CLXVI.—*The Dicarbazyls. Part II. 9 : 9′-Dicarbazyl and its Halogen Derivatives.*

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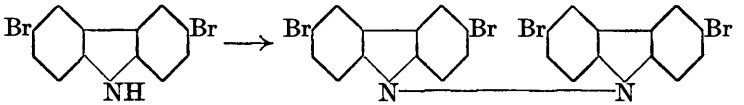
WIELAND and GAMBARJAN (*Ber.*, 1906, **39**, 1506) have stated that no bisdiphenylenehydrazine (9 : 9′-dicarbazyl) is produced when carbazole is treated with lead peroxide in benzene or with potassium permanganate in cold acetone, although both of these reagents act on diphenylamine giving tetraphenylhydrazine. Later, Perkin and Tucker (J., 1921, **119**, 216) obtained two crystalline dicarbazyls, A and B, and an amorphous product, C, by oxidising carbazole with potassium permanganate in hot acetone. The hydrogen atoms in the 9- and 3-positions of the carbazole molecule are the most reactive, and migration of groups from the 9- to the 3-position is common. Any method, therefore, which will prevent oxidation at one or other of these positions will tend to reduce the number and complexity of the oxidation products. It was with this idea in view that we attempted the oxidation of 3 : 6-dihalogen derivatives of carbazole, in the hope that oxidation would be confined to the imino-group.

When 3 : 6-dibromocarbazole was oxidised by the method of Perkin and Tucker (*loc. cit.*), a tetrabromodicarbazyl was produced. It was expected that, if this were a 9 : 9′-dicarbazyl derivative, it would reduce with comparative ease to 3 : 6-dibromocarbazole. The substance was very stable towards reducing agents, however, and likewise showed no tendency to dissociate (compare tetraphenylhydrazine). Reduction was eventually accomplished with hydriodic acid, carbazole only being produced. 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl* (II) was then synthesised as follows. 3 : 6-Dibromocarbazole (I), on treatment with finely divided potassium in benzene solution, gave a yellow potassium derivative, which was treated (without isolation) with iodine, (II) being produced.



(I.) (II.)

The oxidation product of 3 : 6-dibromocarbazole was found to be identical with (II).

Following on this, the first recorded synthesis of a derivative of 9 : 9′-dicarbazyl, we made attempts to isolate the unsubstituted hydrazine (9 : 9′-dicarbazyl). It seemed highly probable that one of the three compounds of Perkin and Tucker (*loc. cit.*) should have

this structure. Accordingly, each was reduced with hydriodic acid, in order that some clue to its constitution might be obtained. Dicarbazyl A (m. p. 220°) gave only carbazole. Dicarbazyl B (m. p. 265°) gave a substance which we have not yet identified, while the amorphous product C (m. p. 175°) gave carbazole and a high-melting, unknown compound. Since 9 : 9′-dicarbazyl on reduction should give only carbazole, dicarbazyl A seemed the most likely to have this structure. This assumption was readily verified by the direct bromination of dicarbazyl A, 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl (II) being obtained.

The foregoing experiments were repeated, 3 : 6-di-iodocarbazole being used, and dicarbazyl A iodinated.

All attempts to synthesise 9 : 9′-dicarbazyl have met with failure.

It has been shown (Wieland and Gambarjan, *loc. cit.*) that tetraphenylhydrazine may be converted into *NN′*-diphenylbenzidine by the action of cold concentrated sulphuric acid. The analogous conversion of 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl (Tucker, J., 1926, 3033) could not be brought about. *NN′*-Diphenylbenzidine is also obtained by oxidising diphenylamine in acid solution (Wieland, *Ber.*, 1913, **46**, 3296). This method of oxidation was applied to the 3 : 6-dihalogenocarbazoles in the hope that, since the 3 : 3′-compound could not be formed, a 1 : 1′-derivative might result. Only the 9 : 9′-dicarbazyl derivative was obtained, however, when acetic acid and sodium dichromate were used, whilst if sulphuric acid was present in the oxidising solution, a high-melting, amorphous substance was produced.

