366. *The Dicarbazyls. Part VI. Synthesis of* 1 : 1′-*Dicarbazyl.*

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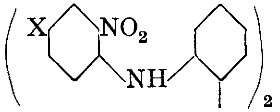
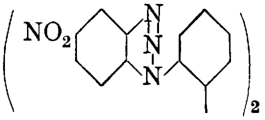
The synthesis of 1 : 1′-dicarbazyl from compounds of the type (I) has been attempted with three compounds: (a) X = H; (b) X = NO_2; (c) X = CN. Synthesis from (a), *i.e.*, from 2 : 2′-di-*o*-nitrophenylaminodiphenyl, has been described (Macrae and Tucker, J., **1933**, 1520). Since this initial material was difficult to obtain, attempts from (b) and (c) were made. That from (c) (I; X = CN) was eventually successful, 2 : 2′-*di-*(2″-*nitro*-4″-*cyanophenylamino*)*diphenyl* having been hydrolysed to the corresponding *carboxylic acid*, which by decarboxylation gave 2 : 2′-di-*o*-nitrophenylaminodiphenyl (I;

X = H), from which, as mentioned above, 1 : 1′-dicarbazyl has been synthesised. Similarly 2 : 2′-*di*-(2″-*amino*-4″-*cyanophenylamino*)*diphenyl* gave the corresponding *carboxylic acid*, which was decarboxylated to give 2 : 2′-di-*o*-aminophenylaminodiphenyl, the intermediate amine in the synthesis of 1 : 1′-dicarbazyl.

(I.)



(II.)



Impracticable routes from (c), the cyano-compound, to this end are described in the experimental part of this paper.

Synthesis from (b) (I; X = NO_2), *i.e.*, from 2 : 2′-*di*-(2″ : 4″-*dinitrophenylamino*)*diphenyl*, by the well-known Graebe–Ullmann method, failed, since reduction of 2 : 2′-*di*-(5″-*nitro*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl* (II) gave unworkable products.

In the course of the synthesis of 1 : 1′-dicarbazyl from 2 : 2′-di-(2″-nitro-4″-cyanophenylamino)diphenyl, it was found that hydrolysis of this compound to the corresponding carboxy-compound was difficult, as was also hydrolysis of 2 : 2′-*di*-(5″-*cyano*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl*; but hydrolysis of 2 : 2′-di-(2″-amino-4″-cyanophenylamino)diphenyl proceeded easily.

Brewin and Turner (J., 1928, 332) find that 4-chloro-3-nitrobenzonitrile and 1-chloro-2 : 4-dinitrobenzene have practically equal reactivity towards piperidine. We find that the former (cyano) compound is less reactive than the latter (nitro) towards 2 : 2′-diaminodiphenyl, for 2 : 2′-di-(2″ : 4″-dinitrophenylamino)diphenyl is obtained by heating 2 : 2′-diaminodiphenyl with 1-chloro-2 : 4-dinitrobenzene, etc., at 140°, whereas for the preparation of 2 : 2′-di-(2″-nitro-4″-cyanophenylamino)diphenyl from the diamine and 4-chloro-3-nitrobenzonitrile a temperature of 150—180° is necessary. At 150°, only the "half-condensation" product, 2-(2″-*nitro*-4″-*cyanophenylamino*)-2′-*aminodiphenyl*, is obtainable. The inability of Brewin and Turner (*loc. cit.*) to distinguish a difference between 1-chloro-2 : 4-dinitrobenzene and 4-chloro-3-nitrobenzonitrile in reactivity towards piperidine may be due to that difference being imperceptible in a very rapid reaction. In the reaction with 2 : 2′-diaminodiphenyl, mentioned above, these two chloro-compounds react relatively slowly, even at elevated temperatures; and the fact that the minimum temperature at which reaction takes place is different for the two shows that a difference in reactivity exists.

Comparison of reactivities of halogen derivatives of benzene is complicated by the fact that the reagent acted upon has a considerable influence on the reaction (Davies, Storrie, and Tucker, J., 1931, 625).

