LXV.—*The Oxidation of α -Dinaphthaxanthens.*By HEMENDRA KUMAR SEN-GUPTA and STANLEY HORWOOD
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THE condensation of α -naphthol with various ketones has been investigated by one of us (Sen-Gupta, T., 1914, **105**, 399). The present communication has arisen out of an investigation of the oxidation of the products of condensation of α -naphthol with acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone respectively. In general, in the oxidation of any particular anhydro-1:1-dihydroxydinaphthylalkylmethane by means of sodium dichromate in glacial acetic acid solution, there are formed simultaneously two products: one, deep orange to red, and the other a brilliant yellow.

The colour of these products suggests that they contain an ortho-quinonoid and a para-quinonoid grouping respectively, and investigation confirms this idea. Thus the orange oxidation products are readily reduced, but form unstable dihydroxy-derivatives. If, however, reduction is effected in the presence of acetylating agents, stable diacetyl derivatives can be isolated. By the action of *o*-phenylenediamine in glacial acetic acid or in alcoholic solution quinoxalines are formed. Whereas the parent anhydro-compounds form mono- and di-nitro-derivatives, the orange oxidation products form mononitro-derivatives only, indicating that one naphthalene group has become oxygenated, leaving the other still free for nitration. The alkyl groups are unaffected in the oxidation process. There is no evidence of xanthone formation. Hence the structure of the orange oxidation products may be represented by I, which

classes them as ortho-diketodialkyl-dihydro- α -dinaphthaxanthens. The nitro-group of the mononitro-derivative is therefore probably present in position 9, the quinoxaline nucleus is formed at positions 5 and 6, and the diacetyl derivative of the unstable reduction product referred to above contains its acetoxy-groups in positions 5 and 6.

5 : 6-Diketo-7 : 7-dimethyl-5 : 6-dihydro- α -dinaphthaxanthen and
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the corresponding methyl ethyl and diethyl compounds normally give mononitro-derivatives, but attempts to prepare a mononitro-derivative of 5:6-diketo-7-methyl-7-*n*-propyl-5:6-dihydro- α -dinaphthaxanthen by the usual method, that is, treatment of the glacial acetic acid solution of the diketo-compound with fuming nitric acid at 100°, have failed. Consequently, nitration was attempted in the *boiling* solution. No nitro-compound separated, but the mixture left, after evaporation, a crystalline residue containing phthalic acid. A similar experiment with 5:6-diketo-7:7-dimethyl-5:6-dihydro- α -dinaphthaxanthen, performed in boiling glacial acetic acid, gave rise likewise to phthalic acid, but mixed with a considerable quantity of a yellow nitro-compound.

The 5:6-diketo-7:7-dialkyl-5:6-dihydro- α -dinaphthaxanthenes are very sensitive to light. If they are preserved in the dark, no decomposition will occur, but exposure to sunlight changes the colour from deep orange to bright scarlet. They are further characterised by high melting points and sparing solubility.

The yellow oxidation products differ notably in properties from the orange oxidation products. The yellow products cannot be nitrated; they can be recovered unchanged from fuming nitric acid. From this it may be inferred that the oxygen atoms are arranged symmetrically in the naphthalene ring systems. They do not give quinoxalines with *o*-phenylenediamine. Their colour and other properties indicate that they possess the para-quinonoid grouping, and their structure is accordingly represented by formula II, that is, they are di-2- α -naphthaquinonyldialkylmethanes.

In all their reactions these substances behave as α -naphthaquinone. Sulphur dioxide has no effect on them, but zinc dust in glacial acetic acid brings about reduction to 5:9-dihydroxy-7:7-dialkyl- α -dinaphthaxanthenes; the expected 1:4:1':4'-tetrahydroxy- $\beta\beta$ -dinaphthyldialkylmethanes cannot be isolated. The course of the reaction is readily explained thus :

Anhydride formation is to be expected in such circumstances. The change III $\rightarrow$ IV is exemplified in numerous instances; for example, Copisarow and Weizmann (T., 1915, **107**, 880) prepared

from di-1-ethoxynaphthylphthalide the stable α -naphthaphthalein and converted this hydroxy-compound into its anhydride, α -naphthafluoran. That the final product of the reduction of di-2- α -naphthaquinonyldialkylmethane is a dihydroxy-compound (IV) is indicated by the formation of the diacetyl, dibenzoyl, and dimethyl derivatives. The diacetoxo-compounds are isomeric with the corresponding 5 : 6-diacetoxo-7 : 7-dialkyl- α -dinaphthaxanthens, prepared by the reduction and subsequent acetylation of the 5 : 6-diketo-7 : 7-dialkyl-5 : 6-dihydro- α -dinaphthaxanthens (I).

