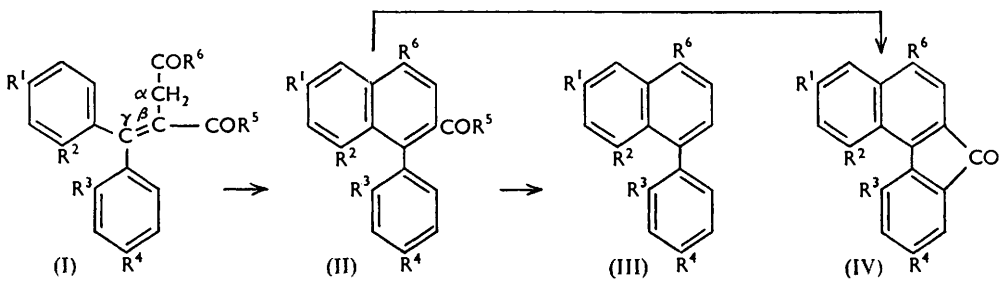
198. 1-*Phenylnaphthalenes. Part IV.* The Cyclisation of Methyl Hydrogen* cis- *and* trans-γ-o-*Methoxyphenyl- and Ethyl Hydrogen* cis- *and* trans-γ-p-*Methoxyphenyl-γ-phenylitaconate to the Corresponding* 1-*Phenylnaphthalenes.*

By F. G. Baddar, Lanson S. El-Assal, and (Mrs.) Victorine B. Baghos.

β-Methyl α-hydrogen *cis-* and *trans-γ-o*-methoxyphenyl-γ-phenylitaconate are converted by acetic anhydride and sodium acetate into methyl 4-acetoxy-8-methoxy-1-phenyl- and methyl 4-acetoxy-1-*o*-methoxyphenyl-2-naphthoate, respectively. The ethyl esters of the *cis-* and *trans-p*-methoxy-isomers give, when similarly treated, ethyl 4-acetoxy-6-methoxy-1-phenyl- and ethyl 4-acetoxy-1-*p*-methoxyphenyl-2-naphthoate, respectively. The acetoxy-compounds are hydrolysed, then methylated and cyclised to the corresponding dimethoxy-3 : 4-benzofluorenones.

cis- and *trans-γ-p-* and *cis-γ-o*-Methoxyphenyl-γ-phenylitaconic anhydride yield with aluminium chloride the corresponding 1-oxo-2-indenylacetic acids, which are cyclised, then methylated to the corresponding dimethoxy-3 : 4-benzofluorenones, identical with the above compounds. However, the *trans-γ-o*-methoxyphenyl-isomer, when similarly treated, gives 4-phenyl-3-coumarinylacetic acid.

The present investigation, a continuation of a previous study (Part II),[1] deals with the Stobbe condensation of monosubstituted benzophenones with succinic esters which gives two stereoisomeric γγ-diarylitaconic acids.



Unless otherwise stated, R¹ to R⁴ are H.

Condensation of 2-methoxybenzophenone with dimethyl succinate gave a mixture of the expected stereoisomeric β-methyl α-hydrogen *cis-* (I; $R^2 = R^5 = OMe$, $R^6 = OH$) † and *trans-γ-o*-methoxyphenyl-γ-phenylitaconate (I; $R^3 = R^5 = OMe$, $R^6 = OH$), from which the latter was obtained crystalline and on hydrolysis gave the *trans*-acid. The mixed esters were cyclised by sodium acetate in acetic anhydride to a mixture from which both esters (II; $R^2 = R^5 = OMe$, $R^6 = OAc$) and (II; $R^3 = R^5 = OMe$, $R^6 = OAc$) were isolated. The derived phenolic acids were converted by methyl sulphate and potassium carbonate in acetone into the dimethoxy-esters (II; $R^2 = R^5 = R^6 = OMe$) and (II; $R^3 = R^5 = R^6 = OMe$), respectively. These were hydrolysed to the acids ($R^5 = OH$) which were decarboxylated to the 1-phenylnaphthalenes (III; R^2 or $R^3 = OMe$, $R^6 = OMe$). The product (III; $R^3 = R^6 = OMe$) was found to be identical with a specimen prepared as follows: α-Methoxynaphthalene was nitrated in acetic acid to 1-methoxy-4-nitronaphthalene [2] which was reduced by aluminium amalgam in ether to 1-methoxy-4-naphthylamine. The amine hydrochloride was converted as usual into

* Part III, *J.*, 1956, 395.

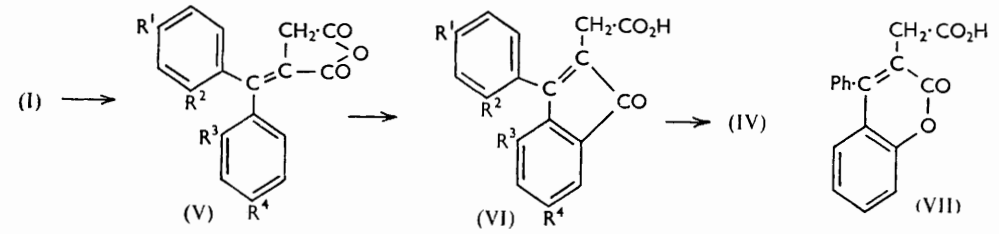
† Here and throughout this paper, all R's are H unless otherwise specified.

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

[2] Hodgson and Smith, *J.*, 1935, 671.

1-iodo-4-methoxynaphthalene,[3] identical with that obtained by the direct iodination of α-methoxynaphthalene with iodine and mercuric oxide in carbon tetrachloride.[4] Ullmann condensation of this iodo-compound with methyl 3-iodo-4-methoxybenzoate gave methyl 4 : 2′-dimethoxy-1-phenylnaphthalene-5′-carboxylate, which on hydrolysis and decarboxylation gave 4-methoxy-1-*o*-methoxyphenylnaphthalene (III; $R^3 = R^6 = OMe$). The acid (II; $R^5 = OH$, $R^2 = R^6 = OMe$) gave, on cyclisation with phosphoric oxide, 2 : 4′-dimethoxy-3 : 4-benzofluorenone (IV; $R^2 = R^6 = OMe$), whereas the acid (II; $R^5 = OH$, $R^3 = R^6 = OMe$) was best cyclised with phosphorus oxychloride [5] in *s*-tetrachloroethane, giving 2 : 5-dimethoxy-3 : 4-benzofluorenone (IV; $R^3 = R^6 = OMe$). However, cyclisation of the latter acid with phosphoric oxide afforded a mixture of the coloured fluorenone and colourless 4-methoxy-1-*o*-methoxyphenyl-2-naphthoic anhydride (predominant).

