Some Derivatives of Diphenylamine.

By S. G. P. PLANT and C. R. WORTHING.

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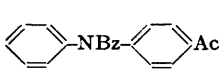
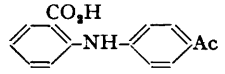
4-Acetyldiphenylamine has been obtained by hydrolysis of the product of a Friedel–Crafts reaction with *N*-benzoyldiphenylamine, and by the decarboxylation of 4-acetyl-2′-carboxydiphenylamine. It has been converted into 4-carboxydiphenylamine by fusion with potassium hydroxide. The action of aniline on *o*-acetylphenyl toluene-*p*-sulphonate has been studied.

FRIEDEL–CRAFTS reactions with carbazole and its *N*-alkyl and *N*-acyl derivatives, and the isomerisation of the *N*-acyl compounds with aluminium chloride, have given various *C*-acylcarbazoles from which the corresponding carbazolecarboxylic acids have been obtained on fusion with potassium hydroxide (see, *e.g.*, Plant and Williams, *J.*, 1934, 1142; Plant, Rogers, and Williams, *J.*, 1935, 741; Mitchell and Plant, *J.*, 1936, 1295). It seemed possible, therefore, that analogous derivatives of diphenylamine might be prepared in similar ways, but the results have been generally disappointing. Apart from *N*-benzoylation in some cases, attempts to introduce acetyl and benzoyl groups into diphenylamine and its *N*-acetyl and *N*-benzoyl derivatives have failed, except in the formation of 4-acetyl-*N*-benzoyldiphenylamine (I), a substance obtained by Chapman (*J.*, 1927, 1743) by rearrangement of *p*-acetylphenyl *N*-phenylbenzimidate. The constitution of this product was established by hydrolysis to 4-acetyldiphenylamine which was also prepared by the decarboxylation of 4-acetyl-2′-carboxydiphenylamine (II) obtained from *p*-aminoacetophenone and potassium *o*-bromobenzoate. It is of interest that Craig (*J. Amer. Chem. Soc.*, 1935, **57**, 195) obtained a small amount of 4-*tert.*-butyldiphenylamine



(I)



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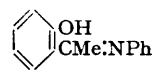

(III)

from diphenylamine and *tert.*-butyl chloride in the presence of aluminium chloride. The heating of *N*-acetyl- and *N*-benzoyl-diphenylamine with aluminium chloride failed to effect rearrangement (cf. Dippy and Wood, *J.*, 1949, 2719).

Fusion of 4-acetyldiphenylamine with potassium hydroxide gave 4-carboxydiphenylamine, prepared by Gilman and Brown (*J. Amer. Chem. Soc.*, 1940, **62**, 3208) by hydrolysis of the ester obtained by heating iodobenzene with methyl *p*-aminobenzoate. This product was shown to be identical (mixed m. p.) with the acid obtained by heating diphenylaminomagnesium iodide in a stream of carbon dioxide at 270° as described by Oddo (*Gazzetta*, 1911, **41**, 255). With the characterisation of the three possible carboxydiphenylamines the structure of Oddo's acid had become reasonably certain, but it appears hitherto not to have been rigidly proved.

In exploring another approach to 4-acetyldiphenylamine it was found that *p*-acetylphenyl toluene-*p*-sulphonate was little affected by boiling aniline. Similar treatment of *o*-acetylphenyl toluene-*p*-sulphonate gave a product which, although having the composition of 2-acetyldiphenylamine, was shown by its reactions to be *o*-(1-phenyliminoethyl)phenol (III). Thus it gave no 5-methylacridine on being heated with glacial acetic acid and a little concentrated sulphuric acid (cf. Jensen and Rethwisch, *J. Amer. Chem. Soc.*, 1928, **50**, 1144), it gave acetanilide on being shaken with acetyl chloride and alkali in acetone, it was hydrolysed to *o*-hydroxyacetophenone and aniline by boiling dilute hydrochloric acid, and the same compound was obtained by heating *o*-hydroxyacetophenone with aniline. It gave a deep reddish-brown colour with ethanolic ferric chloride, and it was soluble in 2N-hydrochloric acid, from which it was recovered by dilution with water, but it did not readily dissolve in dilute aqueous sodium hydroxide. Its structure affords the possibility of intramolecular hydrogen bonding, and this is reflected in its infrared spectrum in Nujol

suspension. Thus there is no absorption indicative of free hydroxyl in the region of 3μ, but there is a diffused broad band in the region of 4μ.

