936. *The Stobbe Condensation with Dimethyl Homophthalate.*

By H. J. E. Loewenthal and R. Pappo.

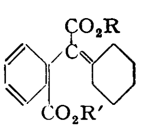
*cyclo*Hexanone, acetone, benzophenone, and benzaldehyde have been condensed with dimethyl homophthalate, in the presence of sodium hydride, to give the expected half-esters in excellent yield. This constitutes an extension of Stobbe's reaction of ketones with dialkyl succinates. Cyclisation and lactonisation of the half-esters obtained have been investigated.

In general, condensation of ketones with a reactive methylene group is difficult to achieve, probably because of the unfavourable equilibrium towards the aldol which is formed primarily. The Stobbe condensation of ketones with alkyl succinates is an exception. Recent work (Johnson, McCloskey, and Dunnigan, *J. Amer. Chem. Soc.*, 1950, **72**, 514) has indicated that, in this reaction, the intermediate aldol condensation product is stabilised by the formation of a saturated five-membered lactone, which is subsequently cleaved, irreversibly, by the alkaline catalyst.

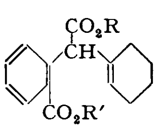
This type of reaction has been extended to dimethyl β-methylglutaconate (Bischof, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1949, **32**, 1920). Here, an unsaturated six-membered lactone might be the intermediate, although comparatively little is known about the stability of such lactones.

Homophthalic acid can be regarded as a homologue of glutaconic acid, so the behaviour of its dimethyl ester in the Stobbe condensation has been studied. Several examples are recorded where derivatives of this acid were condensed with aldehydes. Thus, Mueller (*Annalen*, 1931 **491**, 251) obtained a δ-lactonic acid (probably VI*c*) from the sodium salt of the enol of homophthalic anhydride and benzaldehyde; Dieckmann (*Ber.*, 1914, **47**, 1432) prepared α-benzylidenehomophthalic acid after condensation of the same aldehyde with diethyl homophthalate. By condensing dimethyl homophthalate with a number of ketones, using sodium hydride as catalyst as suggested by Daub and Johnson (*J. Amer. Chem. Soc.*, 1948, **70**, 418), we have obtained the expected half-esters in excellent yield. With *cyclo*hexanone and acetone no Claisen condensation occurred α to the carbonyl group.

An oily mixture of half-esters (I*a* and II*a*) was obtained from *cyclo*hexanone and was hydrolysed to a mixture of the corresponding diacids (I*b* and II*b*). Owing to greater ease of anhydride formation, (II*b*) could be separated, to some extent, from the higher-melting (I*b*) in which the position of the double bond was confirmed by oxidation to *cyclo*hexanone. These products behave similarly to those obtained by Johnson, Davis, Hunt, and Stork (*ibid.*, p. 3021) from *cyclo*hexanone and diethyl succinate.



(I*a*; R = Me, R' = H)
(I*b*; R = R' = H)
(I*c*; R = R' = Me)



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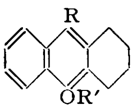
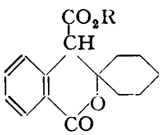
(II*b*; R = R' = H)
(II*c*; R = R' = Me)



(III*a*; R = CO₂Me, R' = Ac)
(III*b*; R = R' = H)



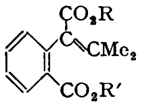
(IV*a*; R = Me)
(IV*b*; R = H)

Cyclisation of the mixture of (I*a*) and (II*a*) with acetic anhydride and acetic acid containing a trace of fused zinc chloride (Fieser and Hershberg, *ibid.*, 1937, **59**, 1028) led to methyl 10-acetoxy-1 : 2 : 3 : 4-tetrahydroanthracene-9-carboxylate (III*a*). Alkaline hydrolysis of this, rather surprisingly, left the carbomethoxy-group unaffected. On the other hand, when the resulting phenolic ester was hydrolysed by acid, the carbomethoxy-group was eliminated, giving 1 : 2 : 3 : 4-tetrahydroanthranol (III*b*), presumably identical with the product obtained by von Braun and Bayer (*Ber.*, 1925, **58**, 2667) by catalytic reduction of anthraquinone or anthrone.

