757. *Dibenz*[b,f]*oxepins and Related Compounds.*

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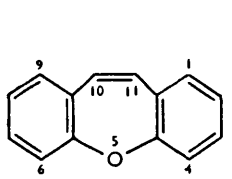
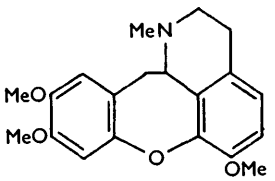
Dibenz[*b*,*f*]oxepin, 2-nitrodibenz[*b*,*f*]oxepin, and a number of their derivatives have been prepared from 2-chloro-5-nitrobenzaldehyde *via* 2-aryloxy-5-nitrobenzaldehydes and the derived 2-aryloxy-5-nitrophenyl-pyruvic and -acetic acids.

Comparatively little is known of the chemistry of dibenz[*b*,*f*]oxepin (I); indeed interest dates from Manske's recent proof [1] that the alkaloid cularine (II) is a derivative of dihydrodibenz[*b*,*f*]oxepin. Before this the ring system was known only in by-products arising from particular applications of Pschorr's phenanthrene synthesis.[2] The parent compound (I) was synthesised by Manske and Ledingham,[3] through reduction and dehydration, from the dibenzoxepinone (III) which they had prepared from *o*-phenoxybenzaldehyde *via* *o*-phenoxyphenylacetic acid. Kulka and Manske [4] also synthesised a number of derivatives modelled on the substitution pattern of the alkaloid although these developments were severely restricted by the poor overall yields. For a practicable synthesis of this type two stages are critical, one being the formation of the diphenyl ether linkage and the other the closure of the central heterocyclic ring. 2-Chloro-5-nitrobenzaldehyde provides a convenient source of 2-aryloxy-5-nitrobenzaldehydes. From it and by using polyphosphoric acid at the cyclisation stage we prepared derivatives of 2-nitrodibenz[*b*,*f*]oxepin in nearly 40% yield, and the parent nitro-compound and dibenz[*b*,*f*]oxepin itself were obtained in yields of 15—20%.



(I)



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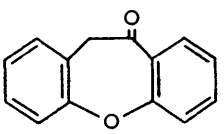

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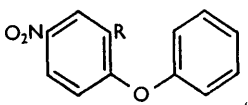

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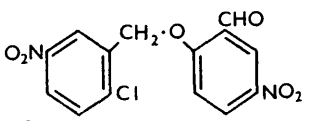


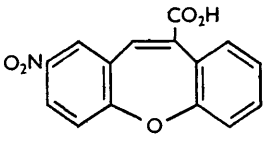
(V)

Based on patent procedure [5] 2-aryloxy-5-nitrobenzaldehydes (IV; R = CHO) were prepared in satisfactory yields by condensing 2-chloro-5-nitrobenzaldehyde with phenol and with methoxyphenols in aqueous alkali. A by-product constantly encountered in these reactions is assigned structure (V). This is in accord with the analytical data and with the formation of a mono-oxime: moreover the same compound was obtained in poor yield from 2-chloro-5-nitrobenzaldehyde and hot aqueous alkali, and in substantial yield by reaction with pre-formed 2-chloro-5-nitrobenzyl alcohol in presence of solid potassium carbonate. 2-Aryloxy-5-nitrobenzaldehydes resemble their 2-arylthio-analogues [6] in forming with concentrated sulphuric acid red solutions of the corresponding xanthylium sulphates. However dilution of such a solution with water does not generally

[1] Manske, *J. Amer. Chem. Soc.*, 1950, **72**, 55.
[2] Pschorr and Knoffler, *Annalen*, 1911, **382**, 53.
[3] Manske and Ledingham, *J. Amer. Chem. Soc.*, 1950, **72**, 4797.
[4] Kulka and Manske, *ibid.*, 1953, **75**, 1322.
[5] Geigy, F.P. 818,032; *Chem. Abs.*, 1938, **32**, 2371.
[6] Campbell, Dick, and Loudon, *J.*, 1941, 747.

lead to an easily separable mixture of the appropriate xanthen and xanthone, as happens in the thio-series, and further description is postponed.

