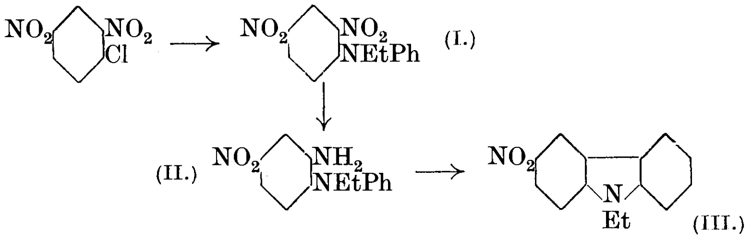
CCCVII.—*Syntheses in the Carbazole Series. The Alleged Synthesis of 3-Nitro-*N*-ethylcarbazole.*

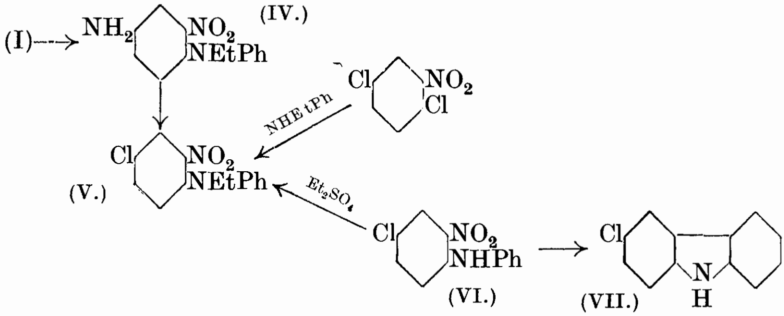
By FREDERICK ROBERT STORRIE and STANLEY HORWOOD TUCKER.

DELÉTRA and ULLMANN (*Arch. Sci. nat. phys. Genève*, 1904, **17**, 78) synthesised a substance which they called *p*-nitroethylcarbazole, *i.e.*, 3-nitro-*N*-ethylcarbazole (III), by the following stages: 1-Chloro-2 : 4-dinitrobenzene and ethylaniline were condensed in alcoholic solution in the presence of fused sodium acetate to form 2 : 4-dinitro-*N*-ethyldiphenylamine (I), which was reduced by means of ammonium sulphide to a substance assumed to be 4-nitro-2-amino-*N*-ethyldiphenylamine (II). The sulphate of this base was diazotised and the resulting solution heated with copper powder to give the alleged *p*-nitroethylcarbazole.



They describe this substance as a red, crystalline powder, m. p. 108° (decomp.), " peu soluble dans l'éther et l'alcool." Stevens and Tucker (J., 1923, **123**, 2143) have pointed out that these properties do not agree with those of the compound they prepared by ethylating 3-nitrocarbazole, which consists of yellow needles, m. p. 125—128°, undecomposed at 230°, very soluble in ether; nor with those of the compound obtained by Meister, Lucius, and Brüning (D.R.P., 259504 7/12/1911), Morgan and Read (J., 1922, **121**, 2715), and others, *viz.*, yellow crystals, m. p. 128°, soluble in alcohol. Thus the substance obtained by Delétra and Ullmann is not 3-nitro-*N*-ethylcarbazole, and all attempts to repeat their preparation have failed.

Those authors ignored the possibility that the 4- instead of (or in addition to) the 2-nitro-group might have been reduced, and on repeating the reduction in alkaline solution we were able to isolate 2-nitro-4-amino-*N*-ethyldiphenylamine only (60% yield). The constitution of this compound (IV) has been established as follows: Diazotisation and treatment of the resulting diazonium chloride solution with (*a*) copper powder or (*b*) cuprous chloride gives 4-*chloro*-2-*nitro*-N-*ethyldiphenylamine* (V), whose constitution has been proved by its synthesis from 1 : 4-dichloro-2-nitrobenzene and ethylaniline, and also by the ethylation of 4-chloro-2-nitrodiphenylamine (VI), in which the nitro-group must be *o*- and not *p*- to the imino-group because 3-chlorocarbazole (VII) was synthesised from it by Ullmann (*Annalen*, 1904, **332**, 93) (confirmed by us).



Since (V) was the only compound isolated in this investigation, it is clear that Delétra and Ullmann's failure to prepare 3-nitro-*N*-ethylcarbazole was due to the reduction of the 4-nitro-group as suggested above.