The crude mixture of acid (I; R^2 or $R^3 = R^5 = OMe$, $R^6 = OH$) was hydrolysed with 10% aqueous-alcoholic potassium hydroxide and *cis*- (I; $R^2 = OMe$, $R^5 = R^6 = OH$) and *trans*-γ-*o*-methoxyphenyl-γ-phenylitaconic acid (I; $R^3 = OMe$, $R^5 = R^6 = OH$) were separated by fractional crystallisation. The configuration of these acids was inferred as follows: (i) The *cis*-anhydride (V; $R^2 = OMe$) was converted by aluminium chloride in



Unless otherwise stated, R^1 to R^4 are H.

nitrobenzene into the yellow 3-*o*-methoxyphenyl-1-oxo-2-indenylacetic acid (VI; $R^2 = OMe$) which was cyclised to 2-acetoxy-4′-methoxy-3 : 4-benzofluorenone (IV; $R^2 = OMe$, $R^6 = OAc$). This was hydrolysed, then methylated, to give the dimethoxy-compound (IV; $R^2 = R^6 = OMe$). (ii) When the *trans*-anhydride (V; $R^3 = OMe$) was similarly treated, it gave the colourless 4-phenyl-3-coumarinylacetic acid (VII).

The structure of the coumarin derivative (VII) was deduced from the following facts: It was unsaturated, contained no methoxyl group, failed to give a 2 : 4-dinitrophenylhydrazone, and when refluxed with aqueous alkali and then treated with methyl sulphate [1] gave *trans*-γ-*o*-methoxyphenyl-γ-phenylitaconic acid (I; $R^3 = OMe$, $R^5 = R^6 = OH$). Its formation is attributed to the demethylating action of aluminium chloride (see Part II [1]). It was also obtained when aluminium chloride was replaced by stannic chloride, and when the *trans*-acid was treated with concentrated sulphuric acid in acetic acid.[6] The same acid was also obtained when α-methyl β-hydrogen *trans*-γ-*o*-methoxyphenyl-γ-phenylitaconate (I; $R^5 = OH$, $R^3 = R^6 = OMe$) (prepared by heating the anhydride with methanol) was heated with zinc chloride in acetic anhydride–acetic acid.[7]

When 4-methoxybenzophenone was similarly condensed with diethyl succinate, it gave an inseparable mixture of ethyl α-hydrogen *cis*- (I; $R^1 = OMe$, $R^5 = OEt$, $R^6 = OH$) and *trans*-γ-*p*-methoxyphenyl-γ-phenylitaconate (I; $R^4 = OMe$, $R^5 = OEt$, $R^6 = OEt$). The product was, therefore, cyclised directly to a mixture of ethyl naphthoates (II; R^1 or $R^4 = OMe$, $R^5 = OEt$, $R^6 = OAc$). Hydrolysis gave the acids ($R^5 = R^6 = OH$) which were methylated, and then decarboxylated, to give 4 : 6-dimethoxy-1-phenyl- (III; $R^1 = R^6 = OMe$) and 4-methoxy-1-*p*-methoxyphenyl-naphthalene (III; $R^4 = R^6 = OMe$).

[3] Cohen, Cook, Hewett, and Girard, *J.*, 1934, 653.
[4] Seer and Ehrenreich, *Monatsh.*, 1913, **34**, 631.
[5] (*a*) Lockett and Short, *J.*, 1939, 787; (*b*) Baddar and El-Assal, *J.*, 1951, 1844.
[6] Borsche, Gillies, Kühn, and Manteuffel, *Annalen*, 1936, **526**, 1.
[7] Johnson and Goldman, *J. Amer. Chem. Soc.*, 1945, **67**, 430.

The last compound was identical with a specimen prepared by Ullmann condensation of 1-iodo-4-methoxynaphthalene with methyl 5-bromo-2-methoxybenzoate and decarboxylation of the resulting acid.

Borsche *et al.*,[6] by cyclisation of the crude mixture of β-ethyl α-hydrogen *cis*- and *trans*-γ-*p*-methoxyphenyl-γ-phenylitaconate with sodium acetate in acetic anhydride, obtained an acetoxy-compound, which was directly hydrolysed to a phenol, m. p. 190—192°. This was claimed by them as a single compound, 4-hydroxy-*x*-methoxy-1-phenyl-2-naphthoic acid. However, it was shown in the present investigation to be a mixture of 4-hydroxy-1-*p*-methoxyphenyl- (II; $R^4 = OMe$, $R^5 = R^6 = OH$) and 4-hydroxy-6-methoxy-1-phenyl-2-naphthoic acid (II; $R^1 = OMe$, $R^5 = R^6 = OH$), m. p. 218·5—219·5° and 214—215°, respectively. The 1-phenylnaphthalene structure of the acids was supported by cyclisation to the red dimethoxy-3 : 4-benzofluorenones.

Hydrolysis of the crude mixture of ethyl hydrogen itaconates gave a mixture of acids from which one of the isomers of γ-*p*-methoxyphenyl-γ-phenylitaconic acid was isolated, but its amount was insufficient for elucidation of its stereochemical nature. The mixed acids were transformed into the anhydrides, which were treated with aluminium chloride in nitrobenzene, to give a mixture of 3-*p*-methoxyphenyl-1-oxo- (VI; $R^1 = OMe$) and 6-methoxy-1-oxo-3-phenyl-2-indenylacetic acid (VI; $R^4 = OMe$), in which the former predominated. These indenylacetic acids undoubtedly came from the *cis*- and *trans*-itaconic acids, respectively.

The structure of the 1-oxo-2-indenylacetic acids was established by cyclisation. The acids (VI; R^1 or $R^4 = OMe$), on cyclisation and hydrolysis, gave 4-hydroxy-2′-methoxy- (IV; $R^1 = OMe$, $R^6 = OH$) and 4-hydroxy-7-methoxy-3 : 4-benzofluorenone (IV; $R^4 = OMe$, $R^6 = OH$), respectively. These gave on methylation the dimethoxyfluorenones identical with the products obtained by cyclisation of the 1-phenyl-2-naphthoic acids (see above). Contrary to statements by Borsche *et al.*[6] cyclisation of the crude mixture of dibasic itaconic acids with concentrated sulphuric acid gave a mixture of 1-oxo-2-indenylacetic acids (VI; $R^1 = OMe$; predominant) and (VI; $R^4 = OMe$), and not the single unidentified product of m. p. 147—149°. The product of Borsche *et al.*[6] was 3-*p*-methoxyphenyl-1-oxo-2-indenylacetic acid (VI; $R^1 = OMe$).

