24. *Union of Aryl Nuclei. Part I. Some Extensions of the Gomberg Reaction.*

By W. S. M. Grieve and D. H. Hey.

Methods for synthesising biaryl compounds by means of reactions involving diazo-compounds are reviewed with special reference to the union of two dissimilar aryl nuclei. Attempts to increase the yields obtained in the reaction, developed by Gomberg and his co-workers (*J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372), between a diazotised base and a neutral aromatic liquid in the presence of aqueous alkali, $Ph{\cdot}N_2{\cdot}OH + PhR \longrightarrow Ph{\cdot}C_6H_4R + N_2 + H_2O$, are unsuccessful. The scope of the reaction is extended to include the use of (a) solid reactants in solution and (b) bases of the naphthalene series; *e.g.*, methyl anthranilate and naphthalene, aniline and diphenyl, *p*-nitroaniline and diphenyl, and *p*-anisidine and benzophenone give *methyl* o-α-*naphthylbenzoate*, *p*-diphenylbenzene, 4′-nitro-*p*-diphenylbenzene, and 4-methoxy-4′-benzoyldiphenyl respectively. The solvent, which is either chloroform or carbon tetrachloride, is not entirely inert. When diazotised aniline is used with carbon tetrachloride, for example, an appreciable quantity of chlorobenzene is formed. This observation is of particular interest in correlating the mechanism of the Gomberg reaction with that of the related reactions of nitrosoacetanilide, phenylazotriphenylmethane, and dibenzoyl peroxide, which is regarded as non-ionic in type. Experimental evidence is also included to show that the two-phase system is an essential feature of the Gomberg reaction, an observation which is in agreement with the representation of the reaction as a non-ionic process. Reactions carried out between diazotised α- and β-naphthylamine and benzene give α- and β-phenylnaphthalene respectively, but in small yield.

SEVERAL methods are available for the preparation of biaryl compounds through the agency of diazonium compounds; *e.g.*, Vorländer and Meyer (*Annalen*, 1902, **320**, 122) prepared a number of symmetrical diphenyl derivatives from aromatic diazonium salts in the presence of ammoniacal cuprous oxide, a reaction which has achieved industrial importance in its application to α-naphthylamine-8-carboxylic acid (I.G., E.P. 278,100). In many cases, however, the reaction follows a different course and gives rise to azo-compounds. Examples of the preparation of symmetrical biaryls from diazonium compounds through the agency of metallic copper (Gattermann, *Ber.*, 1890, **23**, 1226; Knoevenagel, *Ber.*, 1895, **28**, 2049; Ullmann, *Ber.*, 1896, **29**, 1878; Niementowski, *Ber.*, 1901, **34**, 3325; Gerngross and Dunkel, *Ber.*, 1924, **57**, 739; Gerngross, Schachnow, and Jonas, *ibid.*, p. 747) and cuprous chloride (Ullmann and Forgan, *Ber.*, 1901, **34**, 3802; Ullmann and Frentzel, *Ber.*, 1905, **38**, 726) have been recorded, and numerous other agents have also been employed (Griess, *Annalen*, 1866, **137**, 79; Oddo, *Gazzetta*, 1890, **20**, 663; Beeson, *Amer. Chem. J.*, 1894, **16**, 235; Culmann and Gasiorowski, *J. pr. Chem.*, 1889, **40**, 97). The synthesis of unsymmetrical biaryls has also been effected by means of reactions involving diazonium compounds (Hirsch, *Ber.*, 1890, **23**, 3705; 1892, **25**, 1973; Norris, Macintyre, and Corse, *Amer. Chem. J.*, 1903, **29**, 120; Oddo and Curatolo, *Gazzetta*, 1895, **25**, 126; Möhlau and Berger, *Ber.*, 1893, **26**, 1196, 1994; Kühling, *Ber.*, 1895, **28**, 41, 523; 1896, **29**, 165; Bamberger, *Ber.*, 1895, **28**, 403; 1896, **29**, 446; Chatterjee, *J. Indian Chem. Soc.*, 1935, **12**, 410, 690). Some of these methods involve the isolation of dry, or semi-dry, unstable and often explosive intermediates, and in order to overcome this disadvantage Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2339) introduced a procedure which eliminates the necessity of isolating the solid diazo-compound from its aqueous solution. Its use was extended by Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1372). In its simplest form this reaction, which forms the basis of the experimental work in this communication, may be represented thus: $Ph{\cdot}N_2{\cdot}OH + PhR \longrightarrow$ *o*- and *p*-$Ph{\cdot}C_6H_4R + N_2 + H_2O$. Further examples of its use have been described by Grieve and Hey (J., 1932, 1888, 2245; 1934, 1797), Hey (J., 1932, 2636), and Cook and Cook (*J. Amer. Chem. Soc.*, 1933, **55**, 1212).