2-Acetyl-2′-carboxydiphenylamine was prepared from *o*-aminoacetophenone and potassium *o*-bromobenzoate, but attempts to convert it into 2-acetyldiphenylamine by decarboxylation failed. Most of the product was basic, and, although difficult to purify, it gave with concentrated sulphuric acid a yellow solution with a green fluorescence, indistinguishable from that obtained with 5-methylacridine.

It has not been possible to prepare 3-carboxydiphenylamine by fusion of 3-acetyldiphenylamine (Elson and Gibson, *J.*, 1931, 2381) with potassium hydroxide. This acid has been obtained in small yield by Gilman, Van Ess, and Shirley (*J. Amer. Chem. Soc.*, 1944, **66**, 1214) by hydrolysis of the product from the condensation of aniline with methyl *m*-iodobenzoate. A convenient alternative, although again with a small yield, is given below.

Experimental

4-Acetyl-2′-carboxydiphenylamine.—A stirred mixture of *p*-aminoacetophenone (13·5 g.), *cyclo*hexanol (140 c.c.), and potassium *o*-bromobenzoate (10·9 g.) with a little potassium iodide and copper powder was refluxed for 10 hr. After addition of dilute aqueous sodium hydroxide, the *cyclo*hexanol was removed in steam, and the residual solution cooled, filtered, and acidified with hydrochloric acid. *4-Acetyl-2′-carboxydiphenylamine* (6·5 g.; m. p. 160—164°) was obtained when the product was collected after 12 hr., stirred with its own volume of ethanol on a steam-bath for ½ hr., and the solid washed with a little ethanol. Recrystallisation from ethanol gave yellow prisms, m. p. 174° (Found: C, 70·7; H, 5·1. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1%). Its *methyl ester* separated from methanol in pale yellow prisms, m. p. 80° (Found: C, 71·2; H, 5·9. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6%).

4-Acetyldiphenylamine.—(*a*) After the above acid (8 g.) had been heated at 250° until frothing ceased (1—2 hr.), the residue distilled at 235°/17 mm., and the distillate ground with hot ethanol (5 c.c.), *4-acetyldiphenylamine* (2·73 g.) was obtained. Recrystallisation from ethanol gave yellow needles, m. p. 112° (Found: C, 79·5; H, 6·3. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2%). In early preparations this substance was obtained in the less stable form of yellow prisms, m. p. 93°.

(*b*) After a stirred mixture of *N*-benzoyldiphenylamine (10 g.), carbon disulphide (70 c.c.), aluminium chloride (60 g.), and acetyl chloride (20 c.c.) had been refluxed for 5 hr., the solvent was distilled off, and the residue added to ice and dilute hydrochloric acid. When the product was crystallised from ethanol (charcoal), a pale yellow solid (7 g.), m. p. 120—132°, was obtained. This (5 g.) was twice recrystallised from carbon tetrachloride, from which 4-acetyl-*N*-benzoyldiphenylamine was isolated in pale yellow prisms (1·8 g.), m. p. 134—138°. A purer specimen, m. p. 136—138°, of the same substance (mixed m. p.) was obtained by adsorption of a little of the material, m. p. 120—132°, from benzene on alumina (Found: C, 79·7; H, 5·5; N, 4·8. Calc. for $C_{21}H_{17}O_2N$: C, 80·0; H, 5·4; N, 4·4%). After a solution of this benzoyl compound in an excess of aqueous ethanolic potassium hydroxide had been refluxed for 2½ hr. and poured into water, 4-acetyldiphenylamine, pale yellow needles, m. p. 109—110° (from carbon tetrachloride), identical (mixed m. p.) with the above ketone, was obtained.

