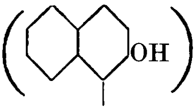
CCCLXXI.—*The Catalytic Production of Polynuclear Compounds. Part I.*

By George Roger Clemo and Robert Spence.

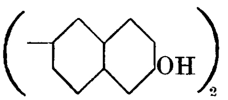
The chemistry of certain polynuclear compounds, some of which have assumed considerable commercial importance, *e.g.*, perylene, is but little known, and accordingly a study has been made in the first instance of certain compounds of intermediate complexity. The present communication deals with dinaphthylene oxides. The literature describes two of these compounds, one from α-naphthol (Merz and Weith, *Ber.*, 1881, **14**, 199), and the other obtained by Dianin (*Ber.*, 1875, **8**, 166) by dehydrating β-dinaphthol with phosphoric oxide. Eckstein (*Ber.*, 1905, **38**, 3660) has proved that compounds stated by Knecht and Unzeitig (*Ber.*, 1880, **13**, 1724) and by Walder (*Ber.*, 1882, **15**, 2166) to be isomeric with Dianin's compound are really identical with it. Further, Merz and Weith (*loc. cit.*) and Niederhausern (*Ber.*, 1882, **15**, 1122) claim to have produced from β-naphthol a specially pure form of Dianin's oxide, but it has now been found that, although the yield of this compound thus obtained is less than 5% of the theoretical, it is really isomeric with Dianin's compound (see p. 2812).

β-Dinaphthol (I) is easily obtained by oxidising β-naphthol with ferric chloride (Dianin, *J. Russ. Phys. Chem. Soc.*, 1874, **6**, 187), and the presence of the 1 : 1′-dinaphthyl linking in it was inferred by Julius (*Ber.*, 1886, **19**, 2549) from the fact that when it was distilled with zinc dust 1 : 1′-dinaphthyl appeared to be formed. Schoepfle, however (*J. Amer. Chem. Soc.*, 1923, **45**, 1566), has shown that a dinaphthylene oxide and not 1 : 1′-dinaphthyl results from this reaction.

Hodgkinson and Limpach (J., 1891, **59**, 1100) distilled sodium 2-naphthol-6-sulphonate and, obtaining a mixture of β-naphthol, a dinaphthyl ether, and a dinaphthylene oxide, suggested that β-dinaphthol might have the constitution (II); whereas Pozzi Escot (*Compt. rend.*, 1904, **138**, 1618), from the fact that azo-derivatives of β-dinaphthol could be prepared, considered that the compound had the formula (III). It has been found, however, that β-dinaphthol, together with a dinaphthylene oxide and a dinaphthylene dioxide (VII), is formed when 1-bromo-2-naphthol is



(I.)



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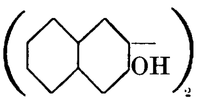
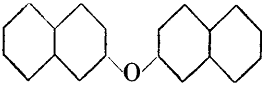


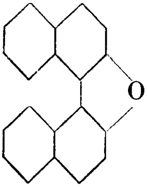
(III.)

treated with copper powder, a result which indicates that (I) is its correct formula.

The dinaphthylene dioxide mentioned above has been prepared recently by Pummerer, Prell, and Rieche (*Ber.*, 1926, **59**, 2159) by heating the copper salt of β-dinaphthol at 280°, and in all probability it has the constitution (VII). The oxide produced by the dehydration of β-dinaphthol, therefore, will be 1 : 1′-dinaphthylene 2 : 2′-oxide (V), a conclusion borne out by its conversion into furoperylene (VI) by treatment with aluminium chloride (Weitzenbock, Seer, and von Bartsch, *Ber.*, 1913, **46**, 1994).



(IV.)



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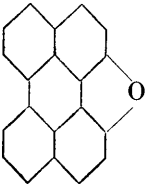

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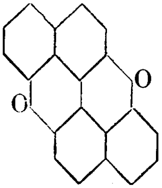
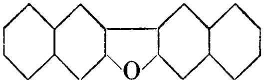


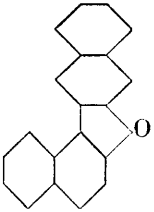
(VII.)