5-Nitro-2-phenoxybenzaldehyde was condensed with aceturic acid and the resultant azlactone converted by acid hydrolysis into 5-nitro-2-phenoxyphenylpyruvic acid (IV; R = CH_2·CO·CO_2H) and hence by oxidation into 5-nitro-2-phenoxyphenylacetic acid (IV; R = CH_2·CO_2H). Each of these acids was cyclised by polyphosphoric acid, the pyruvic acid yielding the carboxylated dibenzoxepin (VI) and the acetic acid yielding the 2-nitro-derivative of the ketone (III). Similarly 2-phenoxyphenylacetic acid, which was prepared from the nitro-compound (IV; R = CH_2·CO_2H) by reduction followed by deamination, was cyclised to the dibenzoxepinone (III) and this product was conveniently isolated as the oxime. It was ascertained that the guaiacol ether, corresponding to the phenyl ether (IV; R = CHO), afforded analogous derivatives of 6-methoxydibenz[*b*,*f*]-oxepin in comparable yields by a similar series of reactions.



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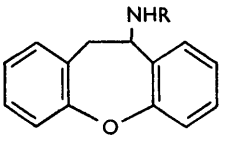

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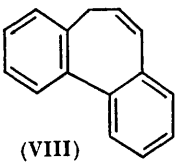
(VIII)

In presence of acetic anhydride, catalytic reduction of the oxime of ketone (III) afforded 10-acetamido-10 : 11-dihydrodibenz[*b*,*f*]oxepin (VII; R = Ac) and hence by hydrolysis the parent base (VII; R = H) which was isolated as the hydrochloride. The position of the nitrogen atom in this base corresponds to that of the nitrogen atom in cularine, but so far attempts to complete the fused *iso*quinoline ring-system of the alkaloid have not been successful. The elements of acetamide were readily eliminated when the acetamido-compound (VII; R = Ac) was heated with phosphoric oxide in xylene and this useful reaction [7] provides an alternative route from (III) to (I).

As a substituted cinnamic acid the compound (VI) was readily decarboxylated, forming 2-nitrodibenz[*b*,*f*]oxepin. It was also readily hydrogenated to 2-amino-10-carboxy-10 : 11-dihydrodibenz[*b*,*f*]oxepin, which was deaminated by standard methods. Manske and Ledingham [3] showed that oxidation of dibenz[*b*,*f*]oxepin by potassium permanganate yields 2 : 2′-dicarboxydiphenyl ether together with a small amount of xanthone. The formation of the latter recalls the oxidation of dibenz*ocyclo*heptatriene (VIII) to phenanthraquinone by sodium dichromate [8] and the associated contrast to oxidation by potassium permanganate whereby compounds of type (VIII) afford mainly homodiphenic acids.[9] This contrast appears indeed to be maintained in dibenz[*b*,*f*]oxepins since, as main products, permanganate oxidation of the acid (VI) yielded 2 : 2′-dicarboxy-4-nitrodiphenyl ether whereas dichromate oxidation gave 2-nitroxanthone. Mathys, Prelog, and Woodward [10] have recently shown that the benzil derivative, which is obtained from the monoketone (III) and selenium dioxide, undergoes benzilic acid rearrangement with exceptional ease. 2-Nitrodibenz[*b*,*f*]oxepin was readily oxidised by osmium tetroxide, affording *cis*-10 : 11-dihydro-10 : 11-dihydroxy-2-nitrodibenz[*b*,*f*]oxepin.

Experimental

Petroleum as solvent refers to light petroleum, b. p. 60—80°. 2-Chloro-5-nitrobenzaldehyde was prepared by nitrating 2-chlorobenzaldehyde.[11]

[7] Cook, Dickson, Ellis, and Loudon, *J.*, 1947, 1074.
[8] Cook, Dickson, and Loudon, *J.*, 1947, 746.
[9] Cf. Tarbell, Frank, and Fanta, *J. Amer. Chem. Soc.*, 1946, **68**, 502.
[10] Mathys, Prelog, and Woodward, *Helv. Chim. Acta*, 1956, **39**, 1095.
[11] Erdmann, *Annalen*, 1893, **272**, 153.

5-Nitro-2-phenoxybenzaldehyde.—2-Chloro-5-nitrobenzaldehyde (40 g.), phenol (20 g.), and sodium hydroxide (10 g.) were heated under reflux with water (400 c.c.) for 2 hr. A vigorous reaction soon set in and the final cold mixture deposited some crystals. The whole was extracted with ether. The filtered ethereal solution, washed with dilute sodium hydroxide then with water, was dried and concentrated. The semi-solid residue was heated with charcoal in benzene and, after recovery, afforded 5-nitro-2-phenoxybenzaldehyde, m. p. 67—68° (from benzene–petroleum) (Found: C, 64·3; H, 3·7. Calc. for $C_{13}H_9O_4N$: C, 64·2; H, 3·7%), in 70% yield.

