CLXVII.—*The Catalytic Production of Polynuclear Compounds. Part II.*

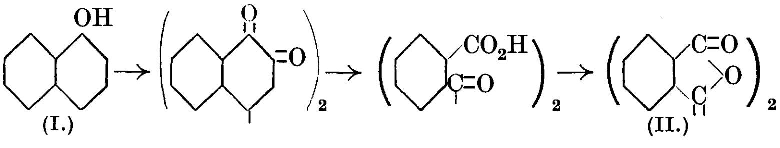
By George Roger Clemo, Joseph George Cockburn, and Robert Spence.

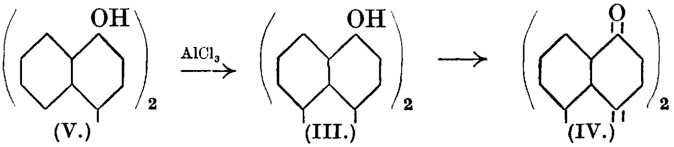
A study of the methods previously described for the catalytic production of polynuclear compounds (Part I, J., 1928, 2811) has led to improvements, and to a more intimate knowledge of the mechanism of the process. The catalytic oxidation of hydrocarbons and related compounds has generally been concerned with reactions in the vapour phase, and, in the case of naphthalene, these usually lead to relatively highly oxygenated compounds such as phthalic anhydride (I. G. Farb. A.G., B.P. 272,557, June 14th, 1926; Caspari, U.S. Pat. 1,674,589, June 19th, 1928). If, however, the catalyst is suspended in the liquid hydrocarbon and an oxygen-bearing gas admitted, less highly oxygenated, intermediate compounds or condensation products can be isolated; *e.g.*, when tetrahydronaphthalene is heated with oxygen in the presence of copper, iron, or nickel oxide, the oxygen attacks the α-carbon atom, giving α-ketotetrahydronaphthalene and some α-hydroxytetrahydronaphthalene (I. G. Farb. A.G., B.P. 318,550, Sept. 5th, 1928).

The velocity of catalytic processes involving both liquid and gaseous reactants must depend on the rate at which they are brought into contact with the catalyst, and the rate of removal of the products. That these conditions are partially effected by a very high speed of stirring has been shown by Reid (*J. Amer. Chem. Soc.*, 1915, **37**, 2112; Rather and Reid, *ibid.*, 1915, **37**, 2115), who found that the reaction between ethylene and benzene to form ethylbenzene in the presence of aluminium chloride can be changed from a very slow to an extremely rapid one by this means. Also King, Swann, and Keyes (*Ind. Eng. Chem.*, 1929, **21**, 1227) found that stirring at 5,000 r.p.m. increased the rate of catalytic oxidation of ethylbenzene from 3·3% to 18%. It has now been found that high-speed stirring considerably accelerates the rate of catalytic oxidation of liquid β-naphthol, good yields of di-β-naphthol being obtained after 15 minutes at 285°. Table I shows the effects of using glass or metal stirrers with or without catalysts. Stirring does not, however, accelerate the catalytic etherification of β-naphthol, the observed rate being approximately that obtained without stirring (Part I, *loc. cit.*).

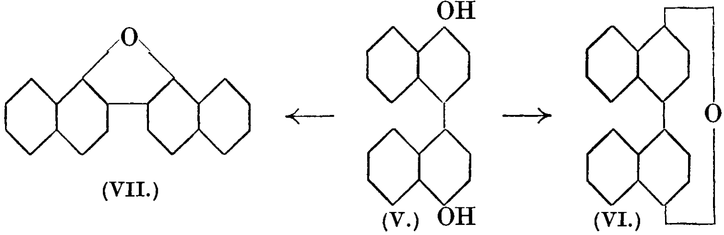
In Part I the catalytic oxidation of β-naphthol by calcium oxide was shown to give *iso*dinaphthylene oxide, to which structure (IX) was given. A further study of this reaction has shown that, if the reaction temperature does not exceed 310°, only di-β-naphthol is formed, but if the temperature rises to 340°, then only (IX) results. When pure di-β-naphthol is heated with lime to 340°, only the *normal* 1 : 1′-dinaphthylene 2 : 2′-oxide is obtained.

