697. *Viridin. Part II.*[1] *Oxidation by Chromic Acid*

By P. McCloskey

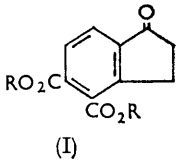
Oxidation of viridin, $C_{20}H_{16}O_6$, with chromic acid yields, in addition to the neutral compound $C_{19}H_{14}O_7$,[1] minor products including three keto-acids, $C_{17}H_{12}O_6$, $C_{11}H_8O_5$, and $C_{12}H_{10}O_4$, and a keto-lactone $C_{12}H_{10}O_3$. The last three compounds have been identified by synthesis as (I; R = H), (II; R = OH), and (II; R = H), respectively.

Viridin, $C_{20}H_{16}O_6$,[1] is converted by oxidation with chromic acid, in acetic acid at ordinary temperature, into a neutral compound, $C_{19}H_{14}O_7$,[1] which crystallises as the reaction proceeds, and a complex mixture of minor products. Three keto-acids, $C_{17}H_{12}O_6$, $C_{11}H_8O_5$, and $C_{12}H_{10}O_4$, and a keto-lactone, $C_{12}H_{10}O_3$, have been isolated in low yields, and the last three compounds identified by synthesis as 1-oxoindane-4,5-dicarboxylic acid (I; R = H), and the 3-methyl-5′-oxo-(1′,2′:6,7)-cyclopentenophthalides (II; R = OH) and (II; R = H) respectively.

The neutral product, $C_{12}H_{10}O_3$, which is optically inactive, contains one active hydrogen and one *C*-methyl group (Kuhn–Roth). It dissolves slowly in cold alkali consuming one

[1] Part I, J. F. Grove, J. S. Moffatt, and E. B. Vischer, preceding Paper.

equivalent, can be recovered in high yield from the acidified solution, and is clearly a lactone. A reactive carbonyl group is detected by semicarbazone and dinitrophenylhydrazone formation, and an adjacent methylene group by the preparation of an oximino-derivative by reaction with pentyl nitrite. The spectral data are consistent with the



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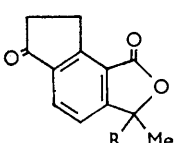

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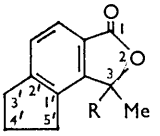

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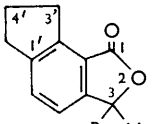


(IV)

presence of a conjugated γ-lactone system, and a conjugated carbonyl group in a five membered ring [$\nu_{max.}$ (chloroform), 1766, 1719 cm.$^{-1}$; $\lambda_{max.}$ (ethanol), ~238, 269, 289 mμ; log ε 4·0, 3·58, 5·55; semicarbazone, $\lambda_{max.}$ (ethanol), 279, 319 mμ; log ε 4·22, 3·89].

Oxidation with cold neutral permanganate converts the lactone into the keto-acid, $C_{12}H_{10}O_4$, which in turn is oxidised by alkaline permanganate under vigorous conditions to benzene-1,2,3,4-tetracarboxylic acid also obtained by oxidising viridin with nitric acid.[1] The preparation of a *neutral O*-acetyl derivative and *normal* and *pseudo*-methyl esters of the keto-acid provides clear evidence for the ring-chain tautomerism of a 3-hydroxyphthalide–*o*-acylbenzoic acid system, further defined as an acetyl- rather than a formylbenzoic acid by a well-marked iodoform reaction and an absence of reducing properties (behaviour shown also by the normal methyl ester); in its cyclic form this acid is a 3-hydroxy-3-methylphthalide. Catalytic reduction of both the keto-lactone and the normal methyl ester of the keto-acid yields the same deoxo-lactone $C_{12}H_{12}O_2$. It follows that the keto-lactone is the 3′- (or 5′-)oxo-derivative of 3-methyl(1′,2′:4,5)cyclopentenophthalide (III; R = H) or of the isomeric 3-methyl(1′,2′:6,7)cyclopentenophthalide (IV; R = H), and that the keto-acid is the corresponding derivative of (III; R = OH) or (IV; R = OH).

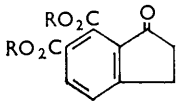
This formulation of the neutral lactone and the related acidic lactol as indan-1-one derivatives is supported by the isolation in very low yield of the dimethyl ester of a keto-dicarboxylic acid, $C_{11}H_8O_5$, from the water-soluble acidic products (after methylation with diazomethane) obtained by oxidising viridin with chromic acid. If this acid represent a stage of oxidation intermediate between the keto-acid, $C_{12}H_{10}O_4$, and benzene-1,2,3,4-tetracarboxylic acid, the analytical and spectral data [obtained for the derived ester: $\nu_{max.}$ (Nujol), 1733, 1717 cm.$^{-1}$; $\lambda_{max.}$ (ethanol), 252, 258, ~300, 304 mμ; log ε 4·07, 4·03, 3·64, 3·65] are only consistent with its being indan-1-one-4,5-dicarboxylic acid (I; R = H) or its 6,7-isomer (V; R = H). In view of the relative inaccessibility of this simplest degradation product, and its close relationship to the other oxidation products, its identification by synthesis was now considered.

The ease with which 1- and 2-naphthols (and their ethers) are cleaved by peracid to yield *o*-carboxycinnamic acid [2,3] which in turn may be oxidised to *o*-phthalic acid [3] suggested that the vicinal aromatic carboxyl groups of the required indanone derivative might be obtained by stepwise oxidation of a suitably hydroxylated (or methoxylated) benzindanone. Moreover, fusion of *o*-carboxycinnamic acid,[4] or treatment with hot, dilute acid,[5] yields phthalide-3-acetic acid (VI) in an easy transformation which comes near to forming the 3-methylphthalide system present in the keto-lactone $C_{12}H_{10}O_3$.

The synthesis of indan-1-one-6,7-dicarboxylic acid (V; R = H) by way of the ketone

[2] J. Böeseken and M. L. v. Königsfeldt, *Rec. Trav. chim.*, 1935, **54**, 316; F. P. Greenspan, *Ind. Eng. Chem.*, 1947, **39**, 847; G. A. Page and D. S. Tarbell, *Organic Syntheses*, 1954, **34**, 8.
[3] H. Fernholz, *Ber.*, 1951, **84**, 110.
[4] S. Gabriel and A. Michael, *Ber.*, 1877, **10**, 2203.
[5] R. Roth, *Ber.*, 1914, **47**, 1598.

(VII) and the *o*-carboxycinnamic acid (VIII) was attempted first because of the ready availability of 2-methoxy-6-substituted naphthalenes by Friedel–Crafts acylation of 2-methoxynaphthalene in nitrobenzene.[6]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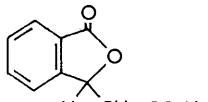
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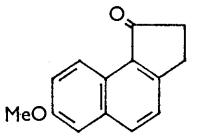
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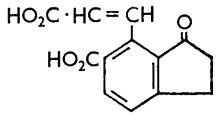
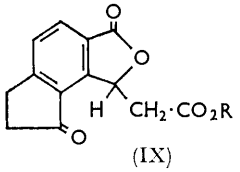

(VIII)

Oxidation of 2-acetyl-6-methoxynaphthalene with hypochlorite gave 6-methoxy-2-naphthoic acid whose chloride underwent Rosenmund reduction to 6-methoxy-2-naphthaldehyde. This was converted by condensation with malonic acid into the naphthylacrylic acid and thence, by catalytic reduction and cyclisation using stannic chloride (or polyphosphoric acid) into the tricyclic ketone (VII) which was oxidised with peracetic acid.

In illustration of the ease of conversion of the required cinnamic acid (VIII) into the isomeric lactonic acid 5′-oxo(1′,2′:4,5)cyclopentenophthalide-3-acetic acid (IX; R = H), the latter was, in fact, found to be the main product of oxidation and was readily isolated as its methyl ester from the crude acidic product after methylation with diazomethane. However, treatment of (IX; R = H) with two equivalents of hot 2N-sodium hydroxide opened the phthalide ring yielding a salt which underwent dehydration at 165—180° [4,7]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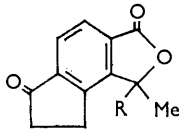
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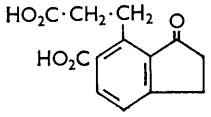

(XI)

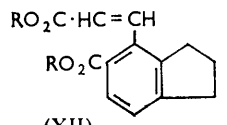
to the salt of β-(5-carboxy-3-oxo-4-indanyl)acrylic acid (VIII), oxidation of which, with alkaline permanganate, then gave the required indan-1-one-6,7-dicarboxylic acid (V; R = H). Confirmation of the substitution pattern assigned to (V) was afforded by the isolation of benzene-1,2,3,4-tetracarboxylic acid as a by-product of this oxidation. The dimethyl ester (V; R = Me) was, however, distinct from the dimethyl ester of the keto-acid $C_{11}H_8O_5$ obtained by oxidation of viridin, a result which virtually identified the degradation product as the acid (I; R = H). This conclusion was verified by catalytic reduction of both esters to dimethyl indane-4,5-dicarboxylate and oxidation of this, with chromic acid in warm acetic acid, to give the ester derived by degradation (I; R = Me) together with a little of its isomer (V; R = Me).

It followed from this identification that the keto-lactone and lactol are probably (II; R = H, OH) or (X; R = H, OH).

