79. *Syntheses of 2-Phenylnaphthalenes.*

By D. H. HEY and S. E. LAWTON.

2-Phenylnaphthalene can be conveniently prepared by the action of nitrosoaceto-2-naphthalide on benzene. By the same general reaction, *viz.*, $R\cdot C_{10}H_6\cdot N(NO)\cdot CO\cdot CH_3 + C_6H_5R' \longrightarrow R\cdot C_{10}H_6\cdot C_6H_4R' + N_2 + CH_3\cdot CO_2H$, 2′-, 4′-, 5-, 6-, and 8-*nitro*-2-*phenylnaphthalene*, 6-*bromo*-2-*phenylnaphthalene*, and 6- and 7-*methoxy*-2-*phenylnaphthalene* are prepared. Nitration of 2-phenylnaphthalene gives 1-*nitro*-2-*phenylnaphthalene*. The six nitro-2-phenylnaphthalenes are reduced to the corresponding amines. The 2′-acetamido-2-phenylnaphthalene thus prepared is identical with the acetyl derivative of the base resulting from the amide of α-chrysenic acid by Hofmann degradation. Reduction of 1-nitro-2-phenylnaphthalene with stannous chloride in hydrochloric acid gives 4-*chloro*-2-*phenyl*-1-*naphthylamine*, but when iron and acetic acid are used, 2-*phenyl*-1-*naphthylamine* is obtained, which on acetylation and nitration gives 4-*nitro*-2-*phenylaceto*-1-*naphthalide*. The 1 : 4-diamino-2-phenylnaphthalene obtained from the latter on hydrolysis and reduction is readily oxidised to 2-phenyl-1 : 4-naphthaquinone. Bromination of 2-phenylnaphthalene gives 1-*bromo*-2-*phenylnaphthalene*. Other compounds described include various *di*- and *tri-nitro*-derivatives of 2-phenylnaphthalene, 2 : 7-*diphenylnaphthalene*, and the *naphthols* derived from 6- and 7-methoxy-2-phenylnaphthalene on demethylation.

NONE of the methods for the preparation of 2-phenylnaphthalene described in the literature appears suitable for its preparation in quantity. By means of the reaction between nitrosoaceto-2-naphthalide and benzene first carried out by Dr. E. C. Butterworth (see Haworth and Hey, this vol., p. 361), the hydrocarbon can be readily and cheaply made available in large quantity. Two simple chemical operations are involved. (1) The optimum conditions for the preparation of nitrosoaceto-2-naphthalide by means of nitrous fumes (Haworth and Hey, *loc. cit.*) and nitrosyl chloride (France, Heilbron, and Hey, this vol., p. 369) have been carefully worked out. In the former method almost quantitative nitrosation can be effected on batches of 25 g. of aceto-2-naphthalide, but in the latter method equally good yields were obtained from quantities of aceto-2-naphthalide up to 150 g. (2) In the reaction of nitrosoaceto-2-naphthalide with benzene, it was not found possible to prevent the production of much red tarry material and the yield of 2-phenylnaphthalene was 25—30%, calculated on the weight of nitrosoaceto-2-naphthalide; this, however, is not regarded as a serious disadvantage owing to the low cost of the initial materials. In the preparation of certain substituted 2-phenylnaphthalenes from substituted nitrosoaceto-2-naphthalides and benzene the formation of red by-products does not take place to the same extent and, as will be noted later, yields of 40—50% are obtained. For comparative purposes the method of preparation of 2-phenylnaphthalene described by Carter and van Loon

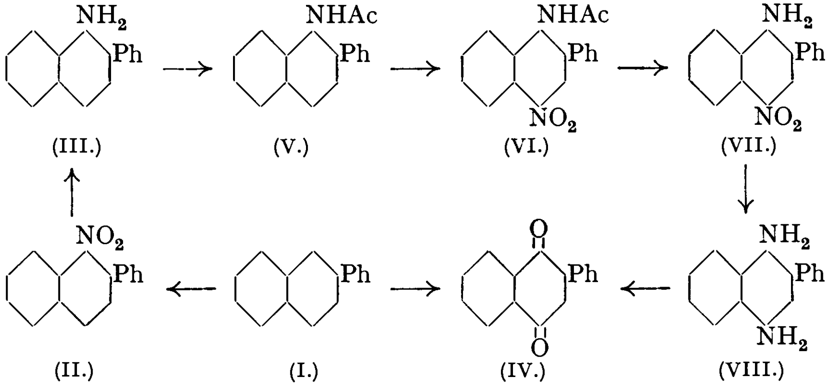
(*J. Amer. Chem. Soc.*, 1938, **60**, 1077) was investigated. They obtained the hydrocarbon in 80—85% yield by refluxing α-amino-β-methoxy-β-phenylpropionic acid with hydrobromic acid, but the amino-acid had to be prepared by a three-stage process from cinnamic acid (*idem, ibid.*, 1937, **59**, 2555) and the overall yield for the four stages was of the order of only 15% (they claim 25—30%). Moreover, the necessary purification of the intermediate products rendered the method tedious as a means of preparing the hydrocarbon in quantity.

(A) *Nitro- and Amino-2-phenylnaphthalenes.*—Under mild conditions of nitration, 2-phenylnaphthalene (I) gives almost exclusively 1-*nitro-2-phenylnaphthalene* (II), m. p. 127°, together with a very small quantity of a *dinitro*-derivative, m. p. 187—188°, probably 1 : 5-dinitro-2-phenylnaphthalene. Under more drastic conditions the product consists of a complex mixture of di- and possibly tri-nitro-derivatives, from which it has not been possible by fractional crystallisation to isolate any pure individual compound. The constitution of the 1-nitro-2-phenylnaphthalene (II) was established by the synthesis of the same substance by the action of diazotised 1-nitro-2-naphthylamine on benzene in the presence of aqueous alkali. The mild nitration of 2-phenylnaphthalene thus resembles that of 2-methylnaphthalene, which yields almost exclusively 1-nitro-2-methylnaphthalene (Schulze, *Ber.*, 1884, **17**, 844; Lesser, *Annalen*, 1914, **402**, 32).

Attempts to prove the constitution of 1-nitro-2-phenylnaphthalene (II) by degradative oxidation were unsuccessful, as also were those of Lesser (*loc. cit.*) in the case of 1-nitro-2-methylnaphthalene.

