1-*Phenylnaphthalenes. Part II.* The Cyclisation of Ethyl Hydrogen γγ-Di-*o*-methoxyphenyl- and γγ-Di-*p*-methoxyphenyl-itaconate to the Corresponding 1-Phenylnaphthalenes.*

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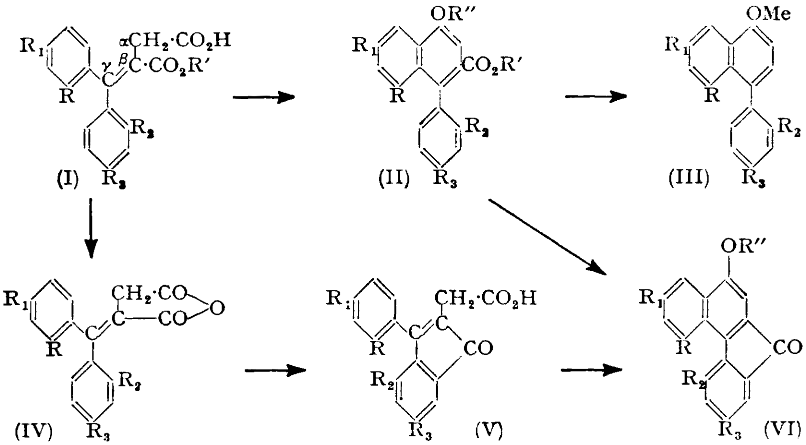
Ethyl hydrogen γγ-di-*o*- and -*p*-methoxyphenylitaconate are converted by use of acetic anhydride and sodium acetate into the corresponding 1-phenylnaphthalene derivatives.

γγ-Di-*p*-methoxyphenylitaconic anhydride yields with aluminium chloride an indenone, which is cyclised and methylated to 2 : 2′ : 7-trimethoxybenzofluorenone. However, the *o*-methoxyphenyl isomer when similarly treated gives 4-*o*-methoxyphenyl-3-coumarinylacetic acid.

SYMMETRICALLY disubstituted benzophenones were condensed with diethyl succinate, potassium *tert.*-butoxide being the catalyst (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 74; 1950, **72**, 511); 2 : 2′-dimethoxybenzophenone thereby gave ethyl hydrogen γγ-di-*o*-methoxyphenylitaconate (I; R = R_2 = OMe, R_1 = R_3 = H, R′ = Et). Use of a suspension of potassium ethoxide in benzene as catalyst gave an unsatisfactory product containing di-*o*-methoxyphenylmethanol, probably formed by a Meerwein–Pondorff type of reduction (cf. Johnson *et al.*, *loc. cit.*, 1947).



Cyclisation of the half-esters (I; R = R_2 = H, R_1 = R_3 = OMe, R′ = Et; and R = R_2 = OMe, R_1 = R_3 = H, R′ = Et) with sodium acetate in acetic anhydride (Borsche *et al.*, *Annalen*, 1936, **526**, 1) gave ethyl 4-acetoxy-6-methoxy-1-*p*-methoxyphenyl- and ethyl 4-acetoxy-8-methoxy-1-*o*-methoxyphenyl-2-naphthoic acid (II; R′ = Et, R″ = Ac; R = R_2 = H, R_1 = R_3 = OMe, and conversely). The derived phenolic acids (II; R = R_2 = R′ = R″ = H, R_1 = R_3 = OMe; and R = R_2 = OMe, R_1 = R_3 =

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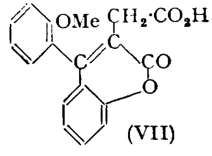
* Part I, *J.*, 1948, 1270.

R′ = R″ = H) were converted by methyl iodide into methyl 4 : 6-dimethoxy-1-*p*-methoxyphenyl- and 4 : 8-dimethoxy-1-*o*-methoxyphenyl-2-naphthoate, respectively. These were hydrolysed to the acids, which were decarboxylated to the corresponding 1-phenylnaphthalene derivatives.

