359. *The Dicarbazyls. Part IV. Synthesis of* 1 : 1′-*Dicarbazyl.*

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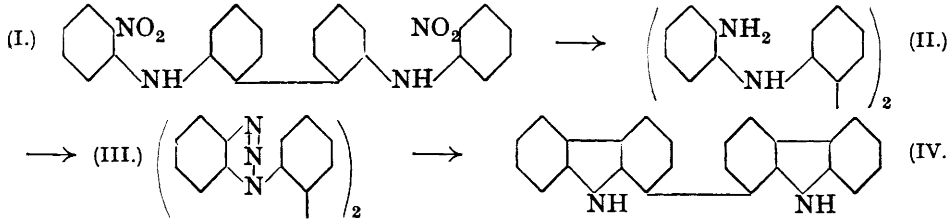
1 : 1′-*Dicarbazyl* has been synthesised from 2 : 2′-diaminodiphenyl according to the scheme :



There is no evidence that it is produced by the oxidation of carbazole (see Perkin and Tucker, J., 1921, **119**, 216; Tucker, J., 1926, 3033; McLintock and Tucker, J., 1927, 1214; Maitland and Tucker, J., 1927, 1388).

All m. p.'s are corrected. Micro-analyses are marked *.

2 : 2′-*Dinitrodiphenyl*.—(1) (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2174; Le Fèvre, J., 1929, 735; Shaw and Turner, this vol., p. 139). *o*-Chloronitrobenzene (200 g.), mixed with copper-bronze (10 g.), was briskly boiled (Pyrex flask, in oil-bath), more copper–bronze (10 g.) being added, until the copper turned grey : the process was repeated until the total quantity of copper-bronze which had been added was 75 g. (time, ½ hour). The mass was allowed to cool until alcohol could be safely added. It was shaken vigorously with the alcohol, and extraction repeated several times. (If the addition of alcohol is delayed until the melt has caked, it is almost impossible to extract with alcohol; in this case the cake is easily extracted with acetone, and the dinitrodiphenyl obtained by distillation of the acetone.) The dark-coloured alcoholic solution (charcoal) gave practically pure 2 : 2′-dinitrodiphenyl, which after recrystallisation from glacial acetic acid gave lemon-yellow crystals, m. p. 124° (75—85 g.; yield, 50—55%).

(2) Niementowski's method (*Ber.*, 1901, **34**, 3327), using *o*-nitroaniline, was also employed. The percentage yield increased with the quantities used. With $\frac{1}{5}$ the quantity recommended, a 29% yield was obtained, and with $\frac{1}{2}$ quantity a 42% yield was never exceeded. Niementowski claims a 60% yield, but the quantities mentioned are difficult to handle.

Method (1), after being developed as above, was distinctly preferable.

2 : 2′-*Diaminodiphenyl* (Niementowski, *loc. cit.*, p. 3329).—Finely-powdered 2 : 2′-dinitrodiphenyl (20 g.) was heated on a water-bath with tin (100 g.) and concentrated hydrochloric acid (200 c.c.) until a clear solution was obtained. (Heating on a sand-bath, or with addition of alcohol, seems to be deleterious.) The solution was treated with excess of caustic soda and extracted with ether. The diaminodiphenyl recovered therefrom separated from ligroin (b. p. 60—80°) in colourless crystals, m. p. 81°. Yield, 80%.