It has now been found that (I) can be converted into (V) by the agency of catalysts such as vanadium pentoxide, and further, that when β-naphthol itself is heated in an open-necked flask at 300° with the trioxide of either tungsten or molybdenum it is converted into the ether (IV); whereas if vanadium pentoxide be used, then, instead of (IV), β-dinaphthol is formed at 300°, and is converted into 1 : 1′-dinaphthylene 2 : 2′-oxide at 340°. If, however, in the latter experiment air is excluded from the flask, by fitting it with a long air condenser, or by the passage of a stream of carbon dioxide, then (IV) only is formed. In the above production of (V) from β-naphthol, therefore, the first reaction is the fairly rapid catalytic air-oxidation to (I), and is followed by catalytic dehydration to (V). All attempts to effect the catalytic air-oxidation of (IV) to (V) have failed. The action of titanium dioxide is intermediate between those of tungsten or molybdenum oxide and vanadium pentoxide, in that it gives a mixture of (IV) and (V) containing a considerable proportion of the former.

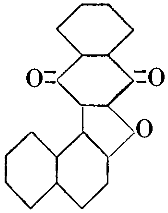
By the action of other catalysts, such as the alkaline-earth oxides, on β-naphthol an oxide isomeric with (V) is easily formed in quantity. This compound, hereinafter called the iso*oxide*, is identical with that obtained in very small yield by Merz and Weith (*loc. cit.*). In this catalytic reaction a second compound, m. p. 300°, is formed, which corresponds to a compound mentioned by Niederhausern (*loc. cit.*), but insufficient has been obtained for investigation. The properties of the *iso*oxide point to its being a structural isomeride of (V) having the constitution (VIII) or (IX), and hence its formation appears to involve unusual reactivity of hydrogen in the β′-position in a mono-β-substituted naphthalene. The formation of 2-hydroxy-3-naphthoic acid from sodium β-naphthoxide is the one well-established case of such β′-reactivity, and indicates that calcium β-naphthoxide also might be reactive in this position.



(VIII.)



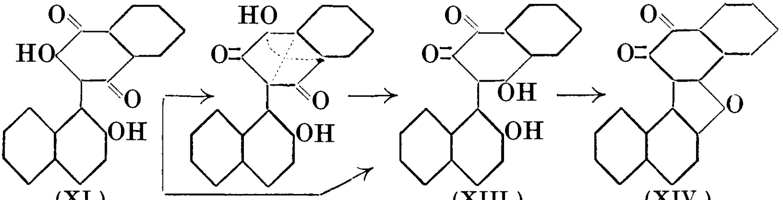
(IX.)



(X.)

Both (V) and the *iso*oxide are stable to almost red-hot zinc dust and are scarcely acted on by fused potassium hydroxide. Reduction with hydriodic acid gives hydrogenated naphthalenes, and oxidation with sulphuric acid gives phthalic acid, in both cases. Chromic acid oxidation, however, destroys (V) but converts the *iso*oxide into a *quinone*, which does not condense with *o*-phenylenediamine and is therefore presumably of the para-type. Such marked difference in behaviour on oxidation suggests that the *iso*oxide is (IX) and not (VIII), for the latter would be expected to give a diquinone if a quinonoid compound were formed. The quinone is therefore probably (X).

When the quinone is distilled with zinc dust the *iso*oxide is regenerated, and on reduction with zinc and acetic anhydride it gives an O-*diacetyl* derivative which still contains the ether linking. The great stability of the furan ring of the *iso*oxide towards alkalis no longer persists in the quinone, however, for when this is treated with alcoholic sodium hydroxide the ring is easily opened to give a *dihydroxydinaphthaquinone*. This compound undergoes a remarkable change on heating: water is lost, but instead of the original *p*-quinone being regenerated an isomeric compound is produced. This forms red needles and condenses easily with *o*-phenylenediamine to give a substituted *phenazine*. It is therefore presumably an o-*quinone*. This transformation is explicable with formula (IX) for the *iso*oxide but not with (VIII): when the furan ring of the quinone (X) is opened, rotation of the top portion of the molecule seems to occur to give (XI), as evidenced by the formation, on treatment with acetic anhydride, of a yellow O-*diacetyl quinone* derivative. If rotation had not taken place, it would be expected that (X) would be re-formed under these conditions. The production of the *o*-quinone (XIV) from (XI), with the loss of water, seems to necessitate the prior formation of (XIII). If this be granted, the reaction appears to involve one or other of two contentious mechanisms, *viz.*, either the migration of a hydrogen atom from one oxygen atom to another in the meta-position with respect to the first, or the migration of the hydrogen in the first instance to an ortho-oxygen atom with temporary formation of the *m*-quinone (XII), followed by a para-migration to give (XIII).