One of the chief characteristics of the reaction is the fact that it gives rise to " amphoteric " or *invariable ortho-para substitution* (Grieve and Hey, J., 1934, 1797), *i.e.*, the phenyl or substituted phenyl group always enters the aromatic nucleus of the second component C_6H_5R at the ortho- and/or para-positions with regard to R, irrespective of the usual directive influence of R with reference to the normal substitution reactions by a kationoid or anionoid reagent. This unusual phenomenon, already noted by Kühling (*loc. cit.*) and Gomberg and Pernert (*loc. cit.*, p. 1379), has been encountered in two other reactions as well as possibly in a third (Hey, J., 1934, 1966), and these additional reactions may therefore be cited as further examples of methods for the preparation of unsymmetrical biaryls. For example, the reaction between nitrosoacylarylamines and an aromatic component (Bamberger, *Ber.*, 1897, **30**, 366; Kliegl and Huber, *Ber.*, 1920, **53**, 1655; Hey, J., 1932, 2636; Grieve and Hey, J., 1934, 1797), *viz.*, $Ar{\cdot}N(NO){\cdot}COR + C_6H_5R' \longrightarrow$ *o*/*p*-$Ar{\cdot}C_6H_4R' + N_2 + R{\cdot}CO_2H$, and also that between a diaroyl peroxide and an aromatic component (Gelissen and Hermans, *Ber.*, 1925, **28**, 285, 476; Hey, J., 1934, 1966; Wieland, Schapiro, and Metzger, *Annalen*, 1934, **513**, 93), *viz.*, $Ar{\cdot}CO{\cdot}O{\cdot}O{\cdot}COAr + C_6H_5R \longrightarrow$ *o*/*p*$Ar{\cdot}C_6H_4R + CO_2 + Ar{\cdot}CO_2H$, may, in selected cases, be of great value in this respect.

Further developments in the methods available for the preparation of unsymmetrical biaryls are obviously desirable and the present communication deals mainly with possible extensions of the Gomberg reaction to include the use of (a) reacting components which are solid at the temperature of the reaction ($< 20°$) and (b) bases of the naphthalene series.

Attempts have also been made to increase the yields by variations in experimental conditions, diazotised aniline and benzene being used, as the ease with which the product (diphenyl) can be isolated enables reliable estimations of yield to be readily obtained. Two methods of procedure are possible: either the diazotised base is added to a cold well-stirred mixture of the second component (which is a neutral aromatic liquid immiscible with water) and sufficient aqueous sodium hydroxide to ensure the mixture being alkaline on the completion of the addition, or the appropriate quantity of aqueous sodium hydroxide is added to the mixture of the aqueous diazonium solution and the second component. The former method is recommended by Gomberg and Pernert (*loc. cit.*) for aniline and the toluidines, and the latter for halogeno- and nitro-anilines. In our experience there is, in most cases, little to choose between the two. By the second method reactions were carried out (a) in presence of magnesium sulphate (cf. Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 250), (b) in presence of copper sulphate, (c) with addition of aqueous ammonia in place of sodium hydroxide, (d) in an atmosphere of nitrogen, solutions saturated with nitrogen being used, (e) with addition of aqueous sodium acetate in place of sodium hydroxide, and (f) in presence of formaldehyde. By the first method reactions were carried out (a) with calcium hydroxide in place of sodium hydroxide, (b) with the addition of lissapol A as an emulsifying agent, (c) at 30° throughout the reaction, and (d) at 50° throughout the reaction. The yield of diphenyl was in no case markedly in excess of that obtained in the usual manner described by Gomberg. In the example studied, however, the reaction proceeded equally well at 30° and artificial cooling is therefore not necessary. At this temperature it is, of course, essential to use the first method of procedure; this modification may be of use with components which would solidify at lower temperatures.

