203. β-*Aroylpropionic Acids. Part IX.* Their Conversion into 1 : 2-Benzanthraquinones.*

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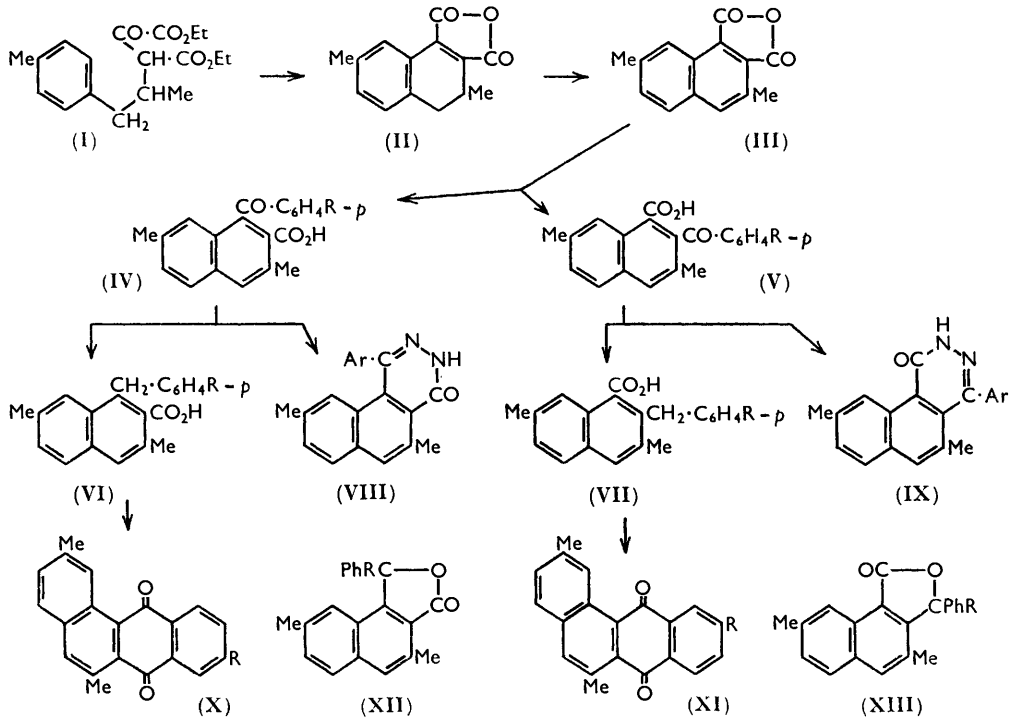
The ester (I) is cyclised with 75% v/v sulphuric acid to 3 : 4-dihydro-3 : 7-dimethylnaphthalene-1 : 2-dicarboxylic anhydride, which is then dehydrogenated to 3 : 7-dimethylnaphthalene-1 : 2-dicarboxylic anhydride. The latter with arylmagnesium halides gives a mixture of 1- and 2-aroyl-3 : 7-dimethyl-2- and -1-naphthoic acid. These are separated and reduced to the corresponding benzylnaphthoic acids, which are cyclised and then oxidised to 1 : 2-benzanthraquinones.

Ethyl β-methyl-γ-*p*-tolylbutyrate [1] was condensed with ethyl oxalate in presence of potassium ethoxide to give the ethoxalyl ester [2] (I), which was cyclised and then dehydrogenated to 3 : 7-dimethylnaphthalene-1 : 2-dicarboxylic anhydride [2] (III). Interaction of this anhydride with phenyl- or *p*-methoxyphenyl-magnesium halide gave a mixture of the aroyl-acids (IV and V; R = H or MeO), the former predominating.



The structure of the acid (IV; R = H) was based on the following facts: (1) On fusion with alkali [3] it gave 3 : 7-dimethyl-2-naphthoic [4] and benzoic acid. (2) It was decarboxylated to 1-benzoyl-3 : 7-dimethylnaphthalene, which on fusion with alkali gave 3 : 7-dimethyl-1-naphthoic acid, 3 : 7-dimethylnaphthalene, and benzoic acid. 3 : 7-Dimethyl-1-naphthoic acid was obtained by refluxing the oxalyl derivative (I) with 30% sulphuric acid and dehydrogenating the product.[2]

* Part VIII, *J.*, 1957, 1699.

[1] Mayer and Stamm, *Ber.*, 1923, **56**, 1424.
[2] Cf. Baddar and Warren, *J.*, 1939, 944.
[3] Cf. Waldmann, *J. prakt. Chem.*, 1930, **127**, 195.
[4] Cf. Coulson, *J.*, 1934, 1406.