The crystals of the dihydroxy-compounds formed in glacial acetic acid solution have been measured. A close crystallographic similarity, pointing to isomorphism, exists between 5 : 9-dihydroxy-7 : 7-dimethyl- α -dinaphthaxanthen and the corresponding diethyl compound. The crystals of 5 : 9-dihydroxy-7-methyl-7-*n*-propyl- α -dinaphthaxanthen, which do not contain acetic acid, do not resemble the above.

5 : 9-Dihydroxy-7 : 7-dimethyl- α -dinaphthaxanthen reacts with chlorine to give a crystalline chloro-derivative.

With the object of elucidating the constitution of the chloro-compound prepared by one of us (Sen-Gupta, *loc. cit.*) by the action of chlorine on anhydro- β -1 : 1-dihydroxydinaphthylpropane, attempts have been made to replace the two hydroxyl groups in 5 : 9-dihydroxy-7 : 7-dimethyl- α -dinaphthaxanthen by chlorine. Thionyl chloride reacts with the compound, and there is formed a crystalline substance which contains chlorine and no sulphur; its investigation is in hand.

Finally, it may be said that the considerations adduced above prove that the anhydrodihydroxydinaphthylparaffins (Sen-Gupta, *loc. cit.*) are 7 : 7-dialkyl- α -dinaphthaxanthens, and they are designated as such in the experimental portion of this paper.

EXPERIMENTAL.

Oxidation of 7 : 7-Dimethyl- α -dinaphthaxanthen (Anhydro- β -1 : 1-dihydroxydinaphthylpropane), $\text{CMe}_2\langle\text{C}_{10}\text{H}_6\text{C}_{10}\text{H}_6\rangle\text{O}$.

Sodium dichromate (25 grams) is added during twenty minutes to a warm solution of 7 : 7-dimethyl- α -dinaphthaxanthen (5 grams) in glacial acetic acid (75 c.c.), the liquid being boiled after each addition. The mixture of orange and yellow crystals which separates is washed with glacial acetic acid until the faintly red filtrate is free from chromium salts. The orange residue is 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro- α -dinaphthaxanthen. The combined filtrates are heated for two hours with more sodium dichromate (10—12

grams) and poured into water. The yellow, flocculent precipitate is $\beta\beta$ -di-2- α -naphthaquinonylpropane.

These two products may also be separated thus :—The mixture is dissolved in a slight excess of boiling glacial acetic acid. Before the solution has attained room temperature it is filtered from the orange crystals—which separate practically pure—and to the filtrate excess of fuming nitric acid is added and the solution maintained at 100° for half an hour. The insoluble nitro-derivative is removed, and the filtrate deposits the yellow product in a pure condition.

5 : 6-Diketo-7 : 7-dimethyl-5 : 6-dihydro- α -dinaphthaxanthen (I) crystallises from glacial acetic acid, or from pyridine diluted with water, in dark orange needles, melting at 287° (Found : C = 81.2; H = 4.7. $C_{23}H_{16}O_3$ requires C = 81.2; H = 4.7 per cent.). It is sparingly soluble in alcohol, acetone, ether, or carbon tetrachloride, but readily soluble in pyridine, benzene, nitrobenzene, or chloroform. It dissolves in concentrated sulphuric acid to form a deep bottle-green solution, which darkens to purple on heating. Bromine, added to the glacial acetic acid solution of the substance, causes, on boiling for a few seconds, the precipitation of salmon-coloured needles. These have not yet been examined.

A mononitro-derivative is obtained by dissolving 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro- α -dinaphthaxanthen in glacial acetic acid, adding excess of fuming nitric acid, and maintaining at 100° for half an hour. The nitro-derivative, which is sparingly soluble in acetic acid, crystallises in long, yellow needles. It is very soluble in hot nitrobenzene. It shows signs of melting and decomposition at 330° (Found : N = 3.8. $C_{24}H_{15}O_5N$ requires N = 3.6 per cent.).

