350. *γγ-Disubstituted Itaconic Acids. Part II.* The Conversion of β-Ethyl α-Hydrogen γ-α-Naphthyl-γ-phenylitaconate into 1-Methoxy-4-phenylphenanthrene and 7-Methoxynaphtho[2,1-c]fluoren-9-one.*

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β-Ethyl α-hydrogen *cis*(Ph/CO_2Et)-γ-α-naphthyl-γ-phenylitaconate is cyclised to ethyl 1-acetoxy-4-phenylphenanthrene-3-carboxylate. The derived phenolic acid (IIb) is converted into 1-methoxy-4-phenylphenanthrene. This acid is cyclised to 7-methoxynaphtho[2,1-*c*]fluoren-9-one which is obtained also from the corresponding itaconic anhydride.

1-Benzoylnaphthalene with diethyl succinate in presence of potassium t-butoxide gives β-ethyl α-hydrogen *cis*(Ph/CO_2Et)-γ-α-naphthyl-γ-phenylitaconate (I). Its structure was assigned by converting it into (probably) 1-methoxy-4-phenylphenanthrene (IIe).

The half-ester (I) was cyclised with sodium acetate in acetic anhydride, giving ethyl 1-acetoxy-4-phenylphenanthrene-3-carboxylate (IIa). The derived phenolic acid (IIb)

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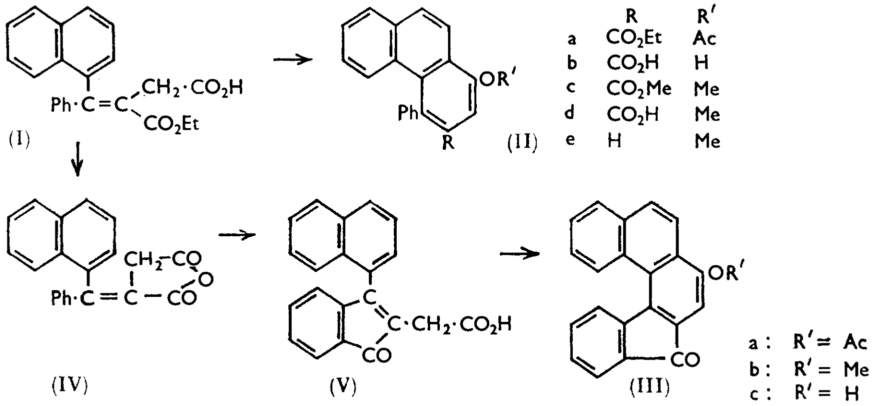
* γγ-Diarylitaconic Acids, *J. Chem. U.A.R.*, 1960, **3**, No. 1, 35, is considered as Part I.

was converted by alkaline dimethyl sulphate into the methoxy-ester (IIc), which was hydrolysed to 1-methoxy-4-phenylphenanthrene-3-carboxylic acid (IId), then decarboxylated to 1-methoxy-4-phenylphenanthrene (IIe).

The structure (IIe) was inferred from the following facts: (i) It depressed the melting point of 4-methoxy-1,1′-binaphthyl prepared by condensing 1-iodo-4-methoxynaphthalene[1] with 1-bromo-2-naphthoic ester in the presence of copper-bronze and decarboxylating the resulting acid. 4-Methoxy-1,1′-binaphthyl would be the final product if the *trans*-(Ph/CO_2Et)-isomer of the acid (I) were subjected to the above reactions. (ii) The ultraviolet spectrum of the ester (IIa) showed maxima at 225 (log ε 4·55) and 257 mμ (log ε 4·61), identical with those of 4-phenylphenanthrene[2] but different from those of 4-methoxy-1,1′-binaphthyl.



Cyclisation of the acid (IId) with phosphoric oxide gave 7-methoxynaphtho[2,1-*c*]-fluoren-9-one (IIIb). The same fluorenone was obtained from the itaconic anhydride (IV) as follows. The anhydride was cyclised with aluminium chloride in nitrobenzene to 3-α-naphthyl-(1-oxo-2-indenyl)acetic acid (V). This was cyclised with acetic anhydride and sodium acetate to the naphthofluorenone (IIIa), which was hydrolysed and then methylated, giving the preceding naphthofluorenone (IIIb).

The infrared spectrum of the acetoxyfluorenone (IIIa) showed stretching frequencies at 1748m, 1700s, and 1200s cm.$^{-1}$, characteristic[3] of aryl acetates, unsaturated cyclic ketones, and the C–O bond of phenolic acetates. The two bands for the acetate group at 1748 and 1200 cm.$^{-1}$ were not present in the spectrum of the ether (IIIb), which showed only a carbonyl stretching frequency at 1710 cm.$^{-1}$.