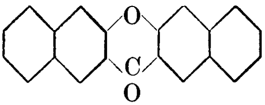


(XI.) (XII.) (XIII.) (XIV.)

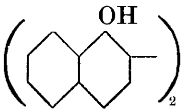
Whilst the above work was progressing an attempt was made to synthesise the symmetrical 2 : 2′-dinaphthylene 3 : 3′-oxide (VIII). The aim of the first series of experiments was to produce the 2 : 2′-dinaphthyl linking and then to introduce the oxygen bridge. 2-Chloro-3-naphthoic acid was treated with copper powder as in the Ullmann reaction (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2184), but only β-naphthoic acid resulted; when ethyl 2-chloro-3-naphthoate was used, the chlorine atom was found to be stable to copper-bronze in boiling nitrobenzene. A similar treatment of either 3-*bromo*-2-*methoxynaphthalene* or its iodo-analogue gave only β-methoxynaphthalene, and 3-*bromo*-β-*naphthol* gave β-naphthol. These 2 : 3-disubstituted naphthalenes were prepared by applying the Hofmann reaction to 2-methoxy-3-naphthoamide. (Fries, *Ber.*, 1925, **58**, 2845, was unable to apply this reaction to 2-hydroxy-3-naphthoamide, as it gave 1-bromo-2-hydroxy-3-naphthoamide instead of the amino-compound.) The second series of experiments aimed at the prior formation of the oxide linking and the subsequent introduction of the dinaphthyl link. The action of tungsten trioxide and of vanadium pentoxide (see p. 2819) on 2-hydroxy-3-naphthoic acid and its ester was investigated with a view to preparing the dinaphthyl ether dicarboxylic acid. Then the Hofmann reaction on the di-amide, followed by diazotisation of the diamino-ether and treatment with ammoniacal copper sulphate (Carpmael, E.P. 278100, 1926), should give the oxide (VIII). Under all the conditions tried, however, the condensation could not be stopped at the ether stage, but easily gave Strohbach's dinaphthaxanthone (XV) (*Ber.*, 1901, **34**, 4144).

The action of catalysts on α-naphthol has also been investigated. Vanadium pentoxide converts it into the α-dinaphthylene oxide of

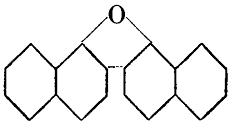
Merz and Weith (*loc. cit.*). The constitution of this compound follows from its preparation by the dehydration of α-dinaphthol. There was no direct evidence for the constitution of the latter compound until Willstätter and Schuler (*Ber.*, 1928, **61**, 362) showed that it is in all probability 1 : 1′-dihydroxy-2 : 2′-dinaphthyl (XVI).



(XV.)



(XVI.)



(XVII.)

Hence α-dinaphthylene oxide would appear to have the constitution (XVII). The same oxide results when α-naphthol is treated with calcium oxide, since, failing a Kaufler type of oxide as the result of a 4 : 4′-dinaphthyl linking, α-naphthol would be expected to form only one dinaphthylene oxide.

EXPERIMENTAL.

β-*Dinaphthol* (I).—1-Bromo-2-naphthol (22 g.), copper bronze (7·5 g.), and iodine (0·5 g.) were heated for 3 hours at 280°. The product was extracted with alkali, the filtered solution acidified with hydrochloric acid, and the precipitate collected and freed from β-naphthol by extraction with boiling water. The residue, crystallised from aqueous alcohol and from glacial acetic acid, gave needles, m. p. 216°, not depressed by admixture with a specimen of β-dinaphthol made by oxidising β-naphthol with ferric chloride (Found : C, 83·5; H, 5·1. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%). From the alkali-insoluble material, boiling acetic acid extracted 1 : 1′-dinaphthylene 2 : 2′-oxide, which separated, on cooling, in needles, m. p. 156° (see below). The residue was crystallised from toluene and gave yellow needles (0·5 g.) of 1 : 1′-dinaphthylene 2 : 8′ : 2′ : 8-dioxide (VII), m. p. 236° (Found : C, 84·5; H, 3·5. Calc. for $C_{20}H_{10}O_2$: C, 85·1; H, 3·5%).