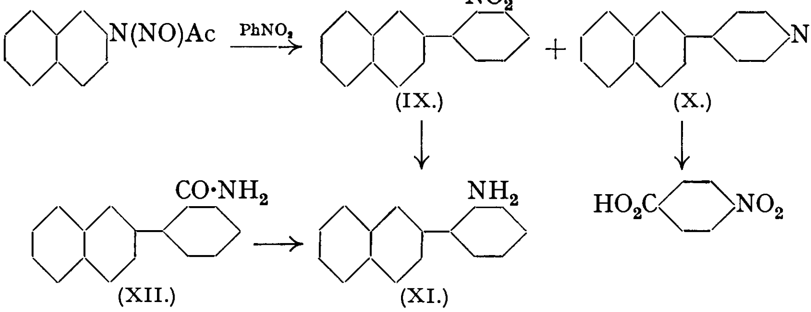
The behaviour of 1-nitro-2-phenylnaphthalene (II) on reduction was similar to that of 1-nitro-2-methylnaphthalene reported by Lesser. Reduction with stannous chloride and hydrochloric acid gave 4-*chloro-2-phenyl-1-naphthylamine*, whereas reduction with iron and acetic acid gave 2-*phenyl-1-naphthylamine* (III). Mild oxidation of 2-phenylnaphthalene (I) with chromic anhydride gives 2-phenyl-1 : 4-naphthaquinone (IV) (Zincke and Breuer, *Annalen*, 1884, **226**, 23; Zincke, *ibid.*, 1887, **240**, 137); under the same conditions, 2'- and 4'-nitro-2-phenylnaphthalene (see below) give rise to the corresponding nitro-2-phenyl-1 : 4-naphthaquinones, but 1-nitro-2-phenylnaphthalene is recovered unchanged. An attempt to convert 2-phenyl-1-naphthylamine into the corresponding nitrile by means of the Sandmeyer reaction gave, not the expected nitrile, but 1-*chloro-2-phenylnaphthalene.*

Nitration of 2-*phenylaceto-1-naphthalide* (V) under mild conditions gave 4-*nitro-2-phenylaceto-1-naphthalide* (VI) in good yield, which was converted on hydrolysis into 4-*nitro-2-phenyl-1-naphthylamine* (VII) and by subsequent reduction into 1 : 4-diamino-2-phenylnaphthalene (VIII). Oxidation of the diamine (VIII) with aqueous chromic acid gave 2-phenyl-1 : 4-naphthaquinone (IV), identical with the product obtained directly from 2-phenylnaphthalene on mild oxidation, thus indicating that nitration of 2-phenylaceto-1-naphthalide had been effected at position 4.



Grieve and Hey (J., 1934, 1797) have shown that the action of nitrosoacetanilide on nitrobenzene yields a mixture of 2- and 4-nitrodiphenyl. It is now shown that, in similar manner, nitrosoaceto-2-naphthalide and nitrobenzene give a mixture of 2'-*nitro-2-phenylnaphthalene* (IX), m. p. 101°, and 4'-*nitro-2-phenylnaphthalene* (X), m. p. 174°, which can be separated either by vacuum sublimation or by distillation in steam. Both nitro-compounds yield the corresponding *nitro-2-phenyl-1 : 4-naphthaquinones* on mild oxidation with chromic anhydride. Reduction of 2′-nitro-2-phenylnaphthalene (IX) gave 2′-amino-2-phenylnaphthalene (XI), which was identified as such by the melting point of its mixture with the base obtained by the Hofmann degradation of the amide (XII) of α-chrysenic acid, as described by Graebe and Hönigsberger (*Annalen*, 1900, **311**, 271). The constitution of the isomeric 4′-nitro-2-phenylnaphthalene (X) was proved by oxidative degradation to *p*-nitrobenzoic acid. Reduction gave *4′-amino-2-phenylnaphthalene.*

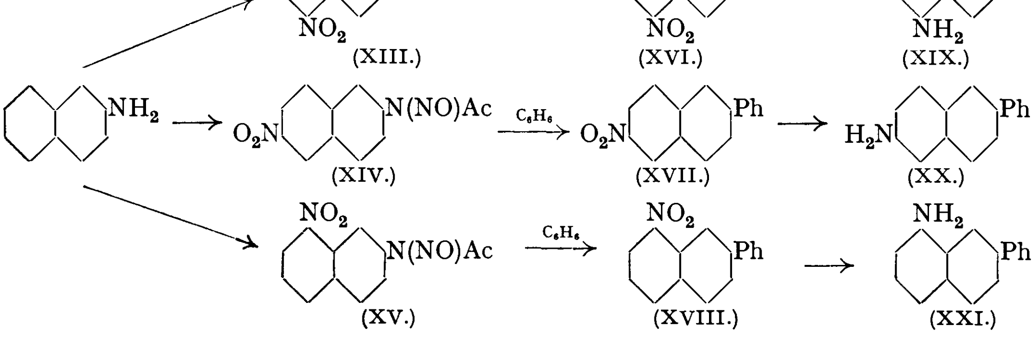
Further nitration of 2′-nitro-2-phenylnaphthalene (IX) gave a product regarded as *1 : 2′-dinitro-2-phenylnaphthalene*, but under similar conditions 4′-nitro-2-phenylnaphthalene (X) was unaffected. Under more drastic conditions 4′-nitro-2-phenylnaphthalene gave a mixture of two trinitro-2-phenylnaphthalenes, probably 1 : 5 : 4′- and *1 : 8 : 4′-trinitro-2-phenylnaphthalene.* Veselý and Kapp (*Rec. Trav. chim.*, 1925, **44**, 360) have shown that further nitration of 1-nitro-2-methylnaphthalene gives a mixture of the 1 : 5- and the 1 : 8-dinitro-derivative.



(IX.) (X.) (XII.) (XI.)

In the same way that 2-phenylnaphthalene is obtained from nitrosoaceto-2-naphthalide and benzene, various nitro-2-phenylnaphthalenes can be obtained from the interaction of nitronitrosoaceto-2-naphthalides with benzene. 1-Nitroaceto-2-naphthalide could not be nitrosated, but this inhibition does not apply when the nitro-group is attached to the second ring in the naphthalene nucleus.

By the methods of nitration due to Friedländer and Szymanski (*Ber.*, 1892, **25**, 2077) and Hodgson and Crook (J., 1936, 1844) 5-nitro- and 8-nitro-2-naphthylamines were prepared from β-naphthylamine; under the conditions of Saunders and Hamilton (*J. Amer. Chem. Soc.*, 1932, **54**, 636) 1-, 6-, and 8-nitro-2-naphthylamines were obtained. The 5-, 6-, and 8-nitro-2-naphthylamines were acetylated, and the resulting acetyl derivatives nitrosated. The nitroso-compounds (XIII, XIV, and XV), on reaction with benzene, yielded *5-nitro-* (XVI), *6-nitro-* (XVII), and *8-nitro-2-phenylnaphthalene* (XVIII) respectively, in yields of 40, 52, and 47%. The three nitro-2-phenylnaphthalenes were reduced to the corresponding *amines* (XIX, XX, XXI), the 5- and the 8-nitro-compound by means of iron



(XIII.) (XVI.) (XIX.) (XIV.) (XVII.) (XX.) (XV.) (XVIII.) (XXI.)

and hydrochloric acid, in order to avoid nuclear chlorination, and the 6-nitro-compound by means of stannous chloride and hydrochloric acid.