Attempts were made to oxidise 1 : 3 : 6 : 8-tetrabromocarbazole, by methods similar to those already described, with a view to obtain 1 : 3 : 6 : 8 : 1′ : 3′ : 6′ : 8′-octabromo-9 : 9′-dicarbazyl. The yield of the oxidation product was very small, however, and it is thought that the bromine atoms in the 1- and 8-positions must exercise some steric effect on the imino-group. This idea is substantiated by the fact that 1 : 3 : 6 : 8-tetrabromocarbazole could not be acetylated by the usual methods, nor could a nitroso-derivative be obtained.

The results obtained in the reduction of the amorphous substance C (Perkin and Tucker, *loc. cit.*) prompted some investigation into the structure of this compound, but so far the results have not justified us in assigning any formula to the substance.

EXPERIMENTAL.

3 : 6-*Dibromocarbazole.*—Some difficulty was experienced in obtaining this compound in quantity. The methods of List (Uerd. a. Rh. D.R.-P. 275,833) and of Mazzara and Leonardi (*Gazzetta*,

1895, **25**, ii, 397) were not suitable. A modification of Mazzara and Leonardi's method (*ibid.*, 1892, **22**, 569) was found to work fairly well, however.

(1) To a solution of 9-benzoylcarbazole (Stevens and Tucker, J., 1923, **123**, 2146; Tucker, *ibid.*, 1926, 546, footnote) (10 g.) in cold glacial acetic acid (140 c.c.), bromine (6 c.c.), dissolved in glacial acetic acid (10 c.c.), was added fairly rapidly. The product, which crystallised almost immediately, was removed after 3—4 hours, washed with a few c.c. of dilute alcohol, and crystallised twice from glacial acetic acid and once from benzene; 3 : 6-dibromo-9-benzoylcarbazole was then obtained in long, white needles, m. p. 213—214° (Found: Br, 37·9. Calc.: Br, 38·2%). The benzoyl derivative (2 g.) was hydrolysed by boiling it for ¼ hour with 5 c.c. of moderately concentrated alcoholic potash; short, white needles (from alcohol) of 3 : 6-dibromocarbazole, m. p. 211—213°, were obtained.

(2) A better method (similar to one described by Lindeman, *Ber.*, 1925, **58**, 2371), which we latterly used exclusively, was to brominate carbazole in carbon disulphide. Carbazole (50 g.) was dissolved in boiling carbon disulphide (600 c.c.), and a solution of bromine (34 c.c.) in carbon disulphide (130 c.c.) was added cautiously. The precipitated product was washed twice with cold carbon disulphide and crystallised twice from absolute alcohol; 3 : 6-dibromocarbazole, m. p. 211—213°, was then obtained (yield, 60%).

Oxidation of 3 : 6-*Dibromocarbazole.*—(1) *With potassium permanganate in acetone.** 3 : 6-Dibromocarbazole (5 g.) was dissolved in pure acetone (40 c.c.), finely powdered potassium permanganate (7 g.) added, and the solution boiled for 2—3 hours on the water-bath. The mixture was then poured into water, and sulphur dioxide passed through the suspension until there remained only a light reddish-brown solid, which was separated and extracted with boiling alcohol. The brown, alcohol-insoluble residue was crystallised twice from benzene, giving small, white cubes of 3 : 6 : 3′ : 6′-*tetrabromo*-9 : 9′-*dicarbazyl*, m. p. 249—250° (Found: Br, 49·2; *M*, cryoscopic in benzene, 629. $C_{24}H_{12}N_2Br_4$ requires Br, 49·4%; *M*, 648). This compound is very slightly soluble in alcohol, fairly easily soluble in acetone or glacial acetic acid, and very soluble in benzene, toluene, or xylene.

(2) *With sodium dichromate in acetic acid.* 3 : 6-Dibromocarbazole (2 g.) was dissolved in glacial acetic acid (40 c.c.), and sodium

* The acetone used in the oxidations described was purified by boiling it (2 l.) with powdered potassium permanganate (20—30 g.) for 1 hour. The acetone was recovered by distillation through a long column, the fraction, b. p. 55—57°, being retained for use.

dichromate (0·4 g.), dissolved in water (0·5 c.c.), was added. The green solution was boiled for ¼ hour and poured into cold water, and the pink precipitate so produced was removed, thoroughly extracted with boiling alcohol (three times with 20 c.c.), and then crystallised twice from benzene. Small, white cubes of 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl, m. p. 249—250°, were obtained.