The fact that 1-benzoylnaphthalene gives on condensation with diethyl succinate *cis*(Ph/CO_2Et)-itaconic acid (I), whereas 6-benzoyltetralin gives a mixture of β-ethyl α-hydrogen *cis*- and *trans*-(Ph/CO_2Et)-γ-phenyl-(5,6,7,8-tetrahydro-2-naphthyl)itaconate,[4] can be explained by consideration of the different conformations of the ion (VI) produced before the formation of the intermediate paraconic acid (VIII). In the case of 1-benzoylnaphthalene, the most stable conformation which is favourable for the formation of the paraconic acid is represented by (VII), in which the bulky naphthyl group is eclipsed with the small hydrogen atom. Extraction of the proton by the basic catalyst (Bu^tO^-) is accompanied by the opening of the lactone ring (cf. VIII) to give the *cis*-itaconic half-ester. However, in the case of 6-benzoyltetralin the tetrahydronaphthyl group can be considered as a 3,4-disubstituted phenyl group. Thus, the two conformations, in which

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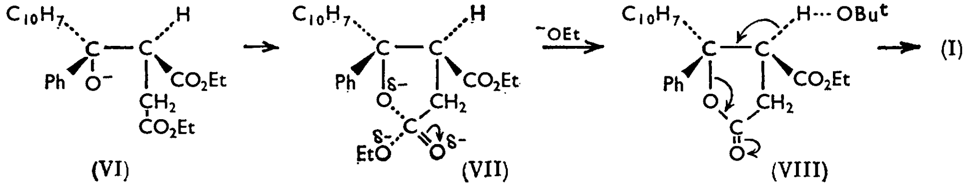
[1] Baddar, El-Assal, and Baghos, *J.*, 1958, 989.

[2] Campbell, *J.*, 1945, 3659.

[3] (*a*) Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1960, pp. 138, 179, 182; (*b*) Hartwell, Richards, and Thompson, *J.*, 1948, 1439.

[4] Hewett, *J.*, 1942, 585.

the hydrogen atom is eclipsed severally with the phenyl and the tetrahydronaphthyl groups, can exist and so *cis*- and *trans*-itaconic half-esters are produced.



The stereochemical configuration of the acids derived from the latter two half-esters is under investigation.

EXPERIMENTAL

Infrared spectra were measured on a Perkin–Elmer Infracord model 137 spectrophotometer for Nujol mulls. Ultraviolet spectra were measured on Zeiss model PMQ II spectrophotometer for ethanol solutions.

β-*Ethyl* α-*Hydrogen* cis(Ph/CO_2Et)-γ-(α-*naphthyl*)-γ-*phenylitaconate* (I).—A solution of potassium t-butoxide [from potassium (4 g.) and t-butyl alcohol (90 ml.)] was treated during 20 min. with a mixture of diethyl succinate (36 g.) and 1-benzoylnaphthalene (24 g.) in t-butyl alcohol (30 ml.), then heated for further 55 min. and worked up as usual.[5,6] The product (20 g.) was oily.

Ethyl 1-*Acetoxy*-4-*phenylphenanthrene*-3-*carboxylate* (IIa).—The crude half-ester (10 g.), sodium acetate (3 g.), and acetic anhydride (45 ml.) were refluxed for 6 hr. and worked up as described by Baddar *et al.*[5] The product crystallised from light petroleum (b. p. 60—80°), to give *ethyl* 1-*acetoxy*-4-*phenylphenanthrene*-3-*carboxylate* (11 g.), m. p. 130—131° (Found: C, 78·0; H, 5·3. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%). It (10 g.) was hydrolysed with 10% alcoholic potassium hydroxide (100 ml.) to the phenolic acid (IIb) (5 g.).

Methyl 1-*Methoxy*-4-*phenylphenanthrene*-3-*carboxylate* (IIc).—The phenolic acid (IIb) (3·5 g.) was heated with dimethyl sulphate (6·5 g.), sodium hydroxide (6 g.), and water (30 ml.) on a boiling-water bath for 30 min. Crystallisation of the product from methanol gave the *ether–ester* (3·8 g.), m. p. 133° (Found: C, 80·2; H, 5·3; OMe, 18·5. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3; OMe, 18·4%).

1-*Methoxy*-4-*phenylphenanthrene*-3-*carboxylic Acid* (IId).—The methoxy-ester (IIc) (3·5 g.) was hydrolysed with 10% alcoholic potassium hydroxide (40 ml.) and worked up as usual. The *acid* (2·5 g.) had m. p. 214° (from methanol) (Found: C, 79·9; H, 4·9; OMe, 9·3. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9; OMe, 9·45%).

