495. *The Preparation and Properties of Some* β-(2- *and* 4-*Aroylphenoxy*)*propionic Acids.*

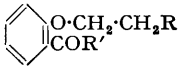
By Elizabeth M. D. Simpson, Muriel L. Tomlinson, and (in part) Helan V. Taylor.

β-(4-Benzoyl-3-hydroxyphenoxy)propionic acid, β-(4-benzoyl-3-methoxyphenoxy)propionic acid, β-(2-benzoyl-5-methoxyphenoxy)propionic acid, and the corresponding 2- and 4-veratroyl compounds have been obtained by interaction of benzoyl and veratroyl chlorides with ethyl β-*m*-methoxyphenoxypropionate in the presence of aluminium chloride. It has been found that these substances are readily dissociated by alkali with the removal of the $-CH_2 \cdot CH_2 \cdot CO_2H$ group and the production of the corresponding phenol. Similar Friedel–Crafts reactions using β-*m*-methoxyphenoxypropionitrile, *m*-di-2′-cyanoethoxybenzene, and *m*-di-2′-carbomethoxyethoxybenzene have also been carried out.

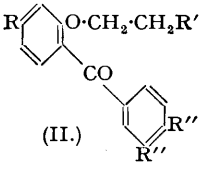
We were interested in the possibility of preparing 1 : 2-benzopyrans by the cyclisation of compounds of the type (I; R = CN or CO_2Et). Previous work having shown that it is difficult to bring about a reaction between acrylonitrile and a phenolic hydroxyl group that is *ortho* to a carbonyl group (Bachman and Levine, *J. Amer. Chem. Soc.*, 1948, **70**, 599; Taylor and Tomlinson, *J.*, 1950, 2724), we decided to investigate the possibility of introducing aroyl groups

into β-*m*-methoxyphenoxypropionitrile and the corresponding ethyl ester under Friedel–Crafts conditions, as an alternative route for the production of substances of the type (I; R = CN or CO_2Et).

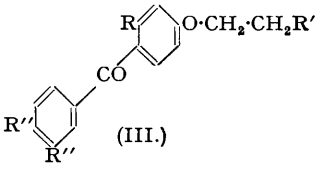
Ray, Silooja, and Wadha (*J. Indian Chem. Soc.*, 1933, **10**, 617) were unsuccessful in their attempt to prepare β-(5-methoxy-2-veratroylphenoxy)propionate (II; R = R″ = OMe, R′ =



(I.)



(II.)



(III.)

CO_2Et) from veratroyl chloride and ethyl β-*m*-methoxyphenoxypropionate: they isolated 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone and a small quantity of a substance, m. p. 175°, which they decided was probably 4-hydroxy-2 : 3′ : 4′-trimethoxybenzophenone. They concluded that the propionic ester residue had been extruded during the Friedel–Crafts reaction to form these compounds.

We began our investigation by using β-*m*-methoxyphenoxypropionitrile, and benzoyl chloride with aluminium chloride in nitrobenzene solution, and from the resulting product obtained β-(4-benzoyl-3-hydroxyphenoxy)propionitrile (III; R = OH, R′ = CN, R″ = H) and a non-phenolic residue which failed to crystallise but afforded β-(2-benzoyl-5-methoxyphenoxy)-propionic acid (II; R = OMe, R′ = CO_2H, R″ = H) on hydrolysis with acid. In a similar reaction with ethyl β-*m*-methoxyphenoxypropionate in the place of the nitrile, the product was found to contain carboxylic, phenolic, and neutral fractions. The acid, removed with sodium carbonate, was β-(2-benzoyl-5-methoxyphenoxy)propionic acid (II; R = OMe, R′ = CO_2H, R″ = H), and the phenolic fraction, extracted with cold dilute sodium hydroxide, afforded β-(4-benzoyl-3-hydroxyphenoxy)propionic acid (III; R = OH, R′ = CO_2H, R″ = H), the ester grouping having been hydrolysed during the extraction. From the neutral part of the reaction product there was isolated, after hydrolysis with dilute acid and careful fractional crystallisation a further quantity of β-(2-benzoyl-5-methoxyphenoxy)propionic acid together with some β-(4-benzoyl-3-methoxyphenoxy)propionic acid (III; R = OMe, R′ = CO_2H, R″ = H).