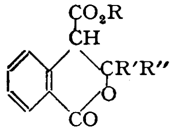
Refluxing the mixture of (I*a*) and (II*a*) with acetic anhydride, acetic acid, and sodium acetate yielded the lactonic methyl ester (IV*a*), which may be the postulated intermediate product in the Stobbe condensation, as it was cleaved to the half-ester (I*a*) by cold alcoholic alkali. The parent lactonic acid (IV*b*) resulted from treatment of the half-ester mixture with boiling hydrobromic acid in acetic acid (cf. Johnson, Davis, *et al.*, *loc. cit.*).

Dehydrogenation of the diester mixture (I*c*) and (II*c*), which was obtained by esterification of the diacids (I*b*) and (II*b*), led ultimately to *o*-benzylbenzoic acid and thence to anthrone. So the condensation of alicyclic or hydroaromatic ketones with esters of homophthalic acid might be utilised in a new general synthesis of anthracene derivatives.

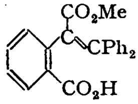
Dimethyl homophthalate and acetone gave a crystalline, homogeneous, half-ester (V*a*). Its formulation as an *iso*propylidene derivative was assured by the fact that the diacid (V*c*), obtained by hydrolysis, gave acetone on oxidation. Its reaction with acetic anhydride, in the presence of sodium acetate, again gave a lactonic ester (VI*a*), and with zinc chloride as catalyst 3-methyl-1-naphthol was formed in small yield. Under the latter conditions, intramolecular ester exchange, leading to the isomeric half-ester (V*b*), appeared to be the main reaction. (A comprehensive discussion of this phenonomenon is given by Johnson and Goldmann, *J. Amer. Chem. Soc.*, 1945, **67**, 430.) The lactonic acid (VI*b*), which was obtained from (V*a*) by treatment with hydrobromic and acetic acids, is possibly identical with the acid obtained by Courtot (*Compt. rend.*, 1915, **160**, 534) by oxidation of 2-1′-indenylpropan-2-ol.



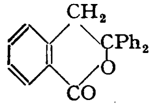
(V*a*; $R = Me, R' = H$)
(V*b*; $R = H, R' = Me$)
(V*c*; $R = R' = H$)



(VI*a*; $R = R' = R'' = Me$)
(VI*b*; $R = H, R' = R'' = Me$)
(VI*c*; $R = R' = H, R'' = Ph$)



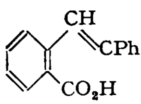
(VII)



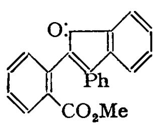
(VIII)

In contrast to the previous half-esters, that (VII) obtained from benzophenone was decarboxylated under strongly acidic conditions, to a mixture of the lactone (VIII) and the unsaturated acid (IX). No lactonic ester or lactonic acid could be obtained, but with zinc chloride as catalyst the indenone derivative (X) was formed in good yield.

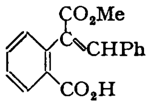
The resistance, towards cyclisation, of the half-ester (XI) from benzaldehyde appeared to indicate that here the phenyl group is *trans* to the aliphatic carbomethoxy-group. Strong acids produced the lactonic acid (VI*c*) from this ester. In Mueller's preparation (*loc. cit.*) of this acid from the sodium salt of the enolate of homophthalic anhydride with benzaldehyde, cleavage was probably avoided. The half-ester (XI) was also formed when dimethyl homophthalate was condensed with benzaldehyde in absolute methanol, in the presence of sodium methoxide, according to Dieckmann (*loc cit.*), who mentioned an " ester salt " as the intermediate product, but did not isolate the highly crystalline half-ester.