In a discussion of the mechanism of this reaction Gomberg and Pernert (*loc. cit.*) conclude that " the success of the reaction is seen at once to lie in the ability of the non-aqueous liquid to extract from the aqueous layer the reactive diazo-compound as fast as it is formed." The present authors are in entire agreement with this statement, which implies that the essential reaction takes place in the non-aqueous medium and is probably non-ionic in character. In confirmation of this view it is now shown that no biaryl formation could be detected when (a) diazotised aniline and aqueous sodium benzoate, (b) diazotised anthranilic acid and aqueous sodium benzoate, or (c) diazotised anthranilic acid and benzene were used as components in the reaction. On the other hand the reaction proceeds in the normal manner when methyl benzoate is used in place of sodium benzoate in reaction (a) (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2343), or when diazotised methyl anthranilate is used in place of anthranilic acid in reaction (c). The two-phase system thus appears to be an essential feature of the reaction, the success of which is dependent upon a favourable partition coefficient.

No experimental work has been reported previously in which the Gomberg reaction has been applied to solid reactants in solution, and the value of the reaction would be considerably enhanced if an extension in this direction could be made. The choice of a suitable solvent is limited, since it must be neutral, immiscible with water, and inert towards the highly reactive diazo-compound. In addition it should possess high solvent power and a reasonably low boiling point. It was impossible to find a solvent entirely inert, but some success attended the use of chloroform and carbon tetrachloride, although in both cases (especially the latter) some reaction with the solvent was evident and the yield of biaryl was, in general, low. The low volatility of the solid reactant, which must be present in excess, unfortunately often adds to the practical difficulty of isolating the desired product.

It was found that from diazotised methyl anthranilate and a solution of naphthalene in carbon tetrachloride, by the use of the normal procedure of Gomberg, *methyl* o-*α-naphthylbenzoate* was obtained. The free acid, obtained on hydrolysis, was converted by ring closure into *meso*benzanthrone, both by the action of aluminium chloride on the acid chloride (cf. Schaarschmidt and Georgeacopol, *Ber.*, 1918, **51**, 1082) and by the action of concentrated sulphuric acid. Further examples of the application of the Gomberg reaction to solutions of solid reactants have been provided by reactions between (a) diazotised aniline and a solution of diphenyl in chloroform and in carbon tetrachloride, which gave rise to *p*-diphenylbenzene, (b) diazotised *p*-nitroaniline and a solution of diphenyl in chloroform, which yielded 4'-nitro-*p*-diphenylbenzene, and (c) diazotised *p*-anisidine and a solution of benzophenone in carbon tetrachloride. In the last reaction 4-methoxy-4'-benzoyldiphenyl was formed, which was identical with the product resulting from the action of benzoyl chloride on 4-methoxydiphenyl in the presence of aluminium chloride, the constitution of which has been proved by an unambiguous synthesis (Hey and Jackson, J., 1936, 802).

When carbon tetrachloride was used as solvent, a considerable quantity of chlorobenzene was found in the product from reactions using diazotised aniline. This observation is of particular significance in correlating the Gomberg reaction with other reactions which give rise to biaryl formation and which, it is held, also proceed most probably by a non-ionic mechanism involving free radicals. It has been shown by Waters (J., 1937, 113) that chlorobenzene is formed when nitrosoacetanilide is dissolved in carbon tetrachloride or chloroform. Wieland and his co-workers (*Annalen*, 1934, **514**, 145) have also shown that, when phenylazotriphenylmethane is heated in carbon tetrachloride solution, chlorobenzene is formed, and a similar result was observed by Böeseken and Gelissen (*Rec. trav. chim.*, 1924, **43**, 869) in the decomposition of dibenzoyl peroxide in carbon tetrachloride. These observations, coupled with evidence from invariable ortho-para aromatic substitution, point to a similar mechanism common to all four reactions and, as indicated elsewhere (Grieve and Hey, J., 1934, 1797; Hey, *ibid.*, p. 1966; Waters, *loc. cit.*), all the available evidence is consistent with a mechanism involving the formation and transient existence of free radicals. If such is the case, only very limited success would be expected to attend the application of the Gomberg reaction to solid reactants in solution, since the highly reactive radicals would also react in large measure with the solvent molecules. The evidence contained in the present communication is entirely in agreement with these conclusions.

Hitherto bases of the naphthalene series have not been used in the Gomberg reaction. Reactions have now been carried out with both diazotised α-naphthylamine and diazotised β-naphthylamine and benzene; α- and β-phenylnaphthalene respectively were obtained, but the yields were small.

EXPERIMENTAL.