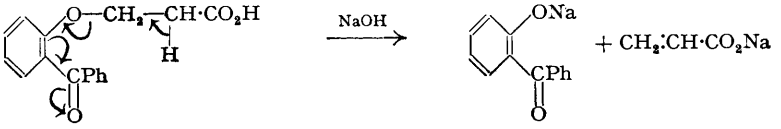
It seemed worth while, in view of these results, to repeat the reaction with veratroyl chloride and ethyl β-*m*-methoxyphenoxypropionate, and in this way we obtained a series of compounds completely analogous to those described above, namely, β-(3-hydroxy-4-veratroylphenoxy)-propionic acid (III; R = OH, R′ = CO_2H, R″ = OMe), β-(3-methoxy-4-veratroylphenoxy)-propionic acid (III; R = R″ = OMe, R′ = CO_2H), and β-(5-methoxy-2-veratroylphenoxy)-propionic acid (II; R = R″ = OMe, R′ = CO_2H). The reaction mixture from a similar experiment with veratroyl chloride and β-*m*-methoxyphenoxypropionitrile gave neutral and phenolic fractions. The former must have contained the isomers (II and III; R = R″ = OMe, R′ = CN), and the latter (III; R = OH, R′ = CN, R″ = OMe). Both fractions, however, failed to crystallise and were investigated by degradation with alkali (see later), and by acid hydrolysis which always gave very poor yields of the expected acids, probably because some demethylation occurs.

Hence, in all these reactions it is clear that the aroyl group is introduced, as would be expected, partly *ortho* to the cyanoethoxy- or carbethoxyethoxy-groups and partly *ortho* to the methoxyl group; the latter may be partly or completely extruded during the reaction but no compound has been isolated that makes it certain that the other substituent is ever removed in this way. All the isolated compounds that had lost this group had been in contact with alkali, which it has been found (see later) effects that kind of decomposition with great ease.

Both possible positions of substitution seem to be attacked in comparable proportions, but it is difficult to estimate these proportions with any accuracy as in no case could all the products be directly crystallised, and in all instances there was a considerable quantity of material that remained as a gummy mass.

It has been found, with substances of the types (II) and (III), that alkali, even under quite mild conditions, removes the cyanoethoxy- and carboxyethoxy-group with the formation of a phenol and presumably acrylonitrile or acrylic acid. This is comparable with the ring opening that occurs with flavanones under the influence of alkali to give *o*-hydroxychalkones, but here, as the group is separated from the rest of the molecule, the reaction is irreversible. This reaction no doubt explains Ray, Silooja, and Wadha's failure (*loc. cit.*) to isolate any β-phenoxypropionic

acids in their investigation, as they hydrolysed their crude ester product with alcoholic alkali which would readily dissociate such substances :



This dissociation also causes considerable loss of materials even with the cold dilute alkali extraction, followed by rapid acidification, that we employed. During the extraction, decomposition products could always be detected by smell, and the product extracted by alkali in the reaction between veratroyl chloride and β-*m*-methoxyphenoxypropionitrile appears to have undergone extensive degradation : β-(5-methoxy-2-aroyl)propionic acids are decomposed rapidly too.