Of the compounds described in Part I derived from the catalytic oxidation or dehydration of naphthols, constitutions could not definitely be assigned to *iso*dinaphthylene oxide, di-α-naphthol, and α-dinaphthylene oxide. Several writers have discussed the constitution of di-α-naphthol, and reached conflicting conclusions. Zincke and Schopfe (*Monatsh.*, 1923, **44**, 370) prepared the perylene derivatives (III) and (IV) by heating di-α-naphthol with aluminium chloride, and Henriques (*Ber.*, 1888, **21**, 1614), oxidising α-naphthol with alkaline permanganate, obtained an acid, $C_{20}H_{14}O_8$, which gave diphthalyl (II) when heated above its melting point; a result confirmed by Dischendorfer (*Monatsh.*, 1928, **50**, 97), who suggested the following mechanism based on the formula (V) for di-α-naphthol.





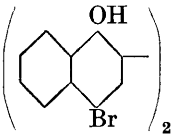
On the other hand, Willstätter and Schuler (*Ber.*, 1928, **61**, 362) prepared the diacetyl derivative of dibromodi-α-naphthol, to which they gave formula (VIII), from 2 : 4-dibromo-α-naphthol, and showed it was identical with that prepared by the bromination and acetylation of the di-α-naphthol obtained from the ferric chloride oxidation of α-naphthol. Further, Corbellini and Debenedetti (*Gazzetta*, 1929, **59**, 391) diazotised naphthidine, obtained from the ferric chloride oxidation of α-naphthylamine and assumed to be the amino-analogue of (V), the same compound being produced by the benzidine transformation of hydrazonaphthalene (Nietzki and Goll, *Ber.*, 1885, **18**, 3254), and, although pure di-α-naphthol could not be obtained, the product, on methylation, yielded its dimethyl derivative, identical with a specimen obtained by methylating di-α-naphthol. The correctness of the formula assumed above for naphthidine has now been proved by reducing 4 : 4′-dinitro-1 : 1′-dinaphthyl, itself prepared from 1-iodo-4-nitronaphthalene (Schoepfle, *J. Amer. Chem. Soc.*, 1923, **45**, 1571), giving 4 : 4′-diamino-1 : 1′-dinaphthyl identical with naphthidine otherwise prepared. Thus di-α-naphthol has the structure (V), and either the α-dinaphthylene oxide produced by its dehydration (Dianin, *J. Russ. Phys. Chem. Soc.*, 1882, **14**, 130) must have the, at present discredited, Kaufler type of formula (VI) or an unusual meta-wandering of the 4 : 4′-dinaphthyl link to the 2 : 2′-position must have occurred to give (VII).



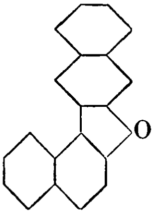
(VII.) (V.) (VI.)

This question has now been settled in favour of the latter alternative, as it has been found that 1 : 1′-*dimethoxy*-2 : 2′-*dinaphthyl*, prepared by the Ullmann reaction from 2-iodo-1-methoxynaphthalene, gives on demethylation with hydriodic acid a mixture of the new 1 : 1′-*dihydroxy*-2 : 2′-*dinaphthyl*, and 2 : 2′-dinaphthylene 1 : 1′-oxide (VII) identical with that obtained from (V). Distillation of the former of these leads to further conversion into the latter. (Under such treatment ordinary di-α-naphthol decomposes.) This migration of the dinaphthyl link in the formation of both (VII) and (IX) indicates that it is not uncommon at about 300°, and has an important bearing on the structure of naphthalene itself. Hitherto signs of such a migration have been observed for the dinaphthyls themselves by Seer and Weitzenbock (*Ber.*, 1913, **46**, 1994) and the migration of a carboxyl group from the 1- to the 3-position occurs in the preparation of β-naphthoic acid.