(B) 2 : 7-*Diphenylnaphthalene*.—2 : 7-Naphthylenediamine was prepared from 2 : 7-dihydroxynaphthalene by the Bucherer reaction (Windaus, *Ber.*, 1924, **57**, 1731). Nitrosation of the diacetyl derivative gave a dinitroso-compound, which on reaction with benzene gave 2 : 7-*diphenylnaphthalene*. In similar manner *diacetyl*-2 : 6-*naphthylenediamine* was obtained from 2 : 6-dihydroxynaphthalene, but in this case nitrosation could not be effected by means of nitrous fumes or nitrosyl chloride.

2 : 7-Diphenylnaphthalene is the first heteronuclear diphenylnaphthalene to be prepared, although all four homonuclear diphenylnaphthalenes are known (Allen and Gilman, *J. Amer. Chem. Soc.*, 1936, **58**, 937; Weiss, Abeles, and Knapp, *Monatsh.*, 1932, **61**, 162; Crawford, *J. Amer. Chem. Soc.*, 1939, **61**, 608).

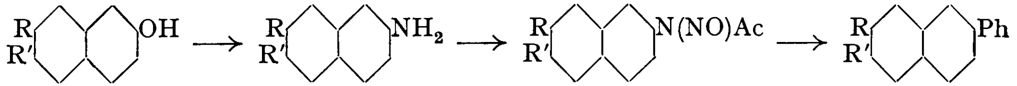
(C) *Bromo-2-phenylnaphthalenes*.—Bromination of 2-phenylnaphthalene gave 1-*bromo*-2-*phenylnaphthalene* identical with the product obtained from 1-amino-2-phenylnaphthalene by means of the Sandmeyer reaction.

Bromination of benzylidene-2-naphthylamine and subsequent hydrolysis as described by Franzen and Eidis (*J. pr. Chem.*, 1913, **88**, 763) gave 1 : 6-dibromo-2-naphthylamine, from which the bromine atom in position 1 was removed with hydriodic acid (Franzen and Stäuble, *ibid.*, 1920, **101**, 68). The resulting 6-bromo-2-naphthylamine was acetylated and nitrosated in the normal manner, and subsequent reaction with benzene gave 6-*bromo*-2-*phenylnaphthalene* in 44% yield, identical with the product obtained from 6-*phenyl*-2-*naphthylamine* by means of the Sandmeyer reaction.

(D) *Hydroxy-2-phenylnaphthalenes*.—6-Hydroxy-2-phenylnaphthalene should be readily obtainable from 6-amino-2-phenylnaphthalene by means of the diazo-reaction, but the availability of the latter, prepared by the method outlined above, is limited, since the 6-nitro-2-naphthylamine from which it is obtained is formed only in small quantity in the nitration of β-naphthylamine by the method of Saunders and Hamilton (*loc. cit.*). An attempt to prepare 6-hydroxy-2-naphthylamine by an alternative method failed because the nitration of 1-bromo-2-naphthol, even under the mildest experimental conditions, gave 1 : 6-dinitro-2-naphthol instead of the expected 6-nitro-1-bromo-2-naphthol. Jacchia (*Annalen*, 1902, **323**, 127) converted 6-nitro-2-naphthylamine-8-sulphonic acid into 6-nitro-2-naphthol-8-sulphonic acid, which on reduction of the nitro-group and elimination of the sulpho-group with sodium amalgam in presence of sodium sulphide gave 6-hydroxy-2-naphthylamine. Since the yields obtained by this method were low, 2 : 6-dihydroxynaphthalene (XXII; R = H, R′ = OH) was converted into 2-hydroxy-6-methoxynaphthalene (XXII; R = H, R′ = OMe), from which 6-methoxy-2-naphthylamine (XXIII; R = H, R′ = OMe) was obtained by means of the Bucherer reaction.

Nitrosation of 6-methoxyaceto-2-naphthalide proceeded normally and subsequent reaction of the nitroso-compound (XXIV; R = H, R′ = OMe) with benzene gave 6-*methoxy*-2-*phenylnaphthalene* (XXV; R = H, R′ = OMe) in 41% yield, from which 6-*hydroxy*-2-*phenylnaphthalene* (XXV; R = H, R′ = OH) was obtained on demethylation.

In similar manner, by the method of Windaus (*loc. cit.*; cf. Fischer and Hammerschmidt, *J. pr. Chem.*, 1916, **94**, 24), 2 : 7-dihydroxynaphthalene (XXII; R = OH, R′ = H) was converted into 2-hydroxy-7-methoxynaphthalene (XXII; R = OMe, R′ = H) and thence into 7-methoxy-2-naphthylamine (XXIII; R = OMe, R′ = H). Nitrosation of 7-methoxyaceto-2-naphthalide, followed by reaction with benzene, gave 7-*methoxy*-2-*phenylnaphthalene* (XXV; R = OMe, R′ = H) in 44% yield, from which 7-*hydroxy*-2-*phenylnaphthalene* (XXV; R = OH, R′ = H) was obtained on demethylation.



(XXII.) (XXIII.) (XXIV.) (XXV.)

Experimental.

Nitrosoaceto-2-naphthalide.—(a) *Nitrous fumes method*. Nitrous fumes (from dilute sulphuric acid and solid sodium nitrite) were passed for 3—4 hours into a solution of aceto-2-naphthalide (25 g.) in a mixture of acetic anhydride (150 c.c.) and glacial acetic acid (200 c.c.) at

8—10°. When the deep green solution was poured into ice-water (500 c.c.) with stirring, nitrosoaceto-2-naphthalide separated as a pale yellow, granular precipitate. This was washed with cold water and dried on a porous tile; the colour changed slowly from pale yellow to reddish-brown [yield, 22 g ; m. p. 80° (decomp.)]. (b) *Nitrosyl chloride method.* A solution of nitrosyl chloride (70 g.) in acetic anhydride (200 c.c.), kept cold by ice–salt, was dropped during 15 minutes into a solution of aceto-2-naphthalide (150 g.) in a mixture of acetic anhydride (1000 c.c.) and glacial acetic acid (1000 c.c.) containing finely powdered, fused sodium acetate (156 g.) in suspension, the reaction mixture being maintained at 5—10° and vigorously stirred. After a further ½ hour's stirring, the mixture was poured into ice-water (2500 c.c.), and the product (140 g.) isolated as described above.

Action of Nitrosoaceto-2-naphthalide on Benzene.—Nitrosoaceto-2-naphthalide (20 g.) was added during 2—3 hours to benzene (1000 c.c.) stirred at room temperature; nitrogen was evolved and the solution became red. After 36 hours the solution was evaporated to half bulk and boiled under reflux for 3—4 hours with hydrochloric acid (200 c.c., *d* 1·2) and granulated tin (25 g.), the latter being added in portions at intervals of about an hour. This treatment removed the red colour. After filtration the benzene layer was separated, the benzene removed, and the residue distilled in a vacuum (100°/10^{-3} mm.). 2-Phenylnaphthalene (5·4 g.) thus obtained crystallised from alcohol in lustrous white flakes, m. p. 101—102°. Basification of the hydrochloric acid layer liberated 2-naphthylamine, m. p. and mixed m. p. 112°, which was extracted with ether. In a preparation on a larger scale nitrosoaceto-2-naphthalide (230 g.), prepared in two batches by method (b) from aceto-2-naphthalide (250 g.), and benzene (8000 c.c.) gave 2-phenylnaphthalene (55 g.). Distillation with superheated steam is more convenient than distillation in a high vacuum (100°/10^{-3} mm.) in the large-scale preparations.