2-2'-Methoxyphenoxy-5-nitrobenzaldehyde (yield 55%), m. p. 111° (from benzene–petroleum) (Found: C, 61·3; H, 3·9; N, 5·3. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0; N, 5·1%), and *2-4'-methoxyphenoxy-5-nitrobenzaldehyde*, m. p. 98° (from benzene–petroleum) (Found: C, 61·3; H, 4·1%), were prepared from *o*- and *p*-methoxyphenol as described for the unmethoxylated compound.

2-(2-Chloro-5-nitrobenzyloxy)-5-nitrobenzaldehyde (V).—(*a*) The ether-insoluble fraction (1—5% yield), found in preparing the foregoing 2-aryloxybenzaldehydes, had m. p. 208° (from benzene) (Found: C, 50·2; H, 2·8; N, 8·6; Cl, 10·75. $C_{14}H_9O_6N_2Cl$ requires C, 49·9; H, 2·7; N, 8·3; Cl, 10·55%) and with hydroxylamine hydrochloride in pyridine afforded the *oxime*, m. p. 194° (from benzene) (Found: C, 47·8; H, 2·9; N, 11·9. $C_{14}H_{10}O_6N_3Cl$ requires C, 47·8; H, 2·8; N, 11·9%). (*b*) It was also obtained (12% yield) when 2-chloro-5-nitrobenzaldehyde (0·5 g.) was heated under reflux (20 min.) with aqueous sodium hydroxide (13 c.c.; 2%). (*c*) *2-Chloro-5-nitrobenzyl alcohol*, m. p. 78° (from petroleum), was prepared by the interaction (4 hr. at 18°) of solutions of 2-chloro-5-nitrobenzaldehyde (3 g.) in methanol (50 c.c.) and sodium borohydride (1 g.) in water (10 c.c.), followed by acidification and evaporation of the methanol (Found: C, 44·8; H, 3·05. $C_7H_6O_3NCl$ requires C, 44·8; H, 3·2%). Equal parts of this alcohol, 2-chloro-5-nitrobenzaldehyde, and potassium carbonate were heated (15 min.) at 100°, affording the product (V) in 80% yield.

2-Methyl-4-(5-nitro-2-phenoxy)benzylidene-5-oxazolone.—Acetic anhydride (2 mol.) aceturic acid (1 mol.), 5-nitro-2-phenoxybenzaldehyde (1 mol.), and potassium hydrogen carbonate (1 mol.) were warmed until the yellow colour of the azlactone was apparent. After 24 hr. at 18° the *azlactone* was collected, washed with hot water, and dried. It formed lemon-yellow needles, m. p. 188° (from benzene–petroleum) (Found: C, 62·9; H, 3·6. $C_{17}H_{12}O_5N_2$ requires C, 63·0; H, 3·7%) (yield 75%). When the azlactone (2 g.) in warm ethanol (5 c.c.) and concentrated sulphuric acid (2 c.c.) was added to ice–water, *ethyl α-acetamido-β-(5-nitro-2-phenoxyphenyl)-acrylate*, m. p. 195—196° (from ethanol) (Found: C, 61·8; H, 5·0. $C_{19}H_{18}O_6N_2$ requires C, 61·6; H, 4·9%), was precipitated.

5-Nitro-2-phenoxyphenylpyruvic Acid.—The foregoing azlactone (10 g.) was heated for 5 hr. with concentrated hydrochloric acid (35 c.c.), water (60 c.c.), and acetic acid (100 c.c.). *5-Nitro-2-phenoxyphenylpyruvic acid*, m. p. 149° (from benzene), crystallised from the filtered hot solution and was augmented by material recovered by dilution of the mother liquor (yield 95%) (Found: C, 60·0; H, 3·8; N, 4·6. $C_{15}H_{11}O_6N$ requires C, 59·8; H, 3·65; N, 4·65%). When the dark-red solution of the acid in aqueous alkali was treated with an excess of hydroxylamine hydrochloride it afforded the *oxime*, m. p. 167° (from benzene) (Found: C, 56·7; H, 3·6. $C_{15}H_{12}O_6N_2$ requires C, 57·0; H, 3·8%).

