

157. *Cyclisations with Hydrazine. Part III.¹ Syntheses of Pentaphene and Dinaphtho[2,1-d : 1',2'-f][1,2]diazocine.*

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Reactions which normally result in nuclear coupling led to reductive dehalogenation of 2-substituted 1-halogenonaphthalenes, except in the case of methyl 1-bromo-2-naphthoate, which, by an Ullmann reaction and further steps, was converted into 1,1'-binaphthyl-2,2'-dialdehyde. Starting with the nuclear coupling of diazotised 3-amino-2-naphthoic acid, a similar synthesis of 2,2'-binaphthyl-3,3'-dialdehyde was carried out. Reaction of hydrazine with the former dialdehyde gave exclusively the cyclic azine (III), whereas the latter dialdehyde underwent reductive cyclisation exclusively, giving pentaphene in 40% overall yield from the amino-acid.

PREVIOUS investigations^{1,2} have shown that reactions of hydrazine with biphenyl compounds containing aldehydo- or keto-groups in the 2,2'-positions give two kinds of tricyclic products. Condensation may occur, giving a cyclic azine, *i.e.*, a dibenzo[*df*][1,2]diazocine, or the carbonyl groups may undergo reductive cyclisation, producing a phenanthrene nucleus. The present paper describes the production of pentacyclic compounds from binaphthyl derivatives. Possible intermediates include the three symmetrical dialdehydes, 1,1'-binaphthyl-2,2'-dialdehyde (II; X = CHO), 2,2'-binaphthyl-3,3'-dialdehyde (V; X = CHO), and 2,2'-binaphthyl-1,1'-dialdehyde (VII). Reductive cyclisation of these would give the pentacyclic hydrocarbons, dibenzo[*cg*]phenanthrene, pentaphene (VI), and picene, respectively. The new dialdehydes, (II) and (V), synthesised as described below, reacted practically quantitatively with hydrazine, the former giving exclusively the cyclic azine (III), and the latter giving exclusively pentaphene (VI).

The required intermediates of the biphenyl series had been prepared^{1,2} by Ullmann coupling of *o*-halogeno-aldehydes or -ketones. Preparation of the dialdehyde (II; X = CHO) was therefore attempted from 1-bromo-2-naphthaldehyde³ (I; X = CHO), obtained from 1-bromo-2-methylnaphthalene, but this bromo-aldehyde, as well as other 2-substituted 1-halogenonaphthalenes, reacted abnormally. Like Hall and Turner,³ we obtained no crystalline product from the bromo-aldehyde under conventional Ullmann conditions, while reaction in refluxing dimethylformamide or nitrobenzene produced up to 50% of 2-naphthaldehyde. Several examples of such reductive dehalogenation, and of other abnormalities in the Ullmann coupling reaction, have been reported.⁴ An unexpected result was also observed when the azine (VIII), obtained from the bromo-aldehyde, was heated with copper. A similar experiment in the benzene series, with the azine of *o*-iodoacetophenone, had given a small yield of 9,10-dimethylphenanthrene, as a result of nuclear coupling accompanied by expulsion of nitrogen, but in the case of compound (VIII) the only non-resinous product was 2-cyanonaphthalene (up to 15%).

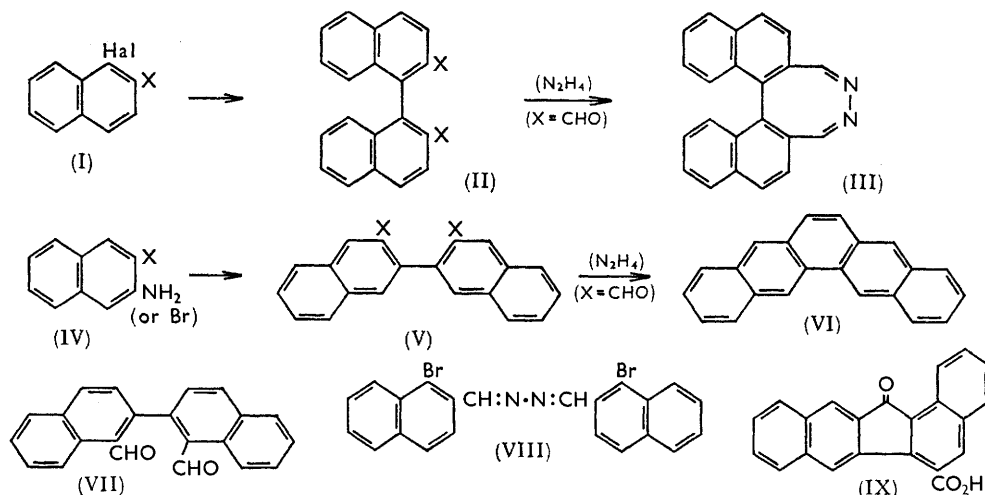
¹ Part II, Bacon and Lindsay, *J.*, 1958, 1382.