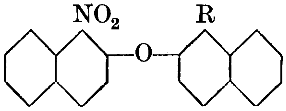
In addition, attempts have been made to prepare ethers of the type (X) (R = H, or a substituent) with a view to the synthesis of dinaphthylene oxides by the ring-closure method of Pschorr (*Ber.*, 1896, **29**, 496), but so far these ethers have not been satisfactorily obtained.



(VIII.)



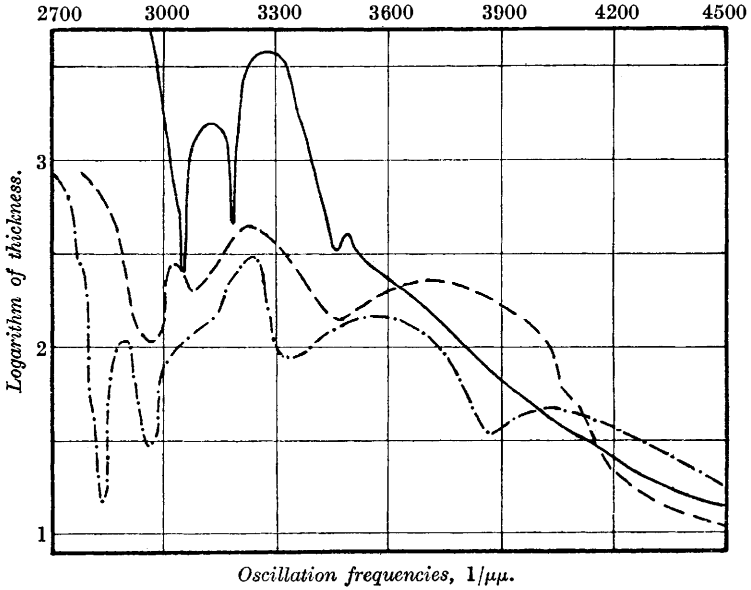
(IX.)



(X.)

Under certain conditions, instead of 1-nitro-β-naphthylamine giving 1-nitro-2-chloro- or -bromo-naphthalene by the Sandmeyer method, it has been found that 1 : 2-dihalogen derivatives result (compare Mascarelli and Martinelli, *Atti R. Accad. Lincei*, 1915, **24**, ii, 25). An interesting example of this anomalous reaction is the production of the hitherto undescribed 2-*chloro*-1-*bromonaphthalene* by diazotisation in hydrochloric acid and subsequent treatment with cuprous bromide.

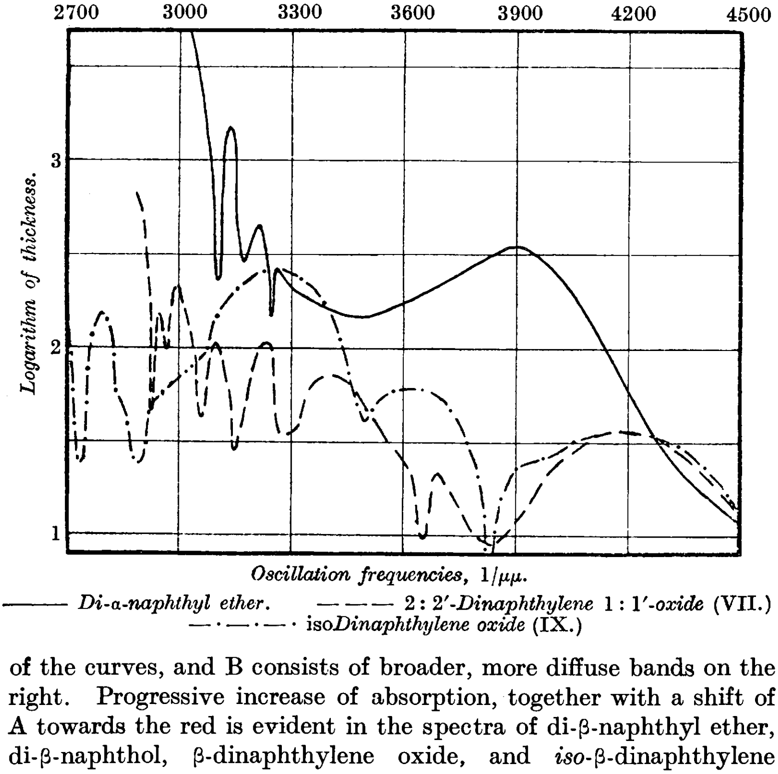
Fig. 1.