A solution of 2-phenylnaphthalene (1 g.) in glacial acetic acid (20 c.c.) was heated on the steam-bath for 10 minutes with a solution of chromic anhydride (3 g.) in 80% acetic acid (10 c.c.). Dilution with water gave 2-phenyl-1 : 4-naphthaquinone (0·8 g.), which crystallised from alcohol in yellow needles, m. p. 109° (cf. Chattaway and Lewis, J., 1894, **65**, 873).

(A) *Nitro- and Amino-2-phenylnaphthalenes.*—*Nitration of 2-phenylnaphthalene.* A mixture of nitric acid (*d* 1·42, 150 c.c.) and glacial acetic acid (75 c.c.) was added to a fine suspension of 2-phenylnaphthalene (10 g.) in glacial acetic acid (75 c.c.), prepared by rapid cooling of the hot solution. After being kept at room temperature overnight, the suspended solid was filtered off, washed with dilute alkali solution and with water, and dried. Two crystallisations from alcohol gave 1-*nitro-2-phenylnaphthalene* (8·5 g.) in hard yellow needles, m. p. 127° (Found : C, 76·9; H, 4·7. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4%). On exposure to diffused sunlight the nitro-compound became pale greenish-yellow, but there was no change in m. p. When the original filtrate from the nitration mixture was poured into water, a yellow oil separated, which was extracted with ether, washed with dilute aqueous alkali, and dried. Removal of the ether left a viscous residue, from which three crystalline products were obtained on treatment with alcohol; (i) m. p. 140—170° (0·3 g.), (ii) m. p. 110—150° (0·3 g.), and (iii) m. p. 114—125° (0·4 g.). Fraction (iii) on further crystallisation gave 1-nitro-2-phenylnaphthalene, but similar treatment of fractions (i) and (ii) yielded only mixtures, m. p. 158—175° and 136—154° respectively. In a second experiment the original filtrate from the nitration mixture was kept for 1 month at room temperature, during which time crystalline 1 : 5-*dinitro-2-phenylnaphthalene* (0·5 g.) separated; after three recrystallisations from glacial acetic acid it was obtained in pale yellow needles, m. p. 187—188° (Found : C, 65·4; H, 3·5. $C_{16}H_{10}O_4N_2$ requires C, 65·3; H, 3·4%). Under more drastic conditions of nitration, *e.g.*, addition of the powdered hydrocarbon to nitric acid (*d* 1·42) at 50°, or treatment with a mixture of nitric acid (*d* 1·42) and sulphuric acid (*d* 1·8) at 50°, the yellow nitration product consisted of mixtures, m. p. 104° to 227°, from which no pure products could be isolated by fractional crystallisation from alcohol or glacial acetic acid.

Attempted oxidation of 1-nitro-2-phenylnaphthalene with chromic anhydride, as described above for the oxidation of 2-phenylnaphthalene to 2-phenyl-1 : 4-naphthaquinone, resulted in the recovery of the nitro-compound unchanged (m. p. and mixed m. p. 126—127°). Under more drastic experimental conditions the nitro-compound was almost completely destroyed.

4-*Chloro-2-phenyl-1-naphthylamine.* A solution of stannous chloride (12 g.) in hydrochloric acid (*d* 1·2, 15 c.c.) was added to a hot solution of 1-nitro-2-phenylnaphthalene (2 g.) in alcohol (50 c.c.). After being heated in an open beaker on the steam-bath for 3 hours, the mixture was made strongly alkaline with concentrated aqueous sodium hydroxide. The base was extracted with ether and dried over potassium hydroxide. Evaporation of the ether left a viscous residue (1·8 g.), from which, after three crystallisations from light petroleum (b. p. 60—80°), 4-*chloro-2-phenyl-1-naphthylamine* was obtained in light brownish needles, m. p. 79° (Found : C, 75·7; H, 5·1. $C_{16}H_{12}NCl$ requires C, 75·8; H, 4·7%). Acetylation by warming with acetic anhydride gave 4-*chloro-2-phenylaceto-*1-*naphthalide,* which crystallised from aqueous alcohol in white plates, m. p. 213° (Found: C, 72·9; H, 4·5. $C_{18}H_{14}ONCl$ requires C, 73·2; H, 4·7%).

2-*Phenyl-*1-*naphthylamine.* Iron dust (12 g.) was added in small portions during 4 hours to a boiling solution of 1-nitro-2-phenylnaphthalene (5 g.) in a mixture of glacial acetic acid (40 c.c.) and water (10 c.c.). After being decanted from undissolved iron, the solution was made strongly alkaline with aqueous sodium hydroxide. The resulting mixture was extracted with ether and removal of the ether from the dried extract left a solid residue (4 g.), which after several crystallisations from light petroleum (b. p. 80—100°) gave 2-*phenyl-*1-*naphthylamine* in light brown needles, m. p. 104° (Found: C, 87·8; H, 5·7. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9%). Acetylation by warming with acetic anhydride gave 2-*phenylaceto-*1-*naphthalide,* which separated from aqueous alcohol in white plates, m. p. 234° (Found: C, 82·65; H, 5·8. $C_{18}H_{15}ON$ requires C, 82·75; H, 5·7%). A portion of the free base (4 g.) in a mixture of hydrochloric acid (*d* 1·2, 24 c.c.) and water (15 c.c.) was diazotised with aqueous sodium nitrite (1·4 g. in 7 c.c.), and the resulting filtered diazonium solution added during 10 minutes to a solution of cuprous cyanide, prepared by the addition of aqueous potassium cyanide (5 g. in 9 c.c.) to aqueous copper sulphate (4·5 g. in 18 c.c.) at 60—70°. The solution was heated on the water-bath for an hour, cooled, and extracted with ether. Removal of the ether from the dried extract left a solid residue, which on sublimation at 100°/10^{-3} mm. gave 1-*chloro-*2-*phenylnaphthalene,* which crystallised from alcohol in white needles, m. p. 82° (Found: Cl, 14·5. $C_{16}H_{11}Cl$ requires Cl, 14·9%).