Catalytic Dehydration of β-*Dinaphthol.* 1 : 1′-*Dinaphthylene* 2 : 2′-*Oxide* (V).—β-Dinaphthol (25 g.) and vanadium pentoxide (1 g.) were gently boiled in a round-bottomed flask for 7 hours. When the product, which contained no alkali-soluble material, was vacuum-distilled, only almost pure 1 : 1′-dinaphthylene 2 : 2′-oxide (12 g.) passed over. This crystallised from benzene in pale yellow needles, m. p. 156° (Found : C, 89·5; H, 4·8. Calc. for $C_{20}H_{12}O$: C, 89·6; H, 4·5%). The oxide gives a purple colour in concentrated sulphuric acid, changing to red and then to dark brown on warming. The picrate has m. p. 164°.

Action of Catalysts on β-*Naphthol.*—(a) *Di*-β-*naphthyl ether* (IV). β-Naphthol (20 g.) and tungsten trioxide (0·5 g.) were heated in a round-bottomed, long-necked flask (250 c.c.), first at 270° and then slowly to 300° as the β-naphthol reacted. After heating for 2 hours, the melt was poured into an excess of boiling caustic soda solution. On cooling, the solid residue was collected (recovered β-naphthol, 3·3 g.), dried (14 g.), and vacuum-distilled. The total distillate (12·5 g.) was crystallised from ligroin and gave colourless plates, m. p. 105°.

(b) β-*Dinaphthol.* β-Naphthol (20 g.) and vanadium pentoxide (0·5 g.) were heated as in (a), for 5 hours, at 300°. The product was extracted with boiling sodium hydroxide solution, in which it was almost completely soluble, and the hot filtered solution was treated with excess of hydrochloric acid. After cooling, the precipitate was collected and extracted with boiling water to remove unchanged β-naphthol. The residual β-dinaphthol (8 g.), after crystallising from glacial acetic acid, had m. p. 216°.

(c) 1 : 1′-*Dinaphthylene* 2 : 2′-*oxide* (V). β-Naphthol (100 g.) and vanadium pentoxide (1 g.) were heated in a flask for 5 hours, the temperature rising slowly from 270° to 340°. The product was extracted with alkali, and β-naphthol (4 g.) and crude β-dinaphthol (13 g.) were obtained from the extract. The dark alkali-insoluble residue was dried (50 g.) and distilled, giving 43 g. of a pale yellow solid which, when crystallised from benzene–alcohol to free it from a little di-β-naphthyl ether, gave 1 : 1′-dinaphthylene 2 : 2′-oxide (30 g.), m. p. 156°.

(d) iso*Dinaphthylene oxide* (IX). β-Naphthol (100 g.) and calcium oxide (1 g.) were heated as in (c) for 10 hours, the temperature being raised slowly from 270° to 340°. The product was treated with alkali to free it from unchanged β-naphthol, and the residue distilled. The distillate, a colourless solid (44 g.), was extracted with benzene (300 c.c.), leaving 0·5 g. of the solid of m. p. 300° (see p. 2812). Alcohol (300 c.c.) was added to the extract; the colourless plates of the iso*oxide* (30 g.) thus obtained, after recrystallisation from glacial acetic acid, melted at 158—159°; mixed m. p. with (V), 130—140° (Found : C, 89·3 ; H, 4·4. $C_{20}H_{12}O$ requires C, 89·6 ; H, 4·5%). The compound is easily soluble in benzene, less soluble in alcohol, and gives in sulphuric acid an orange-red solution, which changes through scarlet, purple, and blue to light brown on warming.

*Dibromo*iso*dinaphthylene Oxide.*—When the *iso*oxide (3·6 g.), dissolved in carbon disulphide, was slowly treated with bromine (2·5 c.c.), colourless needles of the *dibromo*-compound separated (5·9 g.), which, after recrystallisation from benzene and from acetic acid, had m. p. 193° (Found : Br, 37·4. $C_{20}H_{10}OBr_2$ requires Br, 37·6%).

Oxidation of 1 : 1′-*Dinaphthylene* 2 : 2′-*Oxide* (V) *and of the* iso-

Oxide.—(a) *With sulphuric acid.* Concentrated sulphuric acid (50 c.c.) and either of the above two oxides (7 g.), with a little mercury and copper sulphate as catalyst, were heated together. On distillation, phthalic acid (1·3 g.) (anhydride, m. p. 128°) passed over.

