767. *An Approach to the Synthesis of Morphenol.*

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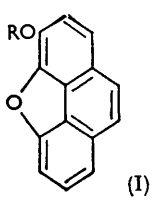
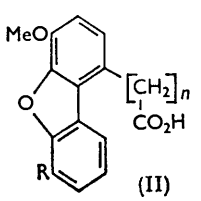
Attempts to synthesise morphenol have produced the related 1,2,3,8,9,9a-hexahydro-5-methoxy-8-oxophenanthro[4,5-*bcd*]furan (IX; R = OMe).

Morphine furnishes a variety of non-nitrogenous degradation products,[1] including morphenol (I; R = H), which has not yet been synthesised. For instance, Burger and Avakian [2] failed to cyclise the acid (II; R = H, n = 1) to the phenanthrol (III; R = H); similarly [3] the acid (II; R = OMe, n = 1) resisted conversion into the ketone (III; R = OMe), and the analogous propionic acid [4] (II; R = OMe, n = 2) gave the indenone (IV)



(I)



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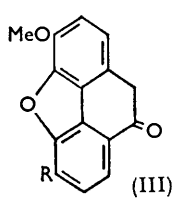

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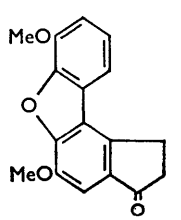


(IV)

rather than a phenanthro[4,5-*bcd*]furan. Our attempts to synthesise morphenol have also been unsuccessful and have been discontinued. This paper reports certain results, including the synthesis of a congener of morphenol, namely, the derivative (IX; R = OMe).

[1] Manske, " The Alkaloids," Academic Press, New York, 1960, Vol. II, p. 1.
[2] Burger and Avakian, *J. Amer. Chem. Soc.*, 1940, **62**, 226.
[3] Gilman and Cheney, *J. Amer. Chem. Soc.*, 1939, **61**, 3149.
[4] Hogg, *Iowa State College J. Sci.*, 1945, **20**, 15.

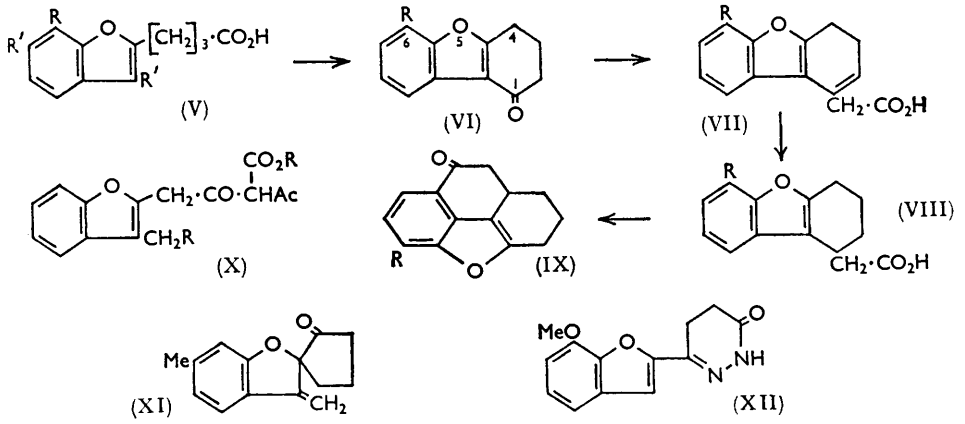
Previous attempts to prepare morphenol have commenced from fully aromatic systems.[2-4] Since morphenol contains an inherently strained fused-ring system our synthetic investigations, which are essentially illustrated by the sequence (V; R = OMe, R′ = H) ⟶ (IX), have utilised partially hydroaromatic precursors in which it was hoped that the greater flexibility would assist cyclisations of the type (VIII) ⟶ (IX) [cf., *e.g.*, the synthesis of (±)-lysergic acid [5]].