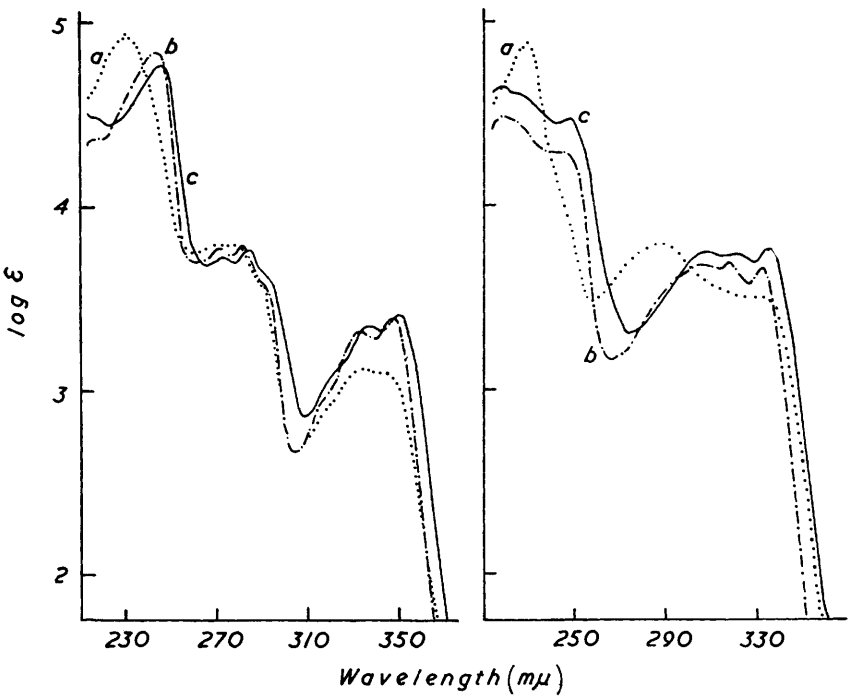
The structure of the isomeric acid (V; R = H) was established as follows: it gave on alkali fission [5] 3 : 7-dimethyl-1-naphthoic acid and benzoic acid; and it was decarboxylated to 2-benzoyl-3 : 7-dimethylnaphthalene, which was cleaved by alkali to 3 : 7-dimethylnaphthalene, benzoic acid, and 3 : 7-dimethyl-2-naphthoic acid.

Attempts to cyclise the keto-acids (IV and V; R = H) directly were not successful. They were, therefore, reduced with hydrazine hydrate in presence of sodium glycollate and ethylene glycol to the benzyl derivatives (VI and VII; R = H). Each reaction mixture contained also a neutral nitrogenous substance, probably the phthalazines (VIII and IX; Ar = Ph).

The benzylnaphthoic acids (VI and VII; R = H) were cyclised with concentrated sulphuric acid to the corresponding 1 : 2-benzanthrones, which were directly oxidised with sodium dichromate to 2′ : 4-dimethyl-1 : 2-benzanthraquinone (X = XI; R = H).

FIG. 1. *Absorption spectra of* (*a*) 3 : 7-*dimethyl-2-naphthoic acid and compounds* (*b*) (XII; R = H) *and* (*c*) (XII; R = Ph).

FIG. 2. *Absorption spectra of* (*a*) 3 : 7-*dimethyl-1-naphthoic acid and compounds* (*b*) (XIII; R = H) *and* (*c*) (XIII; R = Ph).



The measurements were made on a Beckman DU spectrophotometer kindly made available by NAMRO 3, *Cairo.*

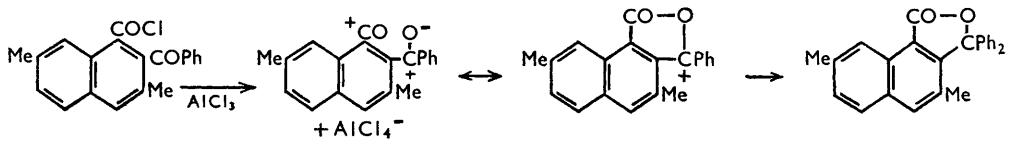
The structure of the keto-acid (IV; R = OMe) was deduced from the fact that on alkali fission it gave 3 : 7-dimethyl-2-naphthoic and *p*-hydroxybenzoic acid. The isomeric acid (V; R = OMe), when similarly treated, was not cleaved but only demethylated. These keto-acids were reduced by zinc dust and alkali to the benzyl acids (VI and VII; R = OMe), which were cyclised and then oxidised to the benzanthraquinones (X and XI; R = OMe).

When the keto-acids (IV and V; R = H) were reduced with zinc amalgam and hydrochloric acid, or with zinc dust and alkali, they gave lactones (XII and XIII; R = H). The infrared spectrum of the former lactone included the characteristic stretching

[5] Cf. Braun, Manz, and Reinsch, *Annalen*, 1929, **468**, 277.

frequency for αβ-unsaturated γ-lactones [6] (1760—1740 cm.$^{-1}$). The absorption spectra of the two lactones (Figs. 1*b* and 2*b*) were identical with those of the corresponding 2- and 1-naphthoic acids (Figs. 1*a* and 2*a*).