——— *Di-β-naphthyl ether.* — — — 2 : 2′-*Dihydroxy*-1 : 1′-*dinaphthyl.*
— · — · — · 1 : 1′-*Dinaphthylene* 2 : 2′-*oxide.*

Concurrently with the above, and in order to obtain further information regarding the structure of α-dinaphthylene oxide, and the *iso*-oxide (IX), a series of absorption spectra of the substances in alcoholic solutions have been taken (Figs. 1 and 2) with a Hilger all-metal Model E 315 quartz prism spectrograph. The curves show the characteristics observed by de Laszlo (*Proc. Roy. Soc.*, 1926, *A*, **111**, 362; *Z. physikal. Chem.*, 1925, **118**, 382) in the spectra of naphthalene derivatives, and are divisible into two parts, A and B, whose position and character alter with the substituent. Part A consists of the narrower, more intense bands on the left-hand portion of the curves, and B consists of broader, more diffuse bands on the right. Progressive increase of absorption, together with a shift of A towards the red is evident in the spectra of di-β-naphthyl ether, di-β-naphthol, β-dinaphthylene oxide, and *iso*-β-dinaphthylene oxide, showing the damping effect of the introduction of further substituents into the nuclei, and the formation of another ring. It will be observed that α- and β-dinaphthylene oxides and *iso*dinaphthylene oxide have a common band at an oscillation frequency of about 3850. Since the other factors are different in each case, it is reasonable to assume that this band is connected with the five-membered furan ring.

FIG. 2.



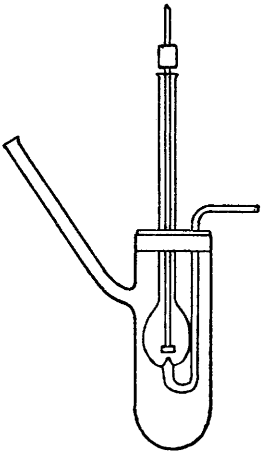
Oscillation frequencies, $1/\mu\mu$.

——— *Di-α-naphthyl ether.* — — — 2 : 2′-*Dinaphthylene* 1 : 1′-*oxide* (VII.)
— · — · — · iso*Dinaphthylene oxide* (IX.)

According to de Laszlo, β-spectra contain relatively larger numbers of bands than α-spectra, and we see that the spectrum of α-dinaphthylene oxide (Fig. 2) contains a greater number of bands relative to di-α-naphthyl ether than does β-dinaphthylene oxide to di-β-naphthyl ether (Fig. 1). Also the ββ-dinaphthyl bands at oscillation frequencies 3204, 3436, and 3556, described by Purvis (J., 1908, **93**, 1322), which seem from their form to belong to A, appear to have their counterparts in the absorption of α-dinaphthylene oxide at 3060, 3145, and 3290. These results therefore agree with formula (VII) for α-dinaphthylene oxide.

In regard to *iso*dinaphthylene oxide, the absorption spectra likewise support the formula 1 : 2′-dinaphthylene 2 : 3′-oxide submitted in Part I from a consideration of its chemical properties. Relative to normal β-dinaphthylene oxide, part A (Fig. 1) shows the shift towards the red region of the spectrum which de Laszlo (*loc. cit.*) observed as a general effect accompanying a change from an α- to a β-linkage.

FIG. 3.



EXPERIMENTAL.