The acid (II; R = R_2 = R′ = H, R_1 = R_3 = OMe, R″ = Me) gave, on cyclisation with phosphoric oxide, 2 : 2′ : 7-trimethoxy-3 : 4-benzofluorenone (VI; R = R_2 = H, R_1 = R_3 = OMe, R″ = Me), also obtained through the following series of reactions: γγ-Di-*p*-methoxyphenylitaconic anhydride (IV; R = R_2 = H, R_1 = R_3 = OMe) (cf. Johnson *et al.*, *loc. cit.*) was cyclised with aluminium chloride in nitrobenzene to 6-methoxy-3-*p*-methoxyphenyl-1-oxo-2-indenylacetic acid (V; R = R_2 = H, R_1 = R_3 = OMe). This keto-acid was cyclised with acetic anhydride and sodium acetate (cf. Borsche *et al.*, *loc. cit.*) to 2-acetoxy-2′ : 7-dimethoxy-3 : 4-benzofluorenone (VI; R = R_2 = H, R_1 = R_3 = OMe, R″ = Ac), which was hydrolysed and then methylated to give the above benzofluorenone. However, when γγ-di-*o*-methoxyphenylitaconic anhydride (IV; R = R_2 = OMe, R_1 = R_3 = H) was treated with aluminium chloride in nitrobenzene, it gave 4-*o*-methoxyphenyl-3-coumarinylacetic acid (VII) instead of the expected compound of type (V). The structure of (VII) was deduced from the fact that, when it was refluxed with sodium hydroxide solution and dimethyl sulphate (cf. Stoermer and Friemel, *Ber.*, 1911, **44**, 1843), it gave γγ-di-*o*-methoxyphenylitaconic acid. Its formation may be due to partial demethylation of γγ-di-*o*-methoxyphenylitaconic anhydride (IV; R = R_2 = OMe, R_1 = R_3 = H) by the aluminium chloride to (IV; R = OMe, R_2 = OH, R_1 = R_3 = H) and conversion of this into (VII) either by rearrangement, or by recyclisation of (I; R = OMe, R_2 = OH, R_1 = R_3 = R′ = H) on acidification of its solution in alkali carbonate.


(VII)

Attempted decarboxylation and lactonisation of γγ-di-*o*-methoxyphenylitaconic acid (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 511) failed, possibly owing to the stabilisation of the carboxyl group in chelation with the *o*-methoxyl group.

Attempts to prepare an authentic specimen of 4 : 8-dimethoxy-1-*o*-methoxyphenylnaphthalene (III; R = R_2 = OMe, R_1 = R_3 = H) by condensation of 1 : 5-dimethoxynaphthalene and diazotised methyl 3-aminoanisate in presence of sodium hydroxide solution (cf. Baddar, *J.*, 1941, **310**) were not successful. Its preparation by the condensation of *o*-iodoanisate with 1-iodo-4 : 8-dimethoxynaphthalene could not be accomplished owing to the failure to obtain a satisfactory yield of the latter compound, from the corresponding amine (cf. Thomson, Race, and Rowe, *J.*, 1947, **354**), or by direct iodination (cf. Derbyshire and Waters, *J.*, 1950, **3694**; Seer and Ehrenreich, *Monatsh.*, 1913, **34**, 631).

Likewise, 2 : 2′-dimethylbenzophenone (Cook, *J.*, 1930, **1091**) failed to condense with diethyl succinate. However, this study is being extended to other mono- and polysubstituted benzophenones.

EXPERIMENTAL

2 : 2′-*Dihydroxybenzophenone*.—A finely powdered mixture of xanthone (2 g.) and potassium hydroxide (1·7 g.) was fused at 205—210° for 20 min. The product was digested with water, and the clear alkaline extract (charcoal) acidified. The precipitated 2 : 2′-dihydroxybenzophenone was filtered off, washed, and dried. On crystallisation from light petroleum (b. p. 40—60°), it was obtained in lemon-yellow crystals (1·4 g.), m. p. 62—63°. Richter (*J. pr. Chem.*, 1883, **28**, 285) and Graebe and Feer (*Ber.*, 1886, **19**, 2609) gave m. p. 59—60° (Found : C, 73·1; H, 4·4; active H, 0·65. Calc. for $C_{13}H_{10}O_3$: C, 72·9; H, 4·6; active H, 0·93%).