Experimental Conditions.—The following reactions were carried out with the object of improving the yield of diphenyl obtainable from diazotised aniline and benzene, one or other of the two general methods of procedure described by Gomberg and Pernert (*loc. cit.*) being used.

(i) Aniline (31 g.), dissolved in hydrochloric acid (*d* 1·16, 83 c.c.), was diazotised at 5° with a concentrated aqueous solution of sodium nitrite. The resulting solution was added to benzene (300 c.c.) and to this mixture, vigorously stirred at 0—5°, was added gradually a solution of sodium hydroxide (32 g.) in water (100 c.c.). Stirring was continued for 8 hours while the temperature was raised slowly to 30—35°. The benzene layer was then separated, washed with dilute hydrochloric acid and with water, dried, and distilled. The crude diphenyl was collected under reduced pressure and redistilled at atmospheric pressure. Weight, 12·5 g.; yield, 24%, calculated on the weight of aniline used. Unless otherwise stated, this method of working up the product was used in all subsequent experiments.

(ii) This reaction was carried out as in (i) except that a solution of magnesium sulphate (35 g. of the heptahydrate) in water (100 c.c.) was added to the mixture of the diazonium solution and the benzene before the addition of the alkali. Weight of diphenyl, 12·5 g.; yield, 24% (cf. Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 250).

(iii) This reaction was carried out as in (ii), but larger quantities were used (47 g. of aniline) and a solution of copper sulphate (50 g. of the pentahydrate) in water (200 c.c.) was added in place of the aqueous magnesium sulphate. Weight of diphenyl, 12 g.; yield, 16%.

(iv) Aqueous ammonia (*d* 0·880, 70 c.c.) was added gradually to a stirred mixture of benzene (350 c.c.) and the diazonium solution, prepared from aniline (47 g.), kept at 0—5°. The temperature was raised gradually to 40° during 12 hours. Weight of diphenyl, 7 g.; yield, 10%.

(v) This reaction was carried out in an atmosphere of nitrogen, solutions previously saturated with this gas being used. The experimental procedure was as in (i), the quantities used being based on 47 g. of aniline. Weight of diphenyl, 17·5 g.; yield, 23%.

(vi) Aqueous sodium acetate (165 g. of the trihydrate in 400 c.c. of water) was added gradually to a cold stirred mixture of the diazonium solution, from 47 g. of aniline, and benzene (350 c.c.). Weight of diphenyl, 4 g.; yield, 5%.

(vii) This reaction was carried out as in (i), quantities based on 47 g. of aniline being used, with the addition of formaldehyde (25 c.c. of 40% solution) prior to the addition of alkali. Since difficulty was experienced in separating the two layers at the end of the reaction, the diphenyl was isolated by prolonged distillation with steam. Weight of diphenyl, 7 g.; yield, 10%.

(viii) A solution of benzenediazonium chloride, prepared from 47 g. of aniline, was added gradually to a stirred mixture of benzene (350 c.c.) and a sludge of slaked lime (46 g.) in water (200 c.c.) at 0—5°. Stirring was continued for 9 hours while the temperature was raised slowly to 40°. The mixture was acidified, and the benzene layer separated and treated as described above. Weight of diphenyl, 17·5 g.; yield, 23%.

(ix) The diazonium solution, prepared from 47 g. of aniline, was added gradually to a stirred mixture of benzene (300 c.c.) and aqueous sodium hydroxide (50 g. in 150 c.c.) with the addition of lissapol A (2 g.). Stirring was continued for 12 hours and the temperature was raised gradually from 5° to about 40°. The diphenyl was distilled in steam. Weight, 17·5 g.; yield, 23%.

(x) This reaction was carried out as in (ix), but no lissapol A was added and the temperature was maintained at 30° throughout the reaction. The diphenyl was distilled in steam. Weight, 20 g.; yield, 26%.

(xi) This reaction was carried out as in (x), but at 50°. Weight of diphenyl, 15 g.; yield, 19%.

The following reactions were carried out to find if the two-phase system of two immiscible liquids is essential.

(xii) An aqueous solution of diazotised aniline was added gradually to an aqueous solution of sodium benzoate at 5° containing a sufficient excess of alkali to neutralise the diazo-solution. No diphenylcarboxylic acid could be detected in the product.

(xiii) An aqueous solution of diazotised anthranilic acid was used in place of the diazotised aniline in reaction (xii). No diphenyldicarboxylic acid was detected.