2 : 2′-*Di*-o-*nitrophenylaminodiphenyl* (I).—2 : 2′-Diaminodiphenyl (10 g.), *o*-chloronitrobenzene (80 g.), and barium carbonate (40 g.) were heated (air-bath; mercury thermoregulator) at 230° for 14 hours. [The carbon dioxide evolved measured 730 c.c. at 20°/760 mm. Apparently several reactions take place, so the volume of carbon dioxide evolved is only a useful indication of the course of the reaction. In the formation of (I) from 10 g. of diamine theory requires 1217 c.c., but it is not advisable to continue heating until this quantity has been collected.] The melt was steam-distilled until no trace of *o*-chloronitrobenzene was left, extracted with alcohol (50 c.c.) and then with acetone several times. The alcoholic extract slowly deposited scarlet crystals, and the acetone (evaporated) beetle-green leaflets. Both forms crystallised from anisole in ruby-red rhombs, m. p. 188·5—189·5° (3 g.; yield, 12%) (Found: C, 67·5; H, 4·4; N, 13·1. $C_{24}H_{18}O_4N_4$ requires C, 67·6; H, 4·2; N, 13·1%). The *amine* is practically insoluble in all cold solvents, especially ligroin.

The yield of (I) was unaltered by heating for 137 hours at 215—225° (900 c.c. CO_2), 16 hours at 225—229° (390 c.c. CO_2, from 4·2 g. diamine), when barium carbonate was replaced by calcium carbonate (5 g. diamine for 49 hours at 205—325° giving 670 c.c. CO_2), sodium carbonate (5 g. diamine for 40 hours at 205—215° giving 350 c.c. CO_2), potassium carbonate (5 g. diamine for 35 hours at 210—219° giving 520 c.c. CO_2). In general, to get the same yield of (I), the temperatures to which the reaction mixture required to be heated were, approximately, for potassium carbonate 210—215°, sodium carbonate 215—220°, barium or calcium carbonate 220—230°. The effect of lowering the temperature is instructively shown by an experiment in which potassium carbonate was used: 2 : 2′-Diaminodiphenyl (20 g.), *o*-chloronitrobenzene (150 g.), and potassium carbonate (80 g.) were heated for 35 hours at 205—208°; 2290 c.c. of carbon dioxide were collected. The melt was steam-distilled and extracted with much alcohol. Nearly all dissolved. The cold solution deposited (I) (3 g.). After filtration and evaporation the alcoholic liquor deposited 2-*o*-nitrophenylamino-2′-aminodiphenyl (the half-condensation product, considered below) (6 g.), and then much deep red oil (which, before and after distillation in a vacuum, was soluble in but would not crystallise from the usual solvents). The alcoholic filtrate on standing deposited *oo*′-dinitrodiphenyl ether [0·5 g., crystallised first from methyl alcohol, then from ligroin (b. p. 80—100°), as a felt of colourless crystals which powdered with the softness characteristic of camphor], m. p. 113—114° (uncorr.) alone or mixed with a specimen prepared as given by Haeussermann (*Ber.*, 1896, **29**, 1446, 2083; 1897, **30**, 738, footnote) (Found: *C, 55·6; H, 3·2; *N, 10·8. Calc.: C, 55·4; H, 3·1; N, 10·8%). This substance and carbazole were obtained in varying amounts when the temperature of reaction was higher than the above. For example, when 2 : 2′-diaminodiphenyl (5 g.) and *o*-chloronitrobenzene (50 g.) were heated for 3 hours at 245° (oil-bath temperature; internal temperature about 230°), as in the preparation of *NN*′-di-*o*-nitrophenylbenzidine (Tucker, *loc. cit.*, p. 3034), the only products were *oo*′-dinitrodiphenyl ether (2·3 g.) and carbazole (0·3 g.). The formation of the former is difficult to explain, since no *o*-nitrophenol could be detected in the *o*-chloronitrobenzene, and no carbonate was used in this preparation.

The use of sodium acetate in place of barium carbonate gave no yield of (I), but a golden-yellow crystalline substance from acetone, m. p. above 240°.

Replacement of *o*-chloronitrobenzene by the corresponding bromo- or iodo-compound led to negative results, although carbon dioxide was evolved, and at lower temperatures than with *o*-chloronitrobenzene. Boiling 2 : 2′-diaminodiphenyl and *o*-chloronitrobenzene in quinoline or in diethylaniline solution was likewise without positive result.