If, however, fuming nitric acid is added to the glacial acetic acid solution and the mixture is *boiled*, the reaction will take a different course. The solution was boiled for a quarter of an hour and then evaporated to dryness. The yellow oil thus obtained, on standing, crystallised in small, white needles, which appeared to be phthalic acid.

The Quinoxaline.—A solution of 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro- α -dinaphthaxanthen (1 gram) mixed with *o*-phenylenediamine (0.8 gram) in glacial acetic acid (10 c.c.) is warmed, and the pale yellow, crystalline solid that is deposited is recrystallised from glacial acetic acid and then from alcohol in pale brown needles which melt at 251–252° (Found : C = 84.8; H = 5.0; N = 6.8. $C_{29}H_{20}ON_2$ requires C = 84.5; H = 4.9; N = 6.8 per cent.).

5 : 6-Diacetoxy-7 : 7-dimethyl- α -dinaphthaxanthen. — 5 : 6-Diketo-7 : 7-dimethyl-5 : 6-dihydro- α -dinaphthaxanthen (1 gram) is dissolved in acetic anhydride (10–12 c.c.) and glacial acetic acid

(about 10 c.c.) by boiling, and zinc dust added until the colour is discharged. Fused sodium acetate (3 grams) is now added and the mixture boiled for some time. The acetyl derivative, isolated in the usual manner, is crystallised from glacial acetic acid or alcohol in colourless needles melting at $251-254^\circ$ (Found: C = 75.7; H = 5.1. $C_{27}H_{22}O_5$ requires C = 76.0; H = 5.2 per cent.).

$\beta\beta$ -Di-2- α -naphthaquinonylpropane (II) crystallises from glacial acetic acid, or pyridine diluted with water, in brilliant yellow plates melting at $245-248^\circ$. Fuming nitric acid has no action on it (Found: C = 77.3; H = 4.6. $C_{24}H_{16}O_4$ requires C = 77.5; H = 4.5 per cent.).

Reduction of $\beta\beta$ -Di-2- α -naphthaquinonylpropane to 5:9-Dihydroxy-7:7-dimethyl- α -dinaphthaxanthen (IV).

The propane derivative (1 gram) is dissolved in glacial acetic acid (25 c.c.) and zinc dust gradually added to effect decoloration. The mixture having been boiled for a few minutes and filtered, the reduction product, which separates on cooling, is recrystallised from glacial acetic acid. The product contains a molecule of acetic acid of crystallisation, which it loses at $120-125^\circ$, leaving a pink powder. It turns faintly brown at 240° and melts at 254° (Found: C = 74.7; H = 5.5. $C_{23}H_{18}O_3 \cdot C_2H_4O_2$ requires C = 74.6; H = 5.5 per cent.).

The crystals are monoclinic; $a:b:c = 0.872:1:1.365$; $\beta = 99^\circ 43'$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$, $q\{011\}$. The common habit is elongated along the b -axis and tabular parallel either to $a(100)$, as in Fig. 1, or tabular parallel to $c(001)$. Two small crystals, about 1 mm. in their largest dimension, were found to be measurable, and the mean angular values obtained from these are given below:

FIG. 1.

	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$q\{011\}$.
ϕ	$89^\circ 29' (+31')$	$*49^\circ 19'$	$91^\circ 1' (-1^\circ 1')$	$7^\circ 9' (0^\circ 0')$
ρ	$90^\circ 0' (0^\circ 0')$	$90^\circ 0' (0^\circ 0')$	$*9^\circ 43'$	$*54^\circ 0'$

The above product, containing acetic acid, is very soluble in hot alcohol, giving a violet fluorescing solution. The addition of an equal volume of hot water to this solution effects the precipitation of colourless plates, which become brown at 240° and melt at 254° , as before. The product contains one molecule of alcohol of crystallisation (Found: C = 77.3; H = 6.2. $C_{24}H_{18}O_3 \cdot C_2H_6O$ requires C = 77.3; H = 6.2 per cent.). The crystals are insoluble in light petroleum, soluble in benzene or xylene, and very soluble in ethyl

acetate. The crystals formed in xylene solution contain xylene of crystallisation; they are needle-shaped, and melt at 241—244°. Potassium hydroxide solution dissolves all three crystalline products to apple-green solutions, which become deep green on standing or on warming.