The possibility, implied above, of correlating the keto-lactone and the cyclopentenophthalide-3-acetic acid (IX; R = H) available as an intermediate in the synthesis of (V; R = H) was re-examined. A first step was the elimination of the ketonic carbonyl group from both compounds and in the degradation product this was readily accomplished by catalytic reduction over palladium. When applied to (IX) this method gave a different result, the indanone system remaining intact whilst the phthalide ring suffered smooth hydrogenolysis affording (XI). Clemmensen reduction also gave an unsatisfactory and obscure result with (IX) but succeeded with the ketone (VII) yielding 6-methoxy-1,2-cyclopentenonaphthalene. Oxidation of this with peracetic acid then gave the *o*-carboxycinnamic acid derivative (XII; R = H) which cyclised quantitatively on fusion yielding 4,5-cyclopentenophthalide-3-acetic acid (XIII).

[6] R. D. Haworth and G. Sheldrick, *J.*, 1934, 864; R. Robinson and H. N. Rydon, *J.*, 1939, 1399.
[7] Cf. F. M. Rowe, A. S. Haigh, and A. T. Peters, *J.*, 1936, 1104.

Difficulty in the decarboxylation of the phthalide acetic acid system present in (XIII) was anticipated, and in model experiments some attempt was first made to convert phthalide-3-acetic acid into *o*-acetylbenzoic acid which can be readily reduced to 3-methylphthalide.



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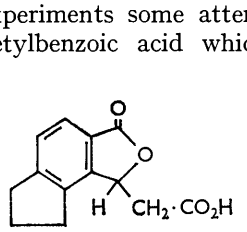

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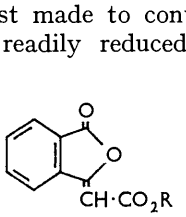


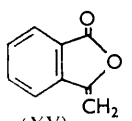
(XIV)

Adaptation of the procedure of Blair *et al.*[8] for oxidising phthalides to *o*-phthalaldehydic acids by way of the *o*-hydroxymethyldimethylbenzamides proved abortive: phthalide-acetic acid remained unchanged on treatment with a cold solution of dimethylamine in ethanol for one week, and was rearranged to *o*-carboxycinnamic acid on heating with the base at 100°.[4]

An alternative route to *o*-acetylbenzoic acid, by way of phthalidylideneacetic acid (XIV; R = H) was more successful. The methyl ester of phthalideacetic acid on treatment with N-bromosuccinimide yielded a bromo-derivative which lost hydrobromic acid smoothly on gentle heating *in vacuo* affording (XIV; R = Me) which was then converted into *o*-acetylbenzoic acid when boiled with dilute hydrochloric acid.[9]

Not unexpectedly, bromination of the methyl ester of the cyclopentenophthalide-3-acetic acid (XIII) under these conditions appeared to take place preferentially in the five-membered ring leading to a heterogeneous product which was not readily dehydrobrominated on heating. However, the easy formation of the phthalidylidene system (XIV) from phthalide acetic acid by way of the bromo-derivative suggested that the same result might be effected by dehydrogenation, and the thermally unstable phthalidylideneacetic acid even simultaneously decarboxylated [10] by a suitable choice of conditions. In the event, distillation of phthalideacetic acid from an intimate mixture with palladised charcoal readily afforded carbon dioxide and a neutral oil from which, by chromatography, methylenephthalide (XV) was isolated, and a trace of 3-methylphthalide separated, and identified by spectroscopy. The difficulty of isolating the required methylenephthalide, which in the crude state rapidly deteriorated,[11] was subsequently avoided, the crude neutral distillate being converted without delay into 3-methylphthalide in satisfactory yield (*ca.* 30% based on phthalideacetic acid) by catalytic hydrogenation.

Distillation of 4,5-cyclopentenophthalide-3-acetic acid (XIII) from palladised charcoal under similar conditions yielded a neutral gum which is considered, by analogy, to consist mainly of 3-methylene-4,5-cyclopentenophthalide (XVI). Immediate hydrogenation of this crude product then gave a gum from which the required 3-methyl-4,5-cyclopentenophthalide (III; R = H) was isolated after separation from an unidentified ketonic by-product by means of the Girard procedure. The deoxolactone derived from viridin was



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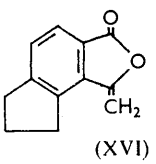

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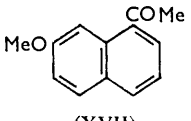

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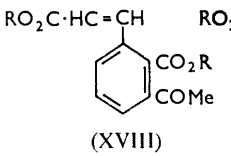

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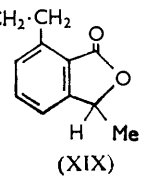


(XIX)

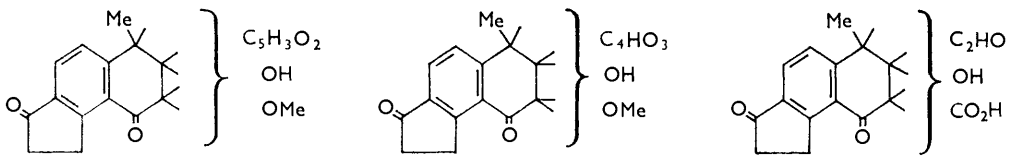
however, different from this product (III; R = H) and must therefore possess the alternative structure (IV; R = H). The parent keto-lactone, $C_{12}H_{10}O_3$, may then be formulated

[8] J. Blair, J. J. Brown, and G. T. Newbold, *J.*, 1955, 708.
[9] Cf. S. Gabriel and A. Michael, *Ber.*, 1877, **10**, 1555.
[10] S. Gabriel, *Ber.*, 1884, **17**, 2521.
[11] Cf. G. Bendz and A. Thalén, *Arkiv Kemi*, 1959, **14**, 519.

as (II; R = H) and the related keto-acid, $C_{12}H_{10}O_4$, as (II; R = OH). These conclusions were now confirmed by synthesis of the keto-lactone as follows.

7-Methoxy-1-naphthoyl chloride was converted by alkylation using dimethylcadmium into 1-acetyl-7-methoxynaphthalene (XVII; R = Me). Oxidation of the corresponding naphthol (or, less satisfactorily, of the naphthol ether itself) with peracetic acid opened the hydroxylated ring yielding the *o*-carboxycinnamic acid (XVIII; R = H) which, as its dimethyl ester (XVIII; R = Me), underwent catalytic hydrogenation with spontaneous formation of the phthalide system in the product (XIX; R = Me). Cyclisation of the corresponding acid (XIX; R = H) occurred on heating it with polyphosphoric acid yielding the required 3-methyl-5'-oxo(1',2':6,7)cyclopentenophthalide (II; R = H) identical with the keto-lactone, $C_{12}H_{10}O_3$, obtained by oxidation of viridin.

The products $C_{19}H_{14}O_7$ and $C_{17}H_{12}O_6$ await detailed examination but comparison of ultraviolet spectra shows that in both of them the chromophoric system present in viridin has survived. Moreover, as may be seen from the infrared spectra, two of the carbonyl groups present in viridin ($\nu_{max.}$ 1692, 1675 cm.$^{-1}$) [1] can be recognised in both these products



(XX) (XXI) (XXII)

($\nu_{max.}$ 1710, 1679 and 1700, 1670 cm.$^{-1}$, respectively), and can be accounted for as aryl-conjugated carbonyl groups, in five- and six-membered rings, which ultimately appear in the indanone and phthalide systems of the minor degradation products discussed above. These conclusions can be stated in terms of the partial structures (XX), (XXI), and (XXII) for viridin and the oxidation products $C_{19}H_{14}O_7$ and $C_{17}H_{12}O_6$ respectively.

Experimental

Melting points are corrected. Infrared spectra were obtained on Nujol mulls and ultraviolet spectra were measured in ethanol. Light petroleum had b. p. 60—80°.

Preparation of the Degradation Products.—Several of the minor products obtained by oxidation of viridin with cold chromic acid are also formed by hot oxidation of the major product $C_{19}H_{14}O_7$.[1] Better yields were generally obtained by such stepwise oxidation rather than by direct hot oxidation of viridin.

(i) *By oxidation of viridin.* Viridin (5 g.) in 95% acetic acid (200 ml.) was treated with chromic oxide (6·25 g.) in 95% acetic acid (125 ml.) during 15 min. at 15—20° and then set aside. A crystalline solid (1·5 g.) which separated was filtered off after 18 hr., washed with water and methanol, and recrystallised from acetic acid yielding yellowish prisms of the product, $C_{19}H_{14}O_7$,[1] m. p. 283—288°.

The filtrates from four such oxidations were combined, diluted with an equal volume of water, and set aside at 0° for 24 hr. and then filtered yielding more (2 g.) of the same product. The filtrate was evaporated on the water-bath under reduced pressure, the residue neutralised with saturated sodium hydrogen carbonate and the resulting mixture treated successively as follows: (*a*) extracted with ether (8 × 1 l.), the extract washed with a little water, dried, and evaporated yielding brown *neutral* solid (0·87 g.); (*b*) acidified with 20% sulphuric acid, set aside for 2 days at 0°, and then filtered yielding an *acidic* solid (1·52 g.); (*c*) extracted with ether (12 × 1 l.), the extract washed with water (6 × 100 ml.), dried, and evaporated affording a brown *acidic* gum (2·6 g.), and (*d*) extracted with ether continuously for 2 weeks, the extract dried over sodium sulphate, and evaporated affording an *acidic* brown oil (1·38 g.). Fractions (*a*) to (*d*) were subsequently combined with corresponding fractions obtained by oxidation of the product $C_{19}H_{14}O_7$ (see below).