2 : 2′- *and* 4 : 4′-*Dimethoxybenzophenone*.—These were prepared by the methylation of the corresponding dihydroxy-compounds (21·4 g.), with methyl sulphate (50·4 g.) and potassium carbonate (55·2 g.) in acetone (200 ml.) (15 hours' refluxing). 4 : 4′-Dimethoxybenzophenone formed needles (*ca.* 29 g.) (from ethyl alcohol), m. p. 145—146° (Schnackenberg and Scholl, *Ber.*, 1903, **36**, 654, gave m. p. 144°); 2 : 2′-dimethoxybenzophenone (*ca.* 22 g.) had m. p. 104—105° (from methanol).

*Ethyl 4-Acetoxy-6-methoxy-*1-p-*methoxyphenyl-2-naphthoate* (II; R = R_2 = H, R_1 = R_3 = OMe, R′ = Et, R″ = Ac).—A mixture of crude ethyl hydrogen γγ-di-*p*-methoxyphenylitaconate (Johnson *et al.*, *loc. cit.*) (3·7 g.), sodium acetate (0·8 g.), and acetic anhydride (20 ml.)

was refluxed for 5 hr. The product was cooled, acetic anhydride decomposed, and the insoluble oil extracted with benzene. The extract was washed successively with water, sodium carbonate solution, and water, and dried ($CaCl_2$). Distillation of the solvent left a brown oily mass (*ca.* 3·2 g.), which solidified on trituration with ether. On crystallisation from acetone, the ester was obtained in aggregates, m. p. 198—199° (Found : C, 70·6; H, 5·5; OMe, 24·0. $C_{23}H_{22}O_6$ requires C, 70·1; H, 5·6; OMe, 23·6%).

4-Hydroxy-6-methoxy-1-p-methoxyphenyl-2-naphthoic Acid.—The above ester on hydrolysis with 10% alcoholic potassium hydroxide, and working up as usual, afforded the *acid* (1·8 g.) which after crystallisation from glacial acetic acid had m. p. 219—220° (shrinking at 218°) (Found : C, 69·8; H, 4·9; OMe, 21·3. $C_{19}H_{16}O_5$ requires C, 70·2; H, 4·9; OMe, 19·1%). Its *ethyl ester* after crystallisation from benzene had m. p. 199—200° (shrinking at 197°) (Found : C, 72·1; H, 5·7; OMe, 25·2. $C_{21}H_{20}O_5$ requires C, 71·6; H, 5·7; OMe 26·4%). Methylation of the foregoing acid (3·3 g.) by methyl iodide (6 ml.) and potassium carbonate (3 g.) in acetone (15 ml.) (12 hours' refluxing) afforded *methyl* 4 : 6-*dimethoxy*-1-p-*methoxyphenyl*-2-*naphthoate* (3·4 g.) in aggregates, m. p. 127—128° (Found : C, 71·4; H, 5·6; OMe, 37·7. $C_{21}H_{20}O_5$ requires C, 71·6; H, 5·6; OMe, 35·2%), from benzene.

On hydrolysis with 10% alcoholic potassium hydroxide (II; $R = R_2 = H$, $R_1 = R_3 = OMe$, $R' = R'' = Me$) gave the corresponding *acid*, in pale yellow flakes, m. p. 205—206° (from glacial acetic acid) (Found : C, 70·7; H, 5·3; OMe, 27·4. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3; OMe, 27·4%).

