86. *The Oxidation of Diphenylamine and of its* N-*Derivatives. Part I. Oxidation of* $>N{\cdot}CH_2R$ *to* $>N{\cdot}CO{\cdot}R$.

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N-Alkyl- and *N*-aralkyl-diphenylamines have been prepared, and their oxidation by potassium permanganate in acetone or pyridine studied. *N*-Ethyldiphenylamine and certain of its nitro- and bromo-derivatives give *N*-acetdiphenylamides, and *N*-benzyldiphenylamine gives *N*-benzdiphenylamide; all other *N*-substituted diphenylamines investigated either do not react or give tetraphenylhydrazine.

N-Benzylcarbazole can be similarly oxidised to *N*-benzoylcarbazole.

A method of preparing dipicrylamine from *N*-acetdiphenylamide is described.

Whereas the oxidation of diphenylamine by potassium permanganate in acetone gives rise to tetraphenylhydrazine, oxidation by sodium dichromate in acid solution gives *NN'*-diphenylbenzidine (Wieland and Gambarjan, *Ber.*, 1906, **39**, 1501; Wieland, *Ber.*, 1913, **46**, 3300; 1919, **52**, 889; Marqueyrol and Muraour, *Bull. Soc. chim.*, 1914, **15**, 186; Sarver and Johnson, *J. Amer. Chem. Soc.*, 1935, **57**, 329. Cf. Kadeira, *Ber.*, 1905, **38**, 3575). Similarly, oxidation of *N*-methyldiphenylamine in acid solution gives rise to *NN'*-diphenyldimethylbenzidine (Wieland, *Ber.*, 1919, **52**, 889; Maitland and Tucker, *J.*, 1927, 1388). On the other hand, oxidation under acid conditions failed to convert *N*-ethyldiphenylamine into a benzidine derivative. Since, however, oxidation of *N*-methyldiphenylamine by potassium permanganate in acetone had given *NN'*-diphenyldimethylbenzidine (Maitland and Tucker, *loc. cit.*), the same oxidising agent was tried on *N*-ethyldiphenylamine, with the quite unexpected result that *N*-acetdiphenylamide was isolated (15%). Modification of the method using pyridine instead of acetone raised the yield (30%).

2-Nitro-, 2 : 4-dinitro-, and 4 : 4'-dibromo-*N*-ethyldiphenylamine also, by oxidation, gave the corresponding *N*-acetyl derivatives, but in small yields: on the other hand *N*-benzyldiphenylamine gave *N*-benzdiphenylamide in excellent yield (70%). The method failed to give the corresponding $>N{\cdot}CO-$ (or $>N{\cdot}C(OH)<$) derivative when tried with *N*-propyl-, *N*-*iso*propyl-, *N*-butyl-, *N*-*iso*butyl-, *N*-amyl-, *N*-β-phenylethyl-, 4 : 4'-dibromo-*N*-propyl-, and 2 : 4 : 2' : 4'-tetrabromo-*N*-ethyl-diphenylamine. The last three were recovered unchanged, but the others gave small yields of tetraphenylhydrazine.

Acyldiphenylamines may arise *via* carbinolamines, $>N{\cdot}CH(OH)R$, the fission and subsequent oxidation of which would explain the formation of tetraphenylhydrazine; *N*-acyldiphenylamines were found to be stable under the conditions employed. Attempts to verify the above suggestion were, however, fruitless; although the reductive condensation of diphenylamine with aldehydes indicates the transitory existence of the carbinolamines (Skita, Keil, and Havemann, *Ber.*, 1933, **66**, 1400) they could not be prepared by interaction of diphenylaminemagnesium bromide and appropriate aldehydes.

N-Alkyl- and -aralkyl-diphenylamines have been prepared by acting upon diphenylamine with (*a*) alcohols and hydrochloric acid (Girard, *Bull. Soc. chim.*, 1875, **23**, 2); (*b*) alkyl sulphates with or without addition of alkali (Ullmann, *Annalen*, 1903, **327**, 104; Wieland, *Ber.*, 1919, **52**, 890; Gibson and Vining, *J.*, 1923, **123**, 831); (*c*) alkyl iodides (Bardz, *Z. angew. Chem.*, 1871, 469) and bromides; (*d*) aldehydes and ketones with hydrogen and a catalyst (Skita, Keil, and Havemann, *loc. cit.*). By modifications of these methods we have prepared the compounds shown in the table in the yields there recorded.