(IX)



(X)



(XI)

The assignment of an unsaturated six-membered ring structure to the lactonic products obtained in these reactions, to the exclusion of the alternative phthalide (five-membered ring) structure, is supported by their infra-red absorption spectra. These show the carbonyl band at 1725 cm.$^{-1}$ (in $CHCl_3$), in good agreement with the value 1720 cm.$^{-1}$ found by Grove and Willis (*J.*, 1951, 878) for aromatic esters, and with the values quoted by them (*loc. cit.*) for six-membered lactones. Aromatic lactones of the phthalide type, according to these authors, should show a band at 1750 cm.$^{-1}$. The lactone esters (IV*a*) and (VI*a*) show only one, unusually broad, carbonyl band, with a peak at 1710 cm.$^{-1}$, which may arise from superposition of the carbonyl and the ester band. The ester band, which is normally situated at about 1740 cm.$^{-1}$ (*loc. cit.*), might be expected to shift towards smaller wave-numbers, under the influence of the phenyl group (for an analogous effect in ethyl diphenylacetate, see Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073).

EXPERIMENTAL

M. p.s are uncorrected. Some analyses are by Drs. Weiler and Strauss, Oxford.

Homophthalic Acid.—This was prepared according to *Org. Synth.*, **29**, 43. Esterification, according to Clinton and Laskovsky's method (*J. Amer. Chem. Soc.*, 1948, **70**, 3136), with methanol, sulphuric acid, and ethylene dichloride gave some *o*-carbomethoxymethylbenzoic acid, m. p. 100—101° (Fieser and Pechet, *J. Amer. Chem. Soc.*, 1946, **68**, 2578, give m. p. 96—97°). The dimethyl ester had b. p. 126—130°/1 mm., m. p. 46—47° (Wegscheider and Glogau, *Monatsh.*, 1903, **24**, 938, give m. p. 39—42°).

General Procedure for the Stobbe Reaction.—The dimethyl ester (15·5 g.), ketone or aldehyde (0·05 mole), and sodium hydride (1·80 g., 0·075 mole) in dry benzene (50—80 c.c.) were stirred at room temperature under nitrogen, with occasional cooling to prevent a rise of temperature above 40°. At the end of the reaction the orange or brown solution, or suspension, was cautiously and slightly acidified with acetic acid, and water was added. The organic layer was extracted with several portions of sodium carbonate solution (5%), and the alkaline extracts were extracted with ether. Acidification of the former precipitated the half-ester. From the neutral portions practically all the excess of dimethyl homophthalate was recovered by distillation.

(A) *Reaction with* cyclo*Hexanone.*—The reaction was complete in 3 hours. The oily mixture of half-esters (I*a*) and (II*a*) was taken up in benzene, and the solvent was removed *in vacuo*. The remaining oil (Found : neutralisation equiv., 276. Calc. for $C_{16}H_{18}O_4$: equiv., 274·3) weighed 15·5 g.

The oil (1·5 g.) was treated on the steam-bath with 2N-sodium hydroxide (15 c.c.) for 1 hour. Acidification gave a mixture (1·2 g.) of the diacids (I*b*) and (II*b*), melting at 161—166°. Four recrystallisations from dilute acetic acid gave α-cyclo*hexylidenehomophthalic acid* (I*b*), m. p. 183—184° (decomp.) (Found : C, 69·1; H, 6·1. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%).

The mother liquors were concentrated to small bulk and diluted with water. The material precipitated (0·40 g.) was dried, finely powdered, and treated at room temperature with acetyl chloride (20 c.c.) for 0·5 hour. The excess of reagent was distilled off and the remaining oil taken up in ether. The ethereal extract was extracted several times with saturated sodium hydrogen carbonate solution, the ether removed, and the oil hydrolysed on the steam-bath with saturated sodium hydrogen carbonate solution (20 c.c.) for 4 hours. The resulting solution was filtered and acidified, to give crude α-cyclo*hexenylhomophthalic acid* (II*b*), m. p. 139—145°. Crystallisation from an insufficient amount of benzene–heptane (2 : 1) gave needles, m. p. 141—143° (Found : C, 69·4; H, 6·8%). This could not be freed completely from the higher-melting isomer.

The diacid (I*b*) (0·30 g.) in water (15 c.c.) containing sodium carbonate (0·25 g.) was treated at 0° with potassium permanganate (0·40 g.) in water (20 c.c.). After 1 hour at room temperature, the mixture was distilled into a solution of 2 : 4-dinitrophenylhydrazine in hydrochloric acid. The precipitated *cyclo*hexanone 2 : 4-dinitrophenylhydrazone (0·16 g.) had m. p. 161—162°. unchanged by admixture with an authentic sample of m. p. 162°.