5-Nitro-2-phenoxyphenylacetic Acid.—To a solution of the foregoing pyruvic acid (6 g.) in aqueous sodium hydroxide (100 c.c.; 10%) kept at 0°, hydrogen peroxide (25 c.c.; 10%) was slowly added. After 4 hr. at 18° the solution was acidified, affording *5-nitro-2-phenoxyphenylacetic acid*, as needles, m. p. 140° (from benzene–petroleum) (Found: C, 61·6; H, 4·0. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0%) (yield, 91%).

2-Nitrodibenz[b,f]*oxepin-10-carboxylic Acid* (VI).—A stirred mixture of 5-nitro-2-phenoxyphenylpyruvic acid (2 g.) and polyphosphoric acid [from syrupy phosphoric acid (14 c.c.) and phosphoric oxide (21 g.)] was heated first for a few minutes at 160° (until it became green-brown), and then at 100° for 2 hr. *2-Nitrodibenzoxepin-10-carboxylic acid* was precipitated by dilution of the cooled solution and, after purification in benzene (charcoal), formed pale yellow crystals, m. p. 224° (from benzene–petroleum) (Found: C, 63·7; H, 3·45; N, 5·05. $C_{15}H_9O_5N$ requires C, 63·6; H, 3·2; N, 4·95%) (yield 75%).

2-Amino-10 : 11-dihydrodibenz[b,f]*oxepin-10-carboxylic Acid.*—2-Nitrodibenzoxepin-10-carboxylic acid in aqueous potassium carbonate was hydrogenated over 2% palladised strontium carbonate, 4 mol. of hydrogen being absorbed. A few crystals of sodium sulphite were added,

and neutralisation of the filtered solution gave the *amine*, m. p. 210° (decomp.) (from ethanol–water) (Found: C, 70·7; H, 4·9. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1%). This, with concentrated hydrochloric acid, formed the *hydrochloride*, m. p. 262° (decomp.) (Found: C, 61·9; H, 4·8. $C_{15}H_{14}O_3NCl$ requires C, 61·75; H, 4·8%).

10 : 11-*Dihydrodibenz*[b,f]*oxepin*-10-*carboxylic Acid*.—The foregoing amine (0·2 g.) was diazotised in dilute hydrochloric acid with sodium nitrite (0·1 g. in 3 c.c. of water) and, after being gently warmed, the filtered solution was treated with hypophosphorous acid (2 c.c.; 30%). After 12 hr. 10 : 11-*dihydrodibenz*[b,f]*oxepin*-10-*carboxylic acid* was collected; it had m. p. 186° (from benzene) (Found: C, 75·3; H, 4·8. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%).

10 : 11-*Dihydro*-2-*nitro*-10-*oxodibenz*[b,f]*oxepin*, m. p. 158° (from benzene–petroleum), was obtained in 80% yield when 5-nitro-2-phenoxyphenylacetic acid was cyclised by polyphosphoric acid at 100° (2 hr.) (Found: C, 66·1; H, 3·55; N, 5·4. $C_{14}H_9O_4N$ requires C, 65·9; H, 3·5; N, 5·5%). Its *oxime* had m. p. 184° (from benzene) (Found: C, 62·0; H, 3·8; N, 10·2. $C_{14}H_{10}O_4N_2$ requires C, 62·2; H, 3·7; N, 10·4%).

5-*Amino*-2-*phenoxyphenylacetic Acid*.—A solution of potassium 5-nitro-2-phenoxyphenylacetate, prepared from the acid (5 g.) and potassium carbonate (2·3 g.) in water (500 c.c.), was hydrogenated over 2% palladised strontium carbonate (1·25 g.). When absorption of hydrogen was complete a few crystals of sodium sulphite were added to poison the catalyst and minimise later formation of coloured products. The filtered solution was neutralised by hydrochloric acid and, after 12 hr. at 0°, 5-*amino*-2-*phenoxyphenylacetic acid* was collected (yield 90%). It had m. p. 148° (from water) (Found: C, 69·0; H, 5·5. $C_{14}H_{13}O_3N$ requires C, 69·1; H, 5·35%) and when treated with concentrated hydrochloric acid yielded the *hydrochloride*, m. p. 230° (decomp.) (Found: C, 60·2; H, 5·25. $C_{14}H_{14}O_3NCl$ requires C, 60·1; H, 5·0%).