Stobbe condensation of 2-methylbenzophenone with diethyl succinate gave a mixture of semi-solid half esters (10% yield) from which one isomer was obtained crystalline. However, 4 : 4′-dimethylbenzophenone gave β-methyl α-hydrogen γγ-di-*p*-tolylitaconate in 90% yield.

That 4 : 4′-dimethoxybenzophenone gives a higher yield (100%) than 4 : 4′-dimethylbenzophenone (90%) may be due to slight deactivation of the carbonyl group by the effect of the methyl group.

The decrease in the yield in the Stobbe condensation in the order, 4 : 4′-dimethoxy- > 2-methoxy- > 2 : 2′-dimethoxy-benzophenone, is undoubtedly due to steric factors. However, the complete failure with 2 : 2′-dimethylbenzophenone cannot be attributed to steric factors only, since even 2-methylbenzophenone gave a very much poorer yield than 2-methoxybenzophenone and 2 : 2′-dimethoxybenzophenone.[1] Although the methyl group is more bulky than the methoxyl group,[8] the difference in bulk [9] could not be solely responsible for this deactivation. Hydrogen-bond formation between the *ortho*-methyl and the carbonyl group may also be a contributing factor.

Experimental

Light petroleum had b. p. 40—60° unless otherwise stated.

1-*Methoxy*-4-*nitronaphthalene*.—A mixture of nitric acid (*d* 1·42) (2·2 ml.; 1·5 mol.) and 98% acetic acid (10 ml.) was added dropwise to a stirred solution of 1-methoxynaphthalene (5·3 g.) in acetic acid (35 ml.) during 3 hr. at ≯10°. The mixture was kept overnight at room

[8] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.
[9] Braude and Forbes, *J.*, 1955, 3776.

temperature. The precipitate was filtered off (*ca.* 2·5 g.; m. p. 82—83°), and gave yellow 1-methoxy-4-nitronaphthalene (from ethanol), m. p. 84—85°. Another crop (*ca.* 1·8 g.) was obtained by the dilution of the acetic acid mother-liquor. Hodgson and Smith [2] give m. p. 85°.

1-*Methoxy*-4-*naphthylamine Hydrochloride*.—Moist aluminium amalgam (2·5 g.) was added to the ethereal solution of 1-methoxy-4-nitronaphthalene (5 g.). Working up as usual gave the amine hydrochloride (*ca.* 4·6 g.).

1-*Iodo*-4-*methoxynaphthalene*.—(i) The amine hydrochloride (3·1 g.) was converted into 1-iodo-4-methoxynaphthalene as described by Cohen *et al.*[3] The *product* was distilled (b. p. 180—200°/2 mm.) and the distillate (0·61 g.) was crystallised from light petroleum (b. p. <40°); it had m. p. 54—55° (Found: I, 43·7. $C_{11}H_9OI$ requires I, 44·7%). It was unstable at room temperature and was best stored under light petroleum in a dark, cool place.

(ii) 1-Methoxynaphthalene (3·2 g.; 1·0 mol.) was iodinated with iodine (5 g.; 1·0 atom-equiv.) in presence of mercuric oxide (2·2 g.), acetic anhydride (2 ml.), and carbon tetrachloride (30 ml.), then worked up as usual.[4] The oily product was distilled and the fraction boiling at 180—200°/2 mm. was collected and crystallised from light petroleum.

4-*Methoxy*-1-o-*methoxyphenylnaphthalene*-5′-*carboxylic Acid*.—A mixture of 1-iodo-4-methoxynaphthalene (5·6 g.), methyl 3-iodo-4-methoxybenzoate (5·8 g.), and copper bronze (7·5 g.) was heated for 5 hr. at 265—270° (ethyl cinnamate bath) with vigorous stirring, and then worked up as usual.[1] The oily product was hydrolysed with 8% methanolic sodium hydroxide (100 ml.); filtration gave the neutral product which crystallised from benzene to give 4 : 4′-dimethoxydinaphthyl, m. p. 260—261° (*ca.* 1·2 g.) (Fernholz and Piazolo [10] give m. p. 257—259°) (Found: C, 84·4; H, 5·9; OMe, 17·85. Calc. for $C_{22}H_{18}O_2$: C, 84·1; H, 5·7; OMe, 19·7%). Acidification of the alkaline solution gave acids (*ca.* 6 g.) which were methylated with dimethyl sulphate (10 g.), potassium carbonate (10·5 g.), and acetone (50 ml.). The product was extracted with boiling methanol, and the soluble fraction (4·5 g.) was hydrolysed with 8% alcoholic alkali (50 ml.) (2 hours' refluxing). The resulting acid was boiled with glacial acetic acid, and the insoluble product was identified as 2 : 2′-dimethoxydiphenyl-5 : 5′-dicarboxylic acid, m. p. >350°. Its methyl ester had m. p. 169—170°, undepressed on admixture with a specimen kindly provided by A. M. Fleifel, Faculty of Science, Cairo University. The acetic acid mother-liquor precipitated, on concentration, a colourless solid which was repeatedly crystallised from methanol, to give 4-*methoxy*-1-o-*methoxyphenylnaphthalene*-5′-*carboxylic acid*, m. p. 276—277° (*ca.* 0·5 g.) (Found: C, 74·2; H, 5·3; OMe, 19·75. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%).

4-*Methoxy*-1-p-*methoxyphenylnaphthalene*-3′-*carboxylic Acid*.—Condensation of 1-iodo-4-methoxynaphthalene (5·6 g.) with methyl 5-bromo-2-methoxybenzoate (5 g.) in presence of copper bronze (7·5 g.) was carried out as reported by Baddar *et al.*[11] for 5-methoxy-3-(6-methoxy-1-naphthyl)benzoic acid. The acid insoluble in benzene was identified as 4 : 4′-dimethoxydiphenyl-3 : 3-dicarboxylic acid, m. p. 236—238°, undepressed on admixture with a sample kindly provided by A. M. Fleifel. The acid soluble in benzene (2·9 g.) was esterified with diazomethane and the ester was fractionated. The fraction of b. p. 250—260°/4 mm. (*ca.* 1 g.) was hydrolysed with 8% methanolic sodium hydroxide. The acid, after being heated in a vacuum for 2 hr. at 100°, was repeatedly crystallised from methanol, to give 4-*methoxy*-1-p-*methoxyphenylnaphthalene*-3′-*carboxylic acid* (0·5 g.), m. p. 173—174° (Found: C, 73·9; H, 5·4; OMe, 21·0%).