Thionyl chloride acted on 5:9-dihydroxy-7:7-dimethyl- α -dinaphthaxanthen with evolution of hydrochloric acid, but although crystalline products were obtained and shown to contain chlorine and not sulphur, no pure compound could be isolated. 5:9-Dihydroxy-7:7-dimethyl- α -dinaphthaxanthen reacts with chlorine in a boiling solution of glacial acetic acid to give pale green crystals, which melt at 242—244°.

5:9-Diacetoxy-7:7-dimethyl- α -dinaphthaxanthen, prepared by boiling the dihydroxy-compound with excess of acetyl chloride until a crystalline precipitate commences to separate, or with acetic anhydride and fused sodium acetate, crystallises from glacial acetic acid in needles melting at 239—241° (Found: C = 75.9; H = 5.1. $C_{27}H_{22}O_5$ requires C = 76.1; H = 5.2 per cent.).

5:9-Dibenzoyloxy-7:7-dimethyl- α -dinaphthaxanthen is prepared by boiling 5:9-dihydroxy-7:7-dimethyl- α -dinaphthaxanthen with sufficient benzoyl chloride to effect solution. After one minute's boiling, the solution, without addition of caustic alkali, is poured into water, and the readily precipitated dibenzoyl derivative separated. It crystallises from glacial acetic acid in pointed laminae, which melt at 239—240°. The crystals contain one molecule of acetic acid (Found: C = 76.6; H = 5.1. $C_{37}H_{26}O_5 \cdot C_2H_4O_2$ requires C = 76.7; H = 4.9 per cent.). When heated at 140°, the crystals lose acetic acid of crystallisation, but the powder melts, as before, at 239—240° (Found: acetic acid = 9.8. $C_{37}H_{26}O_5$, $C_2H_4O_2$ requires acetic acid = 9.8 per cent.). The oven-dried product crystallises from pyridine (Found: C = 80.8; H = 4.9. $C_{37}H_{26}O_5$ requires C = 80.7; H = 4.7 per cent.).

5:9-Dimethoxy-7:7-dimethyl- α -dinaphthaxanthen. — 5:9-Dihydroxy-7:7-dimethyl- α -dinaphthaxanthen (1 gram) is dissolved in potassium hydroxide solution (9 c.c. of 15 per cent.) and the apple-green solution treated with methyl sulphate (0.75 gram), whereupon a salmon-coloured precipitate separates; this is crystallised from amyl alcohol in pale salmon plates, which show signs of change at 280° and melt at 291° (Found: C = 80.7; H = 6.0. $C_{23}H_{22}O_3$ requires C = 81.1; H = 6.0 per cent.).

The substance decomposes when it is heated, and a vapour is evolved having a naphtholic odour. It dissolves in cold concentrated sulphuric acid to a yellow-red solution, which becomes brown on warming. It is insoluble in ethyl acetate, ethyl alcohol, or light

petroleum, slightly soluble in glacial acetic acid, and soluble in acetone, pyridine, amyl alcohol, carbon disulphide, chloroform, aniline, benzene, or nitrobenzene. It crystallises well from amyl alcohol, pyridine, or benzene.

Substance melting at 250°.—The crystals separating from a benzene solution behave abnormally. They are hard, warty, and nearly white; on drying at 120°, they fall to a powder which melts at 250°. A mixture with the above-described dimethoxy-compound melts at 243°. The investigation of the substance is being continued.

Oxidation of 7-Methyl-7-ethyl- α -dinaphthaxanthen (Anhydro- β -dihydroxydinaphthylbutane).

7-Methyl-7-ethyl- α -dinaphthaxanthen is oxidised with sodium dichromate in glacial acetic acid as described under the oxidation of 7:7-dimethyl- α -dinaphthaxanthen, and the resulting orange 5:6-diketo-7-methyl-7-ethyl-5:6-dihydro- α -dinaphthaxanthen and the yellow $\beta\beta$ -di-2- α -naphthaquinonylbutane are separated as in that case.