2 : 4-Dinitro-*N*-methyldiphenylamine provided a similar series of compounds, resulting in the formation of 4-*chloro*-2-*nitro*-N-*methyldiphenylamine.*

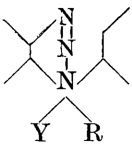
This influence of the alkyl group in causing reduction of the 4-nitro-group in preference to the 2-nitro-group is still under investigation.

Blom (*Helv. Chim. Acta*, 1921, **4**, 1036) failed to synthesise the corresponding carbazoles, starting from 2 : 4-dinitro-4′-R-diphenylamines (R = Cl, OMe, or OEt). A similar explanation to the above, *viz.*, that the 4- and not the 2-nitro-group was reduced, may be advanced; but since Blom gives analyses for the benztriazole compounds intermediately obtained, this is not tenable without further investigation. It is more probable that at the high temperature required the nitro-group effects complete decomposition (but compare Brady, Hewetson, and Klein, J., 1924, **125**, 2401). This same suggestion applies to Delétra and Ullmann's failure to synthesise 3-nitrocarbazole from 2 : 4-dinitrodiphenylamine (*loc. cit.*), in which process the 2-nitro-group was undoubtedly reduced, since 3-aminocarbazole was obtained (Ullmann, *Ber.*, 1898, **31**, 1697; *Annalen*, 1904, **332**, 93).

It is generally assumed that in the reduction of 2 : 4-dinitro-compounds the 2-nitro-group is preferentially reduced; but there are numerous instances showing that whether the 2- or the 4-nitro-group is first attacked is greatly influenced by the nature of the reducing agent, whether alkaline or acid (compare Thiele and

Escales, *Ber.*, 1901, **34**, 2846, on 2 : 4-dinitrostilbene; Nisbet, see below; Anschütz and Heusler, *Ber.*, 1886, **19**, 2161, on 2 : 4-dinitrotoluene; Limpricht, *Ber.*, 1885, **18**, 1400; Nietzki and Almanräder, *Ber.*, 1895, **28**, 2969, on 2 : 4-dinitrodiphenylamine; Claus and Stiebel, *Ber.*, 1887, **20**, 1379, on 1-chloro-2 : 4-dinitrobenzene; Brady, Day, and Reynolds, J., 1929, 2264, on 2 : 4-dinitromethylaniline; and other references given by them).

In the Graebe–Ullmann carbazole synthesis (*Annalen*, 1896, **291**, 16; Ullmann, *Ber.*, 1898, **31**, 1697) a benztriazole derivative is formed [(VIII), after removal of Y and R]. In the synthesis of *N*-alkylcarbazoles from *N*-alkyldiphenylamines it is not likely that triazoles of the type (VIII) are obtained, since carbocyclic structures are synthesised by analogous methods in the synthesis of phenanthrene (Pschorr, *Ber.*, 1896, **29**, 496) and of fluorene (Fischer and Schmidt, *Ber.*, 1894, **27**, 2787).



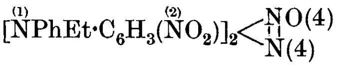
(VIII.)

We have synthesised *N*-ethyl- and *N*-methyl-carbazole by treatment of *N*-ethyl- and *N*-methyl-diphenylamine-2-diazonium chlorides with sodium hydroxide solution (Burton and Gibson, J., 1924, **125**, 2501; see also Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339).

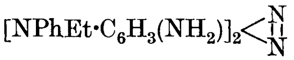
Attempts to reduce preferentially the 2- instead of the 4-nitro-group in these alkylated 2 : 4-dinitrodiphenylamines have been made by employing *acid* reducing agents, *e.g.*, tin and hydrochloric acid, tin and an acetic acid solution of hydrochloric acid, titanous chloride and titanous sulphate in acid solution, but no reduction products could be isolated.

By the action of sodium sulphide in alcoholic solution on 2 : 4-dinitro-*N*-ethyldiphenylamine, two other products were obtained which analyses indicated were (*a*) a nitro-azoxy- (probably 2-*nitro*-4-*azoxy*-) N-*ethyldiphenylamine* (IX) and (*b*) an *aminoazo*-N-*ethyldiphenylamine* (X). Confirmation of the nature of (IX) was obtained from the action of benzoin on 2 : 4-dinitro-*N*-ethyldiphenylamine in alcoholic solution, after Nisbet (J., 1927, 2081).*

(IX.)



$$[\overset{(1)}{\mathrm{N}}\mathrm{PhEt{\cdot}C_6H_3}(\overset{(2)}{\mathrm{N}}\mathrm{O_2})]_2{<}\begin{matrix}\mathrm{NO(4)}\\ \vdots\\ \mathrm{N(4)}\end{matrix}$$



$$[\mathrm{NPhEt{\cdot}C_6H_3(NH_2)}]_2{<}\begin{matrix}\mathrm{N}\\ \vdots\\ \mathrm{N}\end{matrix}$$

(X.)