β-*Methyl* α-*Hydrogen* γ-o-*Methoxyphenyl*-γ-*phenylitaconate*.—A solution of potassium *tert.*-butoxide [from potassium (2·2 g.) and *tert.*-butyl alcohol (50 ml.)] was treated during 20 min. with a mixture of dimethyl succinate (11 g.) and 2-methoxybenzophenone [12] (5·7 g.) in *tert.*-butyl alcohol (10 ml.). The mixture was heated for further 55 min., then worked up as usual.[1, 13] The product (6·8 g.), which solidified, crystallised from benzene–light petroleum to give β-*methyl* α-*hydrogen* trans-γ-o-*methoxyphenyl*-γ-*phenylitaconate* (I; $R^3 = R^5 =$ OMe), m. p. 119—120° (1·2 g.) (Found: C, 70·4; H, 5·7; OMe, 18·0. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5; OMe, 19·0%). The mother-liquor contained an uncrystallisable product which was probably a mixture of the *cis*- and the *trans*-ester.

Cyclisation of β-*Methyl* α-*Hydrogen* γ-o-*Methoxyphenyl*-γ-*phenylitaconates*.—The crude

[10] Fernholz and Piazolo, *Chem. Ber.*, 1954, **87**, 578.
[11] Baddar, Fahim, and Galaby, *J.*, 1955, 465.
[12] Ullmann and Goldberg, *Ber.*, 1902, **35**, 2811.
[13] Johnson and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 511.

mixed esters (6·5 g.), sodium acetate (1·8 g.), and acetic anhydride (30 ml.) were cyclised as described by Baddar *et al.*[1] Distillation of the solvent left a brown oil which was fractionally separated by repeated extraction with light petroleum (b. p. <40°). The soluble fraction (A) (1 g.) proved to be a mixture of methyl 4-acetoxy-1-*o*-methoxyphenyl- and 4-acetoxy-8-methoxy-1-phenyl-2-naphthoate; the insoluble fraction (B) (5 g.) was mainly the former.

4-Hydroxy-1-o-methoxyphenyl-2-naphthoic Acid.—Crude methyl 4-acetoxy-1-*o*-methoxyphenyl-2-naphthoate (3·7 g.) (fraction B) was hydrolysed with 10% alcoholic potassium hydroxide (10 ml.) as usual. The semi-solid acid was digested with boiling benzene, and the insoluble product crystallised from acetic acid, to give *4-hydroxy-1-o-methoxyphenyl-2-naphthoic acid*, m. p. 243—244° (Found: C, 73·0; H, 4·65; OMe, 10·65. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8; OMe, 10·6%). The benzene mother-liquor gave an impure acid.

Methyl 4-Methoxy-1-o-methoxyphenyl-2-naphthoate (II; $R^3 = R^5 = R^6 =$ OMe).—The acid (3 g.) was treated with dimethyl sulphate (5 g.), potassium carbonate (5·2 g.), and acetone (20 ml.) as usual. Crystallisation of the product from benzene–light petroleum gave *methyl 4-methoxy-1-o-methoxyphenyl-2-naphthoate*, m. p. 119·5—120·5° (Found: C, 74·5; H, 5·7; OMe, 26·45. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6; OMe, 28·8%). Hydrolysis of this (3·2 g.) with 10% alcoholic potassium hydroxide (10 ml.) gave the *acid*, m. p. 233—234° (from glacial acetic acid) (Found: C, 73·55; H, 5·4; OMe, 19·6. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%).

4-Methoxy-1-o-methoxyphenylnaphthalene (III; $R^3 = R^6 =$ OMe).—(i) 4-Methoxy-1-*o*-methoxyphenylnaphthalene-3′-carboxylic acid (0·4 g.) was heated with copper bronze (0·5 g.) in quinoline (4 ml.) as usual.[5b] The semi-solid neutral product gave *4-methoxy-1-o-methoxyphenylnaphthalene* (0·34 g.), m. p. 89—90° [from light petroleum (b. p. 80—100°)] (Found: C, 82·5; H, 6·4; OMe, 22·9. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; OMe, 23·5%). (ii) 4-Methoxy-1-*o*-methoxyphenyl-2-naphthoic acid (0·4 g.) was decarboxylated as in (i) (bath-temp. 205—210°). The product, crystallised from light petroleum (b. p. 80—100°), had m. p. 89—90° alone or mixed with the specimen prepared by method (i) (Found: C, 81·45; H, 6·1; OMe, 23·7%).

2 : 5-Dimethoxy-3 : 4-benzofluorenone (IV; $R^3 = R^6 =$ OMe).—Phosphorus oxychloride (0·25 ml.) was added dropwise to a solution of 4-methoxy-1-*o*-methoxyphenyl-2-naphthoic acid (0·4 g.) in *s*-tetrachloroethane (20 ml.), then the mixture was heated for 3 hr. at 140—150°, and worked up as usual.[5] The red product (0·3 g.), crystallised from benzene–light petroleum, gave *2 : 5-dimethoxy-3 : 4-benzofluorenone* in red needles, m. p. 167—168° (Found: C, 78·25; H, 4·8; OMe, 19·75. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8; OMe, 21·4%). When the cyclisation was carried out with phosphoric oxide in benzene, a mixture of the above fluorenone and a colourless product (predominant) was obtained. The latter, crystallised from benzene, gave *4-methoxy-1-o-methoxyphenyl-2-naphthoic anhydride*, m. p. 220—221° (Found: C, 76·7; H, 5·1. OMe, 19·3. $C_{38}H_{30}O_7$ requires C, 76·25; H, 5·0; OMe, 20·7%). Its structure was established by hydrolysis with 20% sodium hydroxide solution to 4-methoxy-1-*o*-methoxy-1-naphthoic acid.