Dey and Doraiswami (*J. Indian Chem. Soc.*, 1933, **10**, 309) have shown that when 1-chloro-2 : 4-dinitrobenzene, 2-chloro-5-nitrobenzonitrile, and 2-chloro-5-nitrobenzoic acid are compared, not only are NO_2 and CN of unequal activating effect (on Cl), but the relative values of influence of NO_2, CN, and CO_2H depend on the type of compound acted upon. Hence the comparison we have made above is only intended to emphasise the difficulty of drawing deductions with regard to relative reactivities after consideration of reaction with only one other type of reactant.

For the nitration of *p*-chlorobenzonitrile the density of the nitric acid used is of fundamental importance. Nitration with acid (cold) of density 1·51 gives a theoretical yield of 4-chloro-3-nitrobenzonitrile; but attempts with 1·49 acid (boiling) give either unchanged *p*-chlorobenzonitrile (after boiling for 1 minute) or a mixture of it with *p*-chlorobenzoic acid (after boiling for 15 minutes). Hydrolysis is complete when *p*-chlorobenzonitrile is heated (15 minutes) with concentrated nitric acid (*d* 1·42).

Although *p*-chlorobenzonitrile requires for nitration nitric acid of density 1·51, *p*-dichlorobenzene and *p*-chlorobenzoic acid are nitrated by acid of density 1·48. Bearing in mind that in *p*-dichlorobenzene the chlorine atoms do not reinforce one another in directive effect, whilst in the other two compounds mentioned the groups present support one another, it is clear that, with regard to nitration in the benzene ring, the cyano-group has a weaker directing power than chlorine or carboxyl. The fact that it is difficult to compare the *m*-directing capacities of the cyano-group and carboxyl gives considerable interest to this sharply defined difference in the action of nitric acid on the compounds mentioned.

After we had, in the course of the above-described work, prepared 2 : 2′-di-(2″ : 4″-dinitrophenylamino)diphenyl, Le Fèvre (J., 1929, 733) described the preparation of this compound. We disagree in several points : we find that the compound crystallises in brick-red prisms, m. p. 233—236° (238—241°, corr.). The substances described by Le Fèvre as melting at 177—178° [considered by him to be 2 : 2′-di-(2″ : 4″-dinitrophenylamino)diphenyl] and 216—217° (considered by him to be *N*-2′ : 4′-dinitrophenylcarbazole) are probably the substances prepared by us, *viz.*, the *salicylidene* derivative of 2-(2″ : 4″-*dinitrophenylamino*)-2′-*aminodiphenyl* (m. p. 178—179·5°) and 2 : 2′-di-(2″ : 4″-dinitrophenylamino)diphenyl (m.p. 233—236°), respectively. We have prepared N-2′ : 4′-*dinitrophenylcarbazole* from carbazole and 1-chloro-2 : 4-dinitrobenzene, and find for it m. p. 188—190°.

We cannot agree with Le Fèvre (*loc. cit.*, p. 735) that " complete absence of steric hindrance during *NN*′-disubstitution " is *proved*; for although, according to his statement, " with the appropriate reagents, disalicylidene, dibenzoyl, diacetyl, and diformyl derivatives are formed *exclusively*," this exclusive formation of *NN*′-di-derivatives does not take place when the reagent is *o*-chloronitrobenzene, 1-chloro-2 : 4-dinitrobenzene, or 4-chloro-3-nitrocyanobenzene; since these give rise to *N*-*mono*substituted and, under slightly more vigorous conditions, the *NN*′-*di*substituted derivatives. Again, by heating 2-*o*-nitrophenylamino-2′-aminodiphenyl with *o*-chloronitrobenzene, only a small yield of 2 : 2′-di-(*o*-nitrophenylamino)diphenyl was produced (Macrae and Tucker, *loc. cit.*, p. 1522). [The supposition that in this reaction the initial product was removed from the reaction by decomposition to 9-*o*-nitrophenylcarbazole is rendered improbable after consideration of the fact that the hydrochloride of 2-*o*-nitrophenylamino-2′-aminodiphenyl on heating gives back unchanged amine and no carbazole derivative (*ibid.*).]