Yields (%) of N-*substituted-diphenylamines.*

N-Substituted-diphenylamine.	Me.	Et.	Pr$^{\alpha}$.	Pr$^{\beta}$.	Bu$^{\alpha}$.	Bu$^{\beta}$.	*n*-Amyl.	Ph·CH$_2$.	Ph·[CH$_2$]$_2$.
By alkyl sulphates	80	65—75	40	—	—	—	—	—	—
By alkyl iodides	40	80	50	50	40	33	30	—	—
By alkyl or aralkyl bromides ...	—	0	2	2	30	—	—	—	45
By aralkyl chloride	—	—	—	—	—	—	—	90—95	—

The alkyl iodides showed most general applicability but the yields steadily decreased with increase of molecular weight of the alkyl group. Chain branching seemed to have little effect—in strong contrast to the effect in the method of Skita, Keil, and Havemann where yields were greatly depressed when a branching methyl radical was attached in the α-position.

Alkylation of diphenylaminemagnesium bromide was successful in the preparation of *N*-ethyldiphenylamine, but unsuccessful for higher members.

N-Ethylcarbazole was unattacked by permanganate in boiling acetone or pyridine, but *N*-benzylcarbazole gave a small amount of *N*-benzoylcarbazole.

Nitration of *N*-acetdiphenylamide with a mixture of concentrated nitric and sulphuric acids gave 2 : 4 : 2′ : 4′-tetranitrodiphenylamine, the intermediate acetyl derivative being very susceptible to hydrolysis. Solution of this tetranitro-derivative in fuming nitric acid followed by addition of sulphuric acid precipitated 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenylamine (dipicrylamine) in almost theoretical yield.

EXPERIMENTAL.

In preparation of the tertiary amines later described, separation from unchanged diphenylamine was effected by one or a combination of the following three methods : the reaction mixture was (1) oxidised by potassium permanganate in acetone—diphenylamine being thus converted into tetraphenylhydrazine—and the tertiary amine obtained by distillation; (2) treated with excess of concentrated hydrochloric acid which precipitated diphenylamine hydrochloride leaving the tertiary amine in solution; (3) treated with acetyl chloride in presence of sodium acetate, and the *N*-acetdiphenylamide separated in crystalline form by adding light petroleum (b. p. 60—80°) and cooling to 0°. Acetic anhydride was less effective, even at the b. p.

For the lowest members method (2) was adopted followed by (3), except that, when *N*-ethyldiphenylamine was being prepared for subsequent oxidation, method (3) was replaced by (1). Method (2) was limited to the *N*-methyl-, *N*-ethyl-, and *N*-propyl-diphenylamines since the higher alkyldiphenylamines are practically insoluble in concentrated hydrochloric acid; these latter were separated by method (3). (Cf. I.G. Farbenindustrie, B.P. 333,349.)

Preparation of N-*Ethyldiphenylamine.*—(A) *Using ethyl sulphate* (Gibson and Vining, *loc. cit.*). Diphenylamine (42·3 g.; 1 mol.), ethyl sulphate (57·7 g. = 49 c.c.; 1·5 mol.), and anhydrous potassium carbonate (51 g.; 1·5 mol.) were mixed and heated in a flask, fitted with a short fractionating column, in an air-bath kept at 175—180° for 2 hours. The mixture was occasionally shaken. A small amount of ethanol, ether, and water distilled. The residue was treated with dilute hydrochloric acid, rendered alkaline, extracted with light petroleum (b. p. 60—80°), and fractionally distilled. The fraction b. p. 150—170°/15 mm. was treated with equal weights of anhydrous sodium acetate and acetyl chloride, the latter being added in four portions with vigorous shaking. The mixture was poured into water, boiled, and extracted whilst warm with light petroleum (b. p. 60—80°). The dried solution was kept for several hours at 0°, filtered from *N*-acetdiphenylamide, and the filtrate fractionally distilled yielding *N*-ethyldiphenylamine, b. p. 152—153°/12 mm. (35 g.; yield, 70%). The yield was slightly reduced when heating was at 165—170°.

(B) *By the Grignard reaction* (cf. Cope, *J. Amer. Chem. Soc.* 1934, **56**, 1578; King, King, and Muir, this vol., p. 5). Diphenylaminemagnesium bromide (1 mol.) was prepared from diphenylamine and ethylmagnesium bromide in ether with exclusion of air. A solution of ethyl sulphate (2 mols.) in ether was added, and *N*-ethyldiphenylamine isolated in the usual way (yield, 80%). Propyl iodide, propyl sulphate, propyl *p*-toluenesulphonate, butyl iodide, and butyl *p*-toluenesulphonate did not react with diphenylaminemagnesium bromide (or iodide) in ether or in boiling toluene or xylene.