Methyl 4 : 8-Dimethoxy-1-phenyl-2-naphthoate (II; $R^2 = R^5 = R^6 =$ OMe).—Crude methyl 4-acetoxy-8-methoxy-1-phenyl-2-naphthoate (1 g.) (fraction A) was hydrolysed by 10% alcoholic potassium hydroxide. Crystallisation of the product from benzene gave 4-hydroxy-1-*o*-methoxyphenyl-2-naphthoic acid, m. p. and mixed m. p. 243—244° (*ca.* 0·2 g.). Distillation of the benzene mother-liquor left a semi-solid mass (*ca.* 0·7 g.) which was methylated with dimethyl sulphate (1·2 g.), potassium carbonate (1·4 g.), and acetone (15 ml.). The product was distilled and the fraction boiling at 250—260°/2 mm. was repeatedly crystallised from methanol, to give *methyl 4 : 8-dimethoxy-1-phenyl-2-naphthoate* (*ca.* 0·3 g.), m. p. 127—128° (depressed to 95—115° on admixture with a specimen of its isomer) (Found: C, 74·5; H, 5·6; OMe, 26·2. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6; OMe, 28·8%).

Hydrolysis of this ester (0·3 g.) with 10% alcoholic potassium hydroxide (10 ml.) (2 hours' refluxing) gave *4 : 8-dimethoxy-1-phenyl-2-naphthoic acid* in colourless aggregates (from benzene–light petroleum), m. p. 180—181°, depressed to 110—120° on admixture with its isomer (Found: C, 74·3; H, 5·15; OMe, 20·7%).

cis- *and* trans-*γ*-o-*Methoxyphenyl-γ-phenylitaconic Acid.*—The crude mixture of β-methyl α-hydrogen *cis-* and *trans-γ-o*-methoxyphenyl-*γ*-phenylitaconate (6·8 g.) was hydrolysed with 10% alcoholic potassium hydroxide (50 ml.). The semi-solid acid (*ca.* 6 g.) was triturated with ether, then repeatedly crystallised from acetic acid, to give trans-*γ*-o-*methoxyphenyl-γ-phenylitaconic acid*, m. p. 201—202° (*ca.* 2·5 g.) (Found: C, 68·7; H, 5·1; OMe, 10·35. $C_{18}H_{16}O_5$

requires C, 69·2; H, 5·1; OMe, 9·9%). The ether used for trituration was evaporated and the residue repeatedly crystallised from benzene, to give cis-γ-o-*methoxyphenyl-γ-phenylitaconic acid* (1·8 g.), m. p. 154—155°, depressed to 105—115° on admixture with the isomer (Found: C, 69·7; H, 5·2; OMe, 9·8%). Hydrolysis of the pure *trans*-half ester (I; $R^3 = R^5 = OMe$, $R^6 = OH$), m. p. 119—120°, gave an acid of m. p. 201—202°, undepressed on admixture with the *trans*-acid.

trans-γ-o-*Methoxyphenyl-γ-phenylitaconic Anhydride* (V; $R^3 = OMe$).—The *trans*-acid, m. p. 201—202° (3 g.), was refluxed with acetyl chloride (30 ml.) for an hour, and then worked up as usual. The product (*ca.* 3 g.) crystallised from benzene–light petroleum, to give trans-γ-o-*methoxyphenyl-γ-phenylitaconic anhydride*, m. p. 155—156° (Found: C, 73·6; H, 4·7; OMe, 10·7. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8; OMe, 10·6%).

cis-γ-o-*Methoxyphenyl-γ-phenylitaconic Anhydride* (V; $R^2 = OMe$).—The *cis*-acid, m. p. 154—155° (2 g.), was similarly treated (2 hours' refluxing), giving cis-γ-o-*methoxyphenyl-γ-phenylitaconic anhydride* (*ca.* 1·8 g.), m. p. 157—158°, depressed to 128—136° on admixture with its isomer and to 133—140° on admixture with its acid (Found: C, 73·8; H, 5·0; OMe, 10·45%).

α-*Methyl* β-*Hydrogen* trans-γ-o-*Methoxyphenyl-γ-phenylitaconate.*—*trans-γ-o*-Methoxyphenyl-γ-phenylitaconic anhydride (1 g.) and absolute methanol (20 ml.) were refluxed for 3 hr., then worked up as usual.[13] Crystallisation from benzene–light petroleum gave α-*methyl* β-*hydrogen* trans-γ-o-*methoxyphenyl-γ-phenylitaconate*, m. p. 140—141°, depressed to 105—115° on admixture with a specimen of the *trans*-half ester obtained by Stobbe condensation (Found: C, 69·9; H, 5·6; OMe, 18·5. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5; OMe, 19·0%).

When the above anhydride was similarly treated with absolute ethanol, the corresponding *ethyl ester*, m. p. 132—133° (from benzene–light petroleum), was obtained (Found: C, 70·6; H, 6·0. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

4-*Phenyl*-3-*coumarinylacetic Acid* (VII).—(i) The *trans*-anhydride (3 g.) was treated in nitrobenzene (30 ml.) with aluminium chloride (2 g.), and worked up as described by Baddar *et al.*[1] Crystallisation of the product from benzene gave 4-*phenyl*-3-*coumarinylacetic acid*, m. p. 189—190°, depressed to 170—175° on admixture with *trans-γ-o*-methoxyphenyl-γ-phenylitaconic acid (Found: C, 72·75; H, 4·3; OMe, 0. $C_{17}H_{12}O_4$ requires C, 72·85; H, 4·3%). (ii) The same anhydride (0·4 g.) and stannic chloride (4 ml.) in *s*-tetrachloroethane (15 ml.) were refluxed at 130—140° for 3 hr. The product, crystallised from benzene, gave the coumarinylacetic acid (0·35 g.), m. p. 189—190°. (iii) The *trans*-half ester (I; $R^3 = OMe$, $R^5 = OH$, $R^6 = OEt$) (0·6 g.), m. p. 132—133°, acetic anhydride (7·5 ml.), glacial acetic acid (7·5 ml.), and zinc chloride (0·08 g.) were refluxed for 2 hr.,[7] then worked up as usual. The oily product (0·6 g.) was hydrolysed with 3% alcoholic potassium hydroxide (10 ml.) (2 hr.). Acidification of the alkaline solution precipitated an acid which on crystallisation from benzene gave the same coumarinylacetic acid, m. p. and mixed m. p. 189—190°. (iv) The *trans*-itaconic acid (I; $R^3 = OMe$; $R^5 = R^6 = OH$) (0·4 g.) was cyclised with concentrated sulphuric acid (40 ml.) and acetic acid (2 ml.), then worked up as described by Borsche *et al.*[6] The product, crystallised from benzene, gave the same coumarinylacetic acid, m. p. and mixed m. p. 189—190°.