These examples indicate that there may be a weak steric effect; but that any steric effect is often negligible in comparison with the polar effect is shown by the following facts : Acetylation and ethylation of diphenylamine, *o*-nitrodiphenylamine, and of 2 : 4-dinitrodiphenylamine are increasingly difficult in this order, *i.e.*, as nitro-groups are introduced. Similarly 2 : 2′-di-*o*-nitrophenylaminodiphenyl can be acetylated (Macrae and Tucker, *loc. cit.*), but 2 : 2′-di-(2″ : 4″-dinitrophenylamino)diphenyl cannot, under the same conditions. These effects are polar.

Again, comparison of the ease of acetylation of *o*-nitrodiphenylamine and of 2 : 2′-di-(*o*-nitrophenylamino)diphenyl does not indicate that there is any appreciable steric hindrance to formation of the *NN*′-diacetyl derivative of the latter (diphenyl compound). On the other hand, comparison of the reactivity of 2 : 4-dinitrodiphenylamine (which can be acetylated) and of 2 : 2′-di-(2″ : 4″-dinitrophenylamino)diphenyl (which cannot be acetylated) forces one to the conclusion that the inhibition of acetylation of the diphenyl derivative *may* be due to steric hindrance.

EXPERIMENTAL.

Attempts to synthesise 1 : 1′-*Dicarbazyl.—Method A. From* 2 : 2′-*di*-(2″ : 4″-*dinitrophenylamino*)*diphenyl.* 2 : 2′-Diaminodiphenyl (Macrae and Tucker, *loc. cit.*, p. 1521) (20 g.), 1-chloro-2 : 4-dinitrobenzene (75 g.), and anhydrous potassium carbonate (30 g.) were heated together, with vigorous stirring, in an oil-bath at 140° for 4 hours. Benzene (250 c.c.) was added to the hot melt, and when cool the insoluble portion was collected and washed with benzene (to remove 1-chloro-2 : 4-dinitrobenzene) and water. 2 : 2′-*Di*-(2″ : 4″-*dinitrophenylamino*)*diphenyl* crystallised at first from acetic anhydride or pyridine in brick-red crystals, m. p. 233—236° (238—241° corr.) (45 g.; yield 80%) (Found : C, 55·7; H, 3·0; N, 16·3. $C_{24}H_{16}O_8N_6$ requires C, 55·8; H, 3·1; N, 16·3%), but afterwards, especially from cold dilute solutions, acetic anhydride gave a mixture of red and yellow crystals, and pyridine, yellow crystals (loss at 150°, 13·5. $C_{24}H_{16}O_8N_6,C_5H_5N$ requires loss, 13·3%). Both yellow compounds gave the same brick-red form, m. p. 233—236°, on heating to remove solvent of crystallisation [cf. 2 : 2′-di-(2″-nitro-4″-cyanophenylamino)diphenyl, p. 1676].

Repetition of Le Fèvre's work (*loc. cit.*) by heating the reactants at about 190° for 10 minutes (effervescence, not " boiling," being observed) gave 2 : 2′-di-(2″ : 4″-dinitrophenylamino)-diphenyl (60% yield). At higher temperatures the yield was reduced. When heating, as above, was for 5 minutes, subsequent extraction with alcohol gave much unchanged 1-chloro-2 : 4-dinitrobenzene, the remainder being removed by extraction with cold benzene. The residue was crystallised from amyl alcohol, and washed with or crystallised from much ethyl alcohol, giving 2-(2″ : 4″-*dinitrophenylamino*)-2′-*aminodiphenyl* in iridescent orange leaflets, m. p. 166—168° (168—170° corr.) after slight softening at 162° (1 g.; yield, 10%) (Found: C, 61·8; H, 4·2; N, 15·7. $C_{18}H_{14}O_4N_4$ requires C, 61·7; H, 4·0; N, 16·0%). A better yield of the compound was obtained when a mixture of 2 : 2′-diaminodiphenyl (2 g.), 1-chloro-2 : 4-dinitrobenzene (2·5 g., *i.e.*, only slight excess), and potassium carbonate (3 g.) in xylene (25 c.c.) was boiled for 1 hour. Xylene was removed, and the residue washed with water, dried, and crystallised twice from amyl alcohol to give the above compound (1·5 g.; yield, 38%). An experiment in which alcohol was used in place of xylene gave the desired compound, but chiefly 2 : 4-dinitrophenetole by a reaction which is found to be generally applicable and will be developed later.