² Bacon and Lindsay, *J.*, 1958, 1375.

³ Hall and E. E. Turner, *J.*, 1955, 1242.

⁴ See, *e.g.*, Braithwaite and Holt, *J.*, 1959, 3025; Forrest, *J.*, 1960, 566 and later papers; Fanta, *Chem. Rev.*, 1946, 38, 139.

Coupling of 1-halogeno-2-methylnaphthalenes was also attempted, but reductive dehalogenation again resulted. 1-Bromo-2-methylnaphthalene was unreactive towards copper, while the 1-iodo-compound gave resin and some 2-methylnaphthalene. The Grignard reagent from 1-bromo-2-methylnaphthalene was treated by methods which are known to produce biaryls. Procedures involving cupric chloride,^{5,6} silver bromide,⁷ or



cobaltous chloride⁸ as coupling agents gave only 2-methylnaphthalene (35–60%). The desired dialdehyde (II; X = CHO) was therefore obtained through the corresponding dicarboxylic ester (II; X = CO₂Me), which had been previously prepared^{3,9,10} by Ullmann coupling of methyl 1-bromo-2-naphthoate (I; X = CO₂Me). This bromo-acid is prepared³ by oxidation of the bromo-aldehyde, since oxidation of 1-bromo-2-methylnaphthalene or 1-bromo-2-bromomethylnaphthalene fails to produce it. The Ullmann reaction gave the best yield of diester under the conditions described by Martin,⁹ but it was desirable to use bromo-ester purified by distillation, since recrystallised samples were liable to retain impurities which were apparently responsible for the extensive reductive dehalogenation to methyl 2-naphthoate (*e.g.*, 40%) observed in some experiments; with dimethylformamide as solvent this dehalogenation was still more extensive.

The dialdehyde (II; X = CHO) was obtained from the diester (II; X = CO₂Me) through the sequence of reactions: X = CO₂Me \rightarrow CH₂·OH \rightarrow CH₂Br \rightarrow CHBr₂ \rightarrow CHO. Reported procedures^{3,10} were used for the first two steps; the second bromination stage was effected very efficiently with *N*-bromosuccinimide; and the tetrabromide readily gave the dialdehyde on treatment with sodium acetate or silver nitrate. *N*-Bromosuccinimide has been used to produce -CHBr₂ groups in some other cases,¹¹ and naphthalene-2,3-dialdehyde has been thus prepared.¹² Direct conversion of the diol (II; X = CH₂·OH) into the dialdehyde was attempted with dinitrogen tetroxide, an oxidant recommended¹³ for the preparation of aromatic monoaldehydes; the isolation of some cyclic azine (III), after treatment with hydrazine, indicated that the resinous oxidation product contained about 20% of the dialdehyde.

⁵ Krzewsky and E. E. Turner, *J.*, 1919, **115**, 559.

⁶ Sakellarios and Kyrimis, *Ber.*, 1924, **57**, 322.

⁷ Gardner and Borgstrom, *J. Amer. Chem. Soc.*, 1929, **51**, 3375.

⁸ Kharasch and Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2316.

⁹ Martin, *J.*, 1941, 679.

¹⁰ Bergmann and Szmuzkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5153.

¹¹ Horner and Winkelmann, *Angew. Chem.*, 1959, **71**, 349.

¹² Ried and Bodem, *Chem. Ber.*, 1956, **89**, 708.

¹³ Field and Grundy, *J.*, 1955, 1110.

Comparable syntheses of biphenyl-2,2'-dialdehyde² from the corresponding dicarboxylic acid were attempted. The route through the derived bishydroxymethyl, bisbromomethyl, and bisdibromomethyl compounds, carried out as in the binaphthyl series, proceeded smoothly. Reduction of the biscarboxydimethylamide with lithium aluminium hydride, as reported¹⁴ for the preparation of *o*-phthalaldehyde, gave insignificant amounts of the dialdehyde. Oxidation of the bishydroxymethyl compound with dinitrogen tetroxide gave a low yield of dialdehyde, the main product being, apparently, the lactone of 2'-hydroxymethylbiphenyl-2-carboxylic acid; the cyclic semiacetal of 2'-hydroxymethylbiphenyl-2-aldehyde is a plausible intermediate.