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* An interesting point about Nisbet's work is that his equation $2R{\cdot}NO_2 + 3CHR(OH){\cdot}CO{\cdot}R = R_2N_2O + 3R{\cdot}CO{\cdot}CO{\cdot}R + 3H_2O$ cannot represent the reaction which is actually taking place, for, in the case of dinitrostilbene, calculating the yield obtained on the amount of benzoin used, one obtains 111% of product. The amount of sodium ethoxide used (a few drops of a 5% solution) cannot account for this yield, and some other action must be occurring: the amount of benzoin used in almost all cases is too little theoretically to give the yields which are stated. We have communicated with Dr. Nisbet but have not been able to arrive at a satisfactory explanation.

In the course of an attempted synthesis of 3 : 6-dicarboxycarbazole, 2-nitro-4-carboxy-4′-methyldiphenylamine was oxidised with potassium permanganate in alkaline solution, but, instead of the expected 2-nitro-4 : 4′-dicarboxydiphenylamine, there was obtained a mixture of *p*-toluidine and 3-nitro-4-hydroxybenzoic acid. These compounds also result from alkaline fission of the diphenylamine, and the observation is in agreement with that recorded by Ikuta (*Annalen*, 1887, **243**, 272).

Attempts to split *o*-nitrodiphenylamine and 2 : 4-dinitro-*N*-ethyldiphenylamine by heating with concentrated potassium hydroxide solution (and also by fusion in the former case) were unsuccessful.

EXPERIMENTAL.

2 : 4-Dinitro-*N*-ethyldiphenylamine was prepared by the method of Delétra and Ullmann (*loc. cit.*) (m. p. 98°; yield, 65%).

*Reduction of 2 : 4-Dinitro-*N*-ethyldiphenylamine.*—(a) *By means of ammonium sulphide.* The method outlined by Delétra and Ullmann was used, and the base isolated as sulphate (m. p. 97—99°; yield 25%).

(b) *By means of sodium trisulphide.* Sodium sulphide crystals ($Na_2S,9H_2O$; 30 g.), powdered sulphur (8 g.), and rectified spirits (1—2 c.c.) were heated until a clear brown solution was obtained. This was added in small quantities to a boiling solution of 2 : 4-dinitro-*N*-ethyldiphenylamine (36 g.) in methylated spirits (200 c.c.), and the mixture boiled under reflux for 2 hours. The solvent was distilled off, and the tarry product washed with water, and extracted with benzene. The dried benzene solution was saturated with dry hydrogen chloride, and a mass of red crystals was obtained. Crystallisation from alcohol containing a little hydrochloric acid gave the *hydrochloride* of 2-nitro-4-amino-*N*-ethyldiphenylamine, reddish-orange leaflets, m. p. 183—185° (decomp.) (Found : Cl, 12·1. $C_{14}H_{16}O_2N_3Cl$ requires Cl, 12·1%); yield 60%. (Any sulphur formed as a by-product in the above preparation remains dissolved in the benzene when the hydrochloride is precipitated.) The action of ammonia on the sulphate or the hydrochloride gives the base, m. p. 86°.

(c) *By means of sodium sulphide.* (i) The use of this reagent in alcoholic solution failed to give any 2-nitro-4-amino-*N*-ethyldiphenylamine.

(ii) 2 : 4-Dinitro-*N*-ethyldiphenylamine (5 g.), saturated sodium sulphide solution (16 g.), and rectified spirits (15 c.c.) were boiled under reflux for 20 hours. The product was poured into water, extracted with benzene, and the extract evaporated. On extraction of the tarry residue with alcohol, light orange-yellow crystals were obtained, m. p. 152—153°. Identical crystals (m. p. and mixed m. p.) were produced when 2 : 4-dinitro-*N*-ethyldiphenylamine (2·8 g.), benzoin (2·1 g.), and alcohol (12 c.c.) containing sodium ethoxide (3 drops of 5% solution) were boiled for 5 mins., the mixture cooled, and the orange-yellow product crystallised from rectified spirit. Hence it is probably *2-nitro-4-azoxy-*N*-ethyldiphenylamine* (IX) (compare Nisbet, *loc. cit.*) (Found: C, 64·0; H, 5·0; N, 15·6. $C_{28}H_{28}O_5N_6$ requires C, 63·9; H, 5·0; N, 16·0%).