In a series of model experiments γ-benzo[*b*]furan-2-ylbutyric acid (V; R = R′ = H) was readily converted into 1,2,3,4-tetrahydro-1-oxodibenzofuran (VI; R = H). Condensation of this with ethyl bromoacetate gave (after dehydration of the intermediate β-hydroxy-ester) 3,4-dihydrodibenzofuran-1-ylacetic acid (VII; R = H) whose light absorption ($\lambda_{max.}$ 238 and 298 mμ) indicates that the double bond is βγ and not αβ with respect to the carboxyl group. Hydrogenation gave the tetrahydro-acid (VIII; R = H) which did not cyclise to the phenanthro[4,5-*bcd*]furan (IX; R = H) under a variety of conditions.

Despite this failure it was hoped that the 5-methoxy-analogue (VIII; R = OMe), required to furnish morphenol, might be more reactive in ring closure. To this end methyl γ-(7-methoxybenzo[*b*]furan-2-yl)butyrate, prepared from *o*-vanillin and methyl 5-chloro-4-oxopentanoate, was converted by Wolff–Kishner reduction into the butyric acid (V; R = OMe, R′ = H): the pyridazinone (XII) was a minor product. Cyclisation of the acid (V; R = OMe, R′ = H) with phosphorus pentoxide gave smoothly the tetrahydrodibenzofuran (VI; R = OMe) but attempts to cyclise by a Friedel–Crafts type catalyst furnished a monochloro-derivative of compound (VI; R = OMe). The dibenzofuran (VI; R = OMe) gave the tetrahydro-acid (VIII; R = OMe) by standard methods. Subsequent direct cyclisation was unsuccessful, but the corresponding acid chloride gave the phenanthro[4,5-*bcd*]furan (IX; R = OMe), albeit in low yield.

The constitution of this product follows from its general properties, elemental analysis, infrared spectrum (ν 1666 cm.$^{-1}$, aromatic-type C=O), and ultraviolet absorption ($\lambda_{max.}$ 246 mμ, log ε 4·22), the ultraviolet absorption of the 2,4-dinitrophenylhydrazone ($\lambda_{max.}$ 394 mμ log ε 4·30), and the method of preparation since cyclisation of the acid (VIII; R = OMe) to furnish a ketone can only occur in accordance with the structure (IX; R = OMe).

We believe this to be the first synthesis of a phenanthrylene oxide of type (IX), but the unsatisfactory yield in the final cyclisation led us to abandon this project.



The constitution of the dibenzofuran (VI; R = H) and hence of (VI; R = OMe) was defined by Wolff–Kishner reduction of the analogue (VI; R = H) to 1,2,3,4-tetrahydrodibenzofuran. This definition is necessary since β-substituted benzofurans of type (X)

[5] Kornfeld, Fornefeld, Kline, Mann, Jones, and Woodward, *J. Amer. Chem. Soc.*, 1954, **76**, 5256.

cyclise [6] to spirans of type (XI), and during this investigation we have shown that acid-catalysed cyclisation of an acid (V; R = H, R′ = Me) similarly gives the spiran (XI), having infrared absorption at 1739s (cyclopentanone C=O) and 804s cm.$^{-1}$ (exocyclic :CH_2). As expected, γ-(6-methyl-3-phenylbenzo[*b*]furan-2-yl)butyric acid resisted cyclisation.

The constitutions of the acid (V; R = H, R′ = Me) and its analogues (see Experimental) follow from their preparation from the corresponding γ-oxobutyric acids which were in turn derived from Friedel–Crafts condensation of 3,6-dimethylbenzofuran with succinic anhydride. This structural assignment is in accord with general principles (see, *e.g.*, Whalley [7,8]) but was proved by an alternative synthesis of γ-(3,6-dimethylbenzo[*b*]-furan-2-yl)-γ-oxobutyric acid, by interaction of 3,6-dimethylcoumariloyl chloride with ethyl sodioacetosuccinate followed by ketonic hydrolysis.

Experimental

1,2,3,4-Tetrahydrodibenzofuran-1-ylacetic acid (VIII; R = H).—The following synthesis was completed before that recorded by Chatterjea [9] and differs in experimental detail.