Biphenyl-2,2'-dialdehyde had given phenanthrene in yields of up to 100% by reaction with hydrazine in acetic acid, ethanol, or other solvents.² 1,1'-Binaphthyl-2,2'-dialdehyde gave only the cyclic azine (III); the yield was nearly quantitative in acetic acid. When treated with hydrazine hydrate in acetic acid, the tetra-acetate of the dialdehyde also gave the cyclic azine, though in low yield and accompanied by *NN'*-diacetylhydrazine. The failure of these reactions to give dibenzo[*cg*]phenanthrene can be attributed to repulsions between the 1,1'-linked naphthalene nuclei, preventing the coplanarity of the aldehydo-groups which is needed for the production of the pentacyclic hydrocarbon. Comparable conditions exist in 6,6'-dimethylbiphenyl-2,2'-dialdehyde, which failed to give 4,5-dimethylphenanthrene with hydrazine.² Syntheses of both dibenzo[*cg*]phenanthrene¹⁰ and 4,5-dimethylphenanthrene have been effected through their 9,10-dihydro-derivatives.

The six-stage route from methyl 1-bromo-2-naphthoate gave ~35% overall yield of the compound (III), which is the first 1,2-diazocine thus to be produced from a dialdehyde. It formed yellow crystals which did not melt or decompose when heated to 360°, and its ultraviolet absorption spectrum was very similar to that of the open-chain azine (VIII) of 1-bromo-2-naphthaldehyde. Light-absorption characteristics have been discussed¹ for the cyclic azines obtained from diketones of the biphenyl series, *i.e.*, dibenzo[*df*][1,2]diazocines. Their absorption curves, as in the case of the compounds (III) and (VIII), are similar to those of related open-chain ketazines containing bulky *ortho*-substituents. A molecular model of the diazocine (III) showed that its heterocyclic ring should possess a "tub" conformation.¹ The infrared absorption spectra of the compounds (III) and (VIII) showed a strong peak, attributed to the C=N group, at 1625 cm.⁻¹; corresponding peaks at 1600—1630 cm.⁻¹ were found¹ in dibenzodiazocines. The subsidiary peak discussed¹ in connexion with the latter compounds was represented by a slight shoulder at ~1600 cm.⁻¹ in the spectra of (III) and (VIII). The only chemical property of compound (III) to be examined was its behaviour in boiling diethylene glycol containing hydrazine, a medium in which the dibenzodiazocines had slowly yielded phenanthrenes.¹ Decomposition occurred, but no dibenzo[*cg*]phenanthrene was isolated.

2,2'-Binaphthyl-3,3'-dialdehyde was prepared from the corresponding dicarboxylic acid (V; X = CO₂H), obtainable by coupling of a suitable naphthalene derivative (IV). Previously 3-bromo-2-naphthoic acid had been used,^{9,15,16} but an improved method was found by diazotising commercially available 2-amino-3-naphthoic acid and coupling the product with cuprous oxide. The subsequent reaction steps were the same as those used in the isomeric series (II). The diol was best produced in high yield by reduction of the dimethyl dicarboxylate, but the acid, its anhydride, or its chloride could also be used.¹⁷ The dibromide was best obtained by treatment of the diol with hydrogen bromide in acetic acid, and the tetrabromide and dialdehyde by the methods used in series (II). Attempts to prepare the dialdehyde by other methods, such as direct oxidation of the diol, were unsuccessful. The dicarboxylic acid (V; X = CO₂H) resembled biphenyl-2,2'-dicarboxylic

¹⁴ Weygand and Tietjen, *Chem. Ber.*, 1951, **84**, 625.

¹⁵ Badger, Jefferies, and Kimber, *J.*, 1957, 1837.

¹⁶ Bergmann and Ikan, *J. Amer. Chem. Soc.*, 1958, **80**, 208.

¹⁷ Cf. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publ., Inc., New York, 1956.

acid in readily giving a cyclic anhydride and cyclic imide, and in undergoing cyclisation in concentrated sulphuric acid. The latter reaction gave dibenzo[*ah*]fluorenone-6-carboxylic acid (IX), a conversion analogous to that of biphenyl-2,2'-dicarboxylic acid into fluorenone-4-carboxylic acid.¹⁸

Reaction of hydrazine with the dialdehyde, or with its tetra-acetate, in acetic acid or ethanol, gave pentaphene in 80—90% yield. The dialdehyde (V) thus behaved like biphenyl-2,2'-dialdehyde² and not like its isomer (II). The yields in all the earlier stages were 80—90% and the six-stage synthesis of the hydrocarbon from 3-amino-2-naphthoic acid was achieved with an overall yield of about 40%. This is substantially better than in previously described syntheses,^{15,16,19} in which overall yields were 10—20%.