Cyclisation of the half-esters. The crude oily mixture (2·0 g.) was refluxed for 2 hours with acetic anhydride (12 c.c.) and acetic acid (12 c.c.) containing fused zinc chloride (0·1 g.). The mixture was cautiously decomposed with an excess of water, and the oil, which separated, was taken up in ether. The extract was washed with dilute sodium carbonate solution and dried ($MgSO_4$), and the ether removed. The residue (1·5 g.), crystallised from methanol and then from heptane, gave *methyl* 10-*acetoxy*-1 : 2 : 3 : 4-*tetrahydroanthracene*-9-*carboxylate* (III*a*) (1·0 g.). Further recrystallisation from methanol gave colourless needles, m. p. 138° (Found : C, 72·4; H, 6·1. $C_{18}H_{18}O_4$ requires C, 72·4; H, 6·2%). The combined mother-liquors were evaporated to small bulk and refluxed with sodium hydroxide solution (12%; 20 c.c.) for 2 hours, under nitrogen. The residue was filtered, and the filtrate saturated with carbon dioxide. The precipitate was filtered off and recrystallised from benzene–heptane, to give *methyl* 10-*hydroxy*-1 : 2 : 3 : 4-*tetrahydroanthracene*-9-*carboxylate* (III*b*) (0·3 g.), leaflets, m. p. 165° (from dilute ethanol) (Found : C, 74·4; H, 6·25. $C_{16}H_{16}O_3$ requires C, 74·8; H, 6·3%).

This phenol (0·3 g.) was refluxed with acetic anhydride (3 c.c.) in the presence of sodium acetate, giving the acetyl derivative (III*a*), m. p. 134—136°, mixed m. p. 135—136°.

1 : 2 : 3 : 4-*Tetrahydro*-10-*anthranol.* The ester (III*b*) (0·05 g.) was refluxed for 6 hours with hydrochloric acid (1 c.c.) and acetic acid (3 c.c.) under nitrogen. Upon cooling, the oil which separated crystallised. Recrystallisation from hexane gave prisms of this phenol (III*c*), m. p. 110—111°, which slowly darkened in air. Von Braun and Bayer (*loc. cit.*) give m. p. 109°

(Found: C, 84·7; H, 7·2. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·15%). The acetate obtained from this by acetic anhydride–sodium acetate, crystallised from hexane in needles, m. p. 111° (the mixed m. p. with (III*b*) was much lower) (von Braun and Bayer, *loc. cit.*, give m. p. 108°) (Found: C, 80·1; H, 7·0. Calc. for $C_{16}H_{16}O_2$: C, 79·8; H, 6·75%).

Lactonisation of the half-esters. (*a*) The oily mixture (4·70 g.) was refluxed for 12 hours with hydrobromic acid, acetic acid, and water (6 : 4 : 2 by vol.; 55 c.c.) (cf. Johnson and Heinz, *J. Amer. Chem. Soc.*, 1949, **71**, 2913). Most of the solvents were distilled off *in vacuo*, and the remaining oil was taken up in ether. The extract was treated with charcoal and filtered, and the ether removed. The residue was treated with hot benzene (40 c.c.), whereupon cyclo*hexane*spiro-3-(3 : 4-*dihydro*iso*coumarin*-4-*carboxylic acid*) (IV*b*) (2·0 g.) separated. Recrystallisation from ethyl acetate–heptane gave needles, m. p. 183—184° (Found: C, 69·4; H, 6·2. Calc. for $C_{15}H_{16}O_4$: C, 69·2; H, 6·2%). A mixture of this with the diacid (I*b*) melted at 165—175°. However, the infra-red spectrum of (IV*b*) revealed the presence of (I*b*) bands at 1726 cm.$^{-1}$ (due to six-membered lactone), and at 1628 cm.$^{-1}$ (due to aromatic, or αβ-unsaturated, carboxyl group), in paraffin oil suspension.