A solution of 2-bromoacetylbenzo[*b*]furan (18·3 g.) in 1 : 1 ether–benzene (200 ml.) was added during 20 min. to a suspension of the sodium derivative of ethyl malonate (13·5 g.) in benzene (100 ml.). After 3 days at room temperature reaction was completed at the b. p. during 15 min. The oily product was hydrolysed during 1½ hr. with boiling 5% sodium hydroxide solution (300 ml.). Acidification then furnished the crude malonic acid (10 g.) which was decarboxylated at 160° during 10 min. Purification of the product from aqueous alcohol gave γ-(benzo[*b*]furan-2-yl)-γ-oxobutyric acid in needles (5·5 g.), m. p. 148° (Found: C, 66·1; H, 4·5. Calc. for $C_{12}H_{10}O_4$: C, 66·1; H, 4·6%). Chatterjea [9] records m. p. 140°.

Reduction of this acid (6 g.) in acetic acid (130 ml.) with zinc amalgam (15 g.) and concentrated hydrochloric acid (25 ml.) during 3 days at room temperature gave γ-benzo[*b*]furan-2-ylbutyric acid which formed prisms (3 g.), m. p. 82°, from light petroleum (b. p. 60—80°) (Found: C, 70·6; H, 6·0. Calc. for $C_{12}H_{12}O_3$: C, 70·6; H, 5·9%). Chatterjea [9] records m. p. 82—83°. A solution of the acid chloride [from the acid (7 g.) and phosphorus pentachloride (8 g.) in chloroform (25 ml.)] in carbon disulphide (120 ml.) containing aluminium chloride (8 g.) was kept at room temperature for 3 days. After isolation in the usual manner, *1,2,3,4-tetrahydro-1-oxodibenzofuran* separated from light petroleum (b. p. 40—60°) in prisms, m. p. 41° (Found: C, 76·7; H, 5·5. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%). This compound was obtained previously [9] as an oil.

Reduction of this dibenzofuran with hydrazine and potassium hydroxide in diethylene glycol at 200° for 6 hr. gave 1,2,3,4-tetrahydrodibenzofuran as an oil, which was characterised as the picrate, orange needles, m. p. 91° (from methanol), identical with an authentic specimen. A mixture of 1,2,3,4-tetrahydro-1-oxodibenzofuran (3 g.), zinc foil (5 g.), methyl bromoacetate (2·5 ml.), and benzene (35 ml.) containing a crystal of iodine was gently warmed until reaction commenced. Next day zinc (0·5 g.) and methyl bromoacetate (0·5 ml.) were added and the mixture was heated under reflux for 1 hr. Isolated in the usual manner, methyl 1,2,3,4-tetrahydro-1-hydroxydibenzofuran-1-ylacetate was obtained as a viscous oil which was dehydrated by oxalic acid (2 g.) in boiling toluene (40 ml.) for 2 hr. The product was saponified during 1 hr. with warm 10% potassium hydroxide solution (30 ml.), to give *3,4-dihydrodibenzofuran-1-ylacetic acid*, needles (1 g.), m. p. 197° (from aqueous alcohol) (Found: C, 73·9; H, 5·4%; Equiv., 238. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%; Equiv., 228).

Hydrogenation of this acid (2·3 g.) in alcohol (50 ml.) with a catalyst prepared from charcoal (0·5 g.) and palladium chloride (0·1 g.) furnished *1,2,3,4-tetrahydrodibenzofuran-1-ylacetic acid* which formed needles (2 g.), m. p. 87°, from light petroleum (b. p. 60—80°) (Found: C, 72·9; H, 6·0. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%).

Methyl 5-Chloro-4-oxopentanoate.—Previous methods [10] for the preparation of this compound probably gave a very impure product. The following process proved satisfactory.

[6] Dean, Halewood, Mongolsuk, Robertson, and Whalley, *J.*, 1953, 1250.
[7] Whalley, *J.*, 1951, 665.
[8] Whalley, *J.*, 1953, 3479.
[9] Chatterjea, *J. Indian Chem. Soc.*, 1957, **34**, 306.
[10] Buchman and Sargent, *J. Amer. Chem. Soc.*, 1945, **67**, 402.