EXPERIMENTAL

1-Bromo-2-naphthoic Acid.—2-Methylnaphthalene was converted into 1-bromo-2-methylnaphthalene,²⁰ and thence with *N*-bromosuccinimide²¹ into 1-bromo-2-bromomethylnaphthalene, m. p. 107° (lit.,²¹ 103.5—105.5°). The latter gave a *thiouonium picrate*, m. p. 235° (Found: C, 41.4; H, 2.5; N, 13.1. C₁₈H₁₄BrN₅O₇S requires C, 41.2; H, 2.7; N, 13.3%). Reaction between the 2-bromomethyl derivative and hexamine²² gave 1-bromo-2-naphthaldehyde, m. p. 118°, which was oxidised^{3,10} to 1-bromo-2-naphthoic acid, m. p. 188—190°; the methyl ester, m. p. 59°, was prepared through the acid chloride.

Behaviour of 1-Halogenonaphthalene Derivatives under Conditions for Nuclear Coupling.—(a) 1-Bromo-2-methylnaphthalene was recovered (90%) after 48 hr. at 200° with copper bronze. Boiling solutions of 2-methyl-1-naphthylmagnesium bromide (0.1 mole) were treated for 1—5 hr. with coupling agents under conditions described in the literature. After hydrolysis, the products consisted of a little unchanged bromide, resin, and 2-methylnaphthalene, which was isolated in the following yields by distillation or by chromatography on alumina: with cupric chloride^{5,6} as coupling agent in ether-benzene (40—50%), with silver bromide⁷ in ether-benzene (70%), with cobaltous chloride⁸ in ether containing ethyl bromide (45%).

(b) Successive nitration,²³ reduction,²³ and diazotisation²⁴ converted 2-methylnaphthalene into 1-iodo-2-methylnaphthalene, b. p. 118°/0.4 mm., reaction of which with copper bronze for 15 hr. at 200°, followed by distillation, gave unchanged iodide (30%), resin, and 2-methylnaphthalene (10%). The iodide gave resin and much unchanged material when bromination with *N*-bromosuccinimide was attempted.

(c) Heating 1-bromo-2-naphthaldehyde with copper, under varied conditions, followed by chromatography, yielded only resins or unchanged material. With an equal weight of copper in refluxing dimethylformamide, the bromo-aldehyde yielded 2-naphthaldehyde (30—50%) after 5 hr., and likewise (50%) in refluxing nitrobenzene, but not in refluxing cyclohexanol.

(d) Methyl 1-bromo-2-naphthoate was heated with copper bronze for 5—7 hr. at 180—190°, as described by Martin,⁹ and gave a variable yield (best, 87%) of dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate, m. p. 159°, b. p. 215—218°/0.4 mm., isolated by extraction with toluene, followed by recrystallisation or vacuum-distillation; there was little reaction at 140—150°. Experiments in which certain samples of the bromo-ester (0.1 mole) were heated with copper bronze (20 g.) at 190° or 280° yielded methyl 2-naphthoate (30—40%), m. p. and mixed m. p. 72°, b. p. 112—120°/0.25 mm., but the normal coupling reaction occurred if these samples were first purified by distillation. With copper in refluxing dimethylformamide an impure sample of bromo-ester gave a 75% yield of methyl 2-naphthoate.

1-Bromo-2-naphthaldehyde Azine.—Reaction between the bromo-aldehyde (0.02 mole) and 60% hydrazine hydrate (0.01 mole) in refluxing ethanol (75 ml.), followed by removal of solvent, left the crude *azine* (95%); recrystallisation from nitrobenzene or vacuum-sublimation gave yellow needles, m. p. 320°, λ_{max}. 282 (log ε 4.46) and 334 μμ (log ε 4.45) (Found: C, 56.8; H, 3.0; N, 6.6. C₂₂H₁₄Br₂N₂ requires C, 56.65; H, 3.0; N, 6.0%). The azine was unchanged

¹⁸ Graebe and Aubin, *Annalen*, 1888, **247**, 257.

¹⁹ Clar and John, *Ber.*, 1931, **64**, 981; Clar and Stewart, *J.*, 1951, 3215.

²⁰ Hall and Mitchell, *J.*, 1951, 1375.

²¹ Newman and Kosak, *J. Org. Chem.*, 1949, **14**, 375.

²² Hewett, *J.*, 1940, 293.