Salicylidene derivative of 2-(2″ : 4″-*dinitrophenylamino*)-2′-*aminodiphenyl.* The amine was heated with salicylaldehyde, and the product crystallised from alcohol, in which it was soluble with difficulty. Recrystallised from acetone, it formed orange-coloured prisms of 2-(2″ : 4″-*dinitrophenylamino*)-2′-*salicylideneaminodiphenyl*, m. p. 178—179·5° (181—182·5° corr.) (Found: C, 66·1; H, 4·0; N, 12·1; *M*, Rast's method, 448. $C_{25}H_{18}O_5N_4$ requires C, 66·1; H, 4·0; N, 12·3%; *M*, 454). It is practically insoluble in cold sodium hydroxide solution, but dissolves slightly on warming to give a reddish solution: this coloration is not due to solution of salicylaldehyde obtained by hydrolysis, since the latter dissolves in alkali to give a yellow solution.

N-2′ : 4′-*Dinitrophenylcarbazole.* A mixture of carbazole (20 g.), 1-chloro-2 : 4-dinitrobenzene (52 g.), and anhydrous potassium carbonate (20 g.) was heated in an oil-bath at 170—180° for 12 hours with frequent shaking and was then extracted with glacial acetic acid (150 c.c., charcoal). The product which crystallised therefrom contained carbazole. Crystallisation from xylene, in which the carbazole remained dissolved, gave orange-brown crystals (powdered, yellow), m. p. 188—190°, of N-2′ : 4-*dinitrophenylcarbazole.* Yield, 50% (Found: C, 64·6; H, 3·3; N, 12·5. $C_{18}H_{11}O_4N_3$ requires C, 64·9; H, 3·3; N, 12·6%). It is sparingly soluble in alcohol.

2 : 2′-*Di*-(2″-*amino*-4″-*nitrophenylamino*)*diphenyl.* 2 : 2′-Di-(2″ : 4″-dinitrophenylamino)-diphenyl (30 g.) was powdered and added to a mixture of rectified spirits (150 c.c.) and ammonia solution (*d* 0·88, 50 c.c.); the mixture was saturated with hydrogen sulphide, then heated on the water-bath for 15 minutes, again saturated with hydrogen sulphide, and reheated. Finally, a dark red solid separated. The intermittent passing of hydrogen sulphide and heating was repeated six times; the contents of the flask were then poured into water. The solid was collected, and the amine extracted as the hydrochloride by repeated treatment with 10% hydrochloric acid. Ammonia solution precipitated therefrom 2 : 2′-*di*-(4″-*nitro*-2″-*aminophenylamino*)*diphenyl.* It crystallised from benzene in small, bright red crystals, m. p. 126° (12 g.; yield, 45%) (Found: N, 18·5. $C_{24}H_{20}O_4N_6$ requires N, 18·4%).

2 : 2′-*Di*-(5″-*nitro*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl.* 2 : 2′-Di-(4″-nitro-2″-aminophenylamino)diphenyl (10 g.) was dissolved in glacial acetic acid (50 c.c.), coarsely powdered sodium nitrite (3 g.) added, and the whole heated to boiling. The product obtained on pouring into water separated from methyl alcohol (solubility 1%), or from other solvents, as an amorphous, yellow powder, m. p. about 140° (9·5 g.; yield, 90%) (Found: N, 23·1. $C_{24}H_{14}O_4N_8$ requires N, 23·4%). It exploded when heated on a spatula.

Method B. From 2 : 2′-*di*-(2″-*nitro*-4″-*cyanophenylamino*)*diphenyl.* The difficulty encountered in method A was essentially the removal of the nitro-groups. This necessity was obviated by the use of 4-chloro-3-nitrobenzonitrile, which was found to be nearly as reactive as 1-chloro-2 : 4-dinitrobenzene (compare Brewin and Turner, *loc. cit.*). It condenses with 2 : 2′-diaminodiphenyl to give the expected two products, *viz.*, 2-(2″-*nitro*-4″-*cyanophenylamino*)-2′-*aminodiphenyl* and 2 : 2′-*di*-(2″-*nitro*-4″-*cyanophenylamino*)*diphenyl.*

Synthesis of 4-*chloro*-3-*nitrobenzonitrile.* Claus and Stiebel's method (*Ber.*, 1887, **20**, 1379) was unsatisfactory.