4 : 6-*Dimethoxy*-1-p-*methoxyphenylnaphthalene* (III; $R = R_2 = H$, $R_1 = R_3 = OMe$).—A stirred solution of 4 : 6-dimethoxy-1-*p*-methoxyphenyl-2-naphthoic acid (0·4 g.) in quinoline (4 ml.), and copper-bronze (0·25 g.) were heated to 205—210° during 30 min. More copper-bronze (0·25 g.) was added portionwise during 2 hr., and stirring and heating were continued for a further hour. The product was worked up as usual, and then crystallised from light petroleum (b. p. 80—100°), giving 4 : 6-*dimethoxy*-1-p-*methoxyphenylnaphthalene* in light brown aggregates (*ca.* 0·3 g.), m. p. 117·5—118·5° (shrinkage at 116°) (Found : C, 77·7; H, 6·1; OMe, 31·9. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1; OMe, 31·8%).

γγ-Di-p-methoxyphenylitaconic Acid (I; $R = R_2 = R' = H$, $R_1 = R_3 = OMe$).—The half-ester (I; $R = R_2 = H$, $R_1 = R_3 = OMe$, $R' = Et$) was hydrolysed with 10% aqueous-alcoholic potassium hydroxide solution (v/v) (2 hours' refluxing) to the acid, m. p. 161—162°.

6-*Methoxy*-3-p-*methoxyphenyl*-1-*oxo*-2-*indenylacetic Acid* (V; $R = R_2 = H$, $R_1 = R_3 = OMe$).—A finely powdered mixture of γγ-di-*p*-methoxyphenylitaconic anhydride (3 g.) (Johnson *et al., loc. cit.*) and aluminium chloride (1·5 g.) was gradually added to stirred and cooled nitrobenzene (15 ml.) at such a rate that the temperature did not exceed 5°. The mixture was kept thereat for a further 3 hr., and then at room temperature for 2 days with occasional stirring. The product was hydrolysed, nitrobenzene removed with steam, and the precipitate filtered off and digested with sodium carbonate solution. The clear alkaline filtrate (charcoal) was acidified, and the red precipitate was filtered off, washed with cold water, and dried (*ca.* 2·8 g.). On repeated crystallisation from benzene, the *keto-acid* formed pink needles, m. p. 181·5—182·5° (Found : C, 69·8; H, 4·7; OMe, 20·6. $C_{19}H_{16}O_5$ requires C, 70·2; H, 4·9; OMe, 19·1%). Its *methyl ester* crystallised from benzene in red, lustrous crystals, m. p. 117—118° (Found : C, 71·3; H, 5·1; OMe, 28·5. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3; OMe, 27·4%), its 2 : 4-*dinitrophenylhydrazone* crystallised from glacial acetic acid in red needles, m. p. 262—263° (Found : N, 11·0. $C_{26}H_{22}O_7N_4$ requires N, 10·8%).

2-*Acetoxy*-2′ : 7-*dimethoxy*-3 : 4-*benzofluorenone* (VI; $R = R_2 = H$, $R_1 = R_3 = OMe$, $R'' = Ac$).—A mixture of the above keto-acid (3 g.), sodium acetate (1 g.), and acetic anhydride (20 ml.) was refluxed for 3 hr. Decomposition of acetic anhydride precipitated a red product which was extracted with benzene. The extract was washed with water and then with sodium carbonate solution and dried ($CaCl_2$). The solid (*ca.* 3·2 g.) left on the evaporation of the solvent was crystallised from benzene, giving 2-*acetoxy*-2′ : 7-*dimethoxy*-3 : 4-*benzofluorenone* in red crystals, m. p. 210—211° (Found : C, 72·3; H, 4·6; OMe, 17·9. $C_{21}H_{16}O_5$ requires C, 72·4; H, 4·6; OMe, 17·8%).