The constitutions allotted to the substances described above are based on the following observations. β-(4-Benzoyl-3-hydroxyphenoxy)propionic acid and the corresponding nitrile gave a violet colour with ferric chloride and a deep yellow solution in sodium hydroxide, and therefore the OH and CO groups must be *ortho* to one another in these compounds. This nitrile could be hydrolysed to the above acid, and methylated to form a nitrile which, on hydrolysis, yielded an acid identical with the one, regarded as β-(4-benzoyl-3-methoxyphenoxy)propionic acid, which was isolated from the Friedel–Crafts reaction product. In addition, both β-(4-benzoyl-3-hydroxyphenoxy)propionic acid and its nitrile were decomposed by alkali to give 2 : 4-dihydroxybenzophenone, identified by direct comparison (mixed m. p.) with a specimen made by Komarowski and von Kostanecki's method (*Ber.*, 1894, **27**, 1997). β-(2-Benzoyl-5-methoxyphenoxy)propionic acid gave no colour with ferric chloride and dissolved in aqueous sodium hydroxide to form a colourless solution, but when it was warmed or kept a yellow colour developed and acid then precipitated 2-hydroxy-4-methoxybenzophenone, the m. p. of which was not depressed by admixture with an authentic specimen. β-(4-Benzoyl-3-methoxyphenoxy)propionic acid, which also gave no colour with ferric chloride or sodium hydroxide, was decomposed by the latter reagent to give 4-hydroxy-2-methoxybenzophenone, which does not appear to have been previously described. It does not colour ferric chloride but it gives a very faintly yellow solution with sodium hydroxide.

Similar properties were observed with the veratroyl analogues, and they were converted into the expected benzophenones with alkali. 4-Hydroxy-2 : 3′ : 4′-trimethoxybenzophenone, obtained from β-(3-methoxy-4-veratroylphenoxy)propionic acid, melted at 179°, and gave no colour with ferric chloride and a pale yellow solution in sodium hydroxide. The substance to which Ray and his collaborators allotted this constitution melted at 175° and gave a faint ferric chloride reaction, yet there seems no doubt that these substances are identical. (The yellowing with alkali that we observed in this compound and the benzene analogue may be caused by traces of the *o*-hydroxy-isomer, but the absence of a ferric chloride reaction indicates that this is not present in appreciable quantity.)

Benzoyl chloride reacts with *m*-di-2′-carbomethoxyethoxybenzene in the presence of aluminium chloride to give 4-benzoyl-1 : 3-di-2′-carbomethoxyethoxybenzene (II; R = O·CH_2·CH_2·CO_2Me, R′ = CO_2Me, R″ = H). Acid hydrolyses this to the corresponding dicarboxylic acid, and treatment with sodium hydroxide at room temperature degrades this acid to β-(4-benzoyl-3-hydroxyphenoxy)propionic acid, identical with the substance described above. Further action of alkali gives 2 : 4-dihydroxybenzophenone. 4-Benzoyl-1 : 3-di-2′-cyanoethoxybenzene (II; R = O·CH_2·CH_2·CN, R′ = CN, R″ = H) has been obtained from benzoyl chloride and 1 : 3-di-2′-cyanoethoxybenzene.

All attempts to cyclise compounds of the type (II) with basic catalysts have so far been unsuccessful because they induce loss of the side chain so readily.

Reduction of 2-hydroxy-4-methoxybenzophenone by Clemmensen's method gave only a poor yield of 2-hydroxy-4-methoxydiphenylmethane, and so the possibility of condensing this substance with acrylonitrile and reoxidation to the ketone was not pursued in an attempt to prepare compounds of the type (II) that was made before the present work was done.

Experimental.