Oxidation and Etherification of β-Naphthol.—β-Naphthol (10 g.) was placed in a small glass bulb (20 c.c.) having a wide tube attached to one end, and a narrow glass tube, drawn out to a jet, sealed in the opposite side and bent so that the apparatus could be immersed in the vapour of boiling benzophenone contained in a jacketing vessel (Fig. 3). Two stirrers of the grooved disc type were used, one of glass and the other consisting of a steel rod with a brass disc at one end. The β-naphthol was immersed in the bath for 15 minutes and reached a temperature of 285° while a flow of approximately 100 c.c. of oxygen per minute was maintained. The product was treated with an excess of boiling water (2·5 l.), dried, and weighed. In the etherification experiments, the product was boiled with excess of potassium hydroxide solution, and the residue washed with water, dried, and weighed.

iso-β-*Dinaphthylene Oxide.*—(1) β-Naphthol (20 g.) contained in a short-necked round-bottomed flask (500 c.c.) was heated to boiling with calcium oxide (0·5 g.), and a slow stream of oxygen directed over the liquid. After 2 hours the boiling point had risen to 330° and the product was poured into a hot solution of sodium hydroxide. The residue (10 g.) was distilled and recrystallised from benzene–

TABLE I.

Stirrer.	R.p.m.	Catalyst.	% Yield dinaphthol.	% Yield ether.
—	—	V_2O_5	2	—
Glass	3000	—	11	—
Metal	3000	—	30	—
Glass	3000	V_2O_5	54	—
Metal	3000	V_2O_5	54	—
Glass	3570	CaO	88·9 (at 310°)	—
Glass	3000	WO_3	—	6·0
Glass	3570	WO_3	—	10·7

alcohol; m. p. 157°, mixed m. p. with *iso*dinaphthylene oxide 157°. The alkali-soluble portion was treated with hydrochloric acid, and the precipitate boiled with water to remove β-naphthol; only di-β-naphthol could be isolated from the residue.

(2) Di-β-naphthol (7·5 g.) and calcium oxide (0·2 g.) were heated at 340—350° for 10 minutes with a stirrer speed of 3570 r.p.m. The crude product after crystallisation from benzene–alcohol had m. p. 144°, not depressed by admixture with normal β-dinaphthylene oxide, but with *iso*dinaphthylene oxide, m. p. 110°.

Naphthidine.—4 : 4′-Dinitro-1 : 1′-dinaphthyl (1 g.) was dissolved in boiling glacial acetic acid (100 c.c.), and zinc dust (5 g.) added. Hydrochloric acid (5 c.c.) was added drop by drop, and after 10 minutes the solution was diluted with an equal volume of water and filtered. The amine was precipitated by addition of solid potassium hydroxide, sufficient to keep the zinc in solution, collected, extracted with a little dilute hydrochloric acid to remove zinc, again heated with sodium hydroxide solution, collected, dried, and distilled at 1 mm. The product crystallised from alcohol in small fan-shaped plates, m. p. 191°, alone or mixed with authentic naphthidine.

2-*Nitro*-1-*methoxynaphthalene.*—Potassium 2-nitro-1-naphthoxide (20 g.) (Burkhardt and Wood, J., 1929, 143), anhydrous sodium carbonate (5 g.), and methyl sulphate (15 c.c.) were heated on the water-bath for 1 hour. The mass was extracted with sodium hydroxide solution, and the residue crystallised from alcohol (20 g., m. p. 80°).

1-*Methoxy*-β-*naphthylamine.*—2-Nitro-1-methoxynaphthalene (10 g.), ferrous sulphate (150 g.), and water (240 c.c.) were heated on the water-bath, and aqueous ammonia (55 c.c., *d* 0·880) added, with shaking, during 1 hour. The amine passed over on steam distillation (5 g., m. p. 49°).

2-*Iodo*-1-*methoxynaphthalene.*—1-Methoxy-β-naphthylamine (5 g.) in 10% sulphuric acid (50 c.c.) was well cooled and treated with sodium nitrite (2 g.) in water (10 c.c.). After ½ hour the solution was filtered, urea (2 g.) added, and the mixture poured into a solution of potassium iodide (9 g.) in 5% sulphuric acid (40 c.c.). The mixture, after standing 1 hour, was heated at 90—100° for ½ hour, and the iodo-compound extracted with ether or steam-distilled; it crystallised from dilute alcohol in needle-like prisms (2—3 g., m. p. 41°).