Method I. *p*-Chlorotoluene ⟶ *p*-chlorobenzoic acid ⟶ 4-chloro-3-nitrobenzoic acid ⟶ acid chloride ⟶ amide ⟶ 4-chloro-3-nitrobenzonitrile.

p-Chlorotoluene (20 g.), glacial acetic acid (250 c.c.), and concentrated sulphuric acid (50 c.c.) in water (50 c.c.) were boiled together and a solution of sodium dichromate (60 g.) in water (100 c.c.) was added during ½ hour with frequent shaking. The whole was then boiled for a further ½ hour. On cooling, pure *p*-chlorobenzoic acid, m.p. 238° (24 g.; yield, nearly theoretical), crystallised (compare *Annalen*, 1866, **139**, 336; *Ber.*, 1875, **8**, 880). A slight amount of oil was also obtained.

p-Chlorobenzoic acid (25 g.) was dissolved by warming in fuming nitric acid (100 c.c., *d* 1·50), and the mixture poured into water; the 4-chloro-3-nitrobenzoic acid obtained was crystallised from alcohol, m. p. 180—181° (yield, theoretical).

4-Chloro-3-nitrobenzoic acid (50 g.) was treated with phosphorus pentachloride (58 g.), the phosphorus oxychloride removed under reduced pressure on the water-bath, dry carbon tetrachloride (80 c.c.) added, and the whole poured into ammonia solution (300 c.c.; *d* 0·88). The acid *amide* (43 g.; yield, 87%) crystallised from water in small colourless needles, m. p. 153—154°, readily soluble in alcohol or benzene (Found: N, 14·1. $C_7H_5O_3N_2Cl$ requires N, 14·0%).

4-Chloro-3-nitrobenzamide (50 g.) was heated at 170°, phosphoric oxide (75 g.) added with vigorous shaking, and the mixture heated for 1 hour. Water was added, then sodium carbonate solution, and after 12 hours the nitrile was collected and crystallised from alcohol, m.p. 101° (uncorr.) (37 g.; yield, 85%).

Method II. Mattaar's method (*Rec. trav. chim.*, 1922, **41**, 25), slightly modified, was much quicker. *p*-Chloroaniline gave *p*-chlorobenzonitrile in 65—70% yield. The latter (10 g.) was added to nitric acid (50 c.c.; *d* 1·51). The solution was poured into water after 20 minutes, and pure 4-chloro-3-nitrobenzonitrile, m. p. 101°, obtained in theoretical yield (Mattaar gives 110°).

Action of Nitric Acid on p-*Chlorobenzonitrile*.—(1) "Commercial" fuming nitric acid (*d* 1·50) contains nitrogen peroxide, and accordingly the density is misleading with regard to the percentage of nitric acid present (Lunge and Rey, *Z. angew. Chem.*, 1891, 165; Lunge and Marchlewski, *ibid.*, 1892, 10; Bousfield, J., 1919, **115**, 48). The fuming nitric acid (*d* 1·51) used in the preparation of 4-chloro-3-nitrobenzonitrile (above) was prepared by distilling concentrated nitric acid (*d* 1·42) with concentrated sulphuric acid (1½ vols.): the faintly greenish-yellow distillate had $d^{15°}$ 1·513. The acid (*d* 1·505) obtained by heating sodium nitrate with concentrated sulphuric acid also effected nitration. Acid of *d* 1·500 (prepared by dilution of acid of *d* 1·51 with water or with concentrated nitric acid of *d* 1·42) gave incomplete nitration unless the reaction mixture was left over-night; a practically theoretical yield was then obtained. Nitric acid of *d* 1·49 (diluted 1·51 acid) would not nitrate *p*-chlorobenzonitrile.