²³ Fierz-David and Mannhart, *Helv. Chim. Acta*, 1937, **20**, 1024.

²⁴ Mayer and Schnecko, *Ber.*, 1923, **57**, 1408.

when heated with an equal weight of copper bronze for 24 hr. at 200°, but decomposition occurred during 5 hr. at 300°. The resinous product, heated under reduced pressure, yielded a white sublimate of impure 2-cyanonaphthalene (5—15%), m. p. 58—61° (lit.,²⁵ 66—67°) (Found: C, 85.5; H, 4.9; N, 10.4. Calc. for C₁₁H₇N: C, 86.2; H, 4.6; N, 9.2%). It showed an infrared absorption peak, attributed to C≡N, at 2238 cm.⁻¹, and hydrolysis in aqueous acetic acid containing sulphuric acid yielded 2-naphthoic acid, m. p. 184° (lit.,²⁵ 184—186°).

2,2'-Bisdibromomethyl-1,1'-binaphthyl.—Reduction of dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate with lithium aluminium hydride³ yielded 2,2'-bishydroxymethyl-1,1'-binaphthyl, m. p. 192°, which was converted with hydrobromic acid in acetic acid³ into 2,2'-bisbromomethyl-1,1'-binaphthyl, melting rather indefinitely at ~150° (lit., 148—149.5°, 151—153°³). This dibromide (0.025 mole) was treated with *N*-bromosuccinimide (0.05 mole; previously kept for 6 hr. under 0.5 mm. pressure) and benzoyl peroxide (0.1 g.) in refluxing carbon tetrachloride (30 ml.) for 15 hr. Evaporation of the solution left 2,2'-bisbromomethyl-1,1'-binaphthyl as a brown powder, which gave colourless needles, m. p. 222°, when recrystallised from benzene—light petroleum (Found: C, 44.3; H, 2.6; Br, 53.1. C₂₂H₁₄Br₄ requires C, 44.2; H, 2.3; Br, 53.5%). Small amounts of lower bromides were removed from mother-liquors by chromatography on alumina; the total yield of tetrabromide was 92%.

1,1'-Binaphthyl-2,2'-dialdehyde.—(a) A mixture of the tetrabromide (3.0 g.) in ethanol (200 ml.) with silver nitrate (4 mol.) in water (50 ml.) was refluxed for 30 min., filtered, concentrated, and cooled. The resulting 1,1'-binaphthyl-2,2'-dialdehyde (80%) gave colourless needles, m. p. 131.5°, when recrystallised from ether (Found: C, 85.0; H, 4.4. C₂₂H₁₄O₂ requires C, 85.2; H, 4.5%). A solution of the dialdehyde in acetic anhydride, containing a drop of sulphuric acid, was kept for 1 hr. at 100° and added to water; the *tetra-acetate* was precipitated; recrystallisation from benzene gave prisms, m. p. 135° (Found: C, 70.2; H, 5.2. C₃₀H₂₆O₈ requires C, 70.0; H, 5.1%).

(b) A solution of the tetrabromide (3.0 g.) and a large excess of anhydrous sodium acetate in acetic acid was heated under reflux for 2 days, concentrated, diluted with water, and extracted with ether, evaporation of which gave crude dialdehyde; it gave crystals (72%) when triturated with ether.

(c) A 10% solution in chloroform of 2,2'-bishydroxymethylbiphenyl and an equal weight of dinitrogen tetroxide¹⁸ was prepared at 0° and kept for 24 hr. at room temperature. Removal of solvent left red resin, from which no dialdehyde could be isolated by recrystallisation, vacuum-sublimation, or chromatography, but treatment with hydrazine in acetic acid or ethanol, as described under (a) below, give cyclic azine in a yield corresponding with a dialdehyde content of ~20% in the resinous oxidation product.

Dinaphtho[2,1-d:1',2'-f][1,2]diazocine.—(a) A solution of 1,1'-binaphthyl-2,2'-dialdehyde (0.6 g.) in refluxing acetic acid (40 ml.) was treated with 60% hydrazine hydrate (0.4 g., 2.5 mol.) in acetic acid (15 ml.) during 45 min., and refluxing was continued for 2 hr. more. The *dinaphthodiazocine* (0.53 g., 88%) was precipitated in fine yellow needles and was recrystallised from chloroform; it did not melt up to 360° and it showed light absorption maxima at 280 (log ε 4.56) and 330 mμ (log ε 4.63) (Found: C, 85.9; H, 4.8; N, 9.1. C₂₂H₁₄N₂ requires C, 86.2; H, 4.6; N, 9.1%). A similar preparation, carried out for 1 hr. in refluxing ethanol, gave the diazocine (15%) and resin. The diazocine (0.2 g.) was incompletely dissolved by refluxing diethylene glycol; on cooling, 70% was unchanged and the rest had resinified. An experiment carried out similarly, but with the addition of 100% hydrazine hydrate (0.1 g.), resulted in rapid dissolution of the diazocine, but yielded only a gum.