An attempt to prepare (I) by heating 2 : 2′-diaminodiphenyl with *o*-nitrophenyl *p*-toluenesulphonate (Ullmann and Nádai, *Ber.*, 1908, **41**, 1872) and (a) quinoline, or (b) sodium acetate gave unworkable oils.

NN′-*Diacetyl*-2 : 2′-*di*-o-*nitrophenylaminodiphenyl* was prepared by boiling 2 : 2′-di-*o*-nitrophenylaminodiphenyl with excess of acetic anhydride containing a trace of concentrated sulphuric acid (essential) for 10 minutes. Unless the acetic anhydride was of good quality, acetylation did not take place. The colour changed from red to pale brown. The solution was poured into water, and the precipitated product crystallised from glacial acetic acid in faintly yellow prisms (Found by heating at 120° : $C_2H_4O_2$, 13·4. $C_{28}H_{22}O_6N_4,C_2H_4O_2$ requires $C_2H_4O_2$, 15·3%). It crystallises from methyl alcohol or ethyl acetate in large, faintly greenish rhombs, m. p. 246—249° (Found : *C, 65·7; H, 4·1; N, 10·9. $C_{28}H_{22}O_6N_4$ requires C, 65·9; H, 4·3; N, 11·0%). The methyl-alcoholic residual liquor deposited a mixture of rhombs and long, pale greenish-yellow needles : the latter were not further examined.

2-o-*Nitrophenylamino-2′-aminodiphenyl* † was prepared in greatest quantity as described under the preparation of 2 : 2′-di-*o*-nitrophenylaminodiphenyl from 2 : 2′-diaminodiphenyl (20 g.), *o*-chloronitrobenzene (150 g.), and potassium carbonate (80 g.) for 35 hours at 205—208° (yield, 6 g. ; 18%). It crystallised best from alcohol in rosettes of orange prisms, m. p. 113—114·5°. It is much more soluble in all solvents than is (I). Orange crystals were also obtained from carbon tetrachloride (Found : N, 13·9. $C_{18}H_{15}O_2N_3$ requires N, 13·8%) or ligroin ; but scarlet crystals were mixed with orange when crystallisation was carried out from methyl alcohol, acetone (and water), benzene (and ligroin) (Found : N, 13·8%). Mixed m. p. determinations also showed that the two forms were of the same substance.

Treatment with hydrochloric acid converted it into the *hydrochloride*, which crystallised very slowly from glacial acetic acid in bright scarlet crystals (Found : N, 12·4. $C_{18}H_{15}O_2N_3,HCl$ requires N, 12·3%). It shrank slightly at 207° and melted at 222° with vigorous evolution of hydrogen chloride, leaving the original amine ; there was no sign of closure of the ring to form *o*-nitrophenylcarbazole. The production of the last-named compound is under consideration.

Heating 2-*o*-nitrophenylamine-2′-aminodiphenyl with *o*-chloronitrobenzene gave only small amounts of (I).

2-o-*Nitrophenylamino-2′-diacetylaminodiphenyl*, prepared by boiling 2-*o*-nitrophenylamino-2′-aminodiphenyl with acetic anhydride for 5 minutes, crystallised from ethyl acetate in bright scarlet prisms, m. p. 192—194° (Found : *C, 67·9; H, 4·9; N, 10·7. $C_{22}H_{19}O_4N_3$ requires C, 67·9; H, 4·9; N, 10·8%).

2 : 2′-*Di*-o-*aminophenylaminodiphenyl* (II).—2 : 2′-Di-*o*-nitrophenylaminodiphenyl (5 g.), glacial acetic acid saturated with hydrogen chloride (75 c.c.), and stannous chloride (5 g.) were boiled together, and, at intervals, three further quantities (5 g. each) of stannous chloride were added, and hydrogen chloride passed into the solution. The red colour gave place to green (about 2 hours). After further heating (2 hours) most of the acetic acid and hydrogen chloride was evaporated, the residue poured into excess of concentrated caustic potash solution, and the precipitate collected, dissolved in dilute hydrochloric acid (charcoal), reprecipitated with alkali, washed, and dried. The salmon-pink product (4·1 g.), recrystallised from toluene and then from ethyl acetate, formed small white needles, m. p. 225—227° (2·2 g. ; 50%) [Found : N, 15·1; *M* (Rast), 380. $C_{24}H_{22}N_4$ requires N, 15·3% ; *M*, 366].