Thionyl chloride (600 g.) was added gradually to methyl hydrogen succinate (400 g.) and the temperature of the mixture kept at 40—50° for 2 hr. The product was distilled, to yield β-methoxycarbonylpropionyl chloride (450 g.), b. p. 86°/12 mm. A solution of this acid chloride (80 g.) in ether (200 ml.) was added during 3 hr. to ethereal diazomethane (2·5 l.) (prepared from 180 g. of methylnitrosourea), and the resultant solution was saturated with hydrogen chloride during 2 hr. at 0°. Next day the solution was washed with water and 2N-sodium hydrogen carbonate, dried, and fractionated, to yield *methyl 5-chloro-4-oxopentanoate* (72 g.), b. p. 120°/13 mm. (Found: Cl, 20·6. $C_6H_9ClO_3$ requires Cl, 21·4%).

1,2,3,4-*Tetrahydro-6-methoxy-1-oxo-dibenzofuran* (VI; R = OMe).—A solution of *o*-vanillin (6 g.) and methyl 5-chloro-4-oxopentanoate (7 g.) in acetone (150 ml.) containing potassium carbonate (50 g.) was heated under reflux for 3 hr., then further quantities of chloro-ketone (2 g.) and potassium carbonate (15 g.) were added and the mixture refluxed for a further 6 hr. Isolated in the usual manner, *methyl γ-(7-methoxybenzo*[b]*furan-2-yl)-γ-oxobutyrate* separated from methanol in needles (8·2 g.), m. p. 85° (Found: C, 64·1; H, 5·5. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%).

A mixture of this ester (7·5 g.), hydrazine hydrate (6 ml.), and diethylene glycol (50 ml.) was heated on the steam-bath for 3 hr., with addition of a solution of potassium hydroxide (5 g.) in diethylene glycol (100 ml.) after 1 hr. The mixture was then kept at 175—185° for 2 hr. The *acid* (V; R = OMe, R′ = H) was isolated in the usual manner and crystallised from light petroleum (b. p. 80—100°) in needles (2·1 g.), m. p. 86° (Found: C, 66·8; H, 6·6. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%). When octan-1-ol was used as the solvent for this reduction similar yields of butyric acid were obtained together with 1,4,5,6-*tetrahydro-6-(7-methoxybenzo*[b]*furan-2-yl)-6-oxopyridazine* (XII) which separated on addition of water to the cooled reaction mixture and from methanol–chloroform formed needles (2·2 g.), m. p. 207° (Found: C, 63·3; H, 4·9; N, 11·2. $C_{13}H_{12}N_2O_3$ requires C, 63·9; H, 5·0; N, 11·5%).

A solution of the acid (V; R = OMe, R′ = H) (4·7 g.) in benzene (400 ml.) containing phosphorus pentoxide (11 g.) was heated under reflux for 8 hr. with stirring. After addition of ice and water to the cooled mixture the benzene layer was separated, washed with 2N-sodium hydrogen carbonate and water, and dried, to yield 1,2,3,4-*tetrahydro-6-methoxy-1-oxodibenzofuran* (3·9 g.) which separated from light petroleum (b. p. 80—100°) in needles, m. p. 119° (Found: C, 72·4; H, 5·2; OMe, 14·2. $C_{12}H_9O_2$·OMe requires C, 72·2; H, 5·6; OMe, 14·4%).

Many attempts to cyclise the acid (V; R = OMe, R′ = H) by Friedel–Crafts reactions yielded a chlorinated product. The following experiment was typical. Aluminium chloride (2 g.) was added to a solution of the acid chloride [prepared from the acid (0·5 g.) and phosphorus pentachloride (2 g.) during 1 hr.] in benzene (20 ml.) at 0°. Next day the product was isolated in the usual manner and purified by chromatography from benzene on activated aluminium oxide, followed by crystallisation from methanol. This gave x-*chloro*-1,2,3,4-*tetrahydro-6-methoxy-1-oxobenzofuran* in plates (0·3 g.), m. p. 170° (Found: C, 62·4; H, 4·4; Cl, 13·8; OMe, 12·7. $C_{12}H_8ClO_2$·OMe requires C, 62·2; H, 4·4; Cl, 14·0; OMe, 12·4%). The 2,4-*dinitrophenylhydrazone* formed red prisms (from benzene), m. p. 209° (decomp.) (Found: C, 53·8; H, 3·5; N, 11·5. $C_{19}H_{15}ClN_4O_6$ requires C, 53·0; H, 3·5; N, 13·0%).