Estimation of the percentages of nitric acid present in the solutions of *d* 1·49 and 1·51 by the method of Kolb (*Ann. Chim. Phys.*, 1867, **10**, 136) gave results in substantial agreement with those obtained by Lunge and Rey (*loc. cit.*).

(2) *p*-Chlorobenzonitrile was kept over-night or boiled (1 min.) with nitric acid (*d* 1·49 or 1·48) and then poured into water. Unchanged material was recovered. Longer boiling (15 mins.) brought about partial hydrolysis but no nitration. Complete hydrolysis to *p*-chlorobenzoic acid was effected by boiling *p*-chlorobenzonitrile with concentrated nitric acid (*d* 1·42) for 15 minutes; pure *p*-chlorobenzoic acid (m. p. 236°; theoretical yield) separated from the hot solution.

Hydrolysis of 4-*Chloro*-3-*nitrobenzonitrile*.—This was effected by boiling (15 mins.) the nitrile (1 g.) with concentrated nitric acid (10 c.c.; *d* 1·42). On cooling, 4-chloro-3-nitrobenzoic acid crystallised (yield, theoretical) (cf. Claus and Kurz, *J. pr. Chem.*, 1888, **37**, 197).

Action of Nitric Acid on p-*Dichlorobenzene and on* p-*Chlorobenzoic Acid*.—The chloro-compound (10·7 g. of the former, or 11·4 g. of the latter) was added to nitric acid (50 c.c.; *d* 1·48), in the case of *p*-chlorobenzoic acid with warming to bring about solution and complete reaction. After 20 minutes the solutions were poured into water and theoretical yields of 1 : 4-dichloro-2-nitrobenzene and 4-chloro-3-nitrobenzoic acid were obtained. Nitration of *p*-chlorobenzoic acid is complete in the *cold* if a greater quantity (75 c.c.) of nitric acid of higher density (*e.g.*, 1·49) is used.

Condensation of 2 : 2′-*Diaminodiphenyl with* 4-*Chloro*-3-*nitrobenzonitrile*.—2 : 2′-Diaminodiphenyl (10 g.), 4-chloro-3-nitrobenzonitrile (50—60 g.), and anhydrous potassium carbonate (15—20 g.) were heated to 160° in 1 hour, maintained thus for another hour, then heated to 180° and maintained at this temperature for 2 hours. The mixture was finally heated at 185° for ½ hour. The dark red, solid mass was heated with water, the aqueous extract decanted, and the residue repeatedly heated with alcohol until a yellow powder was obtained. This was crystallised from anisole to give 2 : 2′-*di*-(2″-*nitro*-4″-*cyanophenylamino*)*diphenyl*, which separated from *warm* concentrated solutions in scarlet cubes, orange when powdered, m. p. 243—248° (Found: C, 65·8; H, 3·4; N, 17·9. $C_{26}H_{16}O_4N_6$ requires C, 65·8; H, 3·4; N, 17·6%). Yield, 15 g. (58%). Crystals from cold, more dilute solutions were canary-yellow needles containing solvent of crystallisation, *e.g.*, from anisole, acetic anhydride, pyridine (orange crystals; loss at 100°, 14%; $C_{24}H_{16}O_4N_6,C_5H_5N$ requires loss, 14·2%), nitrobenzene (loss at 100°, 23·2%; $X,C_6H_5{\cdot}NO_2$ requires loss, 20·5%), benzene (loss at 140°, 13%; X,C_6H_6 requires loss, 14%).

When the above condensation was carried out at 150°, or for several hours in xylene, the alcoholic extract (see above) gave a mixture of yellow crystals of 4-chloro-3-nitrobenzonitrile, and brick-red plates. Hot ether removed the former; the residue (1·5 g.) after crystallisation from alcohol had m. p. 143° and consisted of 2-(2″-*nitro*-4″-*cyanophenylamino*)-2′-*aminodiphenyl* (Found : C, 69·1; H, 4·4; N, 17·0. $C_{19}H_{14}O_2N_4$ requires C, 69·1; H, 4·2; N, 17·0%), sparingly soluble in ether and soluble in dilute acids. Heated with 4-chloro-3-nitrobenzonitrile, it gave 2 : 2′-di-(2″-nitro-4″-cyanophenylamino)diphenyl.