(3) *With sodium dichromate in acetic acid in presence of sulphuric acid* (compare Wieland, *loc. cit.*). An uncrystallisable brown solid, m. p. above 300°, was obtained.

Reduction of 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl.*—This compound proved exceedingly stable towards reducing agents and also towards reagents known to bring about the dissociation of tetra-arylhydrazines. Boiling with zinc and glacial acetic acid (compare Wieland and Gambarjan, *loc. cit.*), or with the same reagents along with hydrochloric acid (Wieland and Haas, *Ber.*, 1922, **55**, 1804), or with tin and alcoholic–hydrochloric acid failed to effect any reduction. Similarly, the action of metallic sodium in an alcohol–benzene or in amyl-alcoholic solution produced no change.

No dissociation could be effected (*a*) by boiling with 2*N*-sulphuric acid (compare Franzen and Zimmerman, *Ber.*, 1906, **39**, 2566), (*b*) by treating an acetic acid solution with concentrated sulphuric acid, (*c*) by boiling in xylene for 1 hour (compare Wieland, *Annalen*, 1911, **381**, 200; 1912, **392**, 156), (*d*) by passing nitric oxide into a toluene solution of the dicarbazyl derivative at 90° (compare Wieland, *loc. cit.*).

Reduction with hydriodic acid. 3 : 6 : 3′ : 6′-Tetrabromo-9 : 9′-dicarbazyl (0·5 g.) was heated at 150° with concentrated hydriodic acid (3 c.c.) for 5 hours. The reaction mixture was then washed into a solution of sulphur dioxide in water. The white product thus obtained was well washed with water and extracted with boiling absolute alcohol, and the alcoholic extract was treated with animal charcoal and evaporated to dryness. The residue crystallised from benzene in white plates, m. p. 235—239°, identical with carbazole. That part of the reduction products which was insoluble in alcohol (0·03 g.) was shown, after recrystallisation from acetone, to be unchanged 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl.

Synthesis of 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl.*—3 : 6-Dibromocarbazole (1 g.) and finely divided potassium (0·5 g.) were boiled together in pure, dry benzene (25 c.c.) for 1 hour. A yellow powder separated which was possibly the potassium derivative. The mixture was cooled, and iodine (0·6 g.) in dry benzene (10 c.c.) added. After ½ hour, the liquid was filtered, the residue washed with benzene containing a little iodine, and the combined filtrate and washings were evaporated almost to dryness; alcohol was then

added. The precipitated solid was extracted three times with boiling alcohol, and the insoluble portion crystallised first from benzene and then from glacial acetic acid, giving white plates, m. p. 249—250°, which were identical with the oxidation product of 3 : 6-dibromocarbazole. Yield 20%. No other products were isolated.

3 : 6-*Di-iodocarbazole* was obtained by Tucker's method (J., 1926, 546). A useful method of purification, which avoids preparation and subsequent hydrolysis of 3 : 6-di-iodo-9-acetylcarbazole, is as follows.

Crude 3 : 6-di-iodocarbazole (1 g.) was dissolved in acetone (20 c.c.), finely powdered potassium permanganate (0·15 g.) added, and the solution boiled for 20 minutes; it was then poured into a solution of sulphur dioxide. The white precipitate, on crystallisation from benzene, gave pure 3 : 6-di-iodocarbazole, m. p. 204—206°. The m. p. of the crude material may thus be raised about 15°.

Oxidation of 3 : 6-*Di-iodocarbazole.*—(1) *With potassium permanganate in acetone.* To a boiling solution of 3 : 6-di-iodocarbazole (2 g.) in a mixture of pure acetone (20 c.c.) and benzene (6 c.c.), a large excess (2—3 g.) of powdered potassium permanganate was added, in 4 portions, during 2 hours. The manganese precipitate was removed and extracted with benzene, the extracts were added to the main filtrate, and the whole was evaporated to dryness. The residue, after being washed with cold acetone, was crystallised from benzene–acetone; small, white cubes of 3 : 6 : 3′ : 6′-*tetraiodo*-9 : 9′-*dicarbazyl*, m. p. 269—270°, were then obtained (Found : I, 60·9; *M*, cryoscopic in benzene, 824. $C_{24}H_{12}N_2I_4$ requires I, 60·8%; *M*, 834). Yield 20%. Much unchanged 3 : 6-di-iodocarbazole was recovered from the acetone washings. 3 : 6 : 3′ : 6′-Tetraiodo-9 : 9′-dicarbazyl closely resembles the tetrabromo-compound. The crystalline form is the same, and the solubilities differ only in being slightly lower for the former.