(*b*) The half-ester mixture (2·75 g.) was refluxed for 4·5 hours with acetic anhydride (20 c.c.), acetic acid (10 c.c.), and fused sodium acetate (1·0 g.) and worked up as for (III*a*). The neutral portion crystallised from hexane, giving the *methyl* ester (IV*a*), m. p. 104—106° (1·7 g.), of the above lactonic acid. Further recrystallisation from the same solvent gave needles, m. p. 108—109° (Found: C, 69·8; H, 6·6. $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6%).

This ester was also obtained from the acid (IV*b*), by diazomethane in ether, with m. p. and mixed m. p. 107—108°. Esterification of (I*b*) in the same way gave an oil.

To the ester (IV*a*) (1·4 g.) in ice-cold ethanol (8 c.c.) ethanolic potassium hydroxide (10%; 5 c.c.) was added. Dilution with ice-water (25 c.c.) gave a clear solution, which was acidified with acetic acid. The oil which separated crystallised on trituration (1·20 g.). Crystallised from hexane, it gave needles of *methyl* α-o-*carboxyphenyl*-α-cyclo*hexylideneacetate* (I*a*), m. p. 114—115° (Found: C, 70·3; H, 6·8. $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6%). Hydrolysis of this gave the diacid (I*b*), m. p. and mixed m. p. 182—183° (decomp.).

Esterification of the half-esters. The oily mixture (7·0 g.) was esterified with methanol, according to Clinton and Laskovsky (*loc. cit.*). Some of the half-ester (1·5 g.) was recovered. The neutral portion was distilled *in vacuo* (130—150°/0·01 mm.), to give an oily mixture of the dimethyl esters (I*c*) and (II*c*) (5·5 g.) (Found: C, 71·0; H, 7·0. Calc. for $C_{17}H_{20}O_4$: C, 70·8; H, 7·0%).

Dehydrogenation and cyclisation to anthrone. The above mixture of diesters (7·0 g.) was heated with palladium–carbon (10%; 1·5 g.) for 10 hours at 250—320° under carbon dioxide. The product was taken up in methanol, filtered from the catalyst, and freed from the solvent. The residue was hydrolysed under reflux with sodium hydroxide solution (12%; 60 c.c.), for 2·5 hours. Acidification gave *o*-benzylbenzoic acid (3·1 g.), which when recrystallised from hexane (charcoal) had m. p. 116—117° undepressed on admixture with an authentic specimen. The crude acid (2·0 g.) was cyclised with sulphuric acid at room temperature to anthrone (1·3 g.), m. p. and mixed m. p. 156—157°.

(B) *Reaction with Acetone.*—Stirring was continued for 3·5 hours. *Methyl* o-*carboxyphenyl*-3-*methylbut*-2-*enoate* (V*a*) (yield 88%), formed needles, m. p. 141°, from benzene–heptane (Found: C, 66·5; H, 6·1. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%).

Hydrolysis of this with 2N-alkali gave the *diacid* (V*c*), needles (from dilute acetic acid), m. p. 198—200° (decomp.) (Found: C, 65·7; H, 5·7. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). Oxidation, as for (I*b*), led to acetone 2 : 4-dinitrophenylhydrazone, m. p. 126—127°, or mixed with an authentic specimen 127—127·5°.

The diacid (2·0 g.) was refluxed for 3 hours with acetyl chloride (60 c.c.). The excess of reagent was removed *in vacuo*, and the residue, crystallised from heptane, gave yellowish prisms of α-iso*propylidenehomophthalic anhydride*, m. p. 136° (1·85 g.) (Found: C, 71·4; H, 5·5. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

The anhydride (1·0 g.) was refluxed for 5 hours with absolute methanol (10 c.c.). Excess of alcohol was distilled off, the oily residue taken up in ether, and the extract was washed with sodium carbonate solution (5%; 3 × 10 c.c.). Each extract was acidified to pH 5 by dropwise addition of acetic acid. This precipitated o-*carbomethoxyphenyl*-3-*methylbut*-2-*enoic acid* (V*b*) (0·6 g.), which formed needles, m. p. 124°, from aqueous ethanol (Found: C, 66·8; H, 6·2. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%). The filtrates were acidified further to pH 3, whereupon the previous half-ester (V*a*) separated (0·2 g.); after one crystallisation from heptane this had m. p. and mixed m. p. 140—141°.