(ii) *By oxidation of the product* $C_{19}H_{14}O_7$. The above product (1·5 g.) in 95% acetic acid (255 ml.) was heated under reflux and treated with chromic oxide (3 g.) in 95% acetic acid (75 ml.)

dropwise during 15 min. and the mixture boiled for a further 30 min. and then set aside overnight. The reaction mixtures obtained by oxidising the product $C_{19}H_{14}O_7$ (total 6·5 g.) in several similar experiments were combined and evaporated under reduced pressure on the water-bath and the residue separated into neutral and acidic products as follows:

Neutral Oxidation Product: 3-*Methyl*-5′-*oxo*-(1′,2′:6,7)*cyclopentenophthalide* (II; R = H).—The residue was neutralised with saturated sodium hydrogen carbonate and extracted with ether (9 × 1 l.). The extract was washed with water, dried, and evaporated yielding a crystalline solid (0·77 g.) which was redissolved in methanol (5 ml.), the solution filtered from insoluble material and concentrated yielding crystals (0·48 g.), m. p. 145—155°. This crude product was combined with similar material (0·19 g.) obtained by crystallisation of neutral fraction (*a*) from the oxidation of viridin (above), sublimed at 130°/0·1 mm., and the sublimate (0·65 g.) crystallised from methanol affording plates, m. p. 157·5—158·5°, of 3-*methyl*-5′-*oxo*-(1′,2′:6,7)-*cyclopentenophthalide* (II; R = H) (Found: C, 71·5; H, 5·3; *C*-Me (Kuhn–Roth), 6·85; active H (Zerewitinov), 0·38%; *M* (Rast), 218. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0; *C*-Me, 7·4; active H, 0·49%; *M*, 202); $\lambda_{max.}$ ~238, 289, 296 mμ; log ε 4·02, 3·55, 3·58; $\nu_{max.}$ (chloroform), 1766, 1719 cm.$^{-1}$ (C=O). The infrared spectrum of this product was identical with that of a synthetic specimen (see below), and no depression of m. p. occurred on mixing. The 2,4-*dinitrophenylhydrazone* formed orange prisms, m. p. 294—296° (decomp.), from ethanol (Found: C, 57·0; H, 3·6; N, 14·4. $C_{18}H_{14}N_4O_6$ requires C, 56·5; H, 3·7; N, 14·65%). The *semicarbazone*, leaflets from aqueous ethanol, softened above 260° and decomposed slowly above 280° (Kofler hot-stage apparatus) (Found: C, 60·3; H, 4·9; N, 15·9. $C_{13}H_{13}N_3O_3$ requires C, 60·2; H, 5·0; N, 16·2%); $\lambda_{max.}$ 279, 319 mμ; log ε 4·22, 3·89. The *oxime* formed needles, m. p. *ca.* 242° (decomp.) (from water) (Found: C, 66·4; H, 5·4; N, 6·9. $C_{12}H_{11}NO_3$ requires C, 66·35; H, 5·1; N, 6·45%).

α-*Oximino-derivative.*—The keto-lactone (100 mg.) in ethanol (1·2 ml.) was treated with concentrated hydrochloric acid (0·15 ml.) and pentyl nitrite (0·2 ml.), the mixture warmed at 40—50° for 15 min., and then set aside at 0° for 1 hr. The solid (91 mg.) was filtered off and crystallised from hot water (charcoal) yielding leaflets of the α-*oximino-derivative*, m. p. 235—240° (decomp.) (Found: C, 62·7; H, 4·0; N, 5·9. $C_{12}H_9NO_4$ requires C, 62·3; H, 3·9; N, 6·1%). $\nu_{max.}$ 1750, 1704 cm.$^{-1}$ (C=O).

Further Reactions of 3-*Methyl*-5′-*oxo*-(1′,2′:6,7)*cyclopentenophthalide* (II; R = H).—(i) *Action of alkali.* The keto-lactone (47 mg.) slowly dissolved when shaken with 0·5N-sodium hydroxide (1 ml.) in the cold yielding a pale yellow solution. Titration with 0·5N-hydrochloric acid (phenolphthalein) showed that 1 equiv. of alkali (0·46 ml.) had been consumed. Acidification of the neutralised solution with concentrated hydrochloric acid gave a sticky, partly crystalline, precipitate which was extracted with ether–benzene. Recovery gave impure keto-lactone (44 mg.), m. p. 150—156° (melt not clear), raised to 156—157·5°, undepressed on admixture with starting material, after extraction with hot methanol and separation from an insoluble neutral solid (4 mg.), m. p. 270—300°. Heating the keto-lactone under reflux with 2N-sodium hydroxide for 4½ hr. followed by acidification converted it into a yellowish powder which melted slowly above 180°. Attempts to purify this material failed.

(ii) *Catalytic reduction.* Absorption of hydrogen (2 mol.) by the keto-lactone (100 mg.) in acetic acid (5 ml.) in the presence of palladium–charcoal (20%; 30 mg.) was complete after 1 hr. Recovery and chromatography of the gummy product on alumina in ether gave a solid (82 mg.) which formed prisms, m. p. 83·5—84·5°, of the deoxo-derivative, 3-*methyl*-6,7-*cyclopentenophthalide* (IV; R = H), from light petroleum (b. p. 40—60°) (Found: C, 76·6; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%); $\lambda_{max.}$ 237, 290, 295 mμ; log ε 3·95, 3·58, 3·58; $\nu_{max.}$ 1752 cm.$^{-1}$ (C=O).

(iii) *Permanganate oxidation.*—The keto-lactone (30 mg.) was stirred with cold 2N-sodium hydroxide (1 ml.) until dissolved (3 hr.). The solution was neutralised by passage of carbon dioxide, and potassium permanganate (32 mg.) in water (1 ml.) added at room temperature during continuous passage of the gas. After reduction of the permanganate was complete (6 hr.) the mixture was filtered, acidified with hydrochloric acid, and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried, and evaporated yielding starting material (17 mg.). Acidification of the aqueous solution and extraction with ether and recovery gave a slightly gummy solid (6 mg.) which, after washing with ether afforded the keto-acid, $C_{12}H_{10}O_4$ (II; R = OH) (see below) as a powder, m. p. *ca.* 196°, undepressed on admixture with the compound m. p. 195—196° obtained by oxidation of viridin.

Acidic Oxidation Products.—(a) *The keto-acid* $C_{17}H_{12}O_6$. The aqueous mother-liquor, after

extraction of neutral products (above) was acidified with 20% sulphuric acid, set aside at 0° for 2 days, and then filtered yielding a pale-brown powder (0·65 g.) which was combined with a similar fraction (*b*) from the oxidation of viridin (above) and reprecipitated from a cold sodium hydrogen carbonate solution by dropwise addition of concentrated hydrochloric acid, washed with water, and dried. Repeated crystallisation from acetic acid yielded pale yellow prisms of a *keto-acid*, which did not melt below 300° [Found (after drying for several hours at 118°/0·1 mm.): C, 64·9; 64·8; H, 4·1, 3·9; OMe, nil. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%]; $\lambda_{max.}$ (water), 247, 316 mμ; log ε 4·44, 4·08; $\nu_{max.}$ 3310 (OH), 1700, 1670, ~1653 cm.$^{-1}$ (C=O).

Methylation of this product (200 mg.), suspended in ether with diazomethane, afforded a *methyl ester* as pale yellow prisms (145 mg.), m. p. 231—232·5°, from methanol (Found: C, 66·3; H, 4·4; OMe, 9·9. $C_{18}H_{14}O_6$ requires C, 66·25; H, 4·3; OMe, 9·5); $\lambda_{max.}$ 241, 300 mμ; log ε 4·4, 4·05; $\nu_{max.}$ 3370, 3110 (OH); 1708, 1696, 1667 cm.$^{-1}$ (C=O).

Catalytic hydrogenation of the methyl ester. Uptake of hydrogen by the methyl ester (50 mg.) in methanol (20 ml.) containing acetic acid (1 drop) in the presence of palladium–charcoal (25%, 25 mg.) was allowed to proceed for 4 days. The mixture was then boiled under reflux, with addition of acetone, to dissolve a crystalline product, filtered, and the filtrate concentrated yielding pale yellow needles (28 mg.) of a *product*, which changed crystalline form with slight softening between 210 and 225°, yielding prisms, m. p. 260—268° (decomp.) (Found: C, 69·5; H, 4·8; OMe, 10·5. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2; OMe, 9·9%); $\nu_{max.}$ 3350—3100 (broad, OH); 1728, 1678 cm.$^{-1}$ (C=O).

(b) *The keto-acid* $C_{12}H_{10}O_4$: 3-*hydroxy*-3-*methyl*-5′-*oxo*-(1′,2′:6,7) *cyclopentenophthalide* (II; R = OH). The aqueous filtrate was extracted with ether (12 × 1 l.) the extract washed with water (3 × 20 ml.), dried, and evaporated, yielding a brown gum (1·45 g.) which was combined with the similar fraction (c) obtained by oxidation of viridin (total *ca.* 4 g.) and extracted portionwise with boiling ether (3 × 1 l.), the extract filtered, and the solution dried and chromatographed on alumina (pH 7·0; 10 g.). Elution with ether (3 l.) and recovery gave a gummy solid which was crystallised from methanol (4 ml.) at 0° yielding a solid (0·82 g.). Successive recrystallisation from water (charcoal), benzene, and methanol afforded prisms, m. p. 195—196°, of 3-*hydroxy*-3-*methyl*-5-*oxo*(1′,2′:6,7)*cyclopentenophthalide* (II; R = OH) (Found: C, 66·0; H, 4·85. $C_{12}H_{10}O_4$ requires C, 66·05; H, 4·6%); $\lambda_{max.}$ (water, 267, 303 mμ; log ε 4·13, 3·52; $\nu_{max.}$ 3250 (OH); 1757, 1700 (in dioxan), 1771, 1724 cm.$^{-1}$ (C=O). This product dissolved slowly, with effervescence, in saturated sodium hydrogen carbonate, and gave the iodoform reaction. It did not reduce ammoniacal silver nitrate. The 2,4-*dinitrophenylhydrazone* formed orange-red crystals, m. p. 260—261° (decomp.), from benzene–methanol (Found: C, 54·6; H, 3·6; N, 14·3. $C_{18}H_{14}N_4O_7$ requires C, 54·3; H, 3·5; N, 14·1%).