(iii) 2 : 4-Dinitro-*N*-ethyldiphenylamine (2 g.), sodium sulphide crystals (15 g.), and rectified spirit (15 c.c.) were boiled under reflux for 20 hours. The reaction mixture was poured into ice-water, and the sticky, dark red solid which was formed was crystallised from alcohol, giving dark red crystals, m. p. 193—194°. From benzene it gave dark red prisms, m. p. 194°. It is possibly an *aminoazo-*N*-ethyldiphenylamine* (X) (Found: C, 74·8; H, 6·9; N, 18·7. $C_{28}H_{30}N_6$ requires C, 74·7; H, 6·7; N, 18·7%).

*Treatment of the Solutions of the Diazonium Salts obtained from 2-Nitro-4-amino-*N*-ethyldiphenylamine.*—Solutions of the diazonium salts were prepared in the usual manner from the sulphate or hydrochloride of the base.

(a) *Sulphate.* Treatment of the diazonium sulphate in aqueous solution with copper-bronze after the method of Delétra and Ullmann, and also with slight modifications thereof (concentration, amount of copper, period of heating, extracting solvent), failed to yield any identifiable solid substance. Treatment of the solid diazonium sulphate (large hexagonal plates) by heating in liquid paraffin to 180° also failed to yield any solid derivative.

(b) *Chloride.* (i) Copper-bronze was added to an aqueous solution of 2-nitro-*N*-ethyldiphenylamine-4-diazonium chloride, and the whole heated on a water-bath until decomposition was complete. The reaction mixture was filtered, and the solid extracted with alcohol. There slowly crystallised from the solution dark red plates, m. p. 81—82°, which proved to be 4-chloro-2-nitro-*N*-ethyldiphenylamine (see below).

(ii) The diazonium chloride solution was added slowly to cuprous chloride in hydrochloric acid solution, and the mixture heated on the water-bath for about an hour, and cooled. The resulting solid was filtered off and extracted with alcohol. Slow crystallisation gave the same red plates as were obtained in (i).

*Synthesis of 4-Chloro-2-nitro-*N*-ethyldiphenylamine.*—(i) 1 : 4-Dichloro-2-nitrobenzene (3 g.), ethylaniline (6 c.c.), and potassium carbonate (2·5 g.) were heated on an oil-bath at 205—215° for 6 hours with stirring. The cooled mixture was washed with dilute hydrochloric acid, then with water, and the product crystallised from alcohol, giving red plates, m. p. 79—80°.

(ii) 4-Chloro-2-nitrodiphenylamine (2 g.) (Ullmann, *Annalen*, 1904, **332**, 93), potassium hydroxide powder (1·35 g.), and acetone (50 c.c.) were heated under reflux until the liquid boiled gently. Then ethyl sulphate (1·6 g.) was added in small quantities, the mixture being well shaken. The colour changed from violet to yellow, and boiling was continued for a short time. The acetone was then distilled off, and the brown oil so formed was washed with concentrated ammonia solution, with water, and then crystallised from alcohol; reddish plates, m. p. 80—81°. The mixed m. p. of the products of these four separate preparations was 79—80·5° (Found : Cl, 13·1. $C_{14}H_{13}O_2N_2Cl$ requires Cl, 12·8%). Hence the substance is 4-*chloro*-2-*nitro*-N-*ethyldiphenylamine*, and the alkaline reduction product of 2 : 4-dinitro-*N*-ethyldiphenylamine is 2-nitro-4-amino-*N*-ethyldiphenylamine.

The Methyl Homologues.—2 : 4-Dinitro-*N*-methyldiphenylamine, prepared by the method of Reitzenstein (*J. pr. Chem.*, 1902, **68**, 255), was reduced in the same way as the ethyl homologue, giving the *hydrochloride* of 2-nitro-4-amino-*N*-methyldiphenylamine, small, dark red prisms, m. p. 177—178° (decomp.) (Found : Cl, 12·6. $C_{13}H_{14}O_2N_3Cl$ requires Cl, 12·6%).