Conversion of 4-*Phenyl*-3-*coumarinylacetic Acid into* trans-γ-o-*Methoxyphenyl-γ-phenylitaconic Acid* (I; $R^3 = OMe$, $R^5 = R^6 = OH$).—A solution of the coumarinylacetic acid (0·5 g.) in sodium hydroxide (0·4 g.) and water (4·5 ml.) was refluxed for 30 min., then heated on the water-bath with dimethyl sulphate (0·8 g.) for 5 hr.[1,14] Crystallisation of the product from acetic acid gave the *trans*-itaconic acid, m. p. and mixed m. p. 201—202° (0·5 g.).

3-o-*Methoxyphenyl*-1-*oxo*-2-*indenylacetic Acid* (VI; $R^2 = OMe$).—Finely powdered aluminium chloride (1·4 g.) was added gradually to a solution of *cis-γ-o*-methoxyphenyl-γ-phenylitaconic anhydride (2 g.) in nitrobenzene (20 ml.), and worked up as usual.[1] The yellow product, crystallised from benzene, gave the yellow *indenylacetic acid*, m. p. 189—190°, depressed to 150—165° on admixture with the coumarinylacetic acid (Found: C, 73·6; H, 4·8; OMe, 11·8. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8; OMe, 10·5%). Its 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in orange-red needles, m. p. 264—265° (Found: N, 11·2. $C_{24}H_{18}O_7N_4$ requires N, 11·8%).

2-*Acetoxy*-4′-*methoxy*-3 : 4-*benzofluorenone* (IV; $R^2 = OMe$, $R^6 = OAc$).—The above indenylacetic acid (2 g.) and sodium acetate (0·8 g.) in acetic anhydride (20 ml.) were refluxed for 5 hr.,

[14] Stoermer and Friemel, *Ber.*, 1911, **44**, 1838.

then worked up. Crystallisation of the product from acetic acid gave 2-*acetoxy*-4'-*methoxy*-3 : 4-*benzofluorenone* in red needles, m. p. 180—181° (Found: C, 75·4; H, 4·2; OMe, 8·65. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4; OMe, 9·75%).

2-*Hydroxy*-4'-*methoxy*-3 : 4-*benzofluorenone* (IV; R^2 = OMe, R^6 = OH).—The acetoxybenzofluorenone (2 g.) with boiling N-sodium hydroxide (10 ml.) gave in 2 hr. the *hydroxybenzofluorenone*, dark-red needles, m. p. 261—263° (from acetic acid) (Found: C, 77·8; H, 4·25; OMe, 12·2. $C_{18}H_{12}O_3$ requires C, 78·3; H, 4·35; OMe, 11·2%).

2 : 4'-*Dimethoxy*-3 : 4-*benzofluorenone* (IV; R^2 = R^6 = OMe).—(i) A mixture of 4 : 8-dimethoxy-1-phenyl-2-naphthoic acid (0·6 g.), benzene (15 ml.), and phosphoric oxide (0·3 g.) was refluxed for 2 hr. The product, crystallised from benzene–light petroleum, gave 2 : 4'-*dimethoxy*-3 : 4-*benzofluorenone*, red needles, m. p. 148—149° (Found: C, 78·45; H, 4·9; OMe, 20·95. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8; OMe, 21·4%). (ii) 2-Hydroxy-4'-methoxy-3 : 4-benzofluorenone (0·5 g.), dimethyl sulphate (0·3 g.), potassium carbonate (0·3 g.), and acetone (15 ml.) gave 2 : 4-dimethoxy-3 : 4-benzofluorenone in red needles, m. p. and mixed m. p. 148—149° (from benzene–light petroleum).

β-*Ethyl* α-*Hydrogen* cis- *and* trans-γ-p-*Methoxyphenyl*-γ-*phenylitaconate*.—4-Methoxybenzophenone[12] (5·7 g.), diethyl succinate (6·5 g.), and a solution of potassium *tert.*-butoxide [from potassium (1·1 g.) and *tert.*-butyl alcohol (25 ml.)] was refluxed for 20 min. under nitrogen. An equal amount of potassium *tert.*-butoxide solution (25 ml.) was added and the mixture was refluxed for a further 20 min.,[1,13] then worked up as usual. The product (*ca.* 8·2 g., 90%) was uncrystallisable. Borsche *et al.*[6] obtained a 75% yield when using sodium ethoxide.

Ethyl 4-*Acetoxy*-6-*methoxy*-1-*phenyl*- and *Ethyl* 4-*acetoxy*-p-*methoxyphenyl*-2-*naphthoate*.—The crude mixture of the above stereoisomeric half-esters (8·5 g.), sodium acetate (2 g.), and acetic anhydride (60 ml.) was refluxed for 5 hr., and worked up as usual. The oily product (*ca.* 8·0 g.) was triturated with ethanol (30 ml.), then repeatedly crystallised from the same solvent to give *ethyl* 4-*acetoxy*-6-*methoxy*-1-*phenyl*-2-*naphthoate* (II; R^1 = OMe, R^5 = OEt, R^6 = OAc) (3 g.), m. p. 125—126° (Found: C, 72·15; H, 5·4. $C_{22}H_{20}O_5$ requires C, 72·5; H, 5·5%). The alcohol used in trituration slowly gave another crop, m. p. 80—82° (*ca.* 1·8 g.). This on repeated crystallisation from benzene–light petroleum gave *ethyl* 4-*acetoxy*-1-p-*methoxy*-2-*naphthoate* (*ca.* 1·8 g.), m. p. 87—88°, depressed to 65—70° on admixture with a specimen of the above isomer (Found: C, 72·8; H, 5·45; OMe, 16·6%). Borsche *et al.*[6] did not obtain these acetoxy-derivatives crystalline.

4-*Hydroxy*-1-p-*methoxyphenyl*-2-*naphthoic Acid* (II; R^4 = OMe, R^5 = R^6 = OH).—This was obtained in a quantitative yield by hydrolysis of the corresponding acetoxy-ester with 10% alcoholic potassium hydroxide. Crystallisation from acetic acid gave the *acid*, m. p. 218·5—219·5°, depressed to 190—195° on admixture with its isomer (II; R^1 = OMe, R^5 = R^6 = OH) (Found: C, 73·4; H, 4·7; OMe, 11·75. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8; OMe, 10·6%).

When the crude acetoxy-esters, m. p. 120—122°, were hydrolysed, and the acid was crystallised from methylene chloride, a crystalline product, m. p. 190—192°, was obtained (cf. Borsche *et al.*[6]). This was an inseparable mixture of the isomeric phenolic acids. The *methyl ester* (obtained by use of methanol and hydrogen chloride and crystallised from benzene) had m. p. 160—161° (Found: C, 73·65; H, 5·2; OMe, 20·0. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%).