2-*Hydroxy*-2′ : 7-*dimethoxy*-3 : 4-*benzofluorenone* (VI ; $R = R_2 = R'' = H$, $R_1 = R_3 = OMe$).—Hydrolysis of acetoxybenzofluorenone with aqueous sodium hydroxide and working up as usual gave the hydroxy-compound, dark-red flakes, m. p. above 320° (from benzene). It was best identified as its methyl ether, which was prepared as follows :

(*a*) A mixture of the above benzofluorenone (0·4 g.), acetone (15 ml.), methyl iodide (2·5 ml.), and potassium carbonate (1·4 g.) was refluxed for 14—16 hr. and worked up as usual. The product was extracted with benzene, and the extract washed with sodium hydroxide solution, followed by water, and dried ($CaCl_2$). Distillation of the solvent and crystallisation of the red solid (*ca.* 0·4 g.) from benzene gave 2 : 2′ : 7-*trimethoxy*-3 : 4-*benzofluorenone*, m. p. 183—184° (Found : C, 75·2; H, 4·9; OMe 29·0. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0; OMe, 29·2%).

(*b*) *Cyclisation* of 4 : 6-*dimethoxy*-1-p-*methoxyphenyl*-2-*naphthoic acid* (II; $R = R_2 = R' =$ H, $R_1 = R_3 =$ OMe, $R'' =$ Me). A mixture of the pure acid (0·4 g.), benzene (15 ml.), and phosphoric oxide (3 g.) was refluxed for 2 hr. Distillation of benzene and crystallisation of the red solid (0·35 g.) from the same solvent gave the trimethoxy-compound in aggregates, m. p. and mixed m. p. 183—184°.

*Ethyl Hydrogen γγ-Di-*o*-methoxyphenylitaconate* (I; $R = R_2 =$ OMe, $R_1 = R_3 =$ H, $R' =$ Et).—A mixture of 2 : 2′-dimethoxybenzophenone (6·1 g.), diethyl succinate (6·5 g.), and a solution of potassium *tert.*-butoxide (from 1·1 g. of metal) in *tert.*-butyl alcohol (25 ml.) was refluxed in nitrogen; the further procedure was essentially the same as that used by Johnson *et al.* (*loc. cit.*) for the 4 : 4′-dimethoxy-analogue. The crude product (*ca.* 3·7 g.) on crystallisation from benzene afforded *ethyl hydrogen γγ-di-*o*-methoxyphenylitaconate*, m. p. 153—154° (efferv.) (Found : C, 68·1; H, 5·8; OMe, 23·1; active H, 0·3. $C_{21}H_{22}O_6$ requires C, 68·1; H, 5·9; OMe, 23·1; active H, 0·3%).

Attempts to carry out the above condensation by use of alcoholic potassium ethoxide or its suspension in benzene (cf. Haworth and Sheldrick, *J.*, 1935, 640) and long refluxing (17—40 hr.) always gave a very poor yield of an uncrystallisable half-ester. The neutral fraction was hydrolysed with 10% aqueous sodium hydroxide, and the insoluble product extracted with benzene. Distillation of the solvent left a residue which crystallised from methanol to give di-*o*-methoxyphenylmethanol, m. p. 85—86°. Ziegler and Ochs (*Ber.*, 1922, **55**, 2273) gave m. p. 85—86° (Found : C, 73·5; H, 6·4; active H, 0·4%; *M*, 227. Calc. for $C_{15}H_{16}O_3$: C, 73·8; H, 6·5; active H, 0·4%; *M*, 244).

*γγ-Di-*o*-methoxyphenylitaconic Acid* (I; $R = R_2 =$ OMe, $R_1 = R_3 = R' =$ H).—The half-ester (4 g.), when hydrolysed with 10% aqueous-alcoholic potassium hydroxide, gave the crude *acid* (*ca.* 3·7 g.), which had m. p. 185—186° after crystallisation from dilute acetic acid (Found : C, 66·1; H, 5·2; OMe, 17·7. $C_{19}H_{18}O_6$ requires C, 66·6; H, 5·2; OMe, 18·1%).