4-*Chloro*-2-*nitro*-N-*methyldiphenylamine*. (i) The foregoing hydrochloride (2 g.) was suspended in dilute hydrochloric acid (30 c.c.; 1 : 10), cooled in ice, and sodium nitrite (0·5 g.) in aqueous solution added slowly. Copper-bronze (1 g.) was added to the filtered mixture, and the whole heated on a water-bath until the solution gave no coloration with a caustic soda solution of β-naphthol. The mixture was cooled, filtered, extracted with ether, and the extract crystallised from alcohol, giving light red prisms, m. p. 67—68°. Recrystallisation gave orange-red prisms, m. p. 71—72° to a red liquid.

(ii) Cuprous chloride treatment of the diazonium chloride, in the same way as for the ethyl compound, yielded the same product, reddish-orange prisms, m. p. 70—71°.

(iii) 1 : 4-Dichloro-2-nitrobenzene (3 g.), methylaniline (6 c.c.), and potassium carbonate (2·5 g.), when heated together for 6 hours at 210°, also gave this substance, m. p. 70—71° (yield, 25%).

(iv) Methylation of 4-chloro-2-nitrodiphenylamine, carried out in the manner described under the ethylation, gave the same product, m. p. 70—71° (yield, 50%); mixed m. p. of all four products, 70—72°. Hence the substance is 4-*chloro*-2-*nitro*-N-*methyldiphenylamine* (Found : Cl, 13·2. $C_{13}H_{11}O_2N_2Cl$ requires Cl, 13·5%).

Synthesis of N-*Methylcarbazole.*—o-*Nitro*-N-*methyldiphenylamine*. A mixture of *o*-nitrodiphenylamine (20 g.; Kehrmann and

Havas, *Ber.*, 1913, **46**, 341) and potassium hydroxide powder (20 g.) in acetone (200 c.c.) was boiled and then allowed to cool somewhat. Methyl sulphate (30 c.c.) was added slowly and cautiously, the reaction being vigorous at first. In the later stages of the addition the mixture was shaken, and finally boiled for 5 mins. It was then poured into water, the supernatant liquid (alkaline) poured off, and the residual red oil treated with ammonia solution (*d* 0·88) —although this is not always necessary. The red oil was separated in a funnel, and directly distilled under reduced pressure; yield 18 g., b. p. 203°/15 mm. o-*Nitro*-N-*methyldiphenylamine* is a dark red oil possessing a fishy odour (Found : N, 12·3. $C_{13}H_{12}O_2N_2$ requires N, 12·3%). *o*-Nitrodiphenylamine distils at 205°/15 mm.

[*Note.*—In the above preparation, if 10 g. of potassium hydroxide (nearly 2 mols.) and 18 c.c. of methyl sulphate (over $1\frac{1}{2}$ mols.) were used, the other quantities being as before, unchanged starting material was recovered. There was also a considerable yield of the required compound (*o*-nitro-*N*-methyldiphenylamine), and a very small quantity of canary-yellow rods which were less soluble in ligroin than was *o*-nitrodiphenylamine, and melted sharply at 172°. This compound was also obtained in the preparation of *o*-nitro-*N*-ethyldiphenylamine. It dissolved in cold dilute hydrochloric acid to give a yellow solution which became colourless on addition of ammonia solution. Small, cream-coloured crystals were precipitated. Since the amount obtained was so small, the examination of the substance is deferred.]

o-*Amino*-N-*methyldiphenylamine.* *o*-Nitro-*N*-methyldiphenylamine (15 g.), alcohol (75 c.c.), concentrated hydrochloric acid (75 c.c.), and excess of tin were boiled in a capacious flask. The action was at first violent. The solution was boiled until clear and pale brown (about 5 mins.), and poured whilst hot into a hot solution of potassium hydroxide (excess). The white paste which settled was dissolved in hot concentrated hydrochloric acid solution containing a little alcohol, and reprecipitated by potassium hydroxide solution. The pale green oil was extracted by carbon tetrachloride, the extract washed with water and dried, the solvent removed, and the residual oil distilled under reduced pressure. A viscid, yellow oil passed over at 182—184°/15 mm. (yield, 8—9 g.); o-*amino*-N-*methyldiphenylamine* turned slightly brown on keeping (Found : N, 14·3. $C_{13}H_{14}N_2$ requires N, 14·1%).

o-*Acetamido*-N-*methyldiphenylamine* was prepared by boiling the above base with acetic anhydride for a few minutes, then pouring the hot mixture into hot water. The pale pink solid precipitated was recrystallised from aqueous alcohol, and finally from alcohol. It separated in large octahedra when nearly pure, but in long, irregular, colourless crystals, m. p. 87—89°, when pure (Found: N, 11·8. $C_{15}H_{16}ON_2$ requires N, 11·7%). It is readily soluble in hot methyl alcohol, ethyl alcohol, glacial acetic acid, carbon tetrachloride, ligroin, or ethyl acetate. If in the acetylation heating is continued, a second substance, m. p. above 118°, is obtained. It can be easily separated, since it is much less soluble in ligroin than is the above acetyl compound, but crystallises therefrom.