(C) *From alkyl iodides.* A mixture of diphenylamine (1 mol.), ethyl iodide (1·5 mols.), and anhydrous potassium carbonate (1·5 mols.) was boiled for 48 hours and *N*-ethyldiphenylamine isolated (yield, 80%). The experiment failed when ethyl bromide replaced the iodide.

Other *N*-alkyldiphenylamines were similarly prepared, using alkyl iodides, in yields given in the table (p. 454).

N-iso*Propyldiphenylamine*, prepared from *iso*propyl iodide, had b. p. 160—165°/15 mm. (22 g.; yield, 52%) (Found : C, 85·2; H, 7·8. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1%).

4 : 4′-*Dibromo*-N-iso*propyldiphenylamine.*—*N*-*iso*Propyldiphenylamine (5 g.) in glacial acetic acid (40 c.c.) was stirred whilst a solution of bromine (7·7 g.) in glacial acetic acid (20 c.c.) was slowly added. When evolution of hydrogen bromide had ceased, the white crystalline *product*, recrystallised from ethanol, had m. p. 92° (8·5 g., yield 96%) (Found : C, 48·7; H, 4·3; N, 3·9. $C_{15}H_{15}NBr_2$ requires C, 48·8; H, 4·1; N, 3·8%).

The dibromo-derivatives of *N*-ethyl-, *N*-propyl-, and *N*-butyl-diphenylamines were similarly prepared (Skita, Keil, and Havemann, *loc. cit.*).

N-n-*Amyldiphenylamine* was prepared as described for the preparation of *N*-*iso*propyldiphenylamine, and also by heating diphenylamine (33·8 g.; 1 mol.), *n*-amyl alcohol (17·6 g.; 1 mol.), and zinc chloride (40 g.; 1·5 mols.) at 120° for 4 hours. After acetylation of the reaction product, and removal of the crystalline *N*-acetdiphenylamide, the residual oil was fractionated and gave *N*-*n*-amyldiphenylamine, b. p. 190—195°/12 mm. (10·5 g.; yield, 21%) (Found : C, 85·3; H, 8·5. $C_{17}H_{21}N$ requires C, 85·35; H, 8·8%). Under these conditions the risk of contamination of the *n*-amyl by isomerised amyl derivatives is slight (Whitmore, Karnatz, and Popkin, *J. Amer. Chem. Soc.*, 1938, **60**, 2540).

N-β-*Phenylethyldiphenylamine.* Diphenylamine (16·9 g.; 1 mol.), β-phenylethyl bromide (37 g.; 2 mols.), and anhydrous potassium carbonate (20 g.; 1·5 mols.) were heated at 130° for 5 hours. After addition of water the separated oil was distilled in a vacuum; β-phenylethyl bromide (b. p. 100°/10 mm.), diphenylamine (b. p. 150—160°/10 mm.) and *N*-β-phenylethyldiphenylamine (b. p. 220—230°/10 mm.) were obtained. The last crystallised from light petroleum (b. p. 40—60°) in large octahedra; it was recrystallised from methanol; the *compound* then had m. p. 61—63° (15 g.; yield 55%) (Found : C, 87·9; H, 6·8; N, 5·1. $C_{20}H_{19}N$ requires C, 87·9; H, 7·0; N, 5·1%). β-Phenylethyl chloride similarly (at 150° for 4 hours) gave the same product (50% yield); but β-phenylethyl iodide (refluxing for 10 hours) gave unchanged diphenylamine and β-phenylethyl iodide, with β-phenylethanol and styrene.

N-*Benzyldiphenylamine.* Diphenylamine (34 g.; 1 mol.), benzyl chloride (30 g.; 1·2 mols.), and anhydrous potassium carbonate (35 g.; 1·2 mols.) were heated at 200° for 2 hours. The melt was steam distilled to remove unchanged benzyl chloride, the residue extracted with light petroleum (b. p. 60—80°), and the isolated *N*-benzyldiphenylamine crystallised from ethanol; it had m. p. 86° (44 g.; yield, 88%).

Oxidation of N-*Ethyldiphenylamine.*—Acetone was purified by Werner's method (*Analyst*, 1933, **58**, 335). Usually it was further boiled for ½ hour with excess of potassium permanganate, distilled, dried, and redistilled.