In the above oxidation, the use of the mixed solvent (acetone–benzene) materially improved the yield of the oxidation product, which was rarely as much as 15% if acetone alone was used (compare Branch and Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 2411).

(2) *With sodium dichromate in glacial acetic acid.* 3 : 6-Di-iodocarbazole (1 g.) was dissolved in glacial acetic acid (80 c.c.), and sodium dichromate (0·5 g.), dissolved in the minimum quantity of water, was added. The solution was boiled for ½ hour. The flocculent precipitate was removed and extracted with alcohol, and the insoluble portion was crystallised, first from benzene–acetone and then from benzene; small, white cubes, m. p. 269—270°, of 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl were thus obtained.

Synthesis of 3 : 6 : 3′ : 6′-*Tetraiodo*-9 : 9′-*dicarbazyl*.—3 : 6-Di-iodocarbazole (1 g.) was added to finely divided potassium (0·3 g.) in pure dry benzene (20 c.c.), and the mixture boiled for 1½ hours. As in the case of 3 : 6-dibromocarbazole, a yellow solid separated. After the mixture had cooled, a solution of iodine (0·5 g.) in dry benzene (10 c.c.) was added with constant shaking. After 1 hour, the liquid was filtered, the residue washed with benzene containing iodine, and the combined filtrate and washings were evaporated to dryness. The solid thus obtained was extracted with alcohol (to remove unchanged 3 : 6-di-iodocarbazole), and the insoluble residue crystallised from benzene (animal charcoal), white cubes, m. p. 269—270°, identical with the oxidation product of 3 : 6-di-iodocarbazole, being deposited.

Reduction of Dicarbazyl A (m. p. 220°).—Dicarbazyl A (0·5 g.) was heated under pressure with concentrated hydriodic acid at 150° for 15 hours. The reaction mixture was washed into water, and the suspension treated with sulphur dioxide to remove free iodine. The separated solid was completely soluble in boiling alcohol, indicating that no dicarbazyl A remained unreduced, since this substance is insoluble in alcohol. The alcoholic solution deposited yellowish needles, which, after one crystallisation from benzene, melted at 235—238° (with sublimation) and were identified with carbazole in the usual way. No other substance could be detected.

Reduction of Dicarbazyl B (m. p. 265°).—The treatment of dicarbazyl B (0·2 g.) with hydriodic acid (3 c.c.) was that described for dicarbazyl A. The product was soluble in alcohol and was a white, non-crystallisable substance, m. p. 100—110°, which has not yet been identified, but is being further investigated.

Reduction of the Amorphous Product C (m. p. 175°).—The substance C (0·5 g.) was heated with concentrated hydriodic acid for 20 hours at 150°. The product of reduction was isolated as in the reduction of dicarbazyls A and B. The major portion of it was soluble in alcohol; the solution deposited small plates, m. p. 235—238°, identical with carbazole. The alcohol-insoluble portion, after repeated extraction with the solvent, melted at 245—260°. It was dissolved in benzene and the solution, after being boiled with animal charcoal for ¼ hour, was filtered into excess of boiling alcohol. The precipitated solid was redissolved in benzene and the foregoing process repeated five or six times; there was then obtained a small amount of a cream-coloured, amorphous substance, m. p. 300—310°, which would not crystallise from any solvent. It is being further investigated.

Bromination of Dicarbazyl A.—It was found essential to use very pure dicarbazyl both in bromination and in iodination. Even an

amount of impurity causing a depression of 2—3° in the m. p. of dicarbazyl A makes it almost impossible to purify the product of halogenation.

Dicarbazyl A (0·5 g.) was dissolved in the minimum quantity of boiling glacial acetic acid, a solution (3·5 c.c.) of bromine (1 c.c.) in glacial acetic acid (9 c.c.) gradually added, and the turbid mixture heated on the water-bath for ½ hour; small, white, glistening plates had then separated. After cooling, these were removed, washed with boiling alcohol, and crystallised twice from benzene, small, hard cubes, m. p. 249—250°, identical with synthetic 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl, being obtained.