Reaction of Benzoyl Chloride with β-m-Methoxyphenoxypropionitrile.—A solution of aluminium chloride (28 g.) in nitrobenzene (80 c.c.) was slowly added, at room temperature, to a mixture containing β-*m*-methoxyphenoxypropionitrile (12·7 g.), benzoyl chloride (10 g.), and nitrobenzene (20 c.c.). After

being kept for 18 hours, the product was decomposed with ice, and nitrobenzene was distilled in steam. The residue was washed, first with dilute acid and then with water, and dissolved in ether. This solution was washed repeatedly with small volumes of aqueous sodium hydroxide (5%), and the aqueous layer was run, as quickly as possible, into dilute hydrochloric acid. A crystalline precipitate separated, and recrystallisation of this from alcohol afforded *β-(4-benzoyl-3-hydroxyphenoxy)propionitrile* as needles (4·5 g.), m. p. 109° raised to 110° by further recrystallisation from the same solvent (Found : C, 71·8; H, 4·5; N, 5·3. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9; N, 5·2%). The ethereal solution was then washed until free from alkali, dried (Na_2SO_4), and evaporated. The residue, which failed to crystallise, was hydrolysed by boiling it with concentrated hydrochloric acid for 7 hours, and then extracted with ether. From this solution, by extraction with sodium carbonate and subsequent acidification, extraction with ether, drying, and evaporation, a gummy product was obtained. This crystallised in contact with alcohol to give a solid (2·9 g.), m. p. 130—138°. Recrystallisation from alcohol afforded *β-(2-benzoyl-5-methoxyphenoxy)propionic acid*, as prisms, m. p. 138·5—140° (Found : C, 68·1; H, 5·3. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). When this was heated on a steam-bath with sodium hydroxide solution (10%) for a few minutes, the originally colourless solution became deep yellow and on acidification yielded 2-hydroxy-4-methoxybenzophenone, m. p. 63° (after recrystallisation), identical (mixed m. p.) with an authentic specimen (Found : C, 73·8; H, 5·4. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%).

β-(4-Benzoyl-3-hydroxyphenoxy)propionic Acid.—When the above nitrile was boiled with concentrated hydrochloric acid for 8—10 hours the corresponding *acid* was obtained; it crystallised from alcohol as needles, m. p. 173—175° sintering at 165° (Found : C, 66·9; H, 4·9. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). This acid and the corresponding nitrile, when boiled for 5 minutes with aqueous sodium hydroxide (10%), gave a yellow solution from which acid precipitated 2 : 4-dihydroxybenzophenone, m. p. 143° (after recrystallisation), identical (mixed m. p.) with an authentic specimen.

β-(4-Benzoyl-3-methoxyphenoxy)propionic Acid.—*β-*(4-Benzoyl-3-hydroxyphenoxy)propionitrile (1 g.) in acetone (10 c.c.) was refluxed for 6 hours with methyl iodide (5 c.c.) and dry potassium carbonate (5 g.). After evaporation of the solvent, water was added and the precipitate was recrystallised from alcohol. *β-(4-Benzoyl-3-methoxyphenoxy)propionitrile* separated as needles (0·8 g.), m. p. 91° (Found : C, 72·5; H, 5·4. $C_{17}H_{15}O_3N$ requires C, 72·6; H, 5·3%). Hydrolysis of this nitrile was effected by boiling it with hydrochloric acid for 1½ hours. The product was extracted with sodium carbonate, as hydrolysis was incomplete, and acidification afforded a precipitate, m. p. about 70°. When this was rubbed with a little cold sodium hydroxide (10% solution) a colourless sodium salt crystallised, decomposition of which gave *β-(4-benzoyl-3-methoxyphenoxy)propionic acid*, which separated from aqueous methanol as prisms that fell to a crystalline powder, m. p. 83—84°, when dried *in vacuo* (Found : C, 68·0; H, 5·2. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). [Acidification of the yellow alkaline solution from which the above sodium salt separated gave some β-(4-benzoyl-3-hydroxyphenoxy)propionic acid, and longer boiling during the hydrolysis caused considerable demethylation.] *β-*(4-Benzoyl-3-methoxyphenoxy)propionic acid and the corresponding nitrile were decomposed when warmed with aqueous sodium hydroxide (10%) to give *4-hydroxy-2-methoxybenzophenone*, which crystallised from alcohol as prisms, m. p. 124° (Found : C, 74·0; H, 5·2. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

Reaction of Benzoyl Chloride with Ethyl β-m-*Methoxyphenoxypropionate.*—Aluminium chloride (15·6 g.) in nitrobenzene (80 c.c.) and ethyl *β-m-*methoxyphenoxypropionate (8·8 g.) and benzoyl chloride (5·6 g.) in nitrobenzene (20 c.c.) were mixed and treated as above. The ethereal extract was then submitted to the following procedures.