Normal methyl ester. Methylation of the keto-acid with diazomethane in ether at 0° afforded the *normal methyl ester*, leaflets, m. p. 107—108°, from methanol–water (1 : 1) (Found: C, 67·0; H, 5·3. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%); $\lambda_{max.}$ 254, ~302, 304 mμ; log ε 3·96, 3·58, 3·59; $\nu_{max.}$ 1719, 1707 cm.$^{-1}$ (C=O).

Treatment of the ester, in methanol, with 2,4-dinitrophenylhydrazine reagent in the cold for 5 min. yielded orange-yellow prisms, m. p. 260—266° (vigorous decomp.), considered to be the mono-2,4-dinitrophenylhydrazone. On standing overnight in contact with the reagent this was converted into the *bis*-2,4-*dinitrophenylhydrazone*, orange crystals, m. p. 299—303° (decomp.), from methanol (Found: C, 50·8; H, 3·5; N, 18·4. $C_{25}H_{20}N_8O_{10}$ requires C, 50·7; H, 3·4; N, 18·9%).

pseudo-*Methyl ester* (II; R = OMe). The normal methyl ester (m. p. 106·5—108°) (30 mg.) in methanol (0·5 ml.) was treated with concentrated hydrochloric acid (1 drop) and set aside for 18 hr. Dilution with cold water then yielded crystals (17 mg.), m. p. 136—137°, after recrystallisation from ether, of the pseudo-*methyl ester* (Found: C, 67·6; H, 5·2. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%); $\lambda_{max.}$ 218, ~238, 289, 298 mμ; log ε 4·68, 3·99, 3·57, 3·66; $\nu_{max.}$ 1753, 1718 cm.$^{-1}$ (C=O).

Acetyl derivative. The keto-acid (10 mg.) was heated under reflux with acetic anhydride (0·5 ml.) for 2 hr. Evaporation gave a gum which afforded leaflets, m. p. 142—144°, from water containing a trace of methanol, of the *acetyl derivative* (II; R = OAc) (Found: C, 64·9; H, 4·75. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%); $\nu_{max.}$ (chloroform), 1786, 1768, 1717 cm.$^{-1}$ (C=O). It was insoluble in saturated sodium hydrogen carbonate. The 2,4-*dinitrophenylhydrazone* formed crystals, m. p. *ca.* 252° (decomp.) (Found: C, 54·9; H, 3·8; N, 13·1. $C_{20}H_{16}N_4O_8$ requires C, 54·55; H, 3·7; N, 12·7%).

α-Oximino-derivative. The keto-acid (50 mg.), suspended in ethanol (0·6 ml.) was treated with concentrated hydrochloric acid (0·08 ml.) and pentyl nitrite (0·1 ml.). After 15 min. at 45° the mixture was cooled, evaporated to half its volume in a current of air, set aside overnight at 0°, and then filtered yielding solid (23 mg.) which crystallised as leaflets (16 mg.) m. p. *ca.* 140°, resolidifying and remelting at 213—216° (decomp.), from hot water [Found (after drying 3 hr. at 78°/0·1 mm.): C, 54·7; H, 4·0; N, 5·1. $C_{12}H_9NO_5,H_2O$ requires C, 54·3; H, 4·15; N, 5·3%); $\nu_{max.}$ 1781, 1724 cm.$^{-1}$ (C=O) and hydroxyl bands.

Catalytic reduction of the normal methyl ester. Absorption of hydrogen (3·2 mol.) by the normal methyl ester (25 mg.) in methanol (4 ml.) in the presence of palladium–charcoal (20%, 100 mg.) occurred during 5 min. and then ceased. The mixture was filtered hot, the filtrate evaporated, and the residual gum (14 mg.) crystallised from ether affording prisms of 3-methyl-6,7-cyclopentenophthalide (IV; R = H), m. p. 82·5—83·5°, undepressed on admixture with the specimen obtained by catalytic reduction of the keto-lactone $C_{12}H_{10}O_3$ (above).

Oxidation of the keto-acid (II; R = OH) *with permanganate.* The keto-acid (25 mg.) in 2N-sodium carbonate (5 ml.) was heated on the steam-bath whilst powdered potassium permanganate (*ca.* 100 mg.) was added portionwise until oxidation appeared to be complete. The mixture was then filtered and the filtrate boiled under reflux with an excess of permanganate for 4 hr., then cooled, and the excess reduced by addition of a few drops of methanol. After filtration the solution was acidified with 2N-sulphuric acid and extracted repeatedly with ether. Evaporation of the dried extract gave a gum which was redissolved in hot water (charcoal), filtered, concentrated (to 0·1 ml.), and treated with concentrated hydrochloric acid (0·5 ml.) yielding solid (0·5 mg.), m. p. 212—220° (decomp.). Methylation of this product (diazomethane) and recovery gave a solid which formed needles from ether, m. p. 128—131° raised to 129—132° on admixture with tetramethylbenzene-1,2,3,4-tetracarboxylate (m. p. 133—134°). On standing for several weeks exposed to air and light both samples of crystals, which were initially colourless, became purple (Cf ref. 23).

Paper chromatography of a second crop of acidic product on Whatman No. 1 paper using a phenol–water system showed the presence of two acids, one of which had the same R_F (0·24) as that of authentic benzene-1,2,3,4-tetracarboxylic acid in the same run. The second acid (R_F 0·4) was not isolated.

Treatment of the keto-acid (II; R = OH) *with alkali.* The keto-acid (50 mg.) was set aside in excess of 0·1N-sodium hydroxide at room temperature, the solution, initially yellow, gradually becoming red. Acidification after 20 hr. gave a pale brown solid (10 mg.), m. p. >300°, and extraction of the mother-liquor with ether and recovery yielded unchanged starting material (39 mg.), m. p. 195—196° after recrystallisation. Treatment of the keto-acid with N-sodium hydroxide for 19 hr. at room temperature converted it completely into the brown amorphous product.

(c) *The keto-acid* $C_{11}H_8O_5$: *1-oxoindane-4,5-dicarboxylic acid* (I; R = H) (*isolated as the dimethyl ester*). The residue obtained by continuous ether extraction of the (manually extracted) aqueous acidic mother-liquor was combined with a similar residue obtained by oxidation of viridin [fraction (d) above] (total, 2·5—3 g.) and treated with excess of diazomethane in ether at 0° for 30 min. The neutral oily product (2·8 g.) was distilled at 0·1 mm. yielding a pale yellow oil (1·2 g.), b. p. 140—200° (bath), and an undistilled residue which was discarded. Treatment of the distillate with methanol gave a solid mixture (263 mg.) separated by fractional crystallisation from ether into prisms (136 mg.), m. p. 106·5—108°, of the normal methyl ester of the keto-acid $C_{12}H_{10}O_4$ (see above), and prisms (92 mg.), m. p. 117—118°, of *dimethyl-1-oxoindane-4,5-dicarboxylate* (Found: C, 63·15; H, 5·0; OMe, 23·8. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·9; 2OMe, 25·0%); $\lambda_{max.}$ 252, ~258, ~300, 304 mμ; log ε 4·07, 4·03, 3·64, 3·65; $\nu_{max.}$ 1733, 1717 cm.$^{-1}$ (C=O). This product was identical with a synthetic specimen (see below).

Catalytic Reduction.—The keto-ester (25 mg.) in methanol (2 ml.) was hydrogenated in the presence of palladium–charcoal (20%; 50 mg.). Uptake of hydrogen (2 mol.) occurred during 10 min. and then ceased abruptly. Recovery gave a gum which afforded prisms (7 mg.), m. p. 51—51·5° (lit.,[12] 45°), of dimethyl indane-4,5-dicarboxylate [12] (Found: C, 66·7; H, 6·4; OMe, 26·0. Calc. for $C_{13}H_{14}O_4$: C, 66·65; H, 6·0; 2OMe, 26·5%); $\lambda_{max.}$ 243, ~284, 290 mμ; log ε 4·02, 3·47, 3·50; $\nu_{max.}$ 1733, 1713 cm.$^{-1}$ (C=O). This was identical with a synthetic specimen (see below).