When the acid chlorides of the keto-acids (IV and V; R = H) were condensed with benzene in presence of aluminium chloride, they did not give rise to 1 : 2-dibenzoyl-3 : 7-dimethylnaphthalene, but to the diphenyl lactones (XII and XIII; R = Ph). The same lactones were obtained by the action of phenylmagnesium bromide on the keto-acids. The structure of the former lactone follows because it has no ketonic properties and its infrared spectrum is very similar to that of the lactone (XII; R = H), showing the characteristic stretching frequency for αβ-unsaturated γ-lactones. In addition, the ultraviolet spectra of the two lactones (Figs. 1*c* and 2*c*) were identical with those of the lactones (XII and XIII; R = H) and with those of the corresponding 2- and 1-naphthoic acids, respectively. When these lactones (R = Ph) were cleaved with alkali they gave benzoic acid with 3 : 7-dimethyl-2- and -1-naphthoic acid, respectively (cf. the alkali fission of diarylphthalides [7]).



The formation of the lactone (XIII; R = Ph) from 2-benzoyl-3 : 7-dimethyl-1-naphthoyl chloride could be explained according to the annexed scheme.[8] The formation of the keto-acid (IV; R = H or OMe) in a greater proportion than (V; R = H or OMe) may be attributed to deactivation of the 2-carbonyl group towards Grignard reagents either by the electron-repelling character or the bulk of the neighbouring methyl group. The direction of alkali fission of the benzoylnaphthoic acids and benzoylnaphthalenes appears to be governed by the electron density at the carbon atoms attached to the carbonyl group.[9]

Experimental

α- *and* β-*Methyl-γ-oxo-γ*-p-*tolylbutyric Acid*.—A cold stirred mixture of methylsuccinic anhydride (30 g., 1 mol.), toluene (40 g., 1·6 mol.), and acetylene tetrachloride (100 g.) was treated portion-wise with aluminium chloride (50 g., 1·4 mol.) at <5°, stirred for 3 hr. at <5°, then for further 3 hr. at room temperature and for 4 hr. at 60—70°, left overnight, and worked up as usual. The product was crystallised from the least amount of acetic acid, to give α-methyl-γ-oxo-γ-*p*-tolylbutyric acid, m. p. 170—171° (33%). The mother-liquor was evaporated to dryness, and the oily residue crystallised from benzene–light petroleum (b. p. 50—60°) to give the β-methyl acid, m. p. 65—66° (54%) (cf. Mayer and Stamm [1]).

Ethyl β-*Methyl-γ*-p-*tolylbutyrate*.—The above β-methyl-γ-keto-acid was reduced by Martin's method to β-methyl-γ-*p*-tolylbutyric acid, b. p. 160—161°/9 mm., in 89% yield. The ethyl ester, b. p. 130—131°/7 mm., was obtained in 94% yield.

3 : 4-*Dihydro*-3 : 7-*dimethylnaphthalene*-1 : 2-*dicarboxylic Acid* (II).—A stirred suspension of powdered potassium (2 g., 1·15 atom-equiv.) in dry ether (100 ml.) was treated with absolute ethanol (2·4 g., 1·15 mol.); when hydrogen ceased to be evolved, freshly distilled ethyl oxalate (12 g., 1·8 mol.) was added in one portion. The mixture was stirred for ½ hr., then treated with ethyl β-methyl-γ-*p*-tolylbutyrate, left for 3 days with occasional stirring, and then worked up as usual.[2] The crude ethoxalyl derivative was stirred with 75% (v/v) sulphuric acid (50 ml.) at 60—70° for 1·5 hr., then poured into ice-cold water. The solid product was extracted with boiling 10% sodium hydroxide solution, and the insoluble fraction filtered off and identified as

[6] Bellamy, " The Infra-red Spectra of Organic Compounds," Methuen and Co., Ltd., London, 1956, p. 159.
[7] Hubacher, *J. Amer. Chem. Soc.*, 1944, **66**, 255.
[8] Burton and Munday, *J.*, 1957, 1727; Baddeley, *Quart. Rev.*, 1954, **8**, 371.
[9] Baddar and Gindy, *J.*, 1944, 450; 1948, 1231.

3 : 7-dimethyl-1-tetralone [10] (1·5 g.), m. p. and mixed m. p. 51°. The acid precipitated on the acidification of the alkaline solution crystallised (charcoal) from alcohol–benzene, to give 3 : 4-*dihydro*-3 : 7-*dimethylnaphthalene*-1 : 2-*dicarboxylic acid*, m. p. 190—191° (gas evolution), in 75% yield (Found: C, 67·9; H, 5·5. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). Larger batches gave a lower yield.

The *anhydride* was obtained in 81% yield by heating the acid (6·8 g.) with acetyl chloride (30 ml.) for 1 hr. Crystallised from light petroleum (b. p. 50—60°), it had m. p. 119—120° (Found: C, 74·1; H, 5·3. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

The dimethyl ester obtained (72%) from the acid and diazomethane was an oil, b. p. 165—170°/5 mm.

3 : 7-*Dimethylnaphthalene*-1 : 2-*dicarboxylic Anhydride* (III).—The above dihydro-anhydride (2·8 g.) was heated with sulphur (0·8 g.) at 210—215° for 1 hr., then worked up as usual. Crystallisation from benzene gave 3 : 7-*dimethylnaphthalene*-1 : 2-*dicarboxylic anhydride* (91%) as needles, m. p. 225—226° (Found: C, 74·2; H, 4·7. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%). The dehydrogenation was also effected by heating the dihydro-anhydride at 260—270° for 6 hr., or by exposing its benzene solution to sunlight (July) for 30 days.