Attempted nitrosation of 1-*nitroaceto-*2-*naphthalide.* Nitrous fumes were passed into a cold solution of 1-nitroaceto-2-naphthalide (2 g.) in a mixture of glacial acetic acid (150 c.c.) and acetic anhydride (100 c.c.). At half hourly intervals small portions were removed and poured into water, but in every case, even after 6 hours, the product was unchanged 1-nitroaceto-2-naphthalide. To a similar solution containing fused sodium acetate (2 g.), an ice-cold solution of nitrosyl chloride (1 g.) in acetic anhydride (5 c.c.) was gradually added. After 20 minutes the mixture was poured into water, but again only unchanged 1-nitroaceto-2-naphthalide (m. p. and mixed m. p. 123°) was precipitated.

Synthesis of 1-*nitro-*2-*phenylnaphthalene.* A solution of diazotised 1-nitro-2-naphthylamine was prepared by dropping a solution of the base (23 g.) in glacial acetic acid into cold stirred nitrosylsulphuric acid, prepared by the gradual addition of dry sodium nitrite (10 g.) to concentrated sulphuric acid (100 c.c.) at 0° (cf. Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4531). Benzene (500 c.c.) was added to the diazonium solution and into the stirred cooled mixture concentrated aqueous sodium hydroxide was dropped until the aqueous layer gave an alkaline reaction. After standing at room temperature for 48 hours, the dark benzene layer was separated, and the aqueous layer extracted with more benzene (250 c.c.). The combined benzene solutions, washed with concentrated hydrochloric acid and with water, were evaporated to dryness, and the residue sublimed at 130°/10^{-3} mm. After crystallisation from alcohol 1-nitro-2-phenylnaphthalene separated in yellow needles, m. p. 127°, both alone and on admixture with the product of the same m. p. obtained above from the nitration of 2-phenylnaphthalene.

4-*Nitro-*2-*phenyl-*1-*naphthylamine.* A solution of 2-phenylaceto-1-naphthalide (2 g.) in hot glacial acetic acid (15 c.c.) was cooled in ice and stirred during the addition of nitric acid (*d* 1·45, 2 c.c.). After standing at room temperature for an hour, the solution was warmed to 40°. The pale yellow solid precipitated by water gave, on crystallisation from alcohol, 4-*nitro-*2-*phenylaceto-*1-*naphthalide* (1·2 g.) in hard yellow prisms, m. p. 230° (Found: C, 70·7; H, 4·7. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6%). The acetyl derivative (1 g.) was boiled under reflux for 6 hours with alcohol (25 c.c.) and hydrochloric acid (*d* 1·2, 5 c.c.), a further quantity (1 c.c.) of hydrochloric acid being added each hour. Dilution with water precipitated the base and crystallisation from alcohol gave 4-*nitro-*2-*phenyl-*1-*naphthylamine* (0·8 g.) in brown needles showing a greenish reflex, m. p. 155° (Found: C, 73·1; H, 4·7. $C_{16}H_{12}O_2N_2$ requires C, 73·1; H, 4·5%).

1 : 4-*Diacetamido-*2-*phenylnaphthalene.* Powdered 4-nitro-2-phenyl-1-naphthylamine (1 g.) was added to a warm solution of stannous chloride (8 g.) in a mixture of hydrochloric acid (*d* 1·2, 10 c.c.) and alcohol (8 c.c.). The whole was heated on the steam-bath for 3 hours, cooled, made strongly alkaline with aqueous sodium hydroxide, and extracted with ether. Evaporation of the ether from the dried extract left a brown oil, which was dissolved in light petroleum (b. p. 60—80°). The diamine separated slowly in brownish needles, m. p. 100—101°, after further crystallisation from light petroleum (b. p. 80—100°). Acetylation by warming with a mixture of glacial acetic acid (1 c.c.) and acetic anhydride (2 c.c.) gave 1 : 4-*diacetamido-*2-*phenylnaphthalene,* which separated from hot glacial acetic acid in small white needles, m. p. 320° (Found: C, 75·65; H, 5·9. $C_{20}H_{18}O_2N_2$ requires C, 75·5; H, 5·7%).

The diamine (0·3 g.) in 20% hydrochloric acid (8 c.c.) was added slowly to a 5% aqueous solution of chromic anhydride (100 c.c.) at 80°. After boiling for 15 minutes, the solution was cooled; it deposited 2-phenyl-1 : 4-naphthaquinone, m. p. 109° after crystallisation from alcohol, both alone and admixed with an authentic specimen prepared by the oxidation of 2-phenylnaphthalene as described above.

Action of nitrosoaceto-2-naphthalide on nitrobenzene. Nitrosoaceto-2-naphthalide (50 g.), prepared as described above, was added during 10 hours to freshly distilled nitrobenzene (1 l.) stirred at room temperature. The solution, which developed a red colour, was stirred for 36 hours, and the nitrobenzene then removed with steam. The residual oil was distilled under reduced pressure to remove the last traces of nitrobenzene; the residue on sublimation at 10^{-3} mm. gave two fractions at 80—100° and 140—180°. The lower fraction, obtained as a pink amorphous solid (8 g.), on repeated crystallisation from alcohol or glacial acetic acid gave *2′-nitro-2-phenylnaphthalene* in pale yellow needles, m. p. 101° (Found : C, 77·1; H, 4·4. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4%). The higher fraction, obtained as a deep red solid (7 g.), on repeated crystallisation first from alcohol and finally from glacial acetic acid yielded *4′-nitro-2-phenylnaphthalene* in red needles, m. p. 174° (Found : C, 77·0; H, 4·4%). Alternatively the two nitro-compounds may be separated by distillation with superheated steam, in which only 2′-nitro-2-phenylnaphthalene is volatile; colouring matter which contaminates the distillate can be removed by boiling with animal charcoal in glacial acetic acid.

2′-Nitro-2-phenylnaphthalene (0·2 g.) in glacial acetic acid (8 c.c.) was heated on the steam-bath for 10 minutes with a solution of chromic anhydride (0·6 g.) in 90% acetic acid (8 c.c.). Dilution with water gave *2′-nitro-2-phenyl-1 : 4-naphthaquinone*, which crystallised from alcohol in yellow needles, m. p. 164° (Found : C, 68·6; H, 3·4. $C_{16}H_9O_4N$ requires C, 68·8; H, 3·2%). Under similar experimental conditions 4′-nitro-2-phenylnaphthalene gave *4′-nitro-2-phenyl-1 : 4-naphthaquinone*, which crystallised from alcohol in greenish-yellow needles, m. p. 223—224° (Found : C, 69·1; H, 3·5%). Further oxidation of 4′-nitro-2-phenyl-1 : 4-naphthaquinone (2 g.) was effected by boiling under reflux for 12 hours in glacial acetic acid (80 c.c.) to which chromic anhydride (10 g.) was gradually added. The precipitate which separated on pouring into water was collected, dissolved in aqueous sodium hydroxide, and filtered. Acidification precipitated *p*-nitrobenzoic acid (0·3 g.), m. p. and mixed m. p. 238° after crystallisation from hot water.