Methyl 4-*Methoxy*-1-p-*methoxyphenyl*-2-*naphthoate* (II; R^4 = R^5 = R^6 = OMe).—The hydroxy-acid (3 g.) was methylated with dimethyl sulphate (5 g.), potassium carbonate (5·2 g.), and acetone (20 ml.). The product, crystallised from benzene–light petroleum, gave *methyl* 4-*methoxy*-1-p-*methoxyphenyl*-2-*naphthoate*, m. p. 121—122° (Found: C, 73·95; H, 5·7; OMe, 27·25. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6; OMe, 28·8%). Hydrolysis of the ester with 15% alcoholic potassium hydroxide gave 4-*methoxy*-1-p-*methoxyphenyl*-2-*naphthoic acid*, m. p. 204—205° (from acetic acid), depressed to 178—200° on admixture with its isomer (Found: C, 74·0; H, 5·1; OMe, 19·6%).

4-*Methoxy*-1-p-*methoxyphenylnaphthalene* (III; R^4 = R^6 = OMe).—(i) *Decarboxylation of* 4-*methoxy*-1-p-*methoxyphenylnaphthalene*-3'-*carboxylic acid*. The acid (0·4 g.) was heated with copper bronze (0·5 g.) in quinoline (4 ml.), and worked up as usual. Crystallisation of the oily product from benzene–light petroleum (b. p. 80—100°) gave 4-*methoxy*-1-p-*methoxyphenyl*-*naphthalene* (0·34 g.), m. p. 104—105° (Found: C, 81·9; H, 6·1; OMe, 20·6. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; OMe, 23·5%).

(ii) *Decarboxylation* of 4-*methoxy*-1-p-*methoxyphenyl*-2-*naphthoic acid*. The acid (0·4 g.)

was decarboxylated as in (i), and the product crystallised from the same solvent to give 4-methoxy-1-*p*-methoxyphenylnaphthalene (0·35 g.), m. p. and mixed m. p. 104—105°. Its m. p. was depressed to 70—80° on admixture with a specimen of 4 : 6-dimethoxy-1-phenylnaphthalene (see below) (Found: C, 81·8; H, 6·1; OMe, 20·2%).

4-Hydroxy-6-methoxy-1-phenyl-2-naphthoic Acid (II; R^1 = OMe, R^5 = R^6 = OH).—This was obtained by the hydrolysis of the acetoxy-ester (3·7 g.) with 10% alcoholic potassium hydroxide. Crystallisation of the product from dilute acetic acid gave *4-hydroxy-6-methoxy-1-phenyl-2-naphthoic acid* (*ca.* 3 g.), m. p. 214—215° (Found: C, 72·9; H, 4·9; OMe, 9·9. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8; OMe, 10·6%). Its *methyl ester* (methanol and hydrogen chloride), crystallised from benzene, had m. p. 216—217° (Found: C, 74·1; H, 5·2; OMe, 19·9. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%).

Methyl 4 : 6-Dimethoxy-1-phenyl-2-naphthoate.—The phenolic acid (3 g.), methylated with dimethyl sulphate (5 g.), potassium carbonate (5·2 g.), and acetone (20 ml.), gave *methyl 4 : 6-dimethoxy-1-phenyl-2-naphthoate* (3·2 g.), m. p. 135·5—136·5° (from benzene–light petroleum) (Found: C, 74·8; H, 5·7; OMe, 27·05. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6; OMe, 28·8%). Hydrolysis of the ester with 10% alcoholic potassium hydroxide gave the *4 : 6-dimethoxy-acid*, m. p. 233—234° (from acetic acid) (*ca.* 3 g.) (Found: C, 73·7; H, 5·15; OMe, 21·1. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2; OMe, 20·1%).

4 : 6-Dimethoxy-1-phenylnaphthalene.—The preceding acid (0·4 g.) was decarboxylated with copper bronze (0·5 g.) in quinoline (4 ml.) at 205—210°; crystallisation from light petroleum (b. p. 80—100°) gave *4 : 6-dimethoxy-1-phenylnaphthalene* (0·35 g.), m. p. 101—102°, depressed to 70—80° on admixture with a specimen of the isomeric 4-methoxy-1-*p*-methoxyphenylnaphthalene (Found: C, 82·2; H, 5·9; OMe, 25·6. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; OMe, 23·5%).

γ-p-Methoxyphenyl-γ-phenylitaconic Acid.—The mixed half-esters (I; R^1 or R^4 = OMe, R^5 = OEt, R^6 = OH) (8·5 g.) was hydrolysed with 10% alcoholic potassium hydroxide (50 ml.). Fractional crystallisation from ether gave a *γ-p-methoxyphenyl-γ-phenylitaconic acid* (*ca.* 0·8 g.), m. p. 183—184° (Borsche *et al.*[6] did not obtain a crystalline product) (Found: C, 69·3; H, 5·1; OMe, 9·25. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1; OMe, 9·9%). Evaporation of the ethereal mother-liquor gave an inseparable mixture of acids, m. p. 145—149° (cleared with gas evolution).

The mixed acids (7·5 g.) were refluxed with acetyl chloride (50 ml.). The anhydrides (7·4 g.) failed to solidify and were used in the following step.

3-p-Methoxyphenyl-1-oxo- and *6-Methoxy-1-oxo-3-phenyl-2-indenylacetic Acid.*—A solution of the above anhydrides (7·4 g.) in nitrobenzene (60 ml.) was treated with aluminium chloride (4 g.) as described for the *o*-methoxy-derivative. The product was fractionally crystallised from benzene, to give *3-p-methoxyphenyl-1-oxo-2-indenylacetic acid* (*ca.* 3 g.) in orange-yellow crystals, m. p. 152—153°, identical with the unidentified product, m. p. 147—149°, obtained by Borsche *et al.*[6] (Found: C, 74·1; H, 4·5; OMe, 10·1. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8; OMe, 10·6%). Its *2 : 4-dinitrophenylhydrazone* was obtained in orange-red needles (from acetic acid), m. p. 250—251° (Found: N, 11·8. $C_{24}H_{18}O_7N_4$ requires N, 11·8%). Borsche *et al.*[6] give m. p. >250°.