The same result was obtained by reducing the nitro-compound (I) with tin, concentrated hydrochloric acid, and alcohol (10 hours). This agreement eliminates the possibility that reduction with acetic acid and hydrogen chloride might have produced a benziminazole.

The *amine* (II) is fairly or slightly soluble in most of the usual solvents, but is insoluble in boiling methyl or ethyl alcohol or ether.

2 : 2′-*Di*-1″ : 2″ : 3″-*benztriazolyldiphenyl* (III).—2 : 2′-Di-*o*-aminophenylaminodiphenyl (2·4 g.) was dissolved in hot glacial acetic acid (200 c.c. ; a large excess to avoid formation of tar) and cooled in ice, and aqueous sodium nitrite (considerable excess) added. The red liquid was left in ice for ½ hour and at room temperature for 3 hours and then slowly diluted with water to produce a slow deposition of pale brown crystals (2·3 g.), which crystallised from benzene in large colourless prisms softening at 184°, m. p 195° (Found : N, 18·4 ; C_6H_6, 16·8. $C_{24}H_{16}N_6,C_6H_6$ requires N, 18·0; C_6H_6, 16·7%). Heated at 120°, the crystals lost benzene, and then melted at 194—196° without decomposition [Found : N, 21·8; *M* (Rast), 379. $C_{24}H_{16}N_6$ requires N, 21·7% ; *M*, 388]. The substance crystallised in rosettes of hexagonal-ended prisms from alcohol, m. p. 178—186° ; similarly from methyl alcohol, or glacial acetic acid ; all probably containing solvent of crystallisation. It was fairly soluble in carbon tetrachloride, ethyl acetate or acetone, and slightly soluble in ether.

1 : 1′-*Dicarbazyl* (IV).—The foregoing benztriazole (2·3 g.) was gently heated to effect a

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† The m. p. of *N*-*o*-nitrophenylbenzidine is 145—148° (uncorr.). It was inadvertently omitted in J., 1926, 3035.

continuous evolution of nitrogen : a yellow fume was produced without explosion. The melt was finally boiled vigorously. It was extracted with benzene (charcoal, 5 minutes), and the benzene evaporated. The residue (1·2 g.) crystallised from carbon tetrachloride in rosettes of greenish needles, m. p. 172—174°; but after recrystallisation from glacial acetic acid diluted with a few drops of water, and then from glacial acetic acid (violet fluorescence), large colourless prisms were obtained (Found : $C_2H_4O_2$, 26·9. $C_{24}H_{16}N_2,2C_2H_4O_2$ requires $C_2H_4O_2$, 26·6%). 1 : 1'-*Dicarbazyl* (freed from acetic acid) is a white powder, m. p. 205—207° [Found : *C, 86·5; H, 4·8; *N, 8·4; *M* (Rast), 328. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·8; N, 8·4%; *M*, 332]. A benzene solution of 1 : 1'-dicarbazyl, diluted with ligroin, gave long needles. It is readily soluble in methyl or ethyl alcohol and very soluble in ethyl acetate, acetone, chloroform or anisole.

1 : 1'-Dicarbazyl is a white substance possessing a slight violet fluorescence. It dissolves in cold concentrated sulphuric acid to give a faintly green solution, unchanged on warming, but turned intense bluish-green on addition of a trace of nitric acid : on warming, the colour fades to yellow. The fluorescence and colour changes are exhibited similarly by carbazole, 9 : 9'-, 3 : 3'-, and the 265°-melting dicarbazyls.

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