2′-Amino-2-phenylnaphthalene. 2′-Nitro-2-phenylnaphthalene (4 g.) was reduced with stannous chloride (24 g.) and hydrochloric acid (*d* 1·2, 30 c.c.) in the manner previously described for the reduction of 1-nitro-2-phenylnaphthalene to 4-chloro-2-phenyl-1-naphthylamine. The crude base (2·5 g.) separated from aqueous alcohol in light brown needles, m. p. 95° alone and on admixture with authentic 2′-amino-2-phenylnaphthalene prepared from chrysene by conversion into the amide of α-chrysenic acid, which was subjected to the Hofmann degradation as described by Graebe and Hönigsberger (*loc. cit.*). The *acetyl* derivative, prepared by warming the base with acetic anhydride, separated from alcohol in small white plates, m. p. 204—205° alone and on admixture with a specimen derived from the amide of α-chrysenic acid (Found : C, 82·5; H, 5·4. $C_{18}H_{15}ON$ requires C, 82·75; H, 5·7%).

4′-Amino-2-phenylnaphthalene. 4′-Nitro-2-phenylnaphthalene (4 g.) was reduced with stannous chloride and hydrochloric acid as described above for 2′-nitro-2-phenylnaphthalene. The crude product (3 g.), after several crystallisations from light petroleum (b. p. 60—80°), gave *4′-amino-2-phenylnaphthalene* in light brown plates, m. p. 99° (Found : C, 87·5; H, 6·1. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9%). Acetylation by warming with acetic anhydride gave *4′-acetamido-2-phenylnaphthalene*, which separated from alcohol in white plates, m. p. 206° (Found : C, 82·9; H, 5·9. $C_{18}H_{15}ON$ requires C, 82·75; H, 5·7%).

Nitration of 2′-nitro-2-phenylnaphthalene. A solution of 2′-nitro-2-phenylnaphthalene (1 g.) in glacial acetic acid (25 c.c.) was cooled in ice and stirred during the addition of nitric acid (*d* 1·5, 4 c.c.). After 1 hour the mixture was heated at 60—70° for 2 hours. On standing overnight in the refrigerator, a pale yellow solid (0·4 g.) separated, which was filtered off, washed, and dried. Four crystallisations from alcohol gave *1 : 2′-dinitro-2-phenylnaphthalene* in pale yellow needles, m. p. 189° (Found : C, 65·05; H, 3·5. $C_{16}H_{10}O_4N_2$ requires C, 65·3; H, 3·4%). Admixture with the dinitro-compound, m. p. 187—188°, obtained from the nitration of 2-phenylnaphthalene as previously described resulted in a depression of m. p. to 150—160°.

Nitration of 4′-nitro-2-phenylnaphthalene. A solution of 4′-nitro-2-phenylnaphthalene (1 g.) in hot glacial acetic acid (20 c.c.) was cooled in ice and stirred during the addition of nitric acid (*d* 1·5, 4 c.c.). After 2 hours' heating at 60—70°, no nitration was effected, as shown by pouring a test portion into water. More nitric acid (*d* 1·5, 4 c.c.) was therefore added, and the solution heated at 60—70° for a further 2 hours. On standing overnight in the refrigerator, a mixture of trinitro-derivatives separated as a yellowish-brown solid (0·3 g.), which was filtered off, washed, and dried. Extraction with boiling alcohol (150 c.c.) left a residue, m. p. 268—270° after several crystallisations from glacial acetic acid (Found: C, 56·3; H, 2·7. $C_{16}H_9O_6N_3$ requires C, 56·6; H, 2·6%). Evaporation of the alcoholic extract to about 50 c.c. resulted in the deposition of a dark yellow solid, which after recrystallisation from alcohol melted at 192—194° (Found: C, 57·0; H, 2·9%). When the original filtrate from the nitration mixture was poured into water, a brownish-yellow solid separated (m. p. 115—150°), but no pure product could be isolated by fractional crystallisation from alcohol.

Preparation of nitroaceto-2-naphthalides. By the action of concentrated sulphuric acid on 2-naphthylamine nitrate, as described by Friedländer and Szymanski (*loc. cit.*) 5- and 8-nitro-2-naphthylamine were prepared, which on acetylation with acetic anhydride yielded the corresponding acetyl derivatives, m. p. 185° and 195° respectively. Nitration of phthaloyl-2-naphthylamine, as described by Hodgson and Crook (*loc. cit.*), gave a further quantity of 5- and 8-nitro-2-naphthylamine. The hydrolysis of the crude nitrophthaloyl-2-naphthylamine was effected, not with ammonia as described by these workers, but by refluxing the product (62 g.) for 6 hours with a mixture of alcohol (500 c.c.) and hydrochloric acid (*d* 1·2, 150 c.c.), a further quantity of hydrochloric acid (15 c.c.) being added each hour. After pouring into water and filtration, the filtrate was made alkaline with aqueous sodium hydroxide. The red precipitate (20 g.) was filtered off, washed, and dried. Crystallisation from alcohol gave 5-nitro-2-naphthylamine, m. p. 143°. The mother-liquors yielded some 8-nitroaceto-2-naphthalide on acetylation and crystallisation as in the method of Friedländer and Szymanski (*loc. cit.*). Nitration of aceto-2-naphthalide (from 200 g. of β-naphthylamine) by the method of Saunders and Hamilton (*loc. cit.*) gave 1-nitro-2-naphthylamine (75 g., m. p. 127°), 6-nitro-2-naphthylamine (8 g., m. p. 203°), and 8-nitro-2-naphthylamine (24 g., m. p. 103·5°), which on acetylation with acetic anhydride gave the corresponding acetyl derivatives, m. p. 123°, 224°, and 195° respectively (cf. Veselý and Jakes, *Bull. Soc. chim.*, 1923, **33**, 942).

5-*Nitro*-2-*phenylnaphthalene.* Nitrous fumes were passed for 3½ hours into a cold solution of 5-nitroaceto-2-naphthalide (10 g.) in a mixture of glacial acetic acid (300 c.c.) and acetic anhydride (300 c.c.). When the whole was poured into ice-water with stirring, 5-nitronitrosoaceto-2-naphthalide separated as a yellow precipitate (8 g.), which was filtered off, washed, and dried on a porous tile [m. p. 84° (decomp.)]. The dry nitroso-compound was added in portions to benzene (400 c.c.) at room temperature. Nitrogen was evolved and the solution developed a red colour. After 36 hours the benzene was removed; the residue on sublimation at 10^{-3} mm. gave a yellow solid, which on crystallisation from alcohol yielded 5-*nitro*-2-*phenylnaphthalene* (3·1 g.) in pale yellow needles, m. p. 89° (Found: C, 77·3; H, 4·0. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4%).