(i) It was extracted with sodium carbonate (10%); acidification of the aqueous layer yielded material (0·7 g.) which crystallised from alcohol, giving *β-*(2-benzoyl-5-methoxyphenoxy)propionic acid, m. p. 135—137° raised by admixture with the acid, m. p. 138·5—140°, above.

(ii) It was repeatedly extracted with small quantities of aqueous sodium hydroxide (5%) which was run directly into hydrochloric acid; crystals (2·0 g.) separated, and on recrystallisation from alcohol afforded *β-*(4-benzoyl-3-hydroxyphenoxy)propionic acid, m. p. 173—175° not depressed by admixture with that prepared as above.

(iii) The ethereal layer was washed with water, dried ($CaCl_2$), and evaporated, yielding a yellow gum (9·5 g.); this failed to solidify and was hydrolysed by prolonged boiling with dilute hydrochloric acid. Non-acidic material was removed by partition between ether and sodium carbonate solution, and acid precipitated, from the aqueous layer, a substance that solidified. Careful fractional crystallisation from alcohol ultimately yielded *β-*(2-benzoyl-5-methoxyphenoxy)propionic acid (3—4 g.), m. p. 138—140° (from alcohol). From the mother-liquors there was obtained *β-*(4-benzoyl-3-methoxyphenoxy)propionic acid (0·4 g.), m. p. 83—85°. This had been purified by conversion into the sparingly soluble sodium salt and subsequent recrystallisation from aqueous methanol. Both specimens were identified (mixed m. p.) with the substances described above.

Reaction between Veratroyl Chloride and Ethyl β-m-*Methoxyphenoxypropionate.*—A mixture of veratroyl chloride (3·5 g.) and ethyl *β-m-*methoxyphenoxypropionate (4·4 g.) in nitrobenzene (20 c.c.) was treated, at room temperature, with aluminium chloride (7 g.) in nitrobenzene (25 c.c.) and submitted to the procedure described above. From the resulting product, rapid extraction with aqueous sodium hydroxide and acidification gave *β-(3-hydroxy-4-veratroylphenoxy)propionic acid*, which crystallised from alcohol and was obtained after repeated recrystallisation, as plates, m. p. 175—177° (0·5 g.) (Found : C, 62·2; H, 5·5. $C_{18}H_{18}O_7$ requires C, 62·4; H, 5·2%). The non-phenolic fraction failed to crystallise and was therefore hydrolysed by prolonged boiling with dilute hydrochloric acid. The resulting acids were extracted with sodium carbonate; fractional crystallisation from alcohol and aqueous alcohol afforded *β-(5-methoxy-2-veratroylphenoxy)propionic acid* (0·75 g.), which separated from alcohol as prisms, m. p. 135—136° (Found : C, 63·5; H, 5·7. $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%). From the mother-liquors there was also obtained *β-(3-methoxy-4-veratroylphenoxy)propionic acid* (0·7 g.), which crystallised from aqueous alcohol as woolly needles, m. p. 127—129° (Found : C, 63·2; H, 5·6%). These three acids were all decomposed by being heated with aqueous sodium hydroxide solution : *β-*(3-hydroxy-

4-veratroylphenoxy)propionic acid gave 2 : 4-*dihydroxy*-3′ : 4′-*dimethoxybenzophenone*, which separated from alcohol as clear prisms, m. p. 149° (Found : C, 65·7; H, 5·4. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·1%); *β*-(5-methoxy-2-veratroylphenoxy)propionic acid gave 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone, m. p. 141° not depressed by admixture with an authentic specimen, and *β*-(3-methoxy-4-veratroylphenoxy)propionic acid gave 4-hydroxy-2 : 3′ : 4′-trimethoxybenzphenone, which crystallised from alcohol as plates m. p. 179° (Found : C, 67·0; H, 5·7. Calc. for $C_{16}H_{16}O_5$: C, 66·7; H, 5·6%).