1,2,3,8,9,9a-*Hexahydro-5-methoxy-8-oxophenanthro*[4,5-bcd]*furan* (IX; R = OMe).—Ethyl bromoacetate (10 ml.) in benzene (50 ml.) was added during ½ hr. to a stirred solution of 1,2,3,4-tetrahydro-6-methoxy-1-oxodibenzofuran (8·1 g.) in benzene (550 ml.) containing zinc turnings (50 g.), heated under reflux. Reaction was initiated by addition of magnesium turnings (0·1 g.) and a crystal of iodine. The stirred mixture was refluxed for 2 hr. and then decomposed by addition of ice and 2N-sulphuric acid. The benzene solution was separated, washed with water, dried, and distilled with the addition of toluene-*p*-sulphonic acid (0·5 g.) to furnish *ethyl 3,4-dihydro-6-methoxydibenzofuran-1-ylacetate* (7·8 g.), needles, m. p. 97° (from alcohol) (Found: C, 71·2; H, 6·4. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%).

A similar reaction gave the corresponding *methyl ester*, needles (from methanol), m. p. 82° (Found: C, 70·8; H, 5·2. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

Hydrogenation of the ethyl dihydro-ester (5 g.) in alcohol (500 ml.) with a catalyst prepared from charcoal (0·5 g.) and palladium chloride (0·2 g.) was complete after 3 hr. 10% Aqueous potassium hydroxide (500 ml.) was added to the clarified solution which was refluxed for 1 hr. After isolation, 1,2,3,4-*tetrahydro-6-methoxydibenzofuran-1-ylacetic acid* (4·2 g.) formed prisms, m. p. 141°, from light petroleum (b. p. 60—80°) (Found: C, 69·3: H, 6·4; OMe, 11·7. $C_{14}H_{13}O_3$·OMe requires C, 69·2; H, 6·2; OMe, 11·9%).

Attempts to form the acid chloride of this acetic acid by using thionyl chloride gave a resin; phosphorus pentachloride in methylene chloride produced a substance which on hydrolysis gave x-*chloro*-1,2,3,4-*tetrahydro*-6-*methoxydibenzofuran*-1-*ylacetic acid* in prisms, m. p. 116° [from light petroleum (b. p. 60—80°)] (Found: Cl, 11·7. $C_{15}H_{15}ClO_4$ requires Cl, 12·1%). Interaction of 1,2,3,4-tetrahydro-6-methoxydibenzofuran-1-ylacetic acid (0·4 g.) and oxalyl chloride (0·5 ml.) in boiling benzene (2 ml.) during 1 hr. furnished 1,2,3,4-*tetrahydro*-6-*methoxydibenzofuran*-1-*ylacetyl chloride* (0·4 g.), b. p. 280°/0·8 mm. (Found: C, 64·9; H, 5·8. $C_{15}H_{15}ClO_3$ requires C, 64·5; H, 5·7%), whence hydrolysis regenerated the starting acid, m. p. and mixed m. p. 141°, having the requisite infrared absorption spectrum. This chloride gave the *anilide*, needles (from methanol), m. p. 158° (Found: C, 75·0; H, 6·6; N, 4·3; Cl, 0. $C_{21}H_{21}NO_3$ requires C, 75·2; H, 6·3; N, 4·2%).

Aluminium chloride (5 g.) was added to a solution of the acid chloride (5 g.) in carbon disulphide (100 ml.) at 0°. After 10 days at this temperature the mixture was decomposed by ice and hydrochloric acid and extracted with benzene and the extract was washed with 2N-sodium hydrogen carbonate to remove acid. Evaporation of the dried benzene solution afforded a neutral oil which, after treatment with boiling aqueous-alcoholic 5N-potassium hydroxide during ½ hr., afforded a residual neutral fraction (*ca.* 1 g.) together with the parent acid (1·5—2 g.). The neutral fraction was chromatographed in benzene on activated aluminium oxide. Elution with 1 : 99 chloroform–benzene gave a ketonic fraction which on crystallisation from methanol furnished 1,2,3,8,9,9a-*hexahydro*-5-*methoxy*-8-*oxophenanthro*[4,5-bcd]*furan* (IX; R = OMe) in needles, m. p. 115° (Found: C, 74·3; H, 6·3%; *M*, 242. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%), *M*, 242), $\lambda_{max.}$ 246, 295, 236 mμ (log ε 4·22, 4·02, 3·88, respectively). The 2,4-*dinitrophenylhydrazone* formed red needles (from benzene), m. p. 282° (decomp.) (Found: C, 59·9; H, 4·5; N, 12·5. $C_{21}H_{18}N_4O_6$ requires C, 59·7; H, 4·3; N, 13·3%).