(b) *With chromic acid.* iso*Dinaphthaquinone oxide* (X). The *iso*oxide (10 g.) was refluxed for 10 minutes with 250 c.c. of a chromic acid mixture (made by dissolving potassium dichromate, 60 g., in concentrated sulphuric acid, 80 g., and water, 270 c.c.), water was then added, and the solid collected. It was crystallised first from acetic acid (solubility, 0·5%) and then from pyridine, bronze leaflets (4·5 g.) being obtained, m. p. 268° (Found: C, 80·2; H, 3·5. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). The *quinone* sublimes unchanged, and gives in sulphuric acid a bluish-green solution which becomes brown on heating.

After 1 : 1′-dinaphthylene 2 : 2′-oxide has been treated with chromic acid as above, no solid is obtained on dilution with water.

Reduction of the Quinone (X). *Diacetoxy*iso*dinaphthylene Oxide.*—The quinone (5 g.) and acetic anhydride (20 c.c.) were refluxed for 15 minutes in presence of zinc dust (5 g.). The liquid was filtered and poured into water with rapid stirring. The colourless solid obtained crystallised from acetic acid in needles (5 g.), m. p. 245—246° (Found : C, 75·0; H, 4·0. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%).

Hydrolysis of the Quinone.—The quinone (4 g.) was refluxed with alcoholic sodium hydroxide (1 l. of 0·5% solution) for 10 hours and the solution was then concentrated to small bulk, diluted with water, and filtered. The filtrate, treated with an excess of hydrochloric acid, gave a reddish-brown precipitate, which was washed with water and dried in a vacuum desiccator (3·8 g.). It crystallised from chloroform in light red prisms with solvent of crystallisation, which was driven off by heating on the water-bath; m. p. 222° (Found : C, 76·0; H, 3·5. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%). *Dihydroxydinaphthaquinone* crystallises from benzene in needles, with benzene of crystallisation, and from acetic acid in rhombohedra.

Diacetoxydinaphthaquinone.—Dihydroxydinaphthaquinone (0·5 g.) was refluxed with acetic anhydride (20 c.c.) and a drop of pyridine for 10 minutes, and the mixture poured into water. The precipitate obtained was crystallised first from glacial acetic acid and then twice from alcohol, giving golden-yellow needles, m. p. 167° (Found : C, 71·7; H, 4·3. $C_{24}H_{16}O_6$ requires C, 72·0; H, 4·0%). This *diacetyl* compound gives a reddish-brown colour with concentrated sulphuric acid, and dissolves in hot potassium hydroxide solution with a red colour, the original dihydroxydinaphthaquinone being precipitated by the addition of hydrochloric acid.

o-*Dinaphthaquinone Oxide* (XIV).—The dihydroxy-quinone (2 g.)

was heated at 250°, and after about 5 minutes evolution of steam ceased. The product crystallised from benzene in deep red needles (1·1 g.), m. p. 255—256° (Found : C, 80·7; H, 3·4. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). The *o-quinone oxide* gives with sulphuric acid a brown colour which turns green on warming.

Condensation to a phenazine. The *o*-quinone oxide (0·3 g.) and *o*-phenylenediamine (0·2 g.) were refluxed in acetic acid (60 c.c.) for ½ hour. After cooling, the solid was collected; it crystallised from glacial acetic acid in yellow needles (0·25 g.), m. p. 240° (Found : N, 7·3. $C_{26}H_{14}ON_2$ requires N, 7·6%).

Action of Copper-bronze on 2-*Chloro*-3-*naphthoic Acid.*—2-Chloro-3-naphthoic acid (10 g.) was dissolved in nitrobenzene (50 c.c.), copper-bronze (25 g.) added, and the mixture refluxed for 2 hours. A solution of sodium hydroxide was then added, the nitrobenzene removed in steam, and the residual alkaline solution filtered and acidified. The resulting precipitate crystallised from acetone in needles (4 g.), m. p. 185°, and gave an amide, m. p. 197°, and was therefore β-naphthoic acid.

2-*Methoxy*-3-*naphthoic Acid.*—2-Hydroxy-3-naphthoic acid (10 g.), treated with methyl sulphate and sodium hydroxide, gave 11 g. of 2-methoxy-3-naphthoic acid. This was converted into the amide, m. p. 170° after crystallising from acetone.