Hydrolysis of 2 : 2′-*Di*-(2″-*nitro*-4″-*cyanophenylamino*)*diphenyl*.—The above compound (2 g.), glacial acetic acid (4 c.c.), and concentrated hydrochloric acid (6 c.c.) were heated in a sealed tube during 2 hours to 200° and there maintained for 1—2 hours. The product was washed with water, and was either employed as such or crystallised by dissolving it in pyridine and adding half the volume of alcohol and then water to the hot solution until a precipitate formed. On cooling, orange-brown, iridescent leaflets of 2 : 2′-*di*-(2″-*nitro*-4″-*carboxyphenylamino*)*diphenyl* separated, m. p. above 300°; it melted, over a free flame, with decomposition (Found : N, 11·1. $C_{26}H_{18}O_8N_4$ requires N, 10·8%). It is soluble to deep red solutions in alkalis, insoluble in the usual solvents or in dioxan or methyl ethyl ketone, and slightly soluble in *cyclo*hexanone or *cyclo*hexanol.

Hydrolysis of the above nitro-cyano-compound (5 g.) as effected with the corresponding amino-cyano-compound (see below) was incomplete (0·5 g. of nitrocarboxy-compound in 4 hours).

Hydrolysis of the nitro-cyano-compound could not be effected by boiling with dilute caustic soda solution (Sandmeyer, *Ber.*, 1885, **18**, 1494), but a peculiar decomposition ensued. The nitro-cyano-compound (1 g.) was heated at 160° with sodium hydroxide (2 g.) in alcohol (10 c.c.) in a sealed tube. The product was added to dilute hydrochloric acid, and the white solid which separated was collected and dissolved in alcohol; on cooling, a grey solid, m. p. above 300°, separated. The mother-liquor gave a substance which after recrystallisation from alcohol melted at 198° and was evidently 3-amino-4-hydroxybenzoic acid, probably obtained by fission of the diphenylamine group (with accompanying reduction) (Storrie and Tucker, J., 1931, 2258).

Attempts to effect hydrolysis by means of nitric acid gave a polynitro-compound, m. p. about 225° (Found : N, 19·5%). Similarly, sulphuric acid solution (80%) was useless, since the product was sulphonated.

Decarboxylation of 2 : 2′-*Di*-(2″-*nitro*-4″-*carboxyphenylamino*)*diphenyl to give* 2 : 2′-*Di*-o-*nitrophenylaminodiphenyl*.—The nitro-carboxy-compound (1 g.) was heated at 320° with copper-bronze (3 g.) in a long evacuated Pyrex tube. Red fumes were evolved; decomposition was complete in a few minutes. The product was extracted with acetone, the extract evaporated to dryness, and the crystalline residue recrystallised from ethyl acetate (or anisole), forming ruby-red rhombs, m. p. 188·5—189·5° (corr.), which were identical (mixed m. p.) with 2 : 2′-di-*o*-nitrophenylaminodiphenyl (Macrae and Tucker, *loc. cit.*).

2 : 2′-*Di*-(2″-*amino*-4″-*cyanophenylamino*)*diphenyl*.—The above nitro-compound (5 g.) was heated for 1 minute with a large excess of stannous chloride (25 g.) and glacial acetic acid saturated with hydrogen chloride (100 c.c.) (heating should not be prolonged). The pale greenish-brown solution was poured into cold concentrated sodium hydroxide solution and the precipitate was filtered from the hot solution, washed with alkali and water, dried, and extracted with boiling alcohol. Practically all dissolved, and from the solution large brown prisms (3·7 g.) were deposited, m. p. 120° (efferv.), and 190—194° after drying at 100°. Recrystallised from alcohol (charcoal), large colourless prisms (2·1 g.) of 2 : 2′-*di*-(2″-*amino*-4″-*cyanophenylamino*)-*diphenyl* were obtained, m. p. 194—197° (Found : C, 75·2; H, 5·1; N, 20·0. $C_{26}H_{20}N_6$ requires C, 75·0; H, 4·8; N, 20·2%).