1 : 1′-*Dimethoxy*-2 : 2′-*dinaphthyl*.—2-Iodo-1-methoxynaphthalene (2 g.), copper powder (1 g.), and iodine (0·1 g.) were heated together for 4—5 hours at 200—210°. The mixture was extracted with ethyl acetate, the solvent removed, and the *product* recrystallised from ligroin; 0·4 g., m. p. 122° (Found : C, 83·8; H, 5·6. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%).

1 : 1′-*Dihydroxy*-2 : 2′-*dinaphthyl and* 2 : 2′-*Dinaphthylene* 1 : 1′-*Oxide*.—1 : 1′-Dimethoxy-2 : 2′-dinaphthyl (0·4 g.) was refluxed with hydriodic acid (5 c.c., *d* 1·5) for 6 hours, and after dilution with water the solid was collected and extracted with aqueous sodium hydroxide, leaving 0·125 g. of residue which, when distilled and crystallised from ligroin (b. p. 80—100°), gave long, colourless, acicular plates, m. p. 183°, not depressed by admixture with 2 : 2′-dinaphthylene oxide made catalytically from α-naphthol (Found : C, 89·5; H, 4·8. Calc. for $C_{20}H_{12}O$: C, 89·5; H, 4·5%). The alkaline filtrate was acidified, and the solid collected (0·25 g.) and distilled. The distillate was extracted with sodium hydroxide, and the extract filtered from the oxide and acidified. The precipitate was collected, dried, and crystallised from ligroin, giving greyish-white prisms, m. p. 212° (Found: C, 83·4; H, 5·1. $C_{20}H_{14}O_2$ requires C, 83·6; H, 5·0%).

1 : 2 - *Dichloronaphthalene*.—1 - Nitro - β - naphthylamine (Friedländer and Littner, *Ber.*, 1915, **48**, 330) (5 g.) in concentrated hydrochloric acid (25 c.c.) was stirred and ice (100 g.) added, followed by the theoretical amount of solid sodium nitrite. After 1 hour's stirring, the liquid was filtered, added to a solution of cuprous chloride (15 g.) in hydrochloric acid (40 c.c.), and left over-night. Steam-distillation then gave 1 : 2-dichloronaphthalene (2 g.), m. p. 35° (Found : Cl, 36·2. Calc. for $C_{10}H_6Cl_2$: Cl, 36·0%).

1 : 2-*Dibromonaphthalene*.—The above diazo-solution, prepared in 10% sulphuric acid (50 c.c.), was added to copper sulphate (5·4 g.) and sodium bromide (15 g.) in water (40 c.c.) containing copper powder (1·5 g.) and steam-distilled; 1 : 2-dibromonaphthalene then passed over (1·5 g., m. p. 68°).

1 : 2-*Di-iodonaphthalene*.—The above diazo-solution in sulphuric acid was added to potassium iodide (15 g.) in water (50 c.c.) and steam-distilled, giving 1 : 2-di-iodonaphthalene (1 g., m. p. 81°).

2-*Chloro*-1-*bromonaphthalene*.—The above diazo-solution in hydrochloric acid was added to cuprous bromide (20 g.) in hydrochloric acid (40 c.c.), and the mixture extracted with ether. The ether was removed, and the residue steam-distilled, giving 2-*chloro*-1-*bromonaphthalene* (0·3 g.), which formed rhombic prisms, m. p. 46°, from ligroin (b. p. 40—60°) (Found: Cl + Br, 47·8. $C_{10}H_6ClBr$ requires Cl + Br, 47·1%).

2-*Chloro*-1-*bromonaphthalene from* 1-*Bromo*-β-*naphthylamine.*—1-Bromo-β-naphthylamine (Morgan, J., 1900, **77**, 819) (5 g.), suspended in hydrochloric acid (40 c.c.), was treated with the theoretical amount of solid sodium nitrite, and the solution added to cuprous chloride (15 g.) in hydrochloric acid (40 c.c.). Steam-distillation yielded 2-chloro-1-bromonaphthalene identical with that just described.

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THE UNIVERSITY OF DURHAM,
ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

THE FRICK CHEMICAL LABORATORY,
PRINCETON UNIVERSITY.

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