N-*Methylcarbazole. Diazotisation of* o-*amino*-N-*methyldiphenylamine.* To the amine (6·5 g.) dissolved in excess of ice-cold dilute hydrochloric acid, sodium nitrite (2·5 g.) dissolved in water (20 c.c.) was gradually added. A small amount of tar was deposited, but, since this eventually gave *N*-methylcarbazole, it was not separated. Excess of dilute sodium hydroxide solution was added, and the mixture was warmed at 60° for 2 hours and finally boiled for 1 hour. The brown oil which was deposited solidified on cooling. It was washed and distilled, pale yellow to clear oil passing over at 250—310°; yield, 3·5 g. Crystallisation from alcohol gave white crystals (1·2 g.), m. p. 88° (clear melt at 91°), unaltered on admixture with *N*-methylcarbazole (m. p. 88—91°).

Synthesis of N-*Ethylcarbazole.*—o-*Nitro*-N-*ethyldiphenylamine* was prepared similarly to the methyl compound, a greater excess of ethyl sulphate being used with boiling for 20 mins. It separates as large, sword-blade, orange crystals from ligroin, m. p. 50—51° (Found: N, 11·8. $C_{14}H_{14}O_2N_2$ requires N, 11·6%). o-*Amino*-N-*ethyldiphenylamine*, prepared in a manner similar to the methyl homologue, distilled at 200°/15 mm., giving a colourless oil which became claret-coloured on exposure to the air (Found: N, 13·2. $C_{14}H_{16}N_2$ requires N, 13·2%). Attempts to prepare the acetyl and benzal derivatives yielded uncrystallisable oils. A hydrochloride could not be obtained in the usual way, but slow evaporation of a solution of the amine in hydrochloric acid solution afforded it as masses of large ink-blue crystals. It was not further characterised but was used directly in the diazotisation process detailed below. However, in experiments in which the period of reduction had been protracted, a thick, purple oil was obtained, which with hydrochloric acid solution gave white needles of a hydrochloride. These were ground with concentrated ammonia solution and gave a white powder which crystallised from ligroin or benzene–ligroin in slightly pink prisms, m. p. 79°, identical (mixed m. p.) with *o*-aminodiphenylamine. The same result was achieved when reduction was effected by boiling *o*-nitro-*N*-ethyldiphenylamine with a great excess of sodium trisulphide in alcohol for 24 hours.

N-*Ethylcarbazole. Diazotisation of* o-*amino*-N-*ethyldiphenylamine.* Either *o*-amino-*N*-ethyldiphenylamine or its hydrochloride was diazotised, and the diazonium solution treated as in the preparation of *N*-methylcarbazole, the final boiling being for 1 min. The pale yellow oil so obtained crystallised from alcohol in blades, m. p. 70° (softening at 68°) (Graebe and von Alderskron, *Annalen*, 1880, **202**, 24, give 67—68°; Hess and Siemann, E.P. 192,376, give 69·9°); mixed m. p. 68—70°.

Decomposition of 2-Nitro-4-carboxy-4′-methyldiphenylamine.—2-Nitro-4-carboxy-4′-methyldiphenylamine (10 g.) (Schopff, *Ber.*, 1887, **22**, 3288) was heated under reflux with potassium hydroxide solution (20 g. of 50%) for 5 hours. The reaction mixture was then steam-distilled, *p*-toluidine (1·8 g.) being obtained from the distillate (m. p. and mixed m. p. 45°, acetyl derivative, m. p. 148°). The residue was neutralised with acetic acid, and unchanged material (5 g.; m. p. 254°) recovered. The filtrate was evaporated, and the solid so obtained was purified by solution in potassium hydroxide solution, followed by precipitation with concentrated hydrochloric acid solution, giving 3-nitro-4-hydroxybenzoic acid, m. p. and mixed m. p. 184° (1 g.); ethyl ester (prepared by the Fischer–Speier method), m. p. 66—68°.

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