Dimethyl 3 : 7-*dimethylnaphthalene*-1 : 2-*dicarboxylate*, prepared by heating the dihydro-ester with sulphur as above, had m. p. 113—114° [from light petroleum (b. p. 60—70°)] (Found: C, 71·0; H, 6·2. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

3 : 4-*Dihydro*-3 : 7-*dimethyl*-1-*naphthoic Acid*.—The crude ethoxalyl derivative (I) (19 g.) was refluxed with 30% (v/v) sulphuric acid (70 ml.) for 30 hr.,[2] the solution being allowed to evaporate to 75% of its volume during the last 6 hr. The product was extracted with sodium carbonate solution, and the neutral fraction was crystallised from light petroleum (b. p. 60—70°) to give 3 : 4-dihydro-3 : 7-dimethylnaphthalene-1 : 2-dicarboxylic anhydride (0·5 g.). The acid product was heated in a vacuum; the fraction which boiled at 160—161°/9 mm. and proved to be β-methyl-γ-*p*-tolylbutyric acid, was rejected. The residue was dissolved in sodium carbonate solution (charcoal), reprecipitated, and crystallised from light petroleum (b. p. 50—60°) to give 3 : 4-*dihydro*-3 : 7-*dimethyl*-1-*naphthoic acid* (2·2 g.), m. p. 114—115° (Found: C, 77·3; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%).

3 : 7-*Dimethyl*-1-*naphthoic Acid*.—Dehydrogenation of the dihydro-acid was carried out with sulphur as mentioned above. Crystallisation from benzene–light petroleum (b. p. 50—60°) gave 3 : 7-*dimethyl*-1-*naphthoic acid*, m. p. 204—205° (Found: C, 78·0; H, 6·0. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

Action of Phenylmagnesium Iodide on 3 : 7-*Dimethylnaphthalene*-1 : 2-*dicarboxylic Anhydride*.—Ethereal phenylmagnesium iodide [from iodobenzene (9·8 g.) and magnesium (1·2 g.)] was added portionwise to a benzene solution (300 ml.) of 3 : 7-dimethylnaphthalene-1 : 2-dicarboxylic anhydride (10 g.). The mixture was refluxed for 1 hr., left overnight at room temperature, then worked up as usual. The acid product was fractionally crystallised from benzene, to give 1-*benzoyl*-3 : 7-*dimethyl*-2-*naphthoic acid* (IV; R = H) in rods (5 g.), m. p. 231—232° (Found: C, 78·7; H, 5·0. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%). The *ethyl ester*, obtained by ethanol and hydrogen chloride and crystallised from ethanol, had m. p. 146—147° (Found: C, 79·7; H, 6·0. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·1%).

The benzene mother-liquor was concentrated, and the precipitated mixture of acids (m. p. 192—194°) was repeatedly crystallised from methanol, to give 2-*benzoyl*-3 : 7-*dimethyl*-1-*naphthoic acid* (V; R = H) in needles, m. p. 217—218° (1·8 g.), depressed to 190—200° on admixture with its isomer (Found: C, 79·3; H, 5·5%).

1-*Benzoyl*-3 : 7-*dimethylnaphthalene*.—(i) 3 : 7-Dimethyl-1-naphthoyl chloride (prepared by thionyl chloride) was distilled in a vacuum (180—185°/5 mm.), and the product crystallised from light petroleum (b. p. below 40°); the *chloride* had m. p. 57—58° (Found: Cl, 16·8. $C_{13}H_{11}OCl$ requires Cl, 16·2%). It (2 g.) was dissolved in benzene (4 g.) and carbon disulphide (12 ml.), treated portionwise with aluminium chloride (2 g., 1·5 mol.), then refluxed for 8 hr. The mixture was worked up as usual, and the product distilled (b. p. 230—235°/2 mm.). On crystallisation from light petroleum (b. p. below 40°) 1-*benzoyl*-3 : 7-*dimethylnaphthalene* was obtained in needles (19%), m. p. 84—85° (Found: C, 87·8; H, 6·1. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%).

(ii) 1-Benzoyl-3 : 7-dimethyl-2-naphthoic acid (1 g.) was decarboxylated with copper-bronze (0·2 g.) in quinoline (2 ml.) (nitrobenzene-bath) in the usual manner. The product was

[10] Weissgerber and Kruber, *Ber.*, 1919, **52**, 346.

extracted with alcohol, then crystallised from light petroleum (b. p. below 40°) to give 1-benzoyl-3 : 7-dimethylnaphthalene, m. p. and mixed m. p. 84—85° (82%).

Its 2 : 4-*dinitrophenylhydrazone* crystallised from pyridine to give the α-*isomer* in dark red aggregates, m. p. 244—246° (Found: N, 13·2. $C_{25}H_{20}O_4N_4$ requires N, 12·7%). The pyridine mother-liquor precipitated, on dilution with water, the β-*isomer*, which crystallised from ethanol in orange rods, m. p. 231—232°, depressed to 210—225° on admixture with the α-isomer (Found: N, 11·9%).