A solution of 4-acetyldiphenylamine (0·5 g.) and a little (+)-camphorsulphonic acid in acetic anhydride (10 c.c.) was refluxed for 1½ hr. and poured into water (100 c.c.). The solid was purified by boiling its solution in ethanol with charcoal for 15 min. and recovered from the filtered liquid by evaporation to small bulk and precipitation with water. Crystallisation from carbon tetrachloride gave N: *4-diacetyldiphenylamine* (0·4 g.) in pale yellow prisms, m. p. 124° (Found: C, 75·9; H, 6·2. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 6·0%). After its solution in aqueous ethanolic potassium hydroxide had been refluxed for 2 hr., addition of water precipitated 4-acetyldiphenylamine, identified by mixed m. p.

4-Acetyldiphenylamine (0·4 g.) in acetone (10 c.c.) was added to potassium hydroxide (2 g.) in water (1 c.c.), and the whole shaken for 15 min. with methyl sulphate (3 c.c.). When the product obtained by pouring the mixture into dilute aqueous potassium hydroxide was crystallised from methanol, *4-acetyl-N-methyldiphenylamine* (0·16 g.) separated in plates, m. p. 87° (Found: C, 79·8; H, 6·5. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7%).

4-Carboxydiphenylamine.—4-Acetyldiphenylamine (0·5 g.) was gradually stirred into a heated, molten mixture of potassium hydroxide (5 g.) and water (0·5 c.c.). When cold, the

whole was extracted with water and the filtered extract acidified with hydrochloric acid. The solid (0·13 g.; m. p. about 150°), after being boiled in ethanol with charcoal, was crystallised from benzene, from which 4-carboxydiphenylamine separated in plates, m. p. 158° (Found: C, 73·5; H, 5·3. Calc. for $C_{13}H_{11}O_2N$: C, 73·2; H, 5·2%).

o- *and* p-*Acetylphenyl Toluene*-p-*sulphonate.*—After a mixture of *o*-hydroxyacetophenone (30 g.), pyridine (90 c.c.), and toluene-*p*-sulphonyl chloride (64 g.) had been heated on a steam-bath for 2 hr. and left overnight, the whole was poured into dilute hydrochloric acid, and the product, which soon solidified, was washed with dilute aqueous sodium hydroxide. Crystallisation from ethanol gave o-*acetylphenyl toluene*-p-*sulphonate* (39 g.) in needles, m. p. 95—98° (Found: C, 61·8; H, 4·6; S, 11·3. $C_{15}H_{14}O_4S$ requires C, 62·1; H, 4·8; S, 11·0%). Its infrared spectrum in Nujol suspension contains a band at 5·89 μ, characteristic of the carbonyl group.

Prepared similarly from *p*-hydroxyacetophenone, p-*acetylphenyl toluene*-p-*sulphonate* separated from methanol in needles (23%), m. p. 72° (Found: C, 62·0; H, 4·6%).

o-(1-*Phenyliminoethyl*)*phenol.*—(*a*) After a mixture of *o*-acetylphenyl toluene-*p*-sulphonate (15 g.) and aniline (150 c.c.) had been refluxed for 24 hr. and poured into excess of dilute hydrochloric acid, the whole was extracted with ether and the extract shaken with dilute aqueous sodium hydroxide. When the solid obtained by acidification of the alkaline solution was crystallised from ethanol, toluene-*p*-sulphonanilide, m. p. 99—102°, identified by mixed m. p., was obtained. After the ethereal extract had been dried ($MgSO_4$) and evaporated, the residue was crystallised from ethanol and o-(1-*phenyliminoethyl*)*phenol* (3·48 g.) isolated in yellow plates, m. p. 84° [Found: C, 79·8; H, 6·2; N, 6·7%; *M* (Rast), 192. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2; N, 6·6%; *M*, 211].