This acid (4 g.) and acetyl chloride (20 ml.) were refluxed for an hour, the excess of chloride was removed (reduced pressure), and the pale yellow crystalline residue was washed with sodium hydrogen carbonate solution, followed by water, and dried The *anhydride* was then obtained (*ca.* 3·7 g.); on crystallisation from benzene–light petroleum (b. p. 40—60°) it had m. p. 140—141° (Found : C, 70·7; H, 5·1; OMe, 19·3. $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9; OMe, 19·1%).

4-*Hydroxy*-8-*methoxy*-1-o-*methoxyphenyl*-2-*naphthoic Acid* (II; $R = R_2 =$ OMe, $R_1 = R_3 = R' = R'' =$ H).—A mixture of the above half-ester (2 g.), sodium acetate (4 g.), and acetic anhydride (10 ml.) was refluxed for 6 hr. and worked up as usual. *Ethyl* 4-*acetoxy*-8-*methoxy*-1-o-*methoxyphenyl*-2-*naphthoate* was obtained as a pale brown, viscous oil, but 2 hours' refluxing with 10% alcoholic potassium hydroxide and working up as usual afforded the crude acid (*ca.* 1·7 g.); trituration with benzene and crystallisation from acetic acid gave crystals, m. p. 246—247° (Found : C, 69·7; H, 4·8. $C_{19}H_{16}O_5$ requires C, 70·2; H, 4·8%). It did not give a 2 : 4-dinitrophenylhydrazone. Its *ethyl ester* had m. p. 162—163° (from benzene) (Found : C, 71·5; H, 5·6; OMe, 24·8. $C_{21}H_{20}O_5$ requires C, 71·6; H, 5·7; OMe, 26·4%).

4 : 8-*Dimethoxy*-1-o-*methoxyphenyl*-2-*naphthoic Acid* (II; $R = R_2 =$ OMe, $R_1 = R_3 = R' =$ H, $R'' =$ Me).—A hot mixture of the foregoing acid (2 g.), acetone (20 ml.), and potassium carbonate (4 g.) was treated portionwise with methyl iodide (6 g.) during 12 hours' refluxing and then worked up as usual. The pale brown oily product was extracted with benzene, and the extract washed and dried ($CaCl_2$). Distillation of benzene left methyl 4 : 8-dimethoxy-1-*o*-methoxyphenyl-2-naphthoate as a pale brown oil. It was therefore hydrolysed with 10% alcoholic potassium hydroxide to the *acid* (2·0 g.), which recrystallised from glacial acetic acid and then had m. p. 175—176° (Found : C, 71·5; H, 5·4; OMe, 26·4. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3; OMe, 27·4%).

4 : 8-*Dimethoxy*-1-o-*methoxyphenylnaphthalene* (III; $R = R_2 =$ OMe, $R_1 = R_3 =$ H).—The above acid (II; $R = R_2 =$ OMe, $R_1 = R_3 = R' =$ H; $R'' =$ Me) (0·4 g.) was decarboxylated with copper-bronze (0·4 g.) in quinoline (4 ml.), exactly as described for the *p*-isomer. Distillation of the solvent and crystallisation of the residue from light petroleum (b. p. 80—100°) gave 4 : 8-*dimethoxy*-1-o-*methoxyphenylnaphthalene*, m. p. 111—112° (Found : C, 78·1; H, 6·1; OMe, 30·6. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1; OMe, 31·8%).

Attempted Preparation of 2 : 4′ : 5-*Trimethoxy*-3 : 4-*benzofluorenone* (VI; $R = R_2 =$ OMe, $R_1 = R_3 =$ H, $R'' =$ Me).—A mixture of 4 : 8-dimethoxy-1-*o*-methoxyphenyl-2-naphthoic acid (1·5 g.), phosphoric oxide (2·5 g.), and benzene (20 ml.) was worked up as described for the *p*-isomer. Distillation of the solvent left a dark, cherry-red viscous oil (*ca.* 1·2 g.), a fraction, b. p. 260—290°/2 mm., of which solidified to a dark red, uncrystallisable mass.