Concentration of the benzene mother-liquor precipitated another fraction which was repeatedly crystallised from the same solvent, to give orange-red *6-methoxy-1-oxo-3-phenyl-2-indenylacetic acid* (*ca.* 0·5 g.), m. p. 175·5—176·5°, depressed to 120—130° on admixture with the isomer (Found: C, 73·8; H, 4·8; OMe, 11·35%). Its *2 : 4-dinitrophenylhydrazone* was obtained in red crystals (from dioxan), m. p. 263—264°, depressed to 230—240° on admixture with the above hydrazone (Found: N, 12·1%). Contrary to Borsche *et al.*[6] cyclisation of the crude mixture of the itaconic acids with sulphuric acid gave mixed acids.

2-Acetoxy-2'-methoxy-3 : 4-benzofluorenone (IV; R^1 = OMe, R^6 = OAc).—3-*p*-Methoxyphenyl-1-oxo-2-indenylacetic acid (3 g.) was cyclised with sodium acetate (1 g.) in acetic anhydride (20 ml.) as usual. Crystallisation of the product (3·1 g.) from acetic acid gave *2-acetoxy-2'-methoxy-3 : 4-benzofluorenone* in yellow plates, m. p. 212—213° (Borsche *et al.*[6] give m. p. 209—210° for an unidentified product) (Found: C, 74·9; H, 4·2; OMe, 10·1. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4; OMe, 9·75%). Hydrolysis of this compound (2 g.) with N-aqueous sodium hydroxide (10 ml.) (2 hr.) gave *2-hydroxy-2'-methoxy-3 : 4-benzofluorenone* in dark red needles (from acetic acid), m. p. 351—352°, depressed to 255—258° on admixture with its isomer (Found: C, 77·7; H, 4·25; OMe, 10·25. $C_{18}H_{12}O_3$ requires C, 78·3; H, 4·35; OMe, 11·2%). Borsche *et al.*[6] give m. p. 255—258° for the unidentified product obtained by

cyclisation of the impure acid, m. p. 190—192°. This was probably a mixture of the two isomeric hydroxy-3 : 4-benzofluorenones.

2 : 2′-*Dimethoxy*-3 : 4-*benzofluorenone* (IV; $R^1 = R^6 = OMe$).—(i) *Cyclisation of* 4 : 6-*dimethoxy*-1-*phenyl*-2-*naphthoic acid.* This was carried out with phosphoric oxide in benzene. Crystallisation of the product from benzene gave 2 : 2′-*dimethoxy*-3 : 4-*benzofluorenone* in red crystalline aggregates, m. p. 175—176° (Found: C, 78·25; H, 4·7; OMe, 25·3. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8; OMe, 21·4%).

(ii) *Etherification of* 2-*hydroxy*-2′-*methoxy*-3 : 4-*benzofluorenone.* This was carried out by dimethyl sulphate, potassium carbonate, and acetone. On crystallisation from benzene, 2 : 2′-dimethoxy-3 : 4-benzofluorenone was obtained in red aggregates (0·5 g.), m. p. and mixed m. p. 175—176° (Found: C, 78·2; H, 4·7; OMe, 19·6%).

2-*Acetoxy*-7-*methoxy*-3 : 4-*benzofluorenone.*—6-Methoxy-1-oxo-3-phenyl-2-indenylacetic acid (0·6 g.) was cyclised with sodium acetate (0·4 g.) in acetic anhydride (10 ml.). On crystallisation from acetic acid, 2-*acetoxy*-7-*methoxy*-3 : 4-*benzofluorenone* (0·5 g.) was obtained in red crystals, m. p. 207—208°, depressed to 168—175° (shrinkage at 160°) on admixture with 2-acetoxy-2′-methoxy-3 : 4-benzofluorenone (Found: C, 75·45; H, 4·4; OMe, 9·65. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4; OMe, 9·75%). This compound (0·5 g.) was hydrolysed with N-aqueous sodium hydroxide (10 ml.) to 2-hydroxy-7-methoxy-3 : 4-benzofluorenone, red crystals (from acetic acid), m. p. >350°.

2 : 7-*Dimethoxy*-3 : 4-*benzofluorenone.*—(i) *Cyclisation* of 4-*methoxy*-1-p-*methoxyphenyl*-2-*naphthoic acid.* The acid was cyclised with phosphoric oxide in benzene, and the product crystallised from benzene to give 2 : 7-*dimethoxy*-3 : 4-*benzofluorenone* in red needles (0·5 g.), m. p. 184—185°, depressed to 140—150° on admixture with 2 : 2′-dimethoxy-3 : 4-benzofluorenone (Found: C, 78·25; H, 4·9; OMe, 19·2. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8; OMe, 21·4%).

(ii) *Methylation of* 2-*hydroxy*-7-*methoxy*-3 : 4-*benzofluorenone.* The phenol was methylated as usual. Crystallisation from benzene gave 2 : 7-dimethoxy-3 : 4-benzofluorenone (0·5 g.), m. p. and mixed m. p. 184—185° (Found: C, 78·3; H, 4·7; OMe, 19·4%).

γγ-Di-p-*tolylitaconic Acid.*—4 : 4′-Dimethylbenzophenone (5·3 g.) was condensed with dimethyl succinate (11 g.) in the presence of a solution of potassium *tert.*-butoxide [from potassium (2·2 g.) in *tert.*-butyl alcohol (50 ml.)] (1·5 hours' refluxing). β-Methyl α-hydrogen *γγ*-di-*p*-tolylitaconate was hydrolysed by 10% alcoholic potassium hydroxide to *γγ-di*-p-*tolylitaconic acid* (7 g., 90%), m. p. 169·5—170·5° (from dilute ethanol) (Found: C, 73·3; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·55; H, 5·8%). The *anhydride*, m. p. 118·5—119·5° (from benzene–light petroleum), was obtained by refluxing the acid (3 g.) with acetyl chloride (20 ml.) (Found: C, 77·8; H, 5·8. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%).

β-*Ethyl* α-*Hydrogen* cis- *and* trans-*γ*-*Phenyl*-*γ*-o-*tolylitaconate.*—2-Methylbenzophenone (4·9 g.) was condensed with dimethyl succinate (13 g.) as described for 2-methoxybenzophenone. The oily half-ester (0·9 g., 10%) was left at 25—30° for several days, triturated with benzene–light petroleum, then repeatedly crystallised from the same solvent, to give β-*ethyl* α-*hydrogen* cis- or trans-*γ*-*phenyl*-*γ*-o-*tolylitaconate* (*ca.* 0·3 g.), m. p. 115—116° (Found: C, 74·3; H, 6·25. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

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