5:6-Diketo-7-methyl-7-ethyl-5:6-dihydro- α -dinaphthaxanthen (I) can be crystallised from glacial acetic acid, or from pyridine diluted with water, in orange needles which melt with decomposition at 276°. The crystals become scarlet when they are exposed to sunlight (Found: C = 81.4; H = 5.1. $C_{24}H_{18}O_3$ requires C = 81.4; H = 5.1 per cent.).

A mononitro-derivative is prepared similarly to its lower homologue; it crystallises in pale salmon-coloured prisms which melt at 301°, showing signs of change at 297° (Found: N = 3.6. $C_{24}H_{17}O_5N$ requires N = 3.5 per cent.).

The quinoxaline is prepared as the corresponding quinoxaline from 5:6-diketo-7:7-dimethyl-5:6-dihydro- α -dinaphthaxanthen. It crystallises from glacial acetic acid containing a small amount of alcohol in short, bright yellow rods, which melt at 236–241° (Found: N = 6.5. $C_{30}H_{22}ON_2$ requires N = 6.6 per cent.). In certain preparations, a bright yellow, crystalline material was obtained which melted at 225–227°. The quinoxaline is soluble in benzene, glacial acetic acid, acetone, ethyl acetate, or pyridine, slightly soluble in alcohol, and insoluble in light petroleum. It dissolves in pyridine to a red solution which exhibits a deep green fluorescence, similar in tint to that of fluorescein. The solution in ethyl acetate is yellow and shows a pale green fluorescence.

5:6-Diacetoxy-7-methyl-7-ethyl- α -dinaphthaxanthen is prepared from 5:6-diketo-7-methyl-7-ethyl-5:6-dihydro- α -dinaphthaxanthen similarly to 5:6-diacetoxy-7:7-dimethyl- α -dinaphthaxanthen. It

crystallises in colourless needles which melt at 242—244° (Found : C = 76·7; H = 5·4. $C_{23}H_{24}O_5$ requires C = 76·4; H = 5·4 per cent.).

$\beta\beta$ -Di-2- α -naphthaquinonylbutane (II) crystallises from glacial acetic acid in yellow laminae which melt at 219—220°. It exhibits all the properties of its lower homologue (Found : C = 77·6; H = 4·9. $C_{24}H_{18}O_4$ requires C = 77·8; H = 4·9 per cent.).

Reduction of $\beta\beta$ -Di-2- α -naphthaquinonylbutane to 5 : 9-Dihydroxy-7-methyl-7-ethyl- α -dinaphthaxanthen (IV).

The reduction proceeds in an entirely analogous manner to that of the corresponding dimethyl compound. Similarly also, the reduction product is quite stable and readily purified.

5 : 9-Dihydroxy-7-methyl-7-ethyl- α -dinaphthaxanthen crystallises from glacial acetic acid in colourless, thick, hexagonal plates containing a molecule of acetic acid of crystallisation, which is removed on exposure to the air (Found : acetic acid = 14·3. $C_{24}H_{20}O_3 \cdot C_2H_4O_2$ requires acetic acid = 14·4 per cent.). The resulting mauve-tinted powder darkens at 285° and melts at 299° (Found : C = 80·9; H = 5·7. $C_{24}H_{20}O_3$ requires C = 80·9; H = 5·6 per cent.). This dihydroxy-compound also crystallises from alcohol; the solution displays a pale violet fluorescence.

5 : 9-Diacetoxy-7-methyl-7-ethyl- α -dinaphthaxanthen, prepared in the usual manner, crystallises from glacial acetic acid in white, warty crystals, which melt at 221—223°. It is sparingly soluble in alcohol (Found : C = 76·3; H = 5·6. $C_{28}H_{24}O_5$ requires C = 76·4; H = 5·5 per cent.).

5 : 9-Dibenzoyloxy-7-methyl-7-ethyl- α -dinaphthaxanthen is formed by heating the dihydroxy-compound with excess of benzoyl chloride for one minute only. The solution is poured into water containing a small amount of alkali, and vigorously stirred, and the product then separates as a white powder. It is sparingly soluble in glacial acetic acid, from which it crystallises well in colourless, short rods melting at 235—237°. It is very soluble in benzene and slightly soluble in alcohol (Found : C = 80·7; H = 5·2. $C_{38}H_{28}O_5$ requires C = 80·8; H = 5·0 per cent.).