Iodination of Dicarbazyl A.—(1) To a solution of pure dicarbazyl A (0·5 g.) and finely divided iodine (0·75 g.) in boiling glacial acetic acid (35 c.c.), concentrated nitric acid (2·5 c.c.) in glacial acetic acid (10 c.c.) was added drop by drop until the iodine colour was discharged. After cooling, the precipitated product was removed and washed with sulphur dioxide solution and boiling alcohol. The residue crystallised from benzene in slightly yellow cubes, m. p. 269—270°, and was identical with synthetic 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl. The yellow colour, which was probably due to slight nitration, was not removed by animal charcoal.

(2) To a solution of dicarbazyl A (0·23 g.) in the minimum quantity of glacial acetic acid were successively added powdered potassium iodide (0·36 g.) and, after slight cooling, powdered potassium iodate (0·5 g.). The whole was boiled until the iodine colour had vanished, and was then poured into a solution of sulphur dioxide. The product was 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl.

9 : 9′-*Dicarbazyl.*—We made several attempts to convert 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl, but without success. Solid 9 : 9′-dicarbazyl, or a solution in glacial acetic acid, was unaffected by cold, and sulphonated by hot, concentrated sulphuric acid. Hydrochloric acid or acetic anhydride, heated under pressure with 9 : 9′-dicarbazyl, produced no change.

Many fruitless attempts were also made to synthesise 9 : 9′-dicarbazyl (i) by removal of sulphur from di-*o*-thiotetraphenylhydrazine (Pesci, *Gazzetta*, 1916, **46**, i, 103; compare Goske, *Ber.*, 1887, **20**, 233), (ii) by the action of halogens on 9-potassiocarbazole. The action of finely divided potassium on carbazole did not give 9-potassiocarbazole as in the case of the halogen derivatives.

Oxidation of 1 : 3 : 6 : 8-*Tetrabromocarbazole.*—Potassium permanganate in acetone would not oxidise this compound.

1 : 3 : 6 : 8-Tetrabromocarbazole (Votoček, *Chem. Ztg.*, 1896, **20**, 190) (1 g.) was dissolved in boiling glacial acetic acid (60 c.c.), and sodium dichromate (0·75 g.) was added. After boiling for 1 hour,

the mixture was poured into water, and the precipitate was separated and extracted with warm acetone. The insoluble residue, after several crystallisations from benzene, gave a minute quantity of small crystals, m. p. above 300°, insoluble in acetone or alcohol and almost so in glacial acetic acid. A sufficient quantity for analysis has not yet been obtained.

Amorphous Substance C, m. p. 175° (Perkin and Tucker, *loc. cit.*). —Analysis of *C* gave C, 86·8; H, 5·1; N, 8·1; *M*, 546. $C_{36}H_{23}N_3$ requires C, 86·9; H, 4·6; N, 8·45%; *M*, 497. Distillation from a paraffin bath at 300° produced carbazole and a residue, which, after purification in a manner similar to that used for the high-melting reduction product of C, was obtained as a cream-coloured solid, m. p. about 320° (Found: C, 86·1, 86·2; H, 4·9, 4·95; N, 8·2, 8·0. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·9; N, 8·4%). No crystalline derivative of this could be obtained, nor any acetyl, methyl or halogen derivative of the amorphous substance C.

The substance C was not produced by prolonged treatment of 9 : 9′-dicarbazyl with potassium permanganate in acetone.

Summary.

(*a*) 3 : 6 : 3′ : 6′-Tetrabromo-9 : 9′-dicarbazyl (m. p. 249—250°) has been prepared by the oxidation of 3 : 6-dibromocarbazole and has been synthesised by the action of iodine on 3 : 6-dibromo-9-potassiocarbazole.

3 : 6 : 3′ : 6′-Tetraiodo-9 : 9′-dicarbazyl has similarly been prepared and synthesised.

(*b*) The dicarbazyl A, m. p. 220°, of Perkin and Tucker (*loc. cit.*), on bromination, gave 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl. It is therefore concluded that dicarbazyl A is 9 : 9′-dicarbazyl.

(*c*) It has not been found possible to convert 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl.

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