2-*Phenoxyphenylacetic Acid*.—5-Amino-2-phenoxyphenylacetic acid (3 g.) was diazotised in concentrated hydrochloric acid (40 c.c.) and water (100 c.c.) at 0° by addition of sodium nitrite (1 g.) in water. The mixture was gently warmed, then at 18° hypophosphorous acid (40 c.c.; 30%) was added. After 12 hr. 2-phenoxyphenylacetic acid was collected; it formed needles, m. p. 89° (Found: C, 73·95; H, 5·4. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%): Manske and Ledingham [3] report m. p. 91°.

10-*Amino*-10 : 11-*dihydrodibenz*[b,f]*oxepin*.—2-Phenoxyphenylacetic acid was heated with polyphosphoric acid first at 160° (5 min.) and then at 100° (2 hr.). The mixture was diluted with water and, after recovery in ether, 10 : 11-dihydro-10-oxodibenz[*b*,*f*]oxepin was obtained as a yellow oil. Without purification, this was converted (2 hr. under reflux) into the corresponding oxime, m. p. 135° (from benzene–petroleum) (Found: C, 74·7; H, 5·1. Calc. for $C_{14}H_{11}O_2N$: C, 74·7; H, 4·9%): the overall yield was 70%: Manske and Ledingham [3] record m. p. 137°. A solution of the oxime in acetic anhydride was hydrogenated in presence of platinic oxide and, after absorption of hydrogen was complete, the resultant solution was filtered, concentrated *in vacuo*, and diluted with water. 10-*Acetamido*-10 : 11-*dihydrodibenz*[b,f]*oxepin*, m. p. 139° (from benzene–petroleum), was thereby obtained in 88% yield (Found: C, 76·0; H, 6·0. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9%). On hydrolysis by dilute hydrochloric acid (4 hr. under reflux) it afforded 10-amino-10 : 11-dihydrodibenz[*b*,*f*]oxepin as the *hydrochloride*, m. p. 265° (decomp.) (from dilute hydrochloric acid) (Found: C, 68·1; H, 5·8. $C_{14}H_{14}ONCl$ requires C, 67·9; H, 5·65%).

Dibenz[b,f]*oxepin*.—10-Acetamido-10 : 11-dihydrodibenz[*b*,*f*]oxepin (0·1 g.), phosphoric oxide (0·2 g.), and xylene (4 c.c.) were heated under reflux for 30 min. The hot solution was decanted, the residue washed with hot xylene, and the combined solutions clarified and evaporated *in vacuo*, affording dibenz[*b*,*f*]oxepin, m. p. 110° (from methanol) (Found: C, 86·4; H, 5·3. Calc. for $C_{14}H_{10}O$: C, 86·6; H, 5·15%): Manske and Ledingham [3] record m. p. 111°.

2-*Nitrodibenz*[b,f]*oxepin*.—2-Nitrodibenz[*b*,*f*]oxepin-10-carboxylic acid (2 g.), copper bronze (10 g.), and quinoline (50 c.c.) were heated under reflux for 4 hr. The cooled mixture was diluted with benzene and filtered, the filtrate being washed with dilute sulphuric acid, water, aqueous sodium carbonate, and water, before being dried, concentrated and clarified by charcoal. Addition of petroleum to the resultant solution gave 2-*nitrodibenz*[b,f]*oxepin*, m. p. 130°, as pale yellow needles (yield 45%) (from methanol) (Found: C, 70·5; H, 3·9; N, 5·9. $C_{14}H_9O_3N$ requires C, 70·3; H, 3·8; N, 5·85%).

cis-10 : 11-*Dihydro*-10 : 11-*dihydroxy*-2-*nitrodibenz*[b,f]*oxepin*.—Pyridine (3 c.c.) was added to a solution of 2-nitrodibenzoxepin (0·28 g.) and osmium tetroxide (0·45 g.) in dry benzene (15 c.c.), and after 10 days petroleum was added to complete precipitation of the dark complex.

The latter was shaken (4 hr.) in chloroform with a solution of mannitol (3 g.) and potassium hydroxide (0·3 g.) in water (30 c.c.). Evaporation of the washed and dried chloroform solution gave the cis-*diol* as needles, m. p. 196° (from benzene–methanol) (Found: C, 61·3; H, 4·0. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0%).