Cyclisation. The ester (V*a*) (4·0 g.) was refluxed with acetic anhydride (30 c.c.) and a 5% solution of fused zinc chloride in acetic acid (5 c.c.) for 12 hours. Working up as usual gave an oil, which was extracted in ethereal solution with sodium carbonate solution (5%). The alkaline extracts were acidified, yielding a mixture (1·15 g.) of the half-esters (V*a* and *b*). These were separated as described for (V*b*). The neutral residue, after evaporation of the ether, was refluxed for 2 hours with sodium hydroxide solution (15%; 12 c.c.) under nitrogen. The solution was filtered and the filtrate saturated with carbon dioxide. The precipitated solid was collected, dried, and recrystallised from hexane, to give yellowish needles of 3-methyl-1-naphthol, m. p. 94—96° (0·3 g.). An authentic specimen, m. p. 92—93° (prepared according to Cope *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 3455), gave a mixed m. p. 92—94°. The alkaline filtrate, on further acidification, gave the diacid (V*c*), m. p. and mixed m. p. 195—200° (decomp.) (1·15 g.).

Lactonisation. (*a*) (V*a*) (3·0 g.) was refluxed for 10 hours, with the acid mixture (36 c.c.) used for preparation of (IV*b*). The solvents were removed *in vacuo*, leaving 3 : 4-*dihydro*-3 : 3-*dimethyl*iso*coumarin*-4-*carboxylic acid* (VI*b*) (2·50 g.), which crystallised from very dilute methanol as leaflets, m. p. 212° (decomp.) (Found : C, 65·4; H, 5·5. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). The mixed m. p. with (V*c*) was 200—205°. Courtot (*loc. cit.*) gives m. p. 225°.

As for (IV*a*), the infra-red absorption of this lactonic acid indicated the presence of the diacid (V*c*), there being bands at 1726 cm.$^{-1}$ (due to a six-membered lactone), at 1708 cm.$^{-1}$ (due to aliphatic carboxyl), and at 1686 cm.$^{-1}$ (due to aromatic, or αβ-unsaturated, carboxyl), in paraffin oil suspension.

(*b*) The half-ester (V*b*) (1·5 g.) was treated with acetic anhydride–acetic acid–sodium acetate, as in the preparation of (IV*a*). The neutral product (1·0 g.) crystallised on trituration with hexane and on recrystallisation therefrom gave needles of *methyl* 3 : 4-*dihydro*-3 : 3-*dimethyl*iso*coumarin*-4-*carboxylate* (VI*a*), m. p. 115—116° (Found: C, 66·9; H, 6·2. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%). This was also obtained by treatment of the lactonic acid (VI*b*) with diazomethane in ether; it then had m. p. and mixed m. p. 115—116°.

Fission of the lactone ring, as described for (I*a*), yielded the half-ester (V*a*), m. p. and mixed m. p. 140—141°.

(C) *Reaction with Benzophenone.*—Stirring was continued overnight. The sodium salt of the half-ester separated as an oil, which gradually crystallised. Acidification gave *methyl* α-o-*carboxyphenyl*-ββ-*diphenylacrylate* (VII), m. p. 201—202° (79%), crystallising from dilute acetic acid as needles, m. p. 202—203·5° (Found : C, 77·2; H, 5·0. $C_{23}H_{18}O_4$ requires C, 77·05; H, 5·1%).

Hydrolysis with 2N-alkali gave the *diacid*, freely soluble in dilute alkali, and forming yellowish needles, m. p. 206—208° (decomp.), from dilute acetic acid (Found : C, 76·7; H, 4·9. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%).

Cyclisation. The foregoing ester (1·0 g.) was refluxed for 8 hours with acetic anhydride (8 c.c.) and a 5% solution (1·5 c.c.) of zinc chloride in acetic acid. A deep red colour developed within 10 minutes. The neutral residue, obtained as usual, crystallised from methanol, to give 2-o-*carbomethoxyphenyl*-3-*phenylindenone* (X) as orange needles, m. p. 150° (0·82 g.). Further recrystallisation from ethanol raised the m. p. to 150·5° (Found : C, 81·4; H, 4·9. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·75%). Its orange-red 2 : 4-*dinitrophenylhydrazone*, needles, m. p. 206—208°, was purified by chromatography from chloroform and crystallisation from chloroform–ethanol (Found : N, 10·9. $C_{29}H_{20}O_6N_4$ requires N, 10·8%).