2-*Benzoyl*-3 : 7-*dimethylnaphthalene*.—This *ketone* was obtained in 82% yield by decarboxylation of 2-benzoyl-3 : 7-dimethyl-1-naphthoic acid as above. It crystallised from light petroleum (b. p. 60—70°) in needles, m. p. 125—126° (Found: C, 87·6; H, 6·2%). Its 2 : 4-dinitrophenylhydrazone gave the α-*isomer* in red needles (from acetic acid), m. p. 235—236° (Found: N, 12·7%), and the β-*isomer* in yellow needles (from ethanol), m. p. 207—209°, depressed to 180—190° on admixture with the α-isomer (Found: N, 13·6%).

1-(α-*Hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene*.—Phenylmagnesium bromide [from bromobenzene (0·72 g.) and magnesium (0·11 g.)] was refluxed with 1-benzoyl-3 : 7-dimethylnaphthalene (1 g.) in benzene (20 ml.) for 2 hr., left at room temperature overnight, then worked up as usual. 1-(α-*Hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene* (63% yield) had m. p. 173—174° (from methanol) (Found: C, 88·4; H, 6·3; active H, 0·23. $C_{25}H_{22}O$ requires C, 88·7; H, 6·55; active H, 0·29%).

Alkali Fission of 1-*Benzoyl*-3 : 7-*dimethyl*-2-*naphthoic Acid*.—The acid (1 g.) was stirred with fused potassium hydroxide (1·5 g.) heated at 220—225° for 35 min., then worked up as usual. The acid product was boiled with water, filtered off while hot, and crystallised from benzene, to give 3 : 7-dimethyl-2-naphthoic acid (0·62 g.), m. p. 228°, depressed to 175—185° on admixture with 3 : 7-dimethyl-1-naphthoic acid (Found: C, 78·5; H, 6·2. Calc. for $C_{13}H_{12}O_2$: C, 78·0; H, 6·0%). Its anilide melted at 238°.[4] The aqueous mother-liquor was made alkaline, concentrated, and acidified to give benzoic acid (0·15 g.), identified by m. p. and mixed m. p.

Alkali Fission of 2-*Benzoyl*-3 : 7-*dimethyl*-1-*naphthoic Acid*.—The acid (0·6 g.) was heated with alkali (1 g.) at 235—250° for 15 min. The mixture was worked up as in the preceding experiment, to give benzoic (0·08 g.) and 3 : 7-dimethyl-1-naphthoic acid (0·34 g.), m. p. and mixed m. p. 204—205°.

Alkali Fission of 1- *and* 2-*Benzoyl*-3 : 7-*dimethylnaphthalene*.—(i) The former ketone (1·2 g.) was fused with potassium hydroxide (2 g.) at 240—250° for 20 min., then worked up as usual. The neutral product, m. p. 110—111° (from ethanol), proved to be 3 : 7-dimethylnaphthalene (0·6 g.) (Found: C, 92·1; H, 7·5. Calc. for $C_{12}H_{12}$: C, 92·3; H, 7·7%). Its picrate was obtained in yellow needles (from alcohol), m. p. 142—143°.[10] The concentrated alkaline filtrate was acidified to give a mixture from which 3 : 7-dimethyl-1-naphthoic, m. p. 204—205° (0·04 g.), and benzoic acid (0·12 g.) were isolated.

(ii) The latter ketone (1·2 g.) was similarly treated at 255—260°, to give 3 : 7-dimethylnaphthalene (0·48 g.), 3 : 7-dimethyl-2-naphthoic acid (0·12 g.), and benzoic acid (0·08 g.).

Di-(1-*benzoyl*-3 : 7-*dimethyl*-2-*naphthoic*) *Anhydride*.—A solution of the acid (0·6 g.) in dry carbon tetrachloride (30 ml.) was refluxed with phosphoric oxide (2 g.) for 4 hr. The mixture was decomposed with dilute hydrochloric acid, and the product crystallised from benzene, to give the *anhydride* (85%), m. p. 290—291° (Found: C, 81·2; H, 5·3. $C_{40}H_{30}O_5$ requires C, 81·3; H, 5·1%).

Di-(2-*benzoyl*-3 : 7-*dimethyl*-1-*naphthoic*) *anhydride* was similarly prepared (82%) (refluxing for 1 hr.; then storage overnight) and had m. p. 304—305° (from benzene) (Found: C, 80·9; H, 5·0%).

The anhydrides were converted into the acids when refluxed with 10% sodium hydroxide solution for 1 hr.

1-α-*Hydroxybenzyl*-3 : 7-*dimethylnaphthalene*-2-*carboxylic Lactone* (XII; R = H).—1-Benzoyl-3 : 7-dimethyl-2-naphthoic acid (2 g.), reduced by Martin's method (30 hr.), gave 1-α-*hydroxybenzyl*-3 : 7-*dimethylnaphthalene*-2-*carboxylic lactone* (64%) (from methanol), m. p. 196—197° (Found: C, 83·1; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

2-α-*Hydroxybenzyl*-3 : 7-*dimethylnaphthalene*-1-*carboxylic Lactone* (XIII; R = H).—This *lactone* was similarly prepared (70%) by the reduction of 2-benzoyl-3 : 7-dimethyl-1-naphthoic acid. It had m. p. 213—214° (from methanol) (Found: C, 83·5; H, 5·5%).