*Reaction between Veratroyl Chloride and β-*m*-Methoxyphenoxypropionitrile.*—Aluminium chloride (29 g.) in nitrobenzene (80 c.c.) was slowly added at room temperature to a mixture of veratroyl chloride (15 g.) and *β-m*-methoxyphenoxypropionitrile (13·2 g.) in nitrobenzene (20 c.c.). Next day, the mixture had set to a jelly and it was decomposed and steam-distilled, etc., as above. The product was dissolved in ether (1500 c.c.), and the solution was extracted with aqueous sodium hydroxide which was subsequently acidified and extracted with ethyl acetate. Both the phenolic fraction thus obtained (17 g.) and the non-phenolic part isolated from the ether (7·5 g.) failed to crystallise.

Non-phenolic fraction. (*a*) When it was boiled with concentrated hydrochloric acid for 5 hours it afforded some *β*-(5-methoxy-2-vertroylphenoxy)propionic acid, m. p. 133—135° (after two crystallisations from alcohol). (*b*) The non-phenolic substance (3·4 g.) was boiled with absolute alcohol (50 c.c.) in which sodium (0·23 g.) had been dissolved. After one hour addition of 2N-hydrochloric acid produced a precipitate, recrystallisation of which from alcohol gave 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone (1·9 g.), m. p. 141°. Next day the aqueous solution had deposited small crystals (m. p. approx. 175°) (0·5 g.), and after two recrystallisations from alcohol this solid was shown to be 4-hydroxy-2 : 3′ : 4′-trimethoxybenzophenone, m. p. 179°. (Identifications were by mixed m. p. determination.)

Phenolic fraction. (*a*) When this substance was boiled with concentrated hydrochloric acid for 1½ hours it gave a product from which sodium carbonate extracted a little *β*-(3-hydroxy-4-veratroylphenoxy)propionic acid, m. p. 174—177° after two recrystallisations from alcohol. (*b*) This material was boiled with sodium hydroxide (10%) until no more ammonia was evolved (about 15 minutes), and acidification then yielded a gum that crystallised slowly in contact with alcohol. Recrystallisation from alcohol afforded 2 : 4-dihydroxy-3′ : 4′-dimethoxybenzophenone. (*c*) When this fraction was shaken with sodium hydroxide and methyl sulphate at room temperature, a good yield of 2 : 4 : 3′ : 4′-tetramethoxybenzophenone, m. p. 107°, separated. (*d*) The phenolic fraction (2 g.) was refluxed for 4 hours with methyl iodide (5 c.c.) and dry potassium carbonate (5 g.) in acetone (50 c.c.) and gave, after addition of water, a product that partly crystallised : the crystals were 2-hydroxy-4 : 3′ : 4′-trimethoxybenzophenone (*i.e.*, methylation was incomplete). The neutral residue, obtained after treatment with alkali, was then boiled with sodium hydroxide (10%) for 15 minutes, and the insoluble portion solidified and was removed. It was 2 : 4 : 3′ : 4′-tetramethoxybenzophenone. Acidification of the aqueous layer then afforded a solid from which 4-hydroxy-2 : 3′ : 4′-trimethoxybenzophenone, m. p. 179°, was obtained. (*e*) When the neutral fraction produced in (*d*) was hydrolysed with concentrated hydrochloric acid and the resulting product was dissolved in ether and extracted with aqueous sodium carbonate, a small quantity of *β*-(3-methoxy-4-veratroylphenoxy)propionic acid, m. p. 127—129°, was obtained. (Identification of all the above substances was by mixed m. p. determination.)

