colourless microcrystals. Its acetyl derivative was identical with that of synthetic 3 : 3′-dicarbazyl (Tucker, *loc. cit.*).

Methylation of 3 : 3′-*Dicarbazyl* (Stevens and Tucker's method, J., 1923, **123**, 2140).—3 : 3′-Dicarbazyl (0·8 g.) was suspended in acetone (40 c.c.), methyl sulphate (2 c.c.) added, and then powdered potassium hydroxide (2 g.). Water was added drop by drop until the potash formed a layer. After boiling for 10 minutes, the solution was poured into water, and the precipitate obtained was washed, dried, and crystallised from benzene three times, giving white needles, m. p. 198—200°. This substance was identical with 9 : 9′-dimethyl-3 : 3′-dicarbazyl prepared by oxidation of 9-methylcarbazole.

Ethylation of 3 : 3′-*Dicarbazyl.*—3 : 3′-Dicarbazyl (0·4 g.) was suspended in acetone (30 c.c.), and ethyl sulphate (5 c.c.) added; powdered potassium hydroxide (10 g.) was then added in small quantities to the boiling solution. On pouring the mixture into water, an oil was obtained (due to the large amount of potash acting on the acetone). After steam distillation, the solid residue was crystallised four times from benzene, and shown to be 9 : 9′-diethyl-3 : 3′-dicarbazyl.

Oxidation of N-*Methyldiphenylamine.*—*N*-Methyldiphenylamine (prepared as described by Gibson and Vining, J., 1923, **123**, 835, and further purified by steam distillation) (5 g.) was dissolved in a cold mixture of concentrated sulphuric acid (20 c.c.) and water (50 c.c.). To the pale yellow solution, sodium dichromate (1·35 g.), dissolved

in water (10 c.c.), was added drop by drop with shaking. A reddish-violet coloration was produced, but was rapidly discharged, and a white precipitate separated. Decoloration was more rapid as the solution became warm. When the last few drops of the dichromate solution had been added (*i.e.*, slight excess over the amount theoretically required), the mauve colour persisted. The colour was removed by treating the mixture with a few drops of sulphurous acid. The separated, salmon-coloured substance (5 g.) was extracted with benzene. Part remained insoluble. The concentrated benzene extract deposited faintly green crystals, which, after several recrystallisations from benzene and finally from acetone, gave white, nacreous laminæ, softening at 167° and melting at 170°, of NN'-*dimethyldiphenylbenzidine* (Found: C, 85·9; H, 6·8; N, 7·9; *M*, by Rast's method, 386. $C_{26}H_{24}N_2$ requires C, 85·7; H, 6·6; N, 7·7%; *M*, 364). On account of the necessary repeated crystallisations the yield of pure product (1·5 g.) was low. No isomeride could, however, be isolated. Crystallisation from ethyl acetate or acetone, without previous use of benzene, failed to purify the product. All solutions possess a faint violet fluorescence.

It crystallises from the usual organic solvents, but is insoluble in alcohol or light petroleum.

N-Methyldiphenylamine, by oxidation with potassium permanganate in acetone, gave *NN'*-dimethyldiphenylbenzidine in small yield.

Methylation of Diphenylbenzidine.—*NN'*-Diphenylbenzidine (1 g.) was dissolved in methyl sulphate (10 c.c.) by warming on the water-bath for 15 minutes. A solution of sodium carbonate in water (35 g. in 200 c.c.) was added during 1 hour, the temperature being kept between 50° and 60°. An oil separated and solidified on cooling. After being washed and dried, the solid was extracted with benzene. Crystals eventually obtained were identical with those of *NN'*-dimethyldiphenylbenzidine prepared by oxidation of *N*-methyldiphenylamine.

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