The same lactones were obtained when the reduction was carried out with zinc dust and 10% sodium hydroxide solution in presence, or in absence, of toluene (20 hours' refluxing).

Alkali Fission of 1- *and* 2-α-*Hydroxybenzyl*-3 : 7-*dimethylnaphthalene*-2- *and* -1-*carboxylic Lactone*.—The lactones were fused with potassium hydroxide at 240—250° for 10 and 20 min., respectively, then worked up as mentioned before. The product contained 3 : 7-dimethyl-2-naphthoic (71%) and 3 : 7-dimethyl-1-naphthoic acid (59%), respectively, together with a small amount of benzoic acid.

1-α-*Hydroxybenzyl*-3 : 7-*dimethyl*-2-*naphthylmethanol*.—1-Benzoyl-3 : 7-dimethyl-2-naphthoic acid (1 g.) was reduced with lithium aluminium hydride (1·5 g.) in ether (30 ml.) and benzene (40 ml.) (6 hours' refluxing), to give 1-α-*hydroxybenzyl*-3 : 7-*dimethyl*-2-*naphthylmethanol* (73%), m. p. 112—113° [from light petroleum (b. p. 60—70°)] (Found: C, 81·7; H, 7·1; active H, 0·59. $C_{20}H_{20}O_2$ requires C, 82·15; H, 6·9; active H, 0·68%).

2-α-*Hydroxybenzyl*-3 : 7-*dimethyl*-1-*naphthylmethanol* was similarly prepared (63%) from 2-benzoyl-3 : 7-dimethyl-1-naphthoic acid (0·5 g.) (10 hours' refluxing), and had m. p. 145—146° [from benzene–light petroleum (b. p. 40—60°)] (Found: C, 82·1; H, 6·6; active H, 0·72%).

When these alcohols (0·6 g.) were oxidised with potassium permanganate (0·5 g.) in 80% (v/v) aqueous acetone (100 ml.) overnight, they gave 1-benzoyl-3 : 7-dimethyl-2-naphthoic and 2-benzoyl-3 : 7-dimethyl-1-naphthoic acid, respectively.

1-*Benzyl*-3 : 7-*dimethyl*-2-*naphthoic Acid* (VI; R = H).—A mixture of 1-benzoyl-3 : 7-dimethyl-2-naphthoic acid (0·5 g.), anhydrous ethylene glycol (5 g.), sodium glycollate (from 0·5 g. of sodium), and 90% hydrazine hydrate (2 g.) was refluxed for 1·5 hr. at 115—120°. The condenser was removed and the temperature of the mixture raised to 220—230° and kept thereat for 6 hr. The whole was worked up as usual. The acid product was crystallised from benzene–light petroleum (b. p. 60—80°), to give 1-*benzyl*-3 : 7-*dimethyl*-2-*naphthoic acid* (30%), m. p. 190—191° (Found: C, 82·5; H, 6·2. $C_{20}H_{18}O_2$ requires C, 82·7; H, 6·25%). The neutral product crystallised from acetic acid, to give 1 : 2-*dihydro*-8 : 2′-*dimethyl*-1-*oxo*-4-*phenyl*-5 : 6-*benzophthalazine* (cf. VIII) (20%), m. p. 302—303° (Found: C, 79·4; H, 5·4; N, 9·2. $C_{20}H_{16}ON_2$ requires C, 80·0; H, 5·4; N, 9·3%). It contained no active hydrogen. Lowering the temperature of the reaction to 200° increased the amount of the neutral product.

2-*Benzyl*-3 : 7-*dimethyl*-1-*naphthoic Acid* (VII; R = H).—This was prepared by reducing 2-benzoyl-3 : 7-dimethyl-1-naphthoic acid with hydrazine hydrate (heating at 130° for 2 hr., then at 260—265° for further 2 hr.). The acid product was crystallised from benzene–light petroleum (b. p. 60—80°) to give 2-*benzyl*-3 : 7-*dimethyl*-1-*naphthoic acid* (34%), m. p. 203—204° (Found: C, 82·6; H, 6·4%). The neutral product crystallised from dioxan, to give 1 : 2-*dihydro*-5 : 3′-*dimethyl*-1-*oxo*-4-*phenyl*-6 : 8-*benzophthalazine* (cf. IX) (25%), m. p. 338—340° (Found: C, 79·3; H, 5·6; N, 9·3%).