Decarboxylation. The half-ester (VII) (5·0 g.) was refluxed for 30 hours, with the acid mixture (100 c.c.) used for the preparation of (IV*b*). The solvents were removed *in vacuo*, and the remaining oily solid was digested with 10% sodium carbonate solution (40 c.c.). The remaining solid was filtered off and recrystallised from dilute methanol. 3 : 4-*Dihydro*-3 : 3-*diphenyl*iso*coumarin* (VIII) (2·45 g.) crystallised from dilute ethanol as needles, m. p. 148—149°, which dissolved with difficulty in hot aqueous alkali (Found : C, 83·5; H, 5·3. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%). Acidification of the alkaline filtrate and recrystallisation from dilute acetic acid gave 2-o-*carboxyphenyl*-1 : 1-*diphenylethylene* (IX) as leaflets, m. p. 169° (Found : C, 83·5; H, 5·3. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%).

The lactone (VIII) (1·0 g.) was refluxed for 3 hours with iodine (0·5 g.) and red phosphorus (0·5 g.) in propionic acid (5 c.c.) containing a trace of water. The hot mixture was filtered, and the filtrate poured into sodium hydrogen sulphite solution (10%). This precipitated o-2 : 2-*diphenylethylbenzoic acid*, which gave needles, m. p. 152—152·5°, from benzene–heptane (Found : C, 83·5; H, 6·1. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). The same acid was obtained by hydrogenation of the unsaturated acid (IX) in ethanol in the presence of Adams's catalyst.

(D) *Reaction with Benzaldehyde.*—The reaction was practically complete after a few minutes.

Methyl α-o-*carboxyphenylcinnamate* (XI) (13·0 g.) crystallised from benzene–heptane as needles, m. p. 153—153·5° (Found : C, 72·5; H, 5·0. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

The same half-ester was obtained in 71% yield by reaction of dimethyl homophthalate with benzaldehyde in absolute methanol containing sodium methoxide, according to Dieckmann (*loc. cit.*). When this reaction was carried out in absolute ethanol containing sodium ethoxide, ester exchange led to the corresponding *ethyl* half-ester (56%), needles, m. p. 172—173°, from ethanol (Found : C, 72·5; H, 5·4. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

Both the above half-esters, with 2N-alkali at 100°, gave α-benzylidenehomophthalic acid as needles (from dilute acetic acid), m. p. 199—200° (decomp.), unchanged on further recrystallisation (Dieckmann, *loc. cit.*, gives m. p. 210°).

With acetic anhydride this diacid gave α-benzylidenehomophthalic anhydride, yellow needles (from heptane), m. p. 133—135° (Dieckmann gives m. p. 135°). When this anhydride was refluxed for 5 hours with absolute methanol, an oily mixture of half-esters was formed, from which only (XI) was isolated pure by repeated recrystallisation.

Lactonisation. The half-ester (XI) (4·0 g.) was refluxed for 12 hours with the acid mixture (40 c.c.) used for preparation of (IV*b*). Working up as usual gave 3 : 4-dihydro-3-phenyl*iso*coumarin-4-carboxylic acid (VI*c*) (2·8 g.). Several recrystallisations from dilute acetic acid gave needles, m. p. 186—187° (Mueller, *loc. cit.*, gives m. p. 185—186°) (Found : C, 71·7; H, 4·7. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5%). The methyl ester (prepared by ethereal diazomethane) formed needles (from methanol and from heptane), m. p. 134—136° (Mueller, *loc. cit.*, gives m. p. 137—138°).

Treatment of (XI) with acetic anhydride–acetic acid–zinc chloride, as for (I*a*) and (II*a*), gave an oily mixture of starting material and of the isomeric half-ester, but only the former could be isolated pure.

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