(b) A 1% solution of 1,1'-binaphthyl-2,2'-dialdehyde tetra-acetate in acetic acid was refluxed with 60% hydrazine hydrate (10 mol.) for 6 hr., then hydrazine (10 mol.) was again added and refluxing continued for 10 hr. longer. Filtration of the cooled solution gave the diazocine (11%) and concentration of the filtrate gave *NN'*-diacetylhydrazine. This compound,²⁶ m. p. 137°, was obtained in yields of up to 80% from hot solutions of hydrazine in acetic acid whenever the hydrazine was not consumed by reaction with a dicarbonyl compound.

2,2'-Binaphthyl-3,3'-dicarboxylic Acid.—A procedure described²⁷ for the coupling of anthranilic acid was modified. 2-Aminonaphthalene-3-carboxylic acid (0.1 mole) was dissolved in aqueous sodium hydrogen carbonate (400 ml., 0.1 mole), the solution filtered, and sodium

²⁵ Elsevier's "Encyclopaedia of Organic Chemistry," Vol. 12B.

²⁶ Harris and Stone, *J. Org. Chem.*, 1958, **23**, 2032.

²⁷ Atkinson, Lawler, Heath, Kimball, and Read, *J. Amer. Chem. Soc.*, 1941, **63**, 730.

nitrite (0.1 mole) added. The mixture, cooled to 0°, was added during 1 hr. to stirred aqueous hydrochloric acid (100 ml., 0.3 mole) at 0°. The resulting diazonium salt solution was filtered and the ice-cold filtrate was introduced, during 1 hr., below the surface of a suspension of cuprous oxide, freshly prepared by treating aqueous copper sulphate (150 ml., 0.14 mole) and concentrated aqueous ammonia (60 ml.) with hydroxylamine hydrochloride (0.14 mole) and sodium hydroxide (0.14 mole) in water (60 ml.). Foaming occurred. After 30 min. the dark green solution was boiled and was acidified, while hot, with hydrochloric acid. The precipitated dicarboxylic acid was filtered off after cooling and purified by dissolution in aqueous sodium hydrogen carbonate, boiling with charcoal, and re-acidification; this yielded a light brown powder (77%), crystallising from ethanol in colourless needles, m. p. 295—297° (lit.,⁹ 298—299°) (Found: C, 77.2; H, 4.1. Calc. for $C_{22}H_{14}O_4$: C, 77.2; H, 4.1%).

Acid Derivatives.—A solution of 2,2'-binaphthyl-3,3'-dicarboxylic acid in acetic anhydride was boiled under reflux for 3 hr. and cooled; the acid *anhydride* separated as needles (76%), m. p. 330—334° after sublimation at 200°/0.1 mm. (Found: C, 81.4; H, 3.8. $C_{22}H_{12}O_3$ requires C, 81.5; H, 3.7%). A solution of the acid in benzene was mixed with an excess of thionyl chloride and boiled under reflux for 24 hr. Cooling and addition of light petroleum gave the *dichloride* (77%), m. p. 207° after recrystallisation from benzene-light petroleum (Found: C, 69.8; H, 3.1; Cl, 18.6. $C_{22}H_{12}Cl_2O_2$ requires C, 69.7; H, 3.2; Cl, 18.7%). Refluxing a solution of the anhydride in methanol for 2 hr. yielded, on cooling, the *methyl hydrogen ester*, which crystallised from methanol as needles, m. p. 249° (Found: C, 77.6; H, 4.8. $C_{23}H_{16}O_4$ requires C, 77.5; H, 4.5%). Similar treatment with ethanol gave the *ethyl hydrogen ester*, crystallising from chloroform as plates, m. p. 254° (Found: C, 77.6; H, 5.0. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%). A solution of the acid chloride in methanol was boiled for 8 hr. and concentrated, yielding the dimethyl ester as needles, m. p. 171° (lit.,⁹ 173—173.5°) (Found: C, 77.8; H, 4.65. Calc. for $C_{24}H_{18}O_4$: C, 77.8; H, 4.9%). Similar treatment with ethanol gave the *diethyl ester* as needles, m. p. 113° (Found: C, 78.2; H, 5.2. $C_{26}H_{22}O_4$ requires C, 78.4; H, 5.6%).