(*b*) When *o*-hydroxyacetophenone (5 g.) was refluxed with aniline (30 c.c.) for 16 hr. and the mixture treated as above, *o*-(1-phenyliminoethyl)phenol (1·5 g.), identified by mixed m. p., was again obtained.

After *o*-(1-phenyliminoethyl)phenol (1 g.) in acetone (30 c.c.) had been added to potassium hydroxide (5·4 g.) in water (2·7 c.c.), the mixture was treated gradually with acetyl chloride (3 c.c.) in acetone (5 c.c.), and the whole shaken for ½ hr., diluted with water, and extracted with ether. The residue obtained when the extract was washed with aqueous alkali and with dilute hydrochloric acid, dried, and evaporated, was crystallised from carbon tetrachloride, from which acetanilide (0·25 g.), m. p. 114°, identified by mixed m. p., separated (Found: C, 70·9; H, 6·8. Calc. for C_8H_9ON: C, 71·1; H, 6·7%).

After *o*-(1-phenyliminoethyl)phenol (2·5 g.) had been refluxed for 2 hr. with hydrochloric acid (12%; 65 c.c.), the solution was diluted with water and extracted with ether. The material (1·3 g.) obtained from the ethereal extract was shown to be *o*-hydroxyacetophenone by conversion into *o*-acetylphenyl toluene-*p*-sulphonate as described above. The aqueous solution was shown to contain aniline by its conversion into acetanilide.

2-*Acetyl*-2′-*carboxydiphenylamine.*—Prepared from *o*-aminoacetophenone as described above for the isomeric compound, 2-*acetyl*-2′-*carboxydiphenylamine* (yield, 16%) separated from ethanol in golden yellow prisms, m. p. 207° (Found: C, 70·8; H, 5·4%).

N: 3-*Diacetyldiphenylamine.*—3-Acetyldiphenylamine (0·5 g.) in acetic anhydride (25 c.c.) containing a little (+)-camphorsulphonic acid was refluxed for 2½ hr. and poured into water. The product was extracted with ether, and the extract washed with aqueous sodium hydroxide, dried ($MgSO_4$), and evaporated. When the residue was crystallised from carbon tetrachloride, N: 3-*diacetyldiphenylamine* (0·37 g.) was obtained; recrystallisation from ethanol gave almost colourless prisms, m. p. 96—97° (Found: C, 75·7; H, 6·0%). When this compound was refluxed for 2 hr. with an excess of aqueous ethanolic potassium hydroxide and the solution poured into water, 3-acetyldiphenylamine was precipitated, having yellow prisms, m. p. and mixed m. p. 88—90° (from carbon tetrachloride).

3-*Carboxydiphenylamine.*—Aniline (150 c.c.), *m*-bromobenzoic acid (20 g.), and anhydrous sodium acetate (15 g.), with a little copper powder and potassium iodide, were refluxed for 24 hr., and the mixture, when cold, poured into an excess of hydrochloric acid (12%). The product was extracted with ether, and the extract filtered and shaken with dilute aqueous sodium carbonate. This aqueous layer was boiled for ½ hr. with charcoal, filtered, and acidified with hydrochloric acid. The precipitated material (7·5 g.; m. p. 137—145°) was refluxed for 20 hr. with methanol (400 c.c.) which had been saturated with hydrogen chloride, most of the solvent was distilled off, and the residue was treated with dilute ammonia solution. The product was collected in ether, the solution dried ($MgSO_4$), the solvent removed, and the residue crystallised from carbon tetrachloride, from which 3-*methoxycarbonyldiphenylamine* (1 g.)

separated in almost colourless plates, m. p. 110—112° (Found: C, 73·9; H, 5·8; N, 6·0. $C_{14}H_{13}O_2N$ requires C, 74·0; H, 5·7; N, 6·2%). After the ester had been refluxed for 3 hr. with an excess of aqueous ethanolic potassium hydroxide, the solution was diluted, filtered, and acidified; 3-carboxydiphenylamine, needles, m. p. 139—141° (from benzene), was precipitated (Found: C, 73·0; H, 5·4%).

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DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, December 20th*, 1954.]