2-2′-*Methoxyphenoxy-5-nitrophenylacetic acid*, m. p. 141° (from benzene–petroleum) (Found: C, 59·6; H, 4·5. $C_{15}H_{13}O_6N$ requires C, 59·4; H, 4·25%), was obtained in 67% overall yield from 2-2′-methoxyphenoxy-5-nitrobenzaldehyde by the methods described for the unmethoxylated compound, *via* 4-(2-2′-*methoxyphenoxy*-5′-*nitrobenzylidene*)-2-*methyl*-5-*oxazolone*, m. p. 197° (decomp.) (Found: C, 61·2; H, 4·1; N, 8·0. $C_{18}H_{14}O_6N_2$ requires C, 61·0; H, 3·95; N, 7·9%), and 2-2′-*methoxyphenoxy*-5-*nitrophenylpyruvic acid*, m. p. 230° (decomp.) (from acetic acid) (Found: C, 57·8; H, 4·1; N, 4·4. $C_{16}H_{13}O_7N$ requires C, 58·0; H, 3·9; N, 4·2%).

10 : 11-*Dihydro*-6-*methoxy*-2-*nitro*-10-*oxodibenz*[b,f]*oxepin*, needles, m. p. 195° (from benzene–petroleum), was formed in 78% yield by cyclisation of the foregoing acetic acid (Found: C, 62·9; H, 4·0. $C_{15}H_{11}O_5N$ requires C, 63·15; H, 3·9%). It yielded the *oxime*, m. p. 211° (from benzene–petroleum) (Found: C, 60·2; H, 4·3. $C_{15}H_{12}O_5N_2$ requires C, 60·0; H, 4·0%).

6-*Methoxy*-2-*nitrodibenz*[b,f]*oxepin*-10-*carboxylic acid*, m. p. 250° (decomp.), was prepared by cyclisation of the appropriate phenylpyruvic acid with polyphosphoric acid (Found: C, 61·5; H, 3·8. $C_{16}H_{11}O_5N$ requires C, 61·3; H, 3·5%) (yield 70%).

2-2′-*Methoxyphenoxyphenylacetic Acid*.—The corresponding 5-nitro-acid was hydrogenated over palladised strontium carbonate, affording (90% yield) 5-*amino*-2-2′-*methoxyphenoxyphenylacetic acid*, m. p. 137° (from methanol–water) (Found: C, 66·0; H, 5·6. $C_{15}H_{15}O_4N$ requires C, 65·9; H, 5·5%), and this was characterised as the *hydrochloride*, m. p. 134° (from water, then benzene–ethanol) (Found: C, 55·1; H, 5·8. $C_{15}H_{16}O_4NCl,H_2O$ requires C, 55·0; H, 5·5%). Deamination, effected as described for the unmethoxylated compound, gave 2-2′-methoxyphenoxyphenylacetic acid, m. p. 90° (from petroleum) (Found: C, 69·3; H, 5·5. Calc. for $C_{15}H_{14}O_4$: C, 69·8; H, 5·4%), for which Manske and Ledingham [3] record m. p. 93°. Cyclisation of this acid by polyphosphoric acid gave 10 : 11-dihydro-6-methoxy-10-oxodibenz[*b*,*f*]oxepin, m. p. 93° (from petroleum; yield 70%) (Found: C, 74·9; H, 5·1. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%), which formed the oxime, m. p. 198° (Found: C, 70·4; H, 5·1. Calc. for $C_{15}H_{13}O_3N$: C, 70·6; H, 5·1%). For these two compounds Manske and Ledingham [3] give m. p. 85 and 196°, respectively.

Oxidation of 2-*Nitrodibenz*[b,f]*oxepin*-10-*carboxylic Acid*.—(*a*) Finely powdered potassium permanganate was gradually added to a solution of the acid in acetone until the pink colour was permanent. Water in small quantities and more of the oxidising agent were then added until the colour persisted for several minutes. The whole was then treated with hot water, acetone was boiled off, and the hot mixture filtered. Acidification of the filtrate gave 2 : 2′-*dicarboxy*-4-*nitrodiphenyl ether*, m. p. 220° (from benzene–petroleum containing a little methanol) (yield, 90%) (Found: C, 55·2; H, 3·2; N, 4·7. $C_{14}H_9O_7N$ requires C, 55·4; H, 3·0; N, 4·6%).

(*b*) A solution of the acid (0·5 g.) and sodium dichromate (0·5 g.) in acetic acid (5 c.c.) was heated under reflux for 1 hr. The cooled solution was diluted with water and extracted with chloroform. Recovery from the washed and dried extract gave 2-nitroxanthone (yield 75%), m. p. and mixed m. p. 202° (Found: C, 65·0; H, 3·15; N, 5·8. Calc. for $C_{13}H_7O_4N$: C, 64·7; H, 2·9; N, 5·8%).

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