*Action of Aluminium Chloride on γγ-Di-*o*-methoxyphenylitaconic Anhydride* (IV; $R = R_2 =$ OMe, $R_1 = R_3 =$ H).—Finely powdered aluminium chloride (1·5 g.) was gradually added to a stirred solution of the anhydride (3 g.) in nitrobenzene (30 ml.) at 0—5°, and the mixture left for 2 days (20—25°), and then worked up as usual. The pale brown product was filtered off, and digested with sodium carbonate solution. Acidification of the clear filtrate (charcoal) precipitated an acid which was filtered off, washed, and dried (*ca.* 2·7 g.). On crystallisation from benzene–light petroleum (b. p. 40—60°), *4-*o*-methoxyphenyl-3-coumarinylacetic acid* was obtained, m. p. 185—186° (depressed to 158—176° on admixture with γγ-di-*o*-methoxyphenylitaconic acid) (Found: C, 69·9; H, 4·8; OMe, 10·6. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·7; OMe, 10·0%). It discharged the colour of alkaline potassium permanganate solution and failed to give a 2 : 4-dinitrophenylhydrazone.

*Conversion of 4-*o*-Methoxyphenyl-3-coumarinylacetic Acid* (VII) *into αα-Di-*o*-methoxyphenylitaconic Acid* (I; $R = R_2 =$ OMe, $R_1 = R_3 = R' =$ H).—A solution of the acid (VII) (0·3 g.) in sodium hydroxide (0·3 g.) and water (1 ml.) was refluxed for 30 min. and kept on a water-bath while being treated portionwise with methyl sulphate (0·32 g.) (cf. Stoermer and Friemel, *Ber.*, 1911, **44**, 1843) for an hour thereafter. The product was extracted with ether, and the extract washed successively with sodium hydroxide solution and with water and dried (Na_2SO_4). Distillation of ether left a viscous, pale brown oil which was directly hydrolysed with 10% alcoholic potash (3 hours' refluxing). The clear aqueous solution (charcoal) was acidified, and the precipitate was filtered off (*ca.* 0·3 g.), and crystallised from dilute acetic acid, giving γγ-di-*o*-methoxyphenylitaconic acid, identical with an authentic specimen.

3-Iodoanisic Acid.—Finely powdered anisic acid (14·8 g.) was iodinated by the method used by Derbyshire and Waters (*loc. cit.*) for iodobenzoic acid, and the precipitate thoroughly extracted with sodium carbonate solution. The clear alkaline extract (charcoal) was acidified, and the precipitate washed and dried (*ca.* 25 g.). On crystallisation from ethyl alcohol, 3-iodoanisic acid was obtained in needles, m. p. 234—235° (Willgerodt and Burkhard, *Annalen*, 1912, **389**, 294, gave m. p. 234°). Its methyl ester crystallised from light petroleum (b. p. 60—80°) in flakes, m. p. 94—95° (Found: C, 37·2; H, 3·1; OMe, 20·8; I, 43·2. Calc. for $C_9H_9O_3I$: C, 36·9; H, 3·1; OMe, 21·4; I, 43·5%).

*Attempted Synthesis of 4 : 8-Dimethoxy-1-*o*-methoxyphenylnaphthalene by Gomberg's Reaction.*—Methyl 3-aminoanisate (9 g.) (von Auwers, *Ber.*, 1897, **30**, 1477) was diazotised, and the solution mixed with one of 1 : 5-dimethoxynaphthalene (Naylor and Gardner, *J. Amer. Chem. Soc.*, 1931, **53**, 4109) (19·2 g.) in carbon tetrachloride (100 ml.); the mixture was stirred at −5° while sodium hydroxide solution (25 ml.; 60%) was gradually added (1 hr.). The temperature was kept at −10° for 1·5 hr., raised to 45° during 3·5 hr., and kept thereat for 5 hr., and the mixture worked up as described by Baddar (*J.*, 1941, 310). Products isolated from both the carbon tetrachloride layer and the sodium hydroxide layer were either uncrystallisable oils or mixtures of crystals, and the yields were so poor that no pure constituents could be separated.

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