6-Methoxy-2-naphthaldehyde.—It was noted (i) that succinoylation of 2-methoxynaphthalene

[12] K. Alder, R. Muders, W. Krane, and P. Wirtz, *Annalen*, 1959, **627**, 59.

in nitrobenzene yields β-(2-methoxy-6-naphthoyl)propionic acid in addition to the 1,2-isomer, Short *et al.*[13] claiming a ratio of 9 : 1 of these two products respectively, and (ii) that oxidation of β-(5-chloro-6-methoxy-2-naphthoyl)propionic acid using sodium hypochlorite leads to the formation of 5-chloro-6-methoxy-2-naphthaldehyde (39%) in addition to the corresponding naphthoic acid.[14] In our hands, however, succinoylation of 2-methoxynaphthalene in nitrobenzene under conditions similar to those used by Short *et al.*[13] gave a mixture of the 1,2- and 2,6-compounds in which the former, unwanted, product predominated.[15] The possibility of using this approach to obtain 6-methoxy-2-naphthaldehyde was therefore not pursued although it was shown that oxidation of both β-(2-methoxy-1-naphthoyl)propionic acid and its 2,6-isomer with sodium hypochlorite gave rise to the corresponding naphthaldehydes (yields of 1% and 33% respectively) in addition to the naphthoic acids. The required 6-methoxy-2-naphthaldehyde was prepared as follows: 6-Methoxy-2-naphthoyl chloride, m. p. 108—110° (lit.,[16] 101°), (12 g.), obtained from 2-acetyl-6-methoxynaphthalene by way of the naphthoic acid,[6] in dry xylene (45 ml.) containing palladium–barium sulphate catalyst (1·1 g.) and quinoline–sulphur regulator (0·1 ml. of stock solution [17]) was heated under reflux and stirred rapidly (Hershberg platinum wire stirrer [18]) during passage of a brisk stream of hydrogen, the exit gases being bubbled through water (50 ml.) containing a measured volume of 2N-sodium hydroxide. Evolution of hydrogen chloride was virtually complete after 3 hr. and the hot mixture was then filtered and set aside overnight. Further filtration now removed a *product* (400 mg.), crystals from benzene, m. p. 224·5—226° after initial softening at *ca.* 140—150° followed by resolidification (Found: C, 76·7; H, 5·4. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%) which was not identified. Evaporation of the filtrate gave a residue of crude aldehyde which, after purification as the bisulphite addition compound and recovery, was distilled, b. p. 192—196°/10 mm., and crystallised from light petroleum as plates of 6-methoxy-2-naphthaldehyde, m. p. 82—82·5° (lit.,[19] 76—78°) (Found: C, 77·2; H, 5·4. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%). The yield of pure product varied, in different experiments, from 45 to 60%.

β-(6-*Methoxy*-2-*naphthyl*)*acrylic Acid*.—6-Methoxy-2-naphthaldehyde (1 g.), malonic acid (1·12 g.), and pyridine (3 ml.) containing piperidine (2 drops) were warmed on a water bath to 85° (15 mm.) during passage of a slow stream of nitrogen, the exit gases being bubbled through barium hydroxide solution. After 1½ hr. at 85° evolution of carbon dioxide became very slow and the mixture was then stirred into powdered ice (20 g.) and concentrated hydrochloric acid (12 ml.), set aside for 18 hr., and the precipitate (1·2 g.) was filtered off and washed with water. Crystallisation from methanol removed a trace of by-product, yellowish needles, m. p. 300—303° (sublimation), and yielded needles of β-(6-*methoxy*-2-*naphthyl*)*acrylic acid* (0·9 g.), m. p. 216·5—217·5° (Found: C, 73·7; H, 5·3. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

β-(6-*Methoxy*-2-*naphthyl*)*propionic Acid*.—A warm solution of β-(6-methoxy-2-naphthyl)-acrylic acid (2·28 g.) in 0·1N-sodium hydroxide (100 ml.) was cooled and the suspension of sodium salt shaken with palladium–strontium carbonate catalyst (*ca.* 3%; 500 mg.) and hydrogen. Uptake of gas (1 mol.) was complete after 30 min. The mixture was filtered and acidified to yield a powder (2·11 g.) which afforded leaflets, m. p. 155·5—156·5° (lit.,[20] 156—157°), from benzene, of β-(6-methoxy-2-naphthyl)propionic acid (Found: C, 73·3; H, 6·2. Calc. for $C_{14}H_{14}O_3$: C, 73·0; H, 6·1%).

6 -*Methoxy*-3′-*oxo*(2′,1′:1,2)*cyclopentenonaphthalene* (VII).—(i) β-(6-Methoxy-2-naphthyl)-propionic acid (1·15 g.) in benzene (7·5 ml.) was treated portionwise with powdered phosphorus pentachloride (1·2 g.) with swirling at room temperature and exclusion of moisture. After standing for 1 hr. the mixture was warmed to 60° for 15 min. and then cooled in a freezing mixture until the benzene started to crystallise. Stannic chloride (1·2 ml.) in benzene (3 ml.) was now added with shaking and the mixture set aside for 6 hr. while a gummy red precipitate became crystalline. Ice was added followed by concentrated hydrochloric acid (10 ml.) and the mixture shaken with ether (50 ml.) until the complex had disintegrated and most of the solid

[13] W. J. Short, H. Stromberg, and A. E. Wiles, *J.*, 1936, 319.
[14] R. Robinson and J. M. C. Thompson, *J.*, 1938, 2009.
[15] Cf. M. Ghosal and P. Bagchi, *Science and Culture* (*India*), 1954, **20**, 197.
[16] K. Fries and K. Schimmelschmidt, *Ber.*, 1925, **58**, 2841.
[17] E. B. Hershberg and J. Cason, *Organic Syntheses*, 1941, **21**, 84.
[18] E. B. Hershberg, *Ind. Eng. Chem. Anal.*, 1936, **8**, 313.
[19] A. Horeau, J. Jacques, and R. Emiliozzi, *Bull. Soc. chim. France*, 1959, 1854.
[20] J. Jacques and A. Horeau, *Bull. Soc. chim. France*, 1948, 711; cf. J. Jacques and A. Horeau, *ibid.*, 1955, 965.

had dissolved. The ether solution was separated and the aqueous layer extracted with ether. The combined ether extracts were washed with 2N-hydrochloric acid, water, 2N-sodium hydroxide, water, and then dried. Evaporation gave a solid (0·99 g.) which was chromatographed on neutral alumina (30 g.) in light petroleum (500 ml.). Recovery of the main product, which was eluted first, gave prisms (0·7 g.), m. p. 154—155°, from light petroleum, of 6-*methoxy*-3′-*oxo*(2′,1′:1,2)*cyclopentenonaphthalene* (Found: C, 79·3; H, 5·9. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%). The 2,4-*dinitrophenylhydrazone* formed red needles, m. p. 286—288°, from benzene (Found: C, 61·6; H, 4·3; N, 14·3. $C_{20}H_{16}N_4O_5$ requires C, 61·2; H, 4·1; N, 14·3%). The *oxime* was precipitated as a crystalline solid when the ketone (63 mg.) was heated under reflux with ethanol (0·75) ml.), hydroxylamine hydrochloride (32 mg.), and anhydrous sodium acetate (38 mg.) for 3 hr., and the mixture then diluted with water. After repeated crystallisation from benzene it formed prisms (33 mg.), m. p. 180—181° (Found: C, 74·5; H, 5·65; N, 6·3. $C_{14}H_{13}NO_2$ requires C, 74·0; H, 5·8; N, 6·2%). A by-product (100 mg.) eluted from the column with benzene, formed pale yellow leaflets, m. p. 221·5—222·5°, from ethanol.

(ii) A mixture of phosphoric oxide (487 mg.) and syrupy phosphoric acid (*d*, 1·7; 260 ml.) was heated on the steam-bath with stirring and exclusion of moisture for 3 hr. β-(6-Methoxy-2-naphthyl)propionic acid (50 g.) was then added during 10 min. and heating and stirring continued for a further 40 min. The mixture was poured on crushed ice (500 g.), stirred until the precipitate became solid, and then filtered. The residue in benzene (1·5 l.) was washed with saturated sodium hydrogen carbonate. Chromatography of the crude product in light petroleum–benzene (2 : 7, 2·2 l.) on neutral alumina (500 g.) afforded 6-methoxy-3′-oxo(2′,1′:1,2)-cyclopentenonaphthalene (VII) as yellowish prisms (35·4 g.), m. p. *ca.* 155° from benzene. More (3·5 g.) product was obtained by further chromatography of the mother-liquor and crystallisation of solid fractions from ether.

Oxidation of 6-*Methoxy*-3′-*oxo*(2′,1′:1,2)*cyclopentenonaphthalene with Peracetic Acid.*—A solution of the ketone (25 g.) in hot acetic acid (187 ml.) was cooled rapidly to produce fine crystals and the suspension then treated at 0° with peracetic acid solution [21] (53 ml. containing 56·2% w/v peracetic acid and 20·6% w/v hydrogen peroxide [22]). The mixture was set aside at 0° for 1 hr. and then at room temperature, with occasional shaking, for 10 days, whilst an orange colour developed and the suspended starting material was replaced by a crystalline product. The mixture was then filtered and the solid (14·1 g.), a mixture of prisms, m. p. 235—240°, and nodules, m. p. 265—275°, both of which were soluble in sodium hydrogen carbonate solution, was washed with water. After attempts to separate the components by fractional crystallisation had failed, the crude product was finely powdered, suspended in ether, and methylated with diazomethane at 0—5° during 1 hr. and the mixture then set aside at room temperature for 2 days. The suspended solid was now dissolved by addition of benzene, the solution washed with sodium hydrogen carbonate solution, and the neutral product recovered as an oil which afforded prisms (7·5 g.) from benzene (35 ml.), m. p. 136—137°, after recrystallisation from methanol, of *methyl* 5′-*oxo*(1′,2′:4,5)-*cyclopentenophthalide*-3-*acetate* (IX; R = Me) (Found: C, 64·5; H, 4·75. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%); $\lambda_{max.}$ ~240, 287, 296 mμ; log ε 4·11, 3·14, 3·20; $\nu_{max.}$ 1768, 1737, 1701 cm.$^{-1}$ (C=O). Concentration of the mother-liquor yielded solid mixtures which were combined (total, 4·4 g.) and chromatographed (see below).

The original reaction filtrate was treated portionwise with sodium metabisulphite until excess of oxidant had been destroyed, evaporated to dryness on the water-bath under reduced pressure, and the residue suspended in ether containing a little methanol and methylated with diazomethane at 0°. The ether solution was washed with sodium hydrogen carbonate solution and the neutral material recovered as a red oil (14 g.) which was chromatographed in benzene on alumina (100 g.). Elution with benzene yielded red, oily (4·5 g.) and gummy (*ca.* 4 g.) fractions which could not be crystallised, nor distilled without decomposition at 0·1 mm. below 280°, more of methyl 5′-oxo(1′,2′:4,5)cyclopentenophthalide-3-acetate (1·1 g.), and a solid (0·82 g.), melting range 90—135°. The last material was combined with the crude product (4·4 g.) from the initial crystallisation of the methyl ester (above) in ether (750 ml.) and chromatographed on alumina in ether and again in light petroleum–ether (2 : 7) thereby affording more of the above methyl ester (0·85 g.) and a solid (1·7 g.) m. p. 95—100°. Crystallisation of the latter from ether gave needles (1·4 g.), m. p. 104—105°, of a *product*, probably methyl β-(5-methoxycarbonyl-3-oxo-4-indanyl)epoxypropionate (Found: C, 62·3; H, 5·0; OMe, 21·8. $C_{15}H_{14}O_6$ requires

[21] F. P. Greenspan, *J. Amer. Chem. Soc.*, 1946, **68**, 907.
[22] D. Swern, *Organic Reactions*, 1953, **7**, 392.

C, 62·1; H, 4·9; 2OMe, 21·4%); $\lambda_{max.}$ 212, 242, 278, 324 mμ; log ε 4·46, 3·95, 4·11, 3·83; $\nu_{max.}$ 1737, 1719 (C=O), 1592 (ar. ring), 1286, 925 cm.$^{-1}$ (epoxide?).

5′-Oxo(1′,2′:4,5)cyclopentenophthalide-3-acetic Acid.—The methyl ester (8 g.) in methanol (50 ml.) was heated under reflux with potassium hydrogen carbonate (8 g.) for 15 hr. The mixture was then evaporated almost to dryness under reduced pressure on the steam-bath. The residue, in water (25 ml.), was acidified with concentrated hydrochloric acid, and the precipitated acid (6·6 g.) crystallised from water affording needles of *5′-oxo(1′,2′:4,5)cyclopentenophthalide-3-acetic acid* (IX; R = H), m. p. 250—253° (Found: C, 63·6; H, 4·1. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%).

β-(5-Carboxy-3-oxo-4-indanyl)acrylic Acid (VIII).—The above lactonic acid (2·48 g.) was dissolved in 2N-sodium hydroxide (10 ml.) and the solution evaporated to dryness on the steam-bath. The residual solid was powdered and heated to 165—180° for 7 hr. After cooling, a portion of the solid, in water, was treated with hydrochloric acid yielding a pale brown microcrystalline powder regarded as *β-(5-carboxy-3-oxo-4-indanyl)acrylic acid* (VIII) which, heated on the Kofler block, partially melted at 180—185° (presumably undergoing lactonisation; see below), resolidified and re-melted at *ca.* 240—245°. The acid was not analysed but was characterised, by methylation with diazomethane, as the *dimethyl ester*, needles, m. p. 135—136° from methanol (Found: C, 66·1; H, 5·1; OMe, 22·5. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·15; 2OMe, 22·6%); $\lambda_{max.}$ 229, 270 mμ; log ε 4·53, 3·9; $\nu_{max.}$ 1726, 1714 (C=O), 1642, 1595, 1575 cm.$^{-1}$ (conjugated ethylenic and aromatic unsaturation). Admixture of this product with the methyl ester of the phthalide acetic acid (above; m. p. 136—137°) caused its m. p. to be depressed some 20°.

Oxidation of β-(5-Carboxy-3-oxo-4-indanyl)acrylic Acid (VIII).—The disodium salt of the acrylic acid (above) (6·5 g.) in water (65 ml.) was treated with potassium permanganate (9·75 g.) in water (195 ml.) during 2½ hr. at 15—20°, rising to 50° towards the end of the addition period. The mixture was finally heated on the steam-bath for 20 min., filtered hot, the residue washed with hot water, and the combined filtrate and washings acidified with concentrated hydrochloric acid and extracted with ether continuously for 4 days. The ether solution was dried and evaporated to yield a yellowish gummy solid (4·4 g.), m. p. 202—215° (decomp.). This crude product contained oxalic acid detected by sublimation at 120—130°/0·1 mm. and methylation of the sublimate to yield leaflets, from ether–light petroleum, m. p. 47—48°, raised slightly on admixture with authentic dimethyl oxalate, m. p. 48—51°.

The crude product (3·9 g.) in methanol (20 ml.) and ether (80 ml.) was methylated with diazomethane at 0° during 5 min. Recovery of neutral product gave a gum (3·6 g.) which was chromatographed on alumina (40 g.) in benzene. Crystallisation of the recovered solid (2·6 g.) from methanol afforded (i) plates (0·81 g.) of *dimethyl-1-oxoindane-6,7-dicarboxylate* (V; R = Me), m. p. 138—139° (Found: C, 62·9; H, 4·9; OMe, 24·6. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·9; 2OMe, 25·0%); $\lambda_{max.}$ 224, 286, 296 mμ; log ε 4·64, 3·13, 3·15; $\nu_{max.}$ 1733, 1716 cm.$^{-1}$ (C=O); and (ii) mixtures (0·6 g.) of prisms, and colourless needles which became purple after exposure for several days to air and light. When this colour change had occurred the two types of crystal could be separated manually thus affording more of the above ester (0·44 g.), and purple needles [23] (0·21 g.) of tetramethylbenzene-1,2,3,4-tetracarboxylate, m. p. 131—133° undepressed on admixture with an authentic specimen. Evaporation of the mother-liquor afforded gum (1·8 g.) which could not be crystallised.

1-Oxoindane-6,7-dicarboxylic Acid (V; R = H).—The dimethyl ester (86 mg.) was heated under reflux with 2N-sodium hydroxide (1 ml.) for 6 hr. and the solution cooled at 0° and acidified with concentrated hydrochloric acid yielding *1-oxoindane-6,7-dicarboxylic acid* (51 mg.) which formed stout yellow rods, m. p. *ca.* 235° (decomp.), from hot water (Found: C, 60·3; H, 4·0. $C_{11}H_8O_5$ requires C, 60·0; H, 3·7%); $\nu_{max.}$ 3540, 3430, 2630, 2535 (OH), 1715, 1703, 1673 cm.$^{-1}$ (C=O). Heating the acid (44 mg.) under reflux with acetic anhydride (1 ml.) for 2 hr., evaporation under reduced pressure, and crystallisation of the gummy product from benzene yielded golden brown leaflets, m. p. 175—179°, of the *anhydride* (Found: C, 65·1; H, 3·3. $C_{11}H_6O_4$ requires C, 65·35; H, 3·0%); $\nu_{max.}$ 1850, 1777, 1718 cm.$^{-1}$ (C=O).

Dimethyl Indane-4,5-dicarboxylate.—Absorption of hydrogen (2 mol.) by dimethyl 1-oxoindane-6,7-dicarboxylate (0·6 g.) in methanol (6 ml.) in the presence of palladium–charcoal (20%; 0·5 g.) was complete after 2½ hr. The mixture was boiled, filtered, and evaporated and the residual gum crystallised from light petroleum (b. p. 40—60°) affording prisms of dimethyl

[23] Cf. L. I. Smith and E. J. Carlson, *J. Amer. Chem. Soc.*, 1939, **61**, 288.

indane-4,5-dicarboxylate, m. p. 51—51·5° (lit.,[12] 45°), identical with the specimen obtained by catalytic reduction of the keto-ester $C_{13}H_{12}O_5$ obtained from viridin (see above).

Dimethyl 1-Oxoindane-4,5-dicarboxylate (I; R = Me).—Dimethyl indane-4,5-dicarboxylate (140 mg.) in acetic acid (0·5 ml.) was treated with chromic oxide (125 mg.) in water (0·1 ml.) and acetic acid (0·25 ml.) at 65° for 1 hr. The mixture was then cooled, diluted with water, and extracted with ether, the extract washed with water, dried, and evaporated. Chromatography of the residual gum (119 mg.) in ether on alumina followed by fractional crystallisation of recovered solid fractions from ether gave (*a*) dimethyl 1-oxoindane-6,7-dicarboxylate (*ca.* 5 mg.), m. p. 136—138° undepressed on admixture with authentic material (above), and (*b*) prisms (19 mg.), m. p. 117—118°, of dimethyl 1-oxoindane-4,5-dicarboxylate (Found: C, 62·8; H, 5·0. Calc. for $C_{13}H_{12}O_5$: C, 62·9; H, 4·9%); the m. p. was undepressed on admixture with the degradation product, $C_{13}H_{12}O_5$, from viridin (see above) and the infrared spectra were identical.

Catalytic Reduction of 5'-Oxo(1',2':4,5)cyclopentenophthalide-3-acetic Acid (IX: R = H).—The lactonic acid (0·5 g.) suspended in acetic acid (10 ml.), with palladium–charcoal (20%; 100 mg.) absorbed hydrogen (1 mol.) during 2 hr. The mixture was filtered and evaporated under reduced pressure and the residue crystallised from hot water yielding needles (0·43 g.), m. p. 195—196·5°, of β-(5-*carboxy*-3-*oxo*-4-*indanyl*)*propionic acid* (Found: C, 62·65; H, 5·0%; Equiv. 122. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·9%; Equiv. 124); $\nu_{max.}$ 3200—2500 (OH); 1702, 1685 cm.$^{-1}$ (C=O). The product readily gave a 2,4-dinitrophenylhydrazone.

6-*Methoxy*-1,2-*cyclopentenonaphthalene*.—Zinc wool (12 g.), mercuric chloride (1 g.), concentrated hydrochloric acid (0·575 ml.), and water (17 ml.) were shaken together for 10 min., the liquid decanted, and the amalgamated zinc covered with water (10 ml.) and concentrated hydrochloric acid (12 ml.). 6-Methoxy-3'-oxo(2',1':1,2)cyclopentenonaphthalene (VII) (5·74 g.) and toluene (20 ml.) were added and the mixture heated under reflux for 36 hr., three portions (2 ml. each) of concentrated hydrochloric acid being added at intervals of 2 hr. followed by an interval of 16 hr., then four more portions at intervals of 2—3 hr. each. The mixture was set aside for 2 days at room temperature and then extracted with ether. Recovery gave a solid (5·37 g.) which was extracted with hot light petroleum (250 ml.), an insoluble residue being rejected. The solution was passed through a column of alumina (50 g.) and the product eluted with the same solvent yielding crystals (3·9 g.), m. p. 91° from light petroleum, of 6-*methoxy*-1,2-*cyclopentenonaphthalene* (Found: C, 84·5; H, 7·2; OMe, 15·35. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1; OMe, 15·65%); $\lambda_{max.}$ 227, 264, 274, 285, 323, 337 mμ; log ε 4·78, 3·64, 3·70, 3·48, 3·36, 3·46.

Oxidation of 6-*Methoxy*-1,2-*cyclopentenonaphthalene*.—A suspension of the finely powdered methoxy-compound (3·7 g.) in acetic acid (27·6 ml.) was treated at 5° with peracetic acid solution [21] (9·2 ml. containing *ca.* 50% w/v peracetic acid and *ca.* 20% hydrogen peroxide [22]) during 20 min. The mixture was set aside for 30 min. at 0° and then the temperature was controlled at 25—30°, by occasional cooling, for 2½ hr. after which the clear red solution was set aside at room temperature for 27 hr. Crude, crystalline β-(5-carboxy-4-indanyl)acrylic acid (XII; R = H) (0·814 mg.), m. p. 182—188°, was now filtered off but attempts to purify this product by recrystallisation caused the m. p. to fall, presumably owing to partial cyclisation to the isomeric phthalide compound (see below). However, a portion was methylated with diazomethane yielding prisms, m. p. 79·5—80·5°, from light petroleum (b. p. 40—60°) containing a trace of ether, of *methyl* β-(5-*methoxycarbonyl*-4-*indanyl*)*acrylate* (XII; R = Me) (Found: C, 69·0; H, 6·3; $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%); $\lambda_{max.}$ 235, 268 mμ; log ε 4·42, 4·11.

The filtrate was set aside for a further 6 days, filtered from a small second crop (34 mg.) of the above acidic product, diluted with water (100 ml.), and extracted repeatedly with ether, the combined extracts being shaken with small portions of sodium metabisulphite until the residual peroxide and peracid were destroyed. Evaporation of the dried ether solution gave a gum (4·15 g.) which was methylated with diazomethane and the neutral product (3·3 g.) then chromatographed on alumina in ether. A first oily fraction (0·35 g.), which was not investigated, was followed by (*a*) a gum (0·38 g.) which, after further chromatography and crystallisation from methanol, yielded yellow needles (24 mg.), m. p. 163—164°, of 2-*methoxy*-5,6-*cyclopenteno*-1,4-*naphthaquinone* (Found: C, 73·3; H, 5·35. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%); $\lambda_{max.}$ 249, 256, 283, 350; log ε 4·10, 4·11, 4·18, 3·62; $\nu_{max.}$ 1678, 1642 (C=O), 1615 cm.$^{-1}$ (aromatic ring); (*b*) a yellowish solid (0·93 g.) which was again chromatographed on alumina in ether yielding prisms (0·32 g.), m. p. 87—88°, from ether of *methyl* 4,5-*cyclopentenophthalide*-3-*acetate* (XIII;

R = Me) (Found: C, 68·1; H, 6·0; OMe, 12·2. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7; OMe, 12·6%); $\lambda_{max.}$ 243, 274, 283, mμ; log ε 4·09, 3·12, 3·06; $\nu_{max.}$ 1759, 1742 cm.$^{-1}$.

Cyclisation of β-(5-carboxy-4-indanyl)acrylic acid (above; 1 g.) occurred when it was melted and maintained at 180—185° for a further 10 min. After cooling, the glassy product was boiled with ether until solid and then crystallised from benzene (charcoal) affording prisms (0·91 g.), m. p. 134—135°, of *4,5-cyclopentenophthalide-3-acetic acid* (XIII; R = H) (Found: C, 67·2; H, 5·3. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%). The methyl ester formed prisms, m. p. 86—87°, from ether–light petroleum, identical with the ester obtained in the peracid oxidation (above).

Decarboxylation of 4,5-Cyclopentenophthalide-3-acetic Acid (XIII; R = H).—The lactonic acid (353 mg.), intimately mixed with palladium–charcoal catalyst (20%; 200 mg.), was heated in a small retort at atmospheric pressure yielding a yellow oily distillate containing some water. The product, in ether (peroxide-free), was washed with sodium hydrogen carbonate solution, dried, and the neutral portion recovered as a gum (80 mg.) which was immediately hydrogenated in methanol in the presence of palladium–charcoal (20%; 50 mg.) to an uptake of *ca.* 1 mol. of gas. The mixture was then filtered and the filtrate evaporated yielding a gum (68 mg.) which readily afforded a mixture of prisms and needles from light petroleum. Repeated chromatography on alumina in light petroleum did not resolve the mixture, but after it had been observed that the needles gave a 2,4-dinitrophenylhydrazone whereas the prisms did not, the recovered solid (27 mg.), m. p. 78—90°, was separated by means of Girard's procedure (Reagent P) into ketonic and non-ketonic fractions. The non-ketonic fraction (19 mg.) now afforded glistening needles, m. p. 104—104·5°, from light petroleum (b. p. 40—60°) of *3-methyl-4,5-cyclopentenophthalide* (III; R = H) (Found: C, 76·5; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%); $\lambda_{max.}$ 244, 275, 284 mμ; log ε 4·05, 3·19, 3·13; $\nu_{max.}$ 1747 cm.$^{-1}$ (C=O).

The ketonic fraction formed needles (6 mg.), m. p. 106—107° (sealed tube) after sublimation at atmospheric pressure; $\lambda_{max.}$ 218, 261 mμ; $E^{1\%}_{1cm.}$ 1442, 808; $\nu_{max.}$ 1720, 1695 cm.$^{-1}$ (C=O).

1-Acetyl-7-methoxynaphthalene.—Dry magnesium turnings (2·06 g.) and dry ether (70 ml.) were stirred and treated dropwise with methyl bromide (10 ml.). The mixture was heated under reflux for 10 min., cooled in ice, and cadmium chloride (7·8 g.; previously dried at 115° for 4 hr.) was added portionwise with stirring during 10 min. The mixture was then heated under reflux until the Gilman test [24] was negative (*ca.* 20 min.). The ether was distilled off on the water-bath, benzene (100 ml.) was added, and distillation continued until half the solvent had been removed. 7-Methoxy-1-naphthoyl chloride [25] (9·4 g.), obtained from 2-methoxynaphthalene by way of 3-methoxyacenaphthaquinone,[26] 2-methoxynaphthalic anhydride [27] and 7-methoxy-1-naphthoic acid,[27] in warm benzene (50 ml.), was now added with stirring during 20 min., the mixture was heated under reflux for a further 1 hr. and then cooled, treated with ice and dilute hydrochloric acid and the layers separated. The aqueous layer was extracted with ether and the combined organic solutions washed with N-sodium hydroxide, dried, and evaporated and the residual solid (8·4 g.) distilled, b. p. *ca.* 120°/0·1 mm., affording prisms, m. p. 66·5—67·5° (lit.[28] 63°), from light petroleum (b. p. 40—60°) of 1-acetyl-7-methoxynaphthalene (7·43 g.) (Found: C, 78·1; H, 6·1. Calc. for $C_{13}H_{12}O_2$: C, 78·0; H, 6·0%).

1-Acetyl-7-hydroxynaphthalene.—The methoxy-compound (1·5 g.) in benzene (25 ml.) was treated with powdered aluminium chloride (3 g.) and heated under reflux whilst the solid dissolved (1 hr.). The mixture was then cooled, poured on ice, treated with 2N-hydrochloric acid, and extracted with ether. The ether solution was washed with water, extracted with N-sodium hydroxide, and the extract washed with ether. Evaporation of the combined ether solutions gave crude starting material (0·22 g.). Acidification of the alkaline solution, extraction with ether, and recovery afforded pale yellow leaflets (0·88 g.), m. p. 154—155° (lit.,[29] 149—150°), from chloroform of 1-acetyl-7-hydroxynaphthalene (Found: C, 77·6; H, 5·5. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%). Concentration of the mother-liquor gave more (0·35 g.) of slightly crude product.

Oxidation of 1-Acetyl-7-hydroxynaphthalene.—The naphthol (1·08 g.) suspended in acetic acid

[24] H. Gilman, in Gilman, *Organic Chemistry*, Vol. I, 2nd edn., p. 496, John Wiley and Sons, New York, 1943.
[25] H. King and T. S. Work, *J.*, 1940, 1307.
[26] H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, 1921, **4**, 342.
[27] R. I. Davies, I. M. Heilbron, and F. Irving, *J.*, 1932, 2715.
[28] N. J. Leonard and A. M. Hyson, *J. Org. Chem.*, 1948, **13**, 164.
[29] N. J. Leonard and A. M. Hyson, *J. Org. Chem.*, 1948, **13**, 164; cf. N. J. Leonard and S. N. Boyd, jun., *ibid.*, 1946, **11**, 419.

(5 ml.) was treated rapidly with peracetic acid solution [21] (1·35 ml. containing 56·5% w/v peracetic acid and 21·3% w/v hydrogen peroxide [22]), the mixture was stirred at 25° ± 3° until the solid had dissolved (3·5 hr.) and then set aside at 15—20° for 22 hr. Water (30 ml.) was then added followed by sodium metabisulphite, portionwise, until excess of peracid was decomposed, and the mixture was then extracted with ether. The acidic product was extracted into saturated sodium hydrogen carbonate, liberated from the aqueous solution by addition of hydrochloric acid, and again extracted with ether, washed with water (1 ml.), dried and methylated with diazomethane. The recovered gummy neutral product (0·8 g.) was chromatographed on alumina (30 g.) in ether yielding a slightly gummy solid (0·61 g.) which afforded prisms (276 mg.), m. p. 96—97°, from ether, of *methyl* β-(3-*acetyl*-2-*methoxycarbonylphenyl*)*acrylate* (XVIII; R = Me) (Found: C, 64·5; H, 5·6; OMe, 23·0. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4; 2OMe, 23·7%); $\lambda_{max.}$ 235, ~275 mμ; log ε 4·25, 3·6; $\nu_{max.}$ 1726, 1687 (C=O); 1645 cm.$^{-1}$ (double bond).

Methyl β-(3-*Methyl*-7-*phthalidyl*)*propionate* (XIX; R = Me).—The unsaturated ester (200 mg.) in methanol (6 ml.) absorbed hydrogen (2 mol.) in the presence of palladium–carbon catalyst (20%; 200 mg.) during 1 hr. The mixture was warmed and filtered and the filtrate evaporated yielding a solid (178 mg.) which was chromatographed on alumina in ether and then afforded prisms (147 mg.), m. p. 63—64°, from ether–light petroleum, of *methyl* β-(3-*methyl*-7-*phthalidyl*)*propionate* (Found: C, 66·9; H, 6·1; OMe, 13·4. $C_{13}H_{14}O_4$ requires C, 66·65; H, 6·0; OMe, 13·25%); $\lambda_{max.}$ 231, 277, 284; log ε 3·96, 3·37, 3·39; $\nu_{max.}$ (in carbon tetrachloride), 1768, 1742 cm.$^{-1}$ (C=O).

β-(3-*Methyl*-7-*phthalidyl*)*propionic Acid* (XIX; R = H).—The above ester (145 mg.) was heated under reflux with 2N-sodium carbonate (2 ml.) for 3·75 hr. The clear solution was then cooled, acidified with concentrated hydrochloric acid, and the precipitate extracted into ether, washed, dried, and recovered as a solid (137 mg.) which gave leaflets, m. p. 140—141°, from benzene of β-(3-*methyl*-7-*phthalidyl*)*propionic acid* (Found: C, 65·35; H, 5·6. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5%).

3-*Methyl*-5′-*oxo*(1′,2′:6,7)*cyclopentenophthalide* (II; R = H).—The above acid (152 mg.) was stirred with polyphosphoric acid (20 g.) at 120—125° for 7 hr. with exclusion of atmospheric moisture. The mixture was set aside 1·5 days and then treated with crushed ice and water and extracted with ether. The extract was washed with saturated sodium hydrogen carbonate, dried, and evaporated and the residual neutral solid (85 mg.) chromatographed on alumina in benzene affording needles (46 mg.), m. p. 156·5—157·5°, from ether, of 3-methyl-5′-oxo(1′,2′:6,7)-cyclopentenophthalide (Found: C, 71·2; H, 5·0. Calc. for $C_{12}H_{10}O_3$: C, 71·3; H, 5·0%). The product had undepressed m. p. on admixture with the keto-lactone degradation product from viridin (above) and the infrared spectra were identical.

Transformations of Phthalide-3-acetic Acid.—(a) *Conversion into* o-*acetylbenzoic acid.*[9] Methylation (diazomethane) of phthalide-3-acetic acid afforded the methyl ester [5] as needles, m. p. 62·5—63°, from ether–light petroleum (Found: C, 64·4; H, 4·9. Calc. for $C_{11}H_{10}O_4$: C, 64·1; H, 4·85%); $\lambda_{max.}$ 227, 272, 279 mμ; log ε 4·00, 3·22, 3·21. The ester (444 mg.) in dry carbon tetrachloride (15 ml.) was heated under reflux with N-bromosuccinimide (384 mg.) for 2 hr. The yellowish solution, which had a sharp acidic odour, was filtered from succinimide (205 mg.), m. p. 112—118°, the filtrate evaporated under reduced pressure, and the residual gum heated on the water-bath *in vacuo* until the acidic odour had disappeared. The product, a slightly gummy solid (460 mg.), afforded crystals, m. p. 162—163° (lit.,[30] 168°), from methanol, of methyl phthalidylidene-3-acetate [30] (XIV; R = Me) (Found: C, 64·75; H, 4·0; OMe, 14·9. Calc. for $C_{11}H_8O_4$: C, 64·7; H, 3·9; OMe, 15·2%); $\lambda_{max.}$ 220, 238, 271, ~279, 305, ~315 mμ; log ε 4·23, 4·23, 4·25, 4·19, 4·00, 3·93.

The unsaturated ester (300 mg.) was heated under reflux with 2N-hydrochloric acid (10 ml.) until evolution of carbon dioxide was negligible (1½ hr.). The solution was cooled and filtered and the product extracted into ether. Recovery gave *o*-acetylbenzoic acid [9] (216 mg.) as needles, m. p. 114·5—115·5° after recrystallisation from ether–light petroleum (b. p. 40—60°) (Found: C, 65·8; H, 5·0. Calc. for $C_9H_8O_3$: C, 65·85; H, 4·9%).

(b) *Conversion into* 3-*methylene phthalide* (XV). An intimate mixture of phthalide-3-acetic acid (0·5 g.) and palladium–charcoal (20%; 0·25 g.) was heated in a small retort over a free flame. Decomposition occurred readily with evolution of carbon dioxide and distillation of a yellowish oil which was dissolved in ether (peroxide-free), washed with saturated sodium hydrogen carbonate, dried, and recovered. The oil (113 mg.) was chromatographed on alumina

[30] S. Gabriel, L. Kornfeld, and C. Grunert, *Ber.*, 1924, **57**, 305.

(15 g.) in ether yielding gummy fractions one of which (16 mg.) yielded needles from ether of 3-methylenephthalide, m. p. 55·5—57°, undepressed on admixture with an authentic specimen [m. p. 56·5—57·5°; Found: C, 73·8; H, 4·2. Calc. for $C_9H_6O_2$: C, 74·0; H, 4·1%; $\lambda_{max.}$ (hexane), 235, 253, 299, 309 mμ; log ε 4·17, 4·20, 3·54, 3·43; $\nu_{max.}$ 1767 (C=O), 1664 cm.$^{-1}$ (methylene)] prepared by thermal decomposition of phthalidylidene-3-acetic acid.[10,31] On storage in a desiccator over phosphoric oxide the sample slowly deteriorated during several weeks with concomitant rise in m. p. and formation of phthalic anhydride.[11]

A later fraction from the chromatogram afforded a gum (12 mg.) identified, after redistillation at 65°/1 mm., as 3-methylphthalide by comparison of ultraviolet and infrared spectra with those of an authentic specimen.

The crude neutral distillate from a similar experiment, in methanol (5 ml.) was immediately hydrogenated in the presence of palladium–charcoal until absorption of gas, initially rapid, became slow. The mixture was then filtered, diluted with water, extracted with ether, and the extract washed with sodium hydrogen carbonate solution, dried, and evaporated yieding 3-methylphthalide as an oil (120 mg.) after distillation at 0·1 mm. (Found: C, 73·0; H, 5·7. Calc. for $C_9H_8O_2$: C, 73·0; H, 5·4%). The infrared spectrum was virtually identical with that of an authentic specimen (see below).

Reduction of o-*Acetylbenzoic Acid to* 3-*Methylphthalide.*—*o*-Acetylbenzoic acid (0·85 g.) in ethanol (5 ml.), together with palladium–charcoal (20%; 0·5 g.), absorbed hydrogen (1 mol.) during 7 hr. The mixture was filtered, diluted with water, and extracted with ether (3 × 20 ml.). The extract was washed with saturated sodium hydrogen carbonate (10 ml.), dried, and evaporated, yielding an oil (0·42 g.) which was chromatographed on alumina in ether. Distillation of the recovered product afforded 3-methylphthalide (Found: C, 72·85; H, 5·35. Calc. for $C_9H_8O_2$: C, 73·0; H, 5·4%); $\lambda_{max.}$ 228, 273, 280 mμ; log ε 3·98, 3·24, 3·22; (in hexane) 224, 230, 264, 270, 277 mμ; log ε 4·00, 3·90, 3·13, 3·16, 3·25; $\nu_{max.}$ 1761 cm.$^{-1}$ (C=O).

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Imperial Chemical Industries Limited, Akers Research Laboratories,
The Frythe, Welwyn, Herts. [*Received, November 24th*, 1964.]

[31] S. Gabriel and A. Neumann, *Ber.*, 1893, **26**, 952.