(xiv) An aqueous solution of diazotised anthranilic acid was added to benzene, and to the resulting mixture aqueous alkali was added, under the conditions described in (i). No diphenylcarboxylic acid was detected.

(xv) A fine suspension of methyl anthranilate (50 g.) in hydrochloric acid (*d* 1·16, 83 c.c.) and water (35 c.c.) was diazotised in the normal manner and added to benzene (350 c.c.). Aqueous sodium hydroxide (27 g. in 100 c.c.) was added gradually to the stirred mixture at 0—5°. Stirring was continued for 12 hours and the temperature was raised gradually to about 30°. The benzene layer was separated, washed with concentrated hydrochloric acid and with water, and distilled. After removal of the benzene the pressure was reduced to 30 mm. and crude methyl diphenyl-2-carboxylate was collected at 190—195°. Redistillation gave the pure ester (17 g.; b. p. 307—308°/740 mm.), which on hydrolysis gave diphenyl-2-carboxylic acid, m. p. and mixed m. p. 110° (Fittig and Ostermayer, *Annalen*, 1873, **166**, 374; Graebe and Rateanu, *Annalen*, 1894, **279**, 260). Treatment with concentrated sulphuric acid at 50° gave fluorenone, m. p. 83° after crystallisation from alcohol (Graebe and Aubin, *Ber.*, 1887, **20**, 847; Weger and Döring, *Ber.*, 1903, **36**, 881).

The Use of Solid Reactants in Solution.—Diazotised methyl anthranilate and naphthalene. A paste of methyl anthranilate (50 g.) in dilute hydrochloric acid (84 c.c. of acid, *d* 1·16, and 40 c.c. of water) was diazotised with aqueous sodium nitrite in the normal manner. Aqueous sodium hydroxide (27 g. in 100 c.c.) was added gradually to a vigorously stirred mixture of the diazonium solution and a solution of naphthalene (100 g.) in carbon tetrachloride (350 c.c.) at 0—5°. Stirring was continued for 10 hours and the temperature of the mixture was raised slowly to 40°. The carbon tetrachloride layer was separated, washed with water, dried, and distilled. After carbon tetrachloride and the excess of naphthalene had been collected, a small intermediate liquid fraction (b. p. 230—250°) was obtained, which consisted of methyl *o*-chlorobenzoate, and finally a fraction, b. p. 300—320°, which solidified when cold. Recrystallisation from methyl alcohol and then from light petroleum (b. p. 80—100°) gave *methyl* o-α-*naphthylbenzoate* in prisms, m. p. 87—88° (Found: C, 82·2; H, 5·1. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%). Hydrolysis of the ester with alcoholic potassium hydroxide yielded *o*-α-naphthylbenzoic acid, m. p. 159—160° (cf. Schaarschmidt and Georgeacopol, *loc. cit.*, p. 1085).

A portion of the acid (0·8 g.), suspended in benzene with the addition of phosphorus pentachloride (0·7 g.), was boiled under reflux for ½ hour; aluminium chloride (2 g.) was then added, and the mixture again boiled until evolution of hydrogen chloride had ceased. The product was poured on ice and distilled with steam to remove benzene. The residual yellowish-brown solid was washed with dilute acid and with alkali. Recrystallisation from acetic acid gave *meso*benzanthrone, m. p. 170°, both alone and on admixture with an authentic specimen.

Ring closure of the acid was also effected by keeping it at room temperature in solution in concentrated sulphuric acid containing 10% of boric acid during several days, the benzanthrone being isolated in the normal manner.

Diazotised aniline and diphenyl. Aqueous sodium hydroxide (100 g. in 250 c.c.) was added slowly to an ice-cold stirred mixture of an aqueous solution of benzenediazonium chloride, prepared from 93 g. of aniline (1 mol.), and a solution of diphenyl (200 g.) in chloroform (600 c.c.). Stirring was continued for 10 hours and the temperature was raised slowly to 40°. The chloroform layer was separated, washed with water, dried, and distilled. The greater part of the excess of diphenyl was collected at atmospheric pressure, but the pressure was reduced to remove the last traces. *p*-Diphenylbenzene, m. p. 206—208°, was extracted from the non-volatile residue by means of a hot mixture of benzene and light petroleum (b. p. 80—100°) (cf. Schultz, *Annalen*, 1874, **174**, 230). In a similar reaction using carbon tetrachloride in place of chloroform, an appreciable quantity of chlorobenzene (16 g.) was collected during the distillation. In a reaction using diazotised aniline, aqueous sodium hydroxide, and carbon tetrachloride alone without any solute, carried out as above, 12 g. of chlorobenzene were obtained from 46·5 g. of aniline.