m-*Di*-2′-*carboxyethoxybenzene.*—*m*-Di-2′-cyanoethoxybenzene (10 g.) (made by Cook and Reed's method, *J.*, 1945, 920), sodium being used as catalyst but the reaction being carried out under reflux conditions) was boiled with concentrated hydrochloric acid (100 c.c.). After about 30 minutes the nitrile had dissolved and the acid crystallised rapidly. Recrystallisation from alcohol gave m-*di*-2′-*carboxyethoxybenzene* as needles, m. p. 184°, sintering at 175°. The m. p. was not changed by further recrystallisation (Found : C, 56·6; H, 5·6. $C_{12}H_{14}O_6$ requires C, 56·7; H, 5·5%) (yield 11·3 g.). This acid (13 g.) was esterified by 2 hours' boiling with methyl alcohol (130 c.c.) and sulphuric acid (5 c.c.) and afforded m-*di*-2′-*carbomethoxyethoxybenzene* as needles (11 g.), m. p. 72·5—74·5° after two recrystallisations from methyl alcohol (Found : C, 59·3; H, 6·4. $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%). The ethyl ester, prepared in a similar way, was obtained as needles, m. p. 39—41°.

4-*Benzoyl*-1 : 3-*di*-2′-*carbomethoxyethoxybenzene.*—Aluminium chloride (53 g.) in nitrobenzene (200 c.c.) was added to a mixture of *m*-di-2′-carbomethoxyethoxybenzene (28 g.) and benzoyl chloride (14 g.) in nitrobenzene (100 c.c.) at 0°. After 12 hours the mixture was worked up in the usual way; the product crystallised from alcohol as orange prisms. Further recrystallisation from the same solvent gave 4-*benzoyl*-1 : 3-*di*-2′-*carbomethoxyethoxybenzene* as large, almost colourless prisms, m. p. 83—85° (14 g.) (Found : C, 65·1; H, 5·8. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%). Treatment with aqueous-alcoholic sodium hydroxide (10%) at room temperature for 2 hours afforded *β*-(4-benzoyl-3-hydroxyphenoxy)propionic acid, m. p. 173—175°, identical (mixed m. p.) with the compound prepared as above, and 1 hour's heating with absolute alcohol containing an equivalent of sodium ethoxide gave a high yield of 2 : 4-dihydroxybenzophenone. Hydrolysis to 4-*benzoyl*-1 : 3-*di*-2′-*carboxyethoxybenzene* was effected by prolonged boiling of it with 2N-hydrochloric acid. This acid crystallised from water or alcohol as prisms, m. p. 159°, sintering at 151° (Found : C, 64·2; H, 5·0. $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%).

4-*Benzoyl*-1 : 3-*di*-2′-*cyanoethoxybenzene.*—This *compound* was prepared from *m*-di-2′-cyanoethoxybenzene and benzoyl chloride in the usual way. It crystallised from alcohol as needles, m. p. 83—85° (Found : C, 70·8; H, 5·2. $C_{19}H_{16}O_3N_2$ requires C, 71·2; H, 5·0%).

2-*Hydroxy*-4-*methoxydiphenylmethane.*—2-Hydroxy-4-methoxybenzophenone (15 g.) was refluxed with amalgamated zinc (150 g.), concentrated hydrochloric acid (180 c.c.), and water (120 c.c.) for 24 hours, further 50-c.c. portions of acid being added from time to time to maintain evolution of hydrogen. The product was then extracted with ether, and the yellow gum that remained after drying and evaporation of the solvent partly crystallised. The solid was separated by prolonged suction, and recrystallisation from light petroleum (b. p. 60—80°) afforded 2-*hydroxy*-4-*methoxydiphenylmethane* as needles, m. p. 51—53° (Found : C, 78·5; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%).

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, May 10th*, 1951.]