2′ : 4-*Dimethyl*-1 : 2-*benzanthraquinone* (X or XI; R = H).—1(or 2)-Benzyl-2(or 1)-naphthoic acid (0·5 g.) was dissolved in concentrated sulphuric acid (8 ml.) and kept at room temperature for 2 hr., then worked up as usual. The benzanthrone formed, which failed to crystallise, was directly oxidised by sodium dichromate (0·7 g.) in acetic acid solution (20 ml.) (½ hr. at room temperature). The product precipitated on dilution with water crystallised from light petroleum (b. p. 40—60°), to give 2′ : 4-dimethyl-1 : 2-benzanthraquinone [11] in yellow needles (70%), m. p. 173° (Found: C, 83·2; H, 4·6. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%).

Action of p-*Methoxyphenylmagnesium Bromide on* 3 : 7-*Dimethylnaphthalene*-1 : 2-*dicarboxylic Anhydride*.—The Grignard reagent [from *p*-bromoanisole (7 g.) and magnesium (0·8 g.)] was added to a solution of 3 : 7-dimethylnaphthalene-1 : 2-dicarboxylic anhydride (8 g.) in benzene (200 ml.)–ether (100 ml.), then refluxed for 1·5 hr. and worked up as usual. The acid product was refluxed with benzene, then extracted with sodium carbonate solution. The benzene solution gave on evaporation unchanged anhydride (0·2 g.). The acid precipitated on acidification of the alkaline extract was crystallised from the least amount of benzene, to give 1-p-*methoxybenzoyl*-3 : 7-*dimethyl*-2-*naphthoic acid* (31%), m. p. 202—203° (Found: C, 75·7; H, 5·7; OMe, 8·9. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4; OMe, 9·3%). The benzene mother-liquor was evaporated, and the residue was triturated with hot light petroleum (b. p. 60—80°), then crystallised from benzene–light petroleum (b. p. 60—80°)to give 2-p-*methoxybenzoyl*-3 : 7-*dimethyl*-1-*naphthoic acid* (12%), m. p. 178—179°, depressed to 160—170° on admixture with the above isomer (Found: C, 75·5; H, 5·5; OMe, 8·6%).

Alkali Fission of 1-p-*Methoxybenzoyl*-3 : 7-*dimethyl*-2-*naphthoic Acid*.—The acid (0·5 g.) was stirred with fused potassium hydroxide (1 g.) at 230—240° for ½ hr., then worked up as usual. The product contained 3 : 7-dimethyl-2-naphthoic acid (0·2 g., 66%), and *p*-hydroxybenzoic

[11] Fieser and Fieser, *J. Amer. Chem. Soc.*, 1933, **55**, 3342.

acid (0·08 g., 39%), m. p. 200—203°, raised to 204—206° on admixture with an authentic specimen.

Alkali Fission of 2-p-*Methoxybenzoyl*-3 : 7-*dimethyl*-1-*naphthoic Acid.*—The fusion was carried out as above, the product was crystallised from benzene to give 2-p-*hydroxybenzoyl*-3 : 7-*dimethyl*-1-*naphthoic acid*, m. p. 210—212° (62%), depressed to 180—190° on admixture with 3 : 7-dimethyl-1-naphthoic acid (Found: C, 75·1; H, 5·2; OMe, 0. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

1-p-*Methoxybenzyl*-3 : 7-*dimethyl*-2-*naphthoic Acid* (VI; R = OMe).—A solution of 1-*p*-methoxybenzoyl-3 : 7-dimethyl-2-naphthoic acid (1 g.) in 10% sodium hydroxide solution (50 ml.) was refluxed with zinc dust (2 g.) for 20 hr., then worked up as usual, to give 1-p-*methoxybenzyl*-3 : 7-*dimethyl*-2-*naphthoic acid* in needles, m. p. 225—226° (from benzene) (0·35 g., 36%) (Found: 78·7; H, 6·5; OMe, 9·6. $C_{21}H_{20}O_3$ requires C, 78·7; H, 6·3; OMe, 9·7%). The neutral product crystallised from methanol, to give 1-α-*hydroxy*-p-*methoxybenzyl*-3 : 7-*dimethylnaphthalene*-2-*carboxylic lactone* in needles, m. p. 202—203° (0·2 g., 20%) (Found: C, 78·7; H, 5·9; OMe, 9·3. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7; OMe, 9·7%).

2-p-*Methoxybenzyl*-3 : 7-*dimethyl*-1-*naphthoic Acid* (VII; R = OMe).—The corresponding keto-acid (0·6 g.) was similarly reduced with zinc dust (2 g.) to give 2-p-*methoxybenzyl*-3 : 7-*dimethyl*-1-*naphthoic acid*, m. p. 212—213° [from benzene–light petroleum (b. p. 40—60°)] (0·2 g.; 34%) (Found: C, 78·8; H, 6·3; OMe, 9·0%).

6-*Methoxy*-2′ : 4-*dimethyl*-1 : 2-*benzanthraquinone* (X; R = OMe).—A solution of 1-*p*-methoxybenzyl-3 : 7-dimethyl-2-naphthoic acid (0·5 g.) in concentrated sulphuric acid (6 ml.) was left at room temperature (30—32°) for 4 hr., then worked up as usual. The resulting benzanthrone was oxidised with sodium dichromate (0·7 g.) in acetic acid (15 ml.) as mentioned above. On crystallisation from ethanol 6-*methoxy*-2′ : 4-*dimethyl*-1 : 2-*benzanthraquinone* was obtained in brownish-yellow needles, m. p. 165—166° (0·35 g., 70%) (Found: C, 79·5; H, 4·9; OMe, 9·6. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1; OMe, 9·8%). It gave a blue solution with concentrated sulphuric acid.