Reduction of this ketone (24 mg.) in methanol (100 ml.) containing sodium borohydride (0·5 g.) and water (5 ml.) furnished the 8-*hydroxy-analogue* which separated from methanol in needles (19 mg.), m. p. 134° (Found: C, 73·8; H, 6·9. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

γ-(3,6-*Dimethylbenzo*[b]*furan*-2-*yl*)-γ-*oxobutyric Acid*.—(*a*) A solution of aluminium chloride (25 g.) in nitrobenzene (45 ml.) was added at 0° to a solution of 3,6-dimethylbenzofuran (15 g.) and succinic anhydride (10 g.) in nitrobenzene (45 ml.). The mixture was kept at 0° for 40 hr., then the product was isolated in the usual manner and purified from methanol, to furnish γ-(3,6-*dimethylbenzo*[b]*furan*-2-*yl*)-γ-*oxobutyric acid* (10 g.) in needles, m. p. 154° (Found: C, 68·3; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%).

γ-(3,7-*Dimethylbenzo*[b]*furan*-2-*yl*)-γ-*oxobutyric acid*, needles, m. p. 174° (from alcohol) (Found: C, 68·5; H, 5·8. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%), and the 3-*methyl analogue*, needles, m. p. 184° (from alcohol) (Found: C, 66·7; H, 5·4. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%), were prepared similarly. Obtained in an analogous way from 3,6-dimethylbenzo[*b*]-furan and phthalic anhydride 2-o-*carboxybenzoyl*-3,6-*dimethylbenzo*[b]*furan* crystallised from alcohol in needles, m. p. 180° (Found: C, 73·8; H, 4·9. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8%).

(*b*) A solution of 3,6-dimethylcoumariloyl chloride [prepared from the acid (4·5 g.) and phosphorus pentachloride (5·5 g.)] in ether (15 ml.) was added gradually to a suspension of ethyl sodioacetosuccinate [from ethyl acetosuccinate (5·1 g.) and sodium (0·5 g.)] in ether (20 ml.). After 10 hours' heating under reflux, the mixture was decomposed by iced water and extracted with ether. The residue obtained on removal of the ether was heated at 50° for 24 hr. with 1·5% sodium hydroxide solution (270 ml.). After removal of a small quantity of insoluble material the solution was acidified, to furnish a mixture of 3,6-dimethylcoumarilic acid and γ-(3,6-dimethylbenzo[*b*]furan-2-yl)-γ-oxobutyric acid. A solution of this mixture in alcohol (50 ml.) containing semicarbazide hydrochloride (5 g.) and anhydrous sodium acetate (3 g.) was refluxed for 1 hr. The sparingly soluble *semicarbazone* of the keto-acid separated on cooling and formed prisms (3·4 g.), m. p. 218° (decomp.), from alcohol (Found: N, 14·0. $C_{15}H_{17}N_3O_4$ requires N, 13·9%).

This semicarbazone (3·2 g.) was decomposed by boiling 10% hydrochloric acid (100 ml.) during 2 hr., to furnish the keto-acid (1·3 g.), m. p. and mixed m. p. 154°, identical with the specimen prepared by method (*a*) (Found: C, 68·2; H, 5·8. Calc. for $C_{14}H_{14}O_4$: C, 68·3; H, 5·7%).

2,3-*Dihydro*-6-*methyl*-3-*methylene*-2′-*oxobenzo*[b]*furan*-2-*spirocyclopentane* (XI).—Reduction of γ-(3,6-dimethylbenzo[*b*]furan-2-yl)-γ-oxobutyric acid (3 g.) with hydrazine hydrate (1·75 g.) and potassium hydroxide (3 g.) in diethylene glycol (35 ml.) was complete after 3 hr. at 140°.