5 : 9-Dimethoxy-7-methyl-7-ethyl- α -dinaphthaxanthen.—The addition of methyl sulphate (0·75 gram) to the pale apple-green solution (which rapidly turned dark bottle-green) of the dihydroxy-compound (1·1 grams) in 15 per cent. potassium hydroxide (5 c.c.) caused the deposition of a green precipitate, which turned brown and finally salmon-coloured. The mixture was warmed on the water-bath for a few minutes and separated. The product was crystallised from glacial acetic acid. At first there separated from the solution long,

sword-shaped, pale salmon crystals, then small, pure white, warty crystals. These melted at the same temperature. Repeated crystallisation gave long, ill-defined, colourless crystals, which melted at 228—230° (Found: C = 80.9; H = 6.3. $C_{26}H_{24}O_3$ requires C = 81.2; H = 6.2 per cent.). The substance resembles 5:9-dimethoxy-7:7-dimethyl- α -dinaphthaxanthen in solubility, but appears to be generally more soluble. It crystallises well from amyl alcohol, in which solvent it gives rise to a faint violet fluorescence.

Oxidation of 7:7-Diethyl- α -dinaphthaxanthen (Anhydro- γ -1:1-dihydroxydinaphthylpentane).

The experiment is conducted as given under the oxidation of the corresponding dimethyl and methyl ethyl compounds.

5:6-Diketo-7:7-diethyl-5:6-dihydro- α -dinaphthaxanthen (I) crystallises from glacial acetic acid in large crystals, which are deep orange when prepared in the dark, but rapidly turn scarlet on the surface when exposed to light. The orange crystals melt at 224—227°. It also crystallises well from pyridine, acetone, or amyl alcohol, and is very soluble in alcohol or benzene (Found: C = 81.5; H = 5.4. $C_{25}H_{20}O_3$ requires C = 81.5; H = 5.4 per cent.).

A mononitro-derivative is obtained in the usual way. It crystallises readily from glacial acetic acid in salmon-red crystals, which melt at 282—284° (Found: N = 3.5. $C_{25}H_{19}O_5N$ requires N = 3.4 per cent.).

The quinoxaline crystallises as yellow rods from a solution containing equal volumes of alcohol and glacial acetic acid, or from pyridine diluted with water. It melts at 218—219°, and is very soluble in glacial acetic acid, and sparingly soluble in alcohol (Found: N = 6.3. $C_{31}H_{24}ON_2$ requires N = 6.4 per cent.).

$\gamma\gamma$ -Di-2- α -naphthaquinonylpentane (II) crystallises from glacial acetic acid, or from pyridine, in yellow plates melting at 251°. Fuming nitric acid has no action upon it (Found: C = 78.2; H = 5.1. $C_{25}H_{20}O_4$ requires C = 78.1; H = 5.2 per cent.).

5:9-Dihydroxy-7:7-diethyl- α -dinaphthaxanthen (IV) is prepared from the preceding compound by reduction with zinc in glacial acetic acid. It crystallises from this acid in the form described below. The crystals become opaque at 90° and one molecule of acetic acid is lost. The pink-tinted powder shows signs of change at 250° and melts at 295° with decomposition (Found: acetic acid = 14.0. $C_{25}H_{22}O_3 \cdot C_2H_4O_2$ requires acetic acid = 14.0 per cent. Found: after removal of the acetic acid, C = 80.8; H = 5.8. $C_{25}H_{22}O_3$ requires C = 81.1; H = 5.9 per cent.).

Crystallographic measurement revealed that the crystals obtained

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from acetic acid solution (containing one molecule of acetic acid), are monoclinic, $a : b = 0.834$; $\beta = 104^\circ 42'$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$. The common habit is shown in Fig. 2, and is tabular parallel to $c\{001\}$ and elongated along the b -axis. The crystals are poor; two, however, were found to be measurable, and the mean angular values obtained were :

	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.
ϕ	$89^\circ 53\frac{1}{2}' (+6\frac{1}{2}')$	$*51^\circ 7'$	$88^\circ 16' (+1^\circ 44')$
ρ	$90^\circ 21\frac{1}{2}' (-21\frac{1}{2}')$	$89^\circ 53' (+7')$	$*14^\circ 42'$

Oxidation of 7-Methyl-7-n-propyl- α -dinaphthaxanthen (Anhydro- β -1 : 1-dihydroxydinaphthylpentane).