6-*Phenyl*-1-*naphthylamine.* A mixture of iron dust (3 g.), 95% alcohol (60 c.c.), and hydrochloric acid (*d* 1·2, 1 c.c.) was boiled under reflux for 15 minutes, 5-nitro-2-phenylnaphthalene (3 g.) then added, and boiling continued for 12 hours with the addition of hydrochloric acid (*d* 1·2, 0·5 c.c.) every 3 hours. The mixture was then made alkaline with sodium carbonate and filtered several times through a fine filter. Distillation of the alcohol left a solid residue, which was dissolved in light petroleum (b. p. 80—100°) and boiled with animal charcoal. When cold, the filtered solution deposited 6-*phenyl*-1-*naphthylamine* (2 g.) in white needles with a faint purple tinge, m. p. 142—143° (Found: C, 87·5; H, 5·9. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9%). Acetylation was effected by warming the base (0·3 g.) with acetic anhydride (1 c.c.). On crystallisation from alcohol 6-*phenylaceto*-1-*naphthalide* separated in white needles, m. p. 131° (Found: C, 82·5; H, 5·8. $C_{18}H_{15}ON$ requires C, 82·75; H, 5·7%).

6-*Nitro*-2-*phenylnaphthalene.* The nitroso-compound of 6-nitroaceto-2-naphthalide was prepared as described above for the corresponding 5-nitro-compound, a solution of 6-nitroaceto-2-naphthalide (10 g.) in a mixture of glacial acetic acid (300 c.c.) and acetic anhydride (150 c.c.) being used. The dry nitroso-compound [9 g., m. p. 86° (decomp.)] was added to benzene (400 c.c.), and the product isolated as described above for the 5-isomeride. 6-*Nitro*-2-*phenylnaphthalene* (4·5 g.) separated from alcohol in pale yellow needles, m. p. 146° (Found: C, 77·2; H, 4·6. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4%).

6-*Phenyl*-2-*naphthylamine.* A solution of stannous chloride (36 g.) in hydrochloric acid (*d* 1·2, 50 c.c.) was added to a solution of 6-nitro-2-phenylnaphthalene (6 g.) in alcohol (100 c.c.). The mixture was heated on the steam-bath for 4 hours in an open beaker. The cooled solution was made strongly alkaline with concentrated aqueous sodium hydroxide and extracted with ether. Evaporation of the dried extract left a solid residue, which on crystallisation from light petroleum (b. p. 80—100°) gave 6-*phenyl*-2-*naphthylamine* (4·5 g.) in light brown needles, m. p. 132° (Found: C, 87·5; H, 5·7. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9%). Acetylation with acetic anhydride in the normal manner gave 6-*phenylaceto*-2-*naphthalide*, which separated from aqueous alcohol in white plates, m. p. 199° (Found : C, 82·8; H, 5·7. $C_{18}H_{15}ON$ requires C, 82·75; H, 5·7%).

8-*Nitro*-2-*phenylnaphthalene*. The nitroso-derivative of 8-nitroaceto-2-naphthalide was prepared from a solution of 8-nitroaceto-2-naphthalide (5 g.) in a mixture of glacial acetic acid (300 c.c.) and acetic anhydride (300 c.c.) as described above for the nitrosation of the 5-isomeride. The dry nitroso-compound [3·6 g., m. p. 86° (decomp.)] and benzene (200 c.c.) gave, as described above in the preparation of 5-nitro-2-phenylnaphthalene, 8-*nitro*-2-*phenylnaphthalene* (1·6 g.), which crystallised from alcohol in yellow needles, m. p. 69° (Found : C, 77·3; H, 4·5. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4%).

7-*Phenyl*-1-*naphthylamine*. An alcoholic solution of 8-nitro-2-phenylnaphthalene (3 g.) was reduced with iron and hydrochloric acid exactly as described above for the reduction of 5-nitro-2-phenylnaphthalene. The solid residue obtained on evaporation of the filtrate was redissolved in alcohol and boiled with animal charcoal. The filtered solution, slightly diluted with water, deposited 7-*phenyl*-1-*naphthylamine* (2 g.) in cream-white needles, m. p. 94° (Found : C, 87·7; H, 6·1. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9%). Acetylation with acetic anhydride in the normal manner gave 7-*phenylaceto*-1-*naphthalide*, which crystallised from alcohol in small plates, m. p. 203° (Found : C, 82·7; H, 5·9. $C_{18}H_{15}ON$ requires C, 82·75; H, 5·7%).

(B) 2 : 7-*Diphenylnaphthalene*.—2 : 7-Naphthylenediamine, prepared from 2 : 7-dihydroxynaphthalene by the Bucherer reaction (Windaus, *loc. cit.*), was acetylated with a mixture of glacial acetic acid and acetic anhydride. The resulting 2 : 7-diacetamidonaphthalene (10 g.) was dissolved in a mixture of glacial acetic acid (200 c.c.) and acetic anhydride (150 c.c.) and into the cooled solution nitrous fumes were passed for 1½ hours. The dinitroso-compound (6·2 g.), precipitated by pouring the reaction mixture into brine with vigorous stirring, was filtered off, washed with water, dried [m. p. 79° (decomp.)], and added in small portions to benzene (300 c.c.). Nitrogen was evolved and the solution developed a red colour. After 36 hours the benzene was removed by distillation, and the residue sublimed in a vacuum. Crystallisation of the sublimate from alcohol gave 2 : 7-*diphenylnaphthalene* (2 g.) in lustrous plates, m. p. 143° (Found : C, 94·4; H, 5·5. $C_{22}H_{16}$ requires C, 94·7; H, 5·3%).

In similar manner 2 : 6-naphthylenediamine (17 g.), prepared from 2 : 6-dihydroxynaphthalene (cf. Windaus, *loc. cit.*), was acetylated by boiling under reflux for 1 hour with a mixture of glacial acetic acid (50 c.c.) and acetic anhydride (15 c.c.). The *diacetyl* derivative (16 g.), which was precipitated on pouring into water, was filtered off, washed with water, and dried; it was insoluble in most organic solvents, but crystallised from nitrobenzene in greenish-yellow needles, m. p. 334—335° (Found : C, 69·65; H, 5·8. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%). Attempts were made to nitrosate it (a) by passing nitrous fumes into a cold stirred suspension (2 g.) in a mixture of glacial acetic acid (70 c.c.) and acetic anhydride (50 c.c.) containing phosphoric oxide (1·5 g.), and (b) by addition of a solution of nitrosyl chloride (1·9 g.) in acetic anhydride (4 c.c.) to a stirred suspension (2·5 g.) in a mixture of glacial acetic acid (40 c.c.) and acetic anhydride (20 c.c.) containing fused sodium acetate (4 g.) at 0°. In both cases the diacetyl-2 : 6-naphthylenediamine was recovered unchanged.