1-*Methoxy*-4-*phenylphenanthrene* (IIe).—1-Methoxy-4-phenylphenanthrene-3-carboxylic acid (1 g.) was decarboxylated by heating it with copper-bronze (2 g.) in quinoline (8 ml.) for 4 hr. and worked up as usual.[5] 1-*Methoxy*-4-*phenylphenanthrene* (0·8 g.) had m. p. 98° [from light petroleum (b. p. 30—50°)] (Found: C, 88·6; H, 5·9; OMe, 12·6. $C_{21}H_{16}O$ requires C, 88·7; H, 5·7; OMe, 10·9%).

7-*Acetoxynaphtho*[2,1-c]*fluoren*-9-*one* (IIIa).—The half-ester (I) (10 g.) was hydrolysed with refluxing 5% alcoholic potassium hydroxide (100 ml.) for 2 hr. Working up as usual gave a semi-solid acid (*ca.* 5 g.) that was converted into its anhydride (IV) by refluxing acetyl chloride (50 ml.) in 1 hr. This anhydride (4 g.), which failed to crystallise, was cyclised with aluminium chloride (1·5 g.) in nitrobenzene (40 ml.). The product, worked up as described by Baddar *et al.*,[5] crystallised from benzene–light petroleum (b. p. 30—50°) to give 3-α-*naphthyl*-(1-*oxo*-2-*indenyl*)*acetic acid* (V) (3·7 g.), m. p. 176°. This acid (3·2 g.) was refluxed with sodium acetate (1·3 g.) and acetic anhydride (35 ml.) for 6 hr., then worked up as before. Crystallisation of the product from glacial acetic acid gave 2-*acetoxynaphtho*[2,1-*a*]*fluorenone* (3·3 g.), m. p. 209° (Found: C, 81·1; H, 4·4. $C_{23}H_{14}O_3$ requires C, 81·6; H, 4·2%).

7-*Methoxynaphtho*[2,1-c]*fluoren*-9-*one* (IIIb).—(i) A solution of 1-methoxy-4-phenylphenanthrene-3-carboxylic acid (1 g.) in benzene (50 ml.) was refluxed with phosphoric oxide (1·3 g.)

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[5] Baddar, El-Assal, and Baghos, *J.*, 1955, 1714.

[6] Johnson and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 511.

for 2 hr. and worked up as usual. The product crystallised from benzene to give the 2-*methoxynaphthofluorenone* (0·85 g.) as red needles, m. p. 177—178° (Found: C, 84·6; H, 4·5; OMe, 9·7. $C_{22}H_{14}O_2$ requires C, 85·1; H, 4·5; OMe, 10·0%).

(ii) The acetate (IIIa) (2 g.) was boiled with N-sodium hydroxide (10 ml.) for 2 hr. and worked up as usual and the phenol (IIIc) (1·7 g.) was methylated with dimethyl sulphate (2·5 g.) and potassium carbonate (2·5 g.) in anhydrous acetone (45 ml.) (10 hours' refluxing). Crystallisation of the product gave the ether (IIIb) (1·8 g.) as red needles, m. p. and mixed m. p. 178—179° (Found: C, 85·4; H, 4·6; OMe, 10·0%).

4'-*Methoxy*-1,1'-*binaphthyl*-2-*carboxylic acid.*—1-Iodo-4-methoxynaphthalene (6 g.),[1] ethyl 1-bromo-2-naphthoate (6 g.), and copper-bronze (9·5 g.) were heated for 6 hr. at 265—270° (ethyl cinnamate bath) with stirring, then worked up as usual.[5] The oily product was hydrolysed with 8% methanolic sodium hydroxide (100 ml.), and the precipitated acid (1·5 g.) crystallised from benzene, giving the *binaphthyl-acid*, m. p. 228—229° (Found: C, 80·6; H, 5·0; OMe, 7·3. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9; OMe, 9·45%).

4-*Methoxy*-1,1'-*binaphthyl.*—The preceding acid (1 g.) was decarboxylated as above at 205—210° (nitrobenzene bath). The product crystallised from ether, giving 4-*methoxy*-1,1'-*binaphthyl* (0·8 g.), m. p. 179—180° (Found: C, 88·8; H, 5·6; OMe, 10·5. $C_{21}H_{16}O$ requires C, 88·7; H, 5·7; OMe, 10·9%), $\lambda_{max.}$ 222 (log ε 4·75) and 297 mμ (log ε 4·16) (identical with $\lambda_{max.}$ of 1,1'-binaphthyl [7]).

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[7] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1955, p. 245.