The reaction is carried out as with the homologues. The viscous reaction mixture deposits the orange and the yellow oxidation products after scratching and long standing; their complete separation is difficult on account of similarity in solubility.

5 : 6-Diketo - 7-methyl-7-n-propyl-5 : 6-dihydro- α -dinaphthaxanthen melts at $219-220^\circ$. It is much more soluble in glacial acetic acid than its homologues (Found: C = 81.5; H = 5.4. $C_{24}H_{20}O_3$ requires C = 81.5; H = 5.4 per cent.).

Attempts to nitrate this compound with fuming nitric acid in glacial acetic acid solution failed. The only product separated from the reaction mixture and identified was phthalic acid.

$\beta\beta$ -Di-2- α -naphthaquinonylpentane (II) crystallises from glacial acetic acid in thick, yellow laminæ melting at $203-204^\circ$. They contain acetic acid of crystallisation, which is removed at 130° . The resulting yellow powder gave C = 78.4; H = 5.4. $C_{25}H_{20}O_4$ requires C = 78.1; H = 5.2 per cent.

Reduction of $\beta\beta$ -Di-2- α -naphthaquinonylpentane to 5 : 9-Dihydroxy-7-methyl-7-n-propyl- α -dinaphthaxanthen (IV).

The reduction product, obtained in the usual way, does not contain acetic acid of crystallisation. It turns slightly brown at 275° , and melts with decomposition at 290° (Found: C = 80.9; H = 6.0. $C_{25}H_{22}O_3$ requires C = 81.1; H = 6.0 per cent.).

Crystallographic examination showed that the crystals are orthorhombic, $a : b : c = 0.704 : 1 : 0.793$. Forms: $b\{010\}$, $a\{100\}$, $o\{111\}$. The common habit (see Fig. 3) is pyramidal, with the pinacoids well developed, although the latter are curved and distorted. Three crystals were measured, and the mean angular values obtained for the form $o\{111\}$ were as follow: ϕ $*54^\circ 51'$; ρ $*54^\circ 1'$.

A *dibenzoyl* derivative of 5 : 9-dihydroxy-7-methyl-7-n-propyl- α -

Fig. 2.

dinaphthaxanthen is obtained in the usual way. It crystallises in colourless rods from glacial acetic acid, and melts at 216—218°. It is almost insoluble in alcohol, very soluble in benzene, and appreciably soluble in carbon tetrachloride.

Summary.

1. The condensation products of α -naphthol and ketones have been shown to be dialkyl substitution products of α -dinaphthaxanthen, in which the alkyl groups are attached to the carbon atom of the pyran ring.

The products examined are those derived from α -naphthol and the ketones, acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone respectively.

2. Oxidation of these 7:7-dialkyl- α -dinaphthaxanthenes has given rise to two series of brightly coloured compounds, orange products containing an ortho-quinonoid grouping, and yellow products containing two para-quinonoid groupings.

3. The orange ortho-diketones are shown to be 5:6-diketo-7:7-dialkyl-5:6-dihydro- α -dinaphthaxanthenes by the preparation therefrom of quinoxalines; and by reduction to hydroxy-compounds, and the formation from these of diacetyl derivatives. The production of a mononitro-derivative and the inability to prepare a dinitro-derivative are in support of the ortho-quinonoid structure, in which one naphthalene ring system is affected and the other unattacked. By further action of the nitrating agent, the orange compounds are oxidised to phthalic acid.

4. The yellow products have been proved to be di-2- α -naphthaquinonyldialkylmethanes by the facts that they do not form quinoxalines and are reducible to 5:9-dihydroxy-7:7-dialkyl- α -dinaphthaxanthenes, the formation of which evidently follows the elimination of water from the intermediately formed tetrahydroxy-reduction products, since stable diacetyl, dibenzoyl, and dimethyl derivatives of the 5:9-dihydroxy-7:7-dialkyl- α -dinaphthaxanthenes have been obtained.

5. The di-2- α -naphthaquinonyldialkylmethanes are unattacked by fuming nitric acid.

6. Their reduction products, 5:9-dihydroxy-7:7-dialkyl- α -dinaphthaxanthenes, have been examined crystallographically.

FIG. 3

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