Diazotised p-*nitroaniline and diphenyl* (with J. L. DUNN). When diazotised *p*-nitroaniline, prepared from 46 g. of *p*-nitroaniline (⅓ mol.), was used in place of diazotised aniline in the previous reaction, 4′-nitro-*p*-diphenylbenzene * was obtained, which was extracted from the non-volatile residue with hot glacial acetic acid. Crystallisation from glacial acetic acid gave golden-yellow needles, m. p. 214—215° (Found: C, 78·2; H, 4·7; N, 5·2. Calc. for $C_{18}H_{13}O_2N$: C, 78·5; H, 4·7; N, 5·1%). On reduction with iron filings and hydrochloric acid in the usual manner, 4′-amino-*p*-diphenylbenzene, m. p. 196—198°, was obtained (cf. Pummerer, Binapfl, Bittner, and Schuegraf, *Ber.*, 1922, **55**, 3095; Pummerer and Bittner, *Ber.*, 1924, **57**, 84).

Diazotised p-*anisidine and benzophenone* (with E. R. B. JACKSON). A solution of *p*-anisidine (50 g.) in hydrochloric acid (*d* 1·16, 100 c.c.) was diazotised with sodium nitrite (28·5 g.) in the normal manner at 0° and added to an ice-cold solution of benzophenone (200 g.) in carbon tetrachloride (350 c.c.). Aqueous sodium hydroxide (30 g. in 100 c.c.) was added to the vigorously stirred, cold mixture during 2 hours. Stirring was continued until the temperature reached that of the room. After standing overnight, the carbon tetrachloride layer was separated, washed with water, and distilled. After removal of the excess of benzophenone under reduced pressure (25 mm.), a viscous oil (3 g.) distilled at 280—285°, which solidified when cold. After crystallisation from benzene–alcohol 4-methoxy-4′-benzoyldiphenyl was obtained in almost colourless leaflets, m. p. 166° alone and in admixture with an authentic specimen (Hey and Jackson, *loc. cit.*) (Found: C, 83·0; H, 6·0. Calc. for $C_{20}H_{16}O_2$: C, 83·3; H, 5·6%).

---

* Since the completion of this work 4′-nitro-*p*-diphenylbenzene has been obtained by Basford (J., 1937, 1442) by another method.

Experiments with α- and β-Naphthylamine.—Diazotised α-naphthylamine and benzene. A suspension of α-naphthylamine (72 g.) in hydrochloric acid (*d* 1·16, 125 c.c.) and water (50 c.c.) was diazotised in the normal manner and added to benzene (400 c.c.). To the mixture, aqueous sodium hydroxide (50 g. in 200 c.c.) was added gradually, with stirring, at 0—5°. After 10 hours with a gradual rise in temperature to 40°, the benzene was removed with steam and the dark solid residue was heated with tin and hydrochloric acid to remove azo-compounds. The insoluble residue was extracted several times with hot benzene. Distillation of the benzene extract yielded α-phenylnaphthalene as a yellow oil, b. p. 320—330°, in small yield. Oxidation with potassium permanganate gave *o*-benzoylbenzoic acid, m. p. 93°, or 125° after dehydration (cf. Möhlau and Berger, *Ber.*, 1893, **26**, 1199).

Diazotised β-naphthylamine and benzene. This reaction was carried out exactly as described above for α-naphthylamine, but half the quantities were used. The residue (41 g.) obtained after steam-distillation was extracted repeatedly with light petroleum (b. p. 80—100°). Evaporation of the extracts deposited β-phenylnaphthalene (4 g.) as a slightly pink, crystalline solid. Recrystallisation from alcohol gave pearl-like flakes, m. p. 100—101° alone and in admixture with an authentic specimen kindly supplied by Dr. F. S. Spring (cf. J., 1934, 1332).

In both reactions with the naphthylamines a considerable quantity of dark insoluble granular material was formed.

The authors thank Professor I. M. Heilbron, F.R.S., for his helpful advice and encouragement, and also Imperial Chemical Industries, Ltd. (Dyestuffs Group), for grants and gifts of chemicals.

THE UNIVERSITY, MANCHESTER. [*Received, November 22nd*, 1937.]