N-Ethyldiphenylamine (2 g. purified by method (2) followed by (1), above) was dissolved in this pure acetone (20 c.c.) and very finely powdered potassium permanganate (5 g.) added in small portions : the mixture was boiled on the water-bath after each addition. After having been boiled for 45 minutes the whole was treated with sulphurous acid to dissolve manganese oxides, and the precipitated oil extracted from the warm solution with light petroleum (b. p. 60—80°). The evaporated extract gave a mixture of crystals and oil; the separated crystals recrystallised from light petroleum as *N*-acetdiphenylamide, m. p. 100° (0·32 g.; yield 15%). The m. p. was not depressed when mixed with an authentic specimen prepared from diphenylamine and boiling acetic anhydride. The separated oil contained unchanged *N*-ethyldiphenylamine.

Addition of sodium bicarbonate, magnesium sulphate, or anhydrous sodium sulphate to the reaction mixture appeared to have no effect; but addition of anhydrous sodium carbonate seemed to give slightly cleaner products. Potassium hydroxide was disadvantageous.

Later it was found that the yield of *N*-acetdiphenylamide was doubled when pyridine replaced the acetone. Calcium permanganate could not be used with pyridine since the two reacted, producing incandescence within the liquid.

The above method was used in the oxidation of other *N*-substituted diphenylamines, except that sodium bicarbonate (equal in weight to that of the permanganate used) was added. It was probably an unnecessary addition.

N-Benzyldiphenylamine, oxidised in acetone by potassium permanganate in presence of sodium bicarbonate, gave *N*-benzdiphenylamide, m. p. 177° (yield, 70%).

4 : 4′-Dibromo-*N*-ethyldiphenylamine similarly oxidised gave 4 : *4′-dibromo-*N*-acetdiphenylamide*, m. p. 180° (yield, 8%). (Found : N, 3·8. $C_{14}H_{11}ONBr_2$ requires N, 3·8%).

2-Nitro-*N*-ethyldiphenylamine gave a mixture from which yellow crystals, m. p. 134—135°, of 2-nitro-*N*-acetdiphenylamide (Kehrmann and Baumgartner, *Helv. Chim. Acta*, 1926, **9**, 673) were separated in very small yield by hand-picking. The corresponding 2 : 4-dinitro-compound gave similarly, by crystallisation from methanol, 2 : 4-dinitro-*N*-acetdiphenylamide, m. p. 154°.

With the other *N*-alkyldiphenylamines oxidation in acetone yielded tetraphenylhydrazine (yield ~15%). This was nearly insoluble in ethanol but crystallised in colourless prisms from ethyl acetate and then from toluene. Owing to the ease with which it turned green it was difficult to raise the m. p. above 144° (Wieland and Gambarjan, *Ber.*, 1906, **39**, 1499; cf. Chattaway and Ingle, *J.*, 1895, **67**, 1091, who give m. p. 147°).

N-*Propiondiphenylamide*.—(*a*) Propionyl chloride and anhydride prepared by the usual methods give poor yields, but the chloride prepared (yield 80%) by means of benzoyl chloride (Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325) gave with diphenylamine in presence of anhydrous sodium acetate an excellent yield of *N*-propiondiphenylamide, m. p. 58° (cf. v. Mayer and Nicolaus, *J. pr. Chem.*, 1861, **82**, 530). (*b*) Diphenylaminemagnesium bromide, prepared in the usual way from ethylmagnesium bromide in ether solution, was treated with ethyl propionate (yield, 52%). (Cf. Hardy, *J.*, 1936, 398.)

Dipicrylamine (2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenylamine).—*N*-Acetdiphenylamide (12 g.) was added to a mixture of concentrated nitric acid (50 c.c.) and concentrated sulphuric acid (25 c.c.) at 15°. On stirring, the amine dissolved and the solution turned green; as the temperature rose spontaneously to 65° the colour changed through brown and orange to red. The temperature was slowly raised to 70—75°; a crystalline yellow precipitate then formed. The mixture was finally heated on the boiling water-bath for 1 minute. 2 : 4 : 2′ : 4′-Tetranitrodiphenylamine, m. p. 198°, was obtained (~100%). (Cf. Kehrmann and Baumgartner, *loc. cit.*, on ease of hydrolysis of the acetyl derivative.) The tetranitrodiphenylamine was dissolved in the minimum quantity of fuming nitric acid (*d* 1·5); addition of concentrated sulphuric acid to this solution precipitated dipicrylamine (exothermic reaction), m. p. 238° (yield, 95%).

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