The anhydride was boiled for 3 hr. with a large excess of concentrated aqueous ammonia, diluted with half its volume of water; about one-third of the anhydride was unchanged. Acidification of the solution yielded the *half-amide* (94% allowing for recovered anhydride), crystallising from methanol as rods, m. p. 219° (Found: C, 77.0; H, 4.6; N, 4.2. $C_{22}H_{15}NO_3$ requires C, 77.4; H, 4.4; N, 4.1%). The half-amide was refluxed for 7 hr. in a mixture of equal volumes of acetic anhydride and acetic acid; cooling gave somewhat impure *imide* (75%), which crystallised from dioxan as needles, m. p. 334° (Found: C, 81.2; H, 4.1; N, 4.9. $C_{22}H_{13}NO_2$ requires C, 81.7; H, 4.1; N, 4.3%). Treatment of the acid chloride with ammonia gave impure diamide, which was fairly readily converted into the dimethyl ester by methanol.

Dibenzo[ah]fluorenone-6-carboxylic Acid.—2,2'-Binaphthyl-3,3'-dicarboxylic acid was dissolved in concentrated sulphuric acid and the purple solution left for 1 hr. at room temperature. Addition to water produced a precipitate of *dibenzo[ah]fluorenone-6-carboxylic acid*, which crystallised from ethanol in orange needles (93%), m. p. 316° (Found: C, 81.4; H, 3.8. $C_{22}H_{12}O_3$ requires C, 81.5; H, 3.7%). When treated with thionyl chloride in benzene it gave the acid chloride, which with refluxing methanol gave the *methyl ester*, m. p. 253° (Found: C, 81.2; H, 4.4. $C_{23}H_{14}O_3$ requires C, 81.6; H, 4.2%).

3,3'-Bishydroxymethyl-2,2'-binaphthyl.—Reduction of dimethyl 2,2'-binaphthyl-3,3'-dicarboxylate with lithium aluminium hydride¹⁵ gave 3,3'-bishydroxymethyl-2,2'-binaphthyl (92%), recrystallisation of which from ethanol and then benzene gave needles, m. p. 242° (lit.,^{15,16} 228—229°, 230°) (Found: C, 84.1; H, 5.9. Calc. for $C_{22}H_{16}O_2$: C, 84.05; H 5.8%). Reductions were also carried out by adding the dicarboxylic acid, acid chloride, or anhydride, dissolved or suspended in ether, to an excess of lithium aluminium hydride in ether, and boiling for 12—20 hr. (typical yields: 80%, 50%, 80%, respectively; m. p. 235—237°).

3,3'-Bisdibromomethyl-2,2'-binaphthyl.—The diol was best converted into the bisbromomethyl compound (91%), with hydrogen bromide¹⁵ in acetic acid; phosphorus tribromide or aqueous hydrobromic acid gave inferior yields. Recrystallisation from benzene gave needles, m. p. 167° (lit.,^{15,16} 165—166°, 172°) (Found: C, 59.9; H, 3.8; Br, 36.1. Calc. for $C_{22}H_{16}Br_2$: C, 60.0; H, 3.6; Br, 36.3%). The dibromide (2.2 g., 0.005 mole) was treated for 8 hr. with *N*-bromosuccinimide (4 mol.) and benzoyl peroxide (0.1 g.) in refluxing carbon tetrachloride (60 ml.); cooling and concentration of the filtrate yielded 3,3'-*bisdibromomethyl-2,2'-binaphthyl* (87%), which crystallised from benzene in plates, m. p. 242° (with some sublimation before melting) (Found: C, 44.35; H, 2.5; Br, 53.3. $C_{22}H_{14}Br_4$ requires C, 44.2; H, 2.3; Br, 53.5%).

2,2'-Binaphthyl-3,3'-dialdehyde.—(a) The preceding tetrabromide (0.002 mole) was treated for 15 hr. with a large excess (5 g.) of anhydrous sodium acetate in refluxing acetic acid (50 ml.), solvent was evaporated under reduced pressure, and the residue treated with water and ether. Concentration of the ethereal solution gave a quantitative yield of *2,2'-binaphthyl-3,3'-dialdehyde*, crystallising from ether in needles, m. p. 195° (Found: C, 84.95; H, 4.5. $C_{22}H_{14}O_2$ requires C, 85.1; H, 4.5%). Alternatively, the tetrabromide was treated with silver nitrate (4 mol.) for 1 hr. in refluxing water-ethanol (1 : 4); concentration of the filtrate from the silver bromide gave the dialdehyde (94%). A solution of the dialdehyde in an excess of acetic anhydride, containing a drop of sulphuric acid, was left at room temperature, then poured into water; the precipitated *tetra-acetate* crystallised from ethanol as needles (84%), m. p. 171° (Found: C, 69.7; H, 5.2. $C_{30}H_{26}O_8$ requires C, 70.0; H, 5.1%).