7-*Methoxy*-2′ : 4-*dimethyl*-1 : 2-*benzanthraquinone* (XI; R = OMe).—2-*p*-Methoxybenzyl-3 : 7-dimethyl-1-naphthoic acid (0·2 g.) was similarly cyclised with concentrated sulphuric acid (4 ml.), then oxidised with sodium dichromate (0·3 g.) in acetic acid (10 ml.) at the b. p. for 5 min. The product crystallised from ethanol, to give 7-*methoxy*-2′ : 4-*dimethyl*-1 : 2-*benzanthraquinone* in fine yellow needles (0·15 g., 76%), m. p. 182—183°, depressed to 150—155° on admixture with the above isomer (Found: C, 79·0; H, 5·2; OMe, 9·3%). It gave a violet solution with concentrated sulphuric acid.

1-*Benzoyl*-3 : 7-*dimethyl*-2-*naphthoyl Chloride.*—The acid (1 g.) was treated with thionyl chloride (2 g.) for 1 hr.; the product crystallised from light petroleum (b. p. below 40°) to give 1-*benzoyl*-3 : 7-*dimethyl*-1-*naphthoyl chloride*, m. p. 163—165° (0·8 g., 76%) (Found: Cl, 11·0. $C_{20}H_{15}O_2Cl$ requires Cl, 11·0%).

2-*Benzoyl*-3 : 7-*dimethyl*-1-*naphthoyl chloride*, similarly prepared in 94% yield, had m. p. 149—150° [from light petroleum (b. p. 40—60°)] (Found: Cl, 10·75%).

1-(α-*Hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene*-2-*carboxylic Lactone* (XII; R = Ph).—(i) A solution of 1-benzoyl-3 : 7-dimethyl-2-naphthoyl chloride (1 g.) in a mixture of carbon disulphide (20 ml.) and benzene (1 g.) was treated with aluminium chloride (1 g.), refluxed for 4 hr., then worked up as usual. The neutral product was crystallised from ethanol, to give 1-(α-*hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene*-2-*carboxylic lactone* in needles, m. p. 225—226° (0·8 g., 71%) (Found: C, 85·3; H, 5·4. $C_{26}H_{20}O_2$ requires C, 85·7; H, 5·5%). It contained no active hydrogen. The m. p. was depressed to 200—212° on admixture with the original keto-acid.

(ii) Di-(1-benzoyl-3 : 7-dimethyl-2-naphthoic) anhydride (1 g.) was treated as in (i). The product contained a mixture of 1-benzoyl-3 : 7-dimethyl-2-naphthoic acid (0·35 g.) and 1-(α-hydroxy-αα-diphenylmethyl)-3 : 7-dimethylnaphthalene-2-carboxylic lactone (0·6 g.).

(iii) The Grignard reagent [from bromobenzene (1·25 g.) and magnesium (0·2 g.)] was added portionwise to a boiling solution of 1-benzoyl-3 : 7-dimethyl-2-naphthoic acid (1 g.) in benzene (50 ml.)–ether (10 ml.), refluxed for 4 hr., then worked up as usual. The neutral product was triturated with light petroleum (b. p. <40°), with few drops of methanol, then crystallised from ethanol to give 1-(α-hydroxy-αα-diphenylmethyl)-3 : 7-dimethylnaphthalene-2-carboxylic lactone (17% yield), m. p. 225—226° (decomp.), undepressed on admixture with the products obtained by methods (i) and (ii).

2-(α-*Hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene*-1-*carboxylic Lactone* (XIII; R = Ph).—This was prepared from 2-benzoyl-3 : 7-dimethyl-1-naphthoyl chloride, the anhydride, or the free acid by the three methods adopted for its isomer in 73, 72, and 34% yield, respectively. It crystallised from ethanol in needles, m. p. 231—232°, depressed to 190—200° when admixed with its isomer (Found: C, 85·1; H, 5·6%). It contained no active hydrogen.

Both lactones were recovered unchanged when refluxed with 10% alcoholic potassium hydroxide solution for 12 hr.

Alkali Fission of 1-(α-*Hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene*-2-*carboxylic Lactone*.—The lactone (0·4 g.) was stirred with fused potassium hydroxide (1 g.) at 265—270° for 20 min., then worked up as usual. The acid product crystallised from benzene to give 3 : 7-dimethyl-2-naphthoic acid in 90% yield. A small amount of crude benzoic acid was isolated.

Alkali Fission of 2-(α-*Hydroxy*-αα-*diphenylmethyl*)-3 : 7-*dimethylnaphthalene*-1-*carboxylic Lactone*.—When the fusion was carried out as above, 3 : 7-dimethyl-1-naphthoic acid was obtained in 73% yield, together with a small amount of crude benzoic acid.

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