(C) *Bromo*-2-*phenylnaphthalenes*.—*Bromination of* 2-*phenylnaphthalene*. Powdered 2-phenylnaphthalene (2 g.) was added to a solution of bromine (2 g.) in glacial acetic acid (12 c.c.) and the mixture was stirred at room temperature for 4 hours and then at 40—50° for 6 hours. Hydrogen bromide was evolved. On pouring into ice-water, an oil separated which solidified; it was filtered off, washed with water, and dried. Two crystallisations from methyl alcohol gave 1-*bromo*-2-*phenylnaphthalene* (1·1 g.) in hard white needles, m. p. 66° (Found : C, 67·45; H, 4·2. $C_{16}H_{11}Br$ requires C, 67·8; H, 3·9%), not depressed by the compound prepared from 2-phenyl-1-naphthylamine as follows : the filtered diazonium solution, prepared by addition of aqueous sodium nitrite (0·6 g. in 4 c.c.) to a fine suspension of 2-phenyl-1-naphthylamine (1·6 g.) in a mixture of hydrochloric acid (*d* 1·2, 6 c.c.) and water (10 c.c.) at 5°, was added slowly to a cold solution of cuprous bromide, prepared by passing sulphur dioxide into an aqueous solution containing copper sulphate (9 g.) and potassium bromide (4·6 g.), in hydrobromic acid (*d* 1·4, 12 c.c.); the reaction was completed on the steam-bath. The cooled mixture was extracted with ether, and evaporation of the ether from the dried extract left a residue, which was dissolved in methyl alcohol and boiled with animal charcoal. The filtered solution deposited 1-bromo-2-phenylnaphthalene, which on recrystallisation separated in white needles, m. p. 66°.

6-*Bromo*-2-*phenylnaphthalene*. A cold solution of 6-bromoaceto-2-naphthalide (10 g.), prepared by the bromination of benzylidene-2-naphthylamine and removal of the bromine atom in the 1-position by treatment of the resulting 1 : 6-dibromo-2-naphthylamine with hydriodic acid, followed by acetylation (Franzen and Eidis, *loc. cit.*; Franzen and Stäuble, *loc. cit.*), in a mixture of glacial acetic acid (350 c.c.) and acetic anhydride (100 c.c.) was treated with nitrous fumes for 3 hours in the normal manner. On pouring into ice-water, 6-bromonitrosoaceto-2-naphthalide (8 g.) separated as a pale yellow precipitate, which was filtered off, washed, and dried [m. p. 82° (decomp.)]. The dry nitroso-compound was added in portions to benzene (400 c.c.). After 36 hours the benzene was removed by distillation, and the residue sublimed at 10^{-3} mm. Crystallisation of the pale yellow sublimate from alcohol gave 6-*bromo*-2-*phenylnaphthalene* (3·4 g.) in large plates, m. p. 132° (Found: C, 67·6; H, 3·9. $C_{16}H_{11}Br$ requires C, 67·8; H, 3·9%), not depressed by the compound prepared from 6-phenyl-2-naphthylamine by means of the Sandmeyer reaction exactly as described above for the preparation of 1-bromo-2-phenylnaphthalene from 2-phenyl-1-naphthylamine. The crude product was sublimed in a vacuum and subsequent crystallisation from alcohol gave 6-bromo-2-phenylnaphthalene in white plates, m. p. 132°.

Nitration of 1-*bromo*-2-*naphthol.* Powdered 1-bromo-2-naphthol (10 g.) (Franzen and Stäuble, *J. pr. Chem.*, 1922, **103**, 367) was added during 1 hour to a stirred mixture of glacial acetic acid (30 c.c.) and nitric acid (*d* 1·42, 5 c.c.) at 0°. After standing overnight, addition of water precipitated 1 : 6-dinitro-2-naphthol (6 g.), m. p. 194—195° (after successive crystallisation from acetic acid and chloroform) both alone and on admixture with an authentic specimen prepared by Bell's method (J., 1932, 2732).

(D) *Hydroxy*-2-*phenylnaphthalenes.*—6-*Hydroxy*-2-*phenylnaphthalene.* Nitrous fumes were passed for 3 hours into a cold solution of 6-methoxyaceto-2-naphthalide (10 g., m. p. 159—160°), prepared from 2 : 6-dihydroxynaphthalene by monomethylation, amination of the hydroxyl group, and subsequent acetylation as described by Windaus (*loc. cit.*), in a mixture of glacial acetic acid (200 c.c.) and acetic anhydride (100 c.c.). On pouring into ice-water, the nitroso-compound (8 g.) was precipitated as a pale yellow, granular solid, which was filtered off, washed, and dried [m. p. 82° (decomp.)]. The dry nitroso-compound was added in small portions to benzene (500 c.c.) at room temperature, and after 36 hours the benzene was removed by distillation. The residue was purified by sublimation in a vacuum, followed by crystallisation from alcohol, which gave 6-*methoxy*-2-*phenylnaphthalene* (3·2 g.) in pale yellow plates, m. p. 148° (Found: C, 87·1; H, 6·2. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%). The methoxy-compound (2 g.) was boiled under reflux for 12 hours with a mixture of hydriodic acid (*d* 1·7, 20 c.c.) and glacial acetic acid (20 c.c.) in a Geissler flask. The precipitate obtained on dilution with water was filtered off, washed, dried, and boiled for 10 minutes in benzene solution with animal charcoal; light petroleum (b. p. 60—80°) was added to the filtrate and, on cooling, 6-*hydroxy*-2-*phenylnaphthalene* (1·4 g.) separated in colourless plates, m. p. 175—176° after recrystallisation from benzene–light petroleum (b. p. 60—80°) (Found: C, 86·9; H, 5·3. $C_{16}H_{12}O$ requires C, 87·3; H, 5·45%).

7-*Hydroxy*-2-*phenylnaphthalene.* 7-Methoxyaceto-2-naphthalide, m. p. 156°, was prepared from 2 : 7-dihydroxynaphthalene by monomethylation (cf. Fischer and Hammerschmidt, *loc. cit.*), followed by amination of the hydroxyl group and acetylation with a mixture of glacial acetic acid and acetic anhydride as described by Windaus (*loc. cit.*). Acetylation of 7-methoxy-2-naphthylamine by boiling with acetic anhydride alone gave *diacetyl*-7-*methoxy*-2-*naphthylamine*, which crystallised from alcohol in long white needles, m. p. 129° (Found: C, 70·35; H, 5·8. $C_{15}H_{15}O_3N$ requires C, 70·0; H, 5·8%). Nitrosation of 7-methoxyaceto-2-naphthalide (10 g.) was effected exactly as described above for the nitrosation of 6-methoxyaceto-2-naphthalide. The dry nitroso-compound [8 g., m. p. 85° (decomp.)] on reaction with benzene (500 c.c.) gave, as described above in the preparation of the 6-isomeride, 7-*methoxy*-2-*phenylnaphthalene* (3·4 g.), which separated from aqueous alcohol, or light petroleum (b. p. 80—100°), in white plates, m. p. 80° (Found: C, 86·9; H, 5·7. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%). Demethylation with a mixture of hydriodic acid and glacial acetic acid, as described above for the 6-isomeride, gave 7-*hydroxy*-2-*phenylnaphthalene*, which separated from benzene–light petroleum (b. p. 60—80°) in pale yellow needles, m. p. 156° (Found: C, 87·15; H, 5·6. $C_{16}H_{12}O$ requires C, 87·3; H, 5·45%).

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