(b) *3,3'-Bishydroxymethyl-2,2'-binaphthyl* was treated with dinitrogen tetroxide as described for its isomer; no dialdehyde was isolated from the product and no pentaphene obtained by treating it with hydrazine.

(c) Treatment of the acid chloride (see above) from *2,2'-binaphthyl-3,3'-dicarboxylic acid* with lithium hydridotri-*t*-butoxyaluminate²⁸ failed to give dialdehyde.

Pentaphene.—*2,2'-Binaphthyl-3,3'-dialdehyde* (0.2 g.) in refluxing acetic acid (15 ml.) was treated during 30 min. with 60% hydrazine hydrate (2.5 mol.) in acetic acid and heating continued for 30 min. Pentaphene began to be precipitated during the addition and it was collected from the cooled solution as yellow leaflets (87%), m. p. 257° (lit.,^{15,16} 257°) (Found: C, 94.7; H, 5.0. Calc. for $C_{22}H_{14}$: C, 94.9; H, 5.1%). It gave the dipicrate, m. p. 186° (lit.,^{15,16} 184°) (Found: C, 55.3; H, 2.8; N, 11.5. Calc. for $C_{34}H_{20}N_6O_{14}$: C, 55.4; H, 2.7; N, 11.4%). A similar preparation from the dialdehyde, carried out during 3 hr. in refluxing ethanol, gave pentaphene (88%). It was also obtained (77%) by reaction between the dialdehyde tetraacetate and an excess of 60% hydrazine hydrate for 10 hr. in refluxing acetic acid. Treatment of *3,3'-bisdibromomethyl-2,2'-binaphthyl* for 4 days with hydrazine and potassium hydroxide in refluxing aqueous ethanol (cf. ref. 2) gave no pentaphene; the tetrabromide was largely unchanged.

Biphenyl-2,2'-dialdehyde.—(a) *2,2'-Bisbromomethylbiphenyl*, prepared² from *2,2'-dimethylbiphenyl*, was heated for 7 hr. with *N*-bromosuccinimide (2 mol.) in refluxing carbon tetrachloride containing a little benzoyl peroxide, and gave *2,2'-bisdibromomethylbiphenyl*²⁹ (77%), m. p. 138°. The tetrabromide (3 g.) was heated with sodium acetate (4 mol.) for 4 hr. in refluxing acetic acid, and the crude biphenyl-*2,2'*-dialdehyde, isolated by evaporation and ether extraction, was redissolved in acetic acid and treated for 4 hr. at the b. p. with hydrazine,² to yield phenanthrene, which was isolated (80% on the tetrabromide) by chromatography.

(b) *2,2'-Bishydroxymethylbiphenyl*, prepared³⁰ from dimethyl biphenyl-*2,2'*-dicarboxylate, was oxidised¹⁸ by dinitrogen tetroxide (1.5 mol.) in chloroform at room temperature for 1–2 days. Chromatography of the product with benzene on alumina yielded the dialdehyde (~15%), m. p. 62°, followed by a second solid fraction (20–65%), which crystallised from benzene as needles, m. p. 134°, and was probably *2'-hydroxymethylbiphenyl-2-carboxylic acid lactone* (lit.,²⁹ m. p. 132°) (Found: C, 79.9; H, 4.8. Calc. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8%). This compound dissolved in hot 30% aqueous potassium hydroxide, and acidification of the solution precipitated a compound, believed to be the hydroxy-acid, m. p. 142° (lit.,²⁹ 146°), which could not be obtained pure owing to ready reconversion into the lactone.

(c) A procedure¹⁴ described for the reduction of the bisdimethylamide of phthalic acid was followed. The acid chloride³¹ of biphenyl-*2,2'*-dicarboxylic acid was converted into the *bisdimethylamide* (77%), obtained as prisms, m. p. 158°, on recrystallisation from water (Found: C, 72.9; H, 6.7; N, 9.2. $C_{18}H_{20}N_2O_2$ requires C, 73.0; H, 6.8; N, 9.4%). Treatment of this with lithium aluminium hydride gave gums, which yielded a *2,4-dinitrophenylhydrazone*,³² but gave not more than 5% of phenanthrene when treated with hydrazine.

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[Received, August 30th, 1962.]

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