2-*Methoxy*-3-*naphthylamine.*—Chlorine, from potassium permanganate (5·3 g.), was passed into an ice-cooled solution of sodium hydroxide (14 g.) in water (100 c.c.). The resulting hypochlorite was added to the finely powdered amide (15 g.) and warmed in a water-bath with stirring, the temperature being kept below 70° until the reaction had subsided. Sodium hydroxide solution was then added, the mixture heated on a water-bath for an hour, the amine extracted with benzene, the benzene removed, and the residue distilled under reduced pressure. The distillate crystallised from methyl alcohol in colourless plates (5 g.), m. p. 109·5° (Found : C, 76·1; H, 6·6; N, 8·4. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·4; N, 8·1%). The *amine* forms an *acetyl* derivative which crystallises from methyl alcohol in colourless plates, m. p. 124—125° (Found : C, 73·0; H, 6·2. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·1%).

3-*Bromo*-2-*methoxynaphthalene.*—2-Methoxy-3-naphthylamine (17 g.), in a mixture of concentrated hydrochloric acid (20 c.c.) and water (150 c.c.), was diazotised with sodium nitrite (7 g.). A solution of cuprous bromide (prepared from copper sulphate, 20 g.) in hydrobromic acid (30 c.c.; *d* 1·44) was cooled in ice, and the diazo-solution added. After ½ hour, the mixture was warmed on the water-bath until no more nitrogen was evolved; the product was then extracted with benzene, and the extract fractionated. The fraction of b. p. 178—190°/16 mm. (6·5 g.) was crystallised from methyl alcohol and then from ligroin (b. p. 40—60°), giving colourless plates, m. p. 76° (Found : Br, 33·2. $C_{11}H_9OBr$ requires Br, 33·75%).

3-*Iodo-2-methoxynaphthalene.*—2-Methoxy-3-naphthylamine (5 g.) was diazotised as above, and an aqueous solution of potassium iodide (5 g.) added. The solution was stirred for ½ hour, heated to boiling, made alkaline, and extracted with benzene. The benzene was removed, and the residue vacuum-distilled, giving a pale yellow oil which solidified; it crystallised from methyl alcohol in colourless prisms, m. p. 65° (Found: I, 44·2. $C_{11}H_9OI$ requires I, 44·7%).

3-*Bromo*-β-*naphthol.* — 3-Bromo-2-methoxynaphthalene (4·5 g.) was refluxed with hydrobromic acid (50 c.c.; *d* 1·44) for 4 hours, and the mixture was then diluted with water and cooled, and the solid collected. This was extracted with sodium hydroxide, the filtered solution acidified, and 3-*bromo*-β-*naphthol* dried and distilled (2 g.). It crystallised from ligroin (b. p. 40—60°) in well-defined needles, m. p. 80—81°; mixed m. p. with 1-bromo-β-naphthol (m. p. 84°), 45—55°. As the bromine determinations were always about 1% low, the product probably contained a small amount of β-naphthol (Found: Br, 34·7. $C_{10}H_7OBr$ requires Br, 35·9%).

The use of hydriodic acid instead of hydrobromic acid for demethylation resulted in both 3-bromo- and 3-iodo-2-methoxynaphthalene being reduced to β-naphthol.

Dinaphthaxanthone.—2-Hydroxy-3-naphthoic acid (6 g.) and tungsten trioxide (0·05 g.) or vanadium pentoxide were heated together for ½ hour, the residue was extracted with alkali, and the insoluble portion was dried and distilled under reduced pressure. The distillate (2 g.) crystallised from glacial acetic acid in long, yellow needles, m. p. 134—135° (Found : C, 85·3; H, 4·1. Calc. for $C_{21}H_{12}O_2$: C, 85·1; H, 4·1%). Ethyl 2-hydroxy-3-naphthoate gave the same result.

2 : 2′-*Dinaphthylene* 1 : 1′-*Oxide* (XVII).—α-Naphthol (20 g.) was heated with vanadium pentoxide (1 g.) for 4 hours, the temperature rising to 340°. The product was extracted with alkali, and the insoluble portion distilled. The distillate crystallised from benzene–alcohol in yellow needles, m. p. 179° (Found : C, 89·2; H, 4·6. Calc. for $C_{20}H_{12}O$: C, 89·6; H, 4·5%).

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