Hydrolysis of 2 : 2′-*Di*-(2″-*amino*-4″-*cyanophenylamino*)*diphenyl to* 2 : 2′-*Di*-(2″-*amino*-4″-*carboxyphenylamino*)*diphenyl*.—The amino-cyano-compound (2·1 g.) was boiled for 1 hour with glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (50 c.c.); more hydrochloric acid (50 c.c.) was then added, and boiling continued (1 hour) (hydrolysis is incomplete in ¾ hour). The solution was evaporated to small bulk, water added, and then sodium hydroxide solution until no more precipitation took place (addition of excess of alkali gave complete solution). The white precipitate was removed, washed, and dried; it separated from nitrobenzene as a pale brown, crystalline powder (1·5 g.), softening at 265°, blackening at 275°, and melting with effervescence at 280° (Found : C, 68·9; H, 4·9; N, 12·4. $C_{26}H_{22}O_4N_4$ requires C, 68·7; H, 4·8; N, 12·3%). It was insoluble in camphor. The white precipitate behaved peculiarly : at first it crystallised from alcohol, but became insoluble after the first crystallisation (similarly from methyl alcohol or ethyl acetate) : it now crystallised as a salmon-tinted powder from amyl alcohol, but, at each subsequent attempt to recrystallise the substance, part remained insoluble. The insoluble portions crystallised normally from nitrobenzene in pale brown crystals. All the crops appeared to consist of the same compound. There was no evidence that the amino-carboxy-compound was losing carbon dioxide in the boiling solutions.

The amino-carboxy-compound (0·8 g.) with a small amount of copper–bronze was carefully heated (free flame) in a long evacuated (15 mm.) Pyrex tube. From the brown residue, toluene extracted a substance which, recrystallised from ethyl acetate, gave pure white micro-needles (0·1 g.), m. p. 225—227° (corr.) alone or mixed with 2 : 2′-di-*o*-aminophenylaminodiphenyl (Macrae and Tucker, *loc. cit.*).

2 : 2′-*Di*-(5″-*cyano*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl*.—A solution of 2 : 2′-di-(2″-amino-4″-cyanophenylamino)diphenyl (2 g.) in glacial acetic acid (20 c.c.) and 10% hydrochloric acid (100 c.c.) was slowly treated with an excess of sodium nitrite solution and finally warmed until effervescence was vigorous. After cooling, the precipitate (1·3 g.) obtained crystallised from glacial acetic acid in white nacreous plates of 2 : 2′-*di*-(5″-*cyano*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl*, m.p. 269° (Found : N, 25·9. $C_{26}H_{14}N_8$ requires N, 25·6%).

Decomposition of 2 : 2′-*Di*-(5″-*cyano*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl*.—The compound (1 g.) was heated at 320° for ½ hour. The product was extracted with glacial acetic acid (charcoal) ; on cooling, a colourless material separated which, recrystallised from glacial acetic acid, gave a compound, m. p. 305—307°, probably 6 : 6′-dicyano-1 : 1′-dicarbazyl.

Hydrolysis of 2 : 2′-*Di*-(5″-*cyano*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl*.—The benztriazole (1 g.) was heated at 160° in a sealed tube for 3 hours with sodium hydroxide (2 g.) in alcohol (10 c.c.). The product was acidified with hydrochloric acid ; the 2 : 2′-*di*-(5″-*carboxy*-1″ : 2″ : 3″-*benztriazolyl*)*diphenyl* obtained separated slowly from acetic anhydride as a white, microcrystalline powder, unmelted at 330° (Found : N, 17·4. $C_{26}H_{16}O_4N_6$ requires N, 17·6%).

Ethylation of 2 : 4-*Dinitrodiphenylamine*.—2 : 4-Dinitrodiphenylamine (10 g.) and potassium hydroxide (10 g., powder) were mixed with alcohol (not acetone) (100 c.c.), and ethyl sulphate (15 c.c.) added to the boiling solution. After dark red oils, which separated on cooling, had been removed, orange crystals of 2 : 4-dinitro-*N*-ethyldiphenylamine, m. p. 98° (uncorr.) (Storrie and Tucker, *loc. cit.*), were deposited in small yield.

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