The resultant γ-(3,6-*dimethylbenzo*[b]*furan*-2-*yl*)*butyric acid* (V; R = H, R′ = Me) (1·8 g.) separated from light petroleum (b. p. 60—80°) in needles, m. p. 80° (Found: C, 71·9; H, 6·5. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). A solution of the acid chloride [prepared from the acid (6 g.) and phosphorus pentachloride (5 g.) in carbon tetrachloride (45 ml.)] in carbon disulphide (40 ml.) containing aluminium chloride (5 g.) was kept for 24 hr. at room temperature. After isolation in the usual manner, the *spiran* (XI) was obtained as an oil (1·4 g.), b. p. 150°/1 mm. (Found: C, 77·8; H, 7·1. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%). The 2,4-*dinitrophenylhydrazone* separated from alcohol–benzene in orange prisms, m. p. 271° (decomp.) (Found: C, 60·4; H, 4·4; N, 13·8. $C_{20}H_{18}N_4O_5$ requires C, 60·9; H, 4·6; N, 14·2%).

γ-(6-*Methyl*-3-*phenylbenzo*[b]*furan*-2-*yl*)-γ-*oxobutyric Acid.*—Prepared by the reaction of 2-hydroxy-4-methylbenzophenone (30 g.) with methyl bromoacetate (15 ml.) in boiling acetone (100 ml.) containing potassium carbonate (40 g.) during 8 hr., *methyl* 2-*benzoyl*-5-*methylphenoxyacetate* separated from methanol in needles (20 g.), m. p. 64° (Found: C, 71·8; H, 5·7. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%).

Cyclisation of this ester (5 g.) in alcohol (40 ml.) with sodium (0·6 g.) occurred during 45 min. at 60°, giving *methyl* 6-*methyl*-3-*phenylbenzo*[b]*furan*-2-*carboxylate*, pale yellow needles (2·5 g.), m. p. 82° (from aqueous methanol) (Found: C, 76·9; H, 5·6. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). Alkaline hydrolysis then furnished 6-methyl-3-phenylcoumarilic acid (quantitatively), needles, m. p. 230° (from methanol). A solution of this acid (8 g.) in quinoline (75 ml.) containing copper powder (0·1 g.) was refluxed for 15 min. The neutral fraction was purified by distillation (b. p. 240°/15 mm.), followed by crystallisation from light petroleum (b. p. 40—60°), giving 6-*methyl*-3-*phenylbenzo*[b]*furan*, plates (7 g.), m. p. 42° (Found: C, 86·6; H, 5·9. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). Reaction of this coumarone (4·5 g.) with succinic anhydride (2·5 g.) in nitrobenzene (40 ml.) containing aluminium chloride (6·5 g.) at room temperature during 24 hr. furnished γ-(6-*methyl*-3-*phenylbenzo*[b]*furan*-2-*yl*)-γ-*oxobutyric acid*, needles (3 g.), m. p. 175° (from alcohol) (Found: C, 73·7; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). The 2,4-*dinitrophenylhydrazone* separated from benzene–alcohol in red prisms, m. p. 234° (Found: N, 11·8. $C_{25}H_{20}N_4O_7$ requires N, 11·5%).

After formation of the hydrazone of this acid (3 g.) at 100° during 30 min. with 90% hydrazine hydrate (2 ml.) in diethylene glycol (40 ml.), potassium hydroxide (6 g.) was added to the mixture and the temperature raised to 140° for 3 hr. From light petroleum (b. p. 60—80°) γ-(6-*methyl*-3-*phenylbenzo*[b]*furan*-2-*yl*)*butyric acid* formed tablets (2 g.), m. p. 98° (Found: C, 77·5; H, 6·3. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%).

Spectra.—Ultraviolet absorption spectra were determined for 95% alcohol solutions with a Unicam S.P. 500 spectrophotometer. The infrared spectral data were obtained for Nujol mulls with a Perkin-Elmer model 21 spectrophotometer.

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