γγ-Disubstituted Itaconic Acids. Part IV.[1] The Stobbe Condensation of 6-Benzoyltetralin and 2-Benzoylnaphthalene with Diethyl Succinate

By **W. I. Awad, F. G. Baddar,* F. A. Fouli,** and **S. M. A. Omran,** Department of Chemistry, Faculty of Science, A'in Shams University, Cairo, Egypt
M. I. B. Selim, Faculty of Engineering, A'in Shams University, Cairo, Egypt

The mixture of *cis*- (I) and *trans*-(Ph/CO_2Et)-3-ethoxycarbonyl-4-phenyl-4-(6-tetralyl)but-3-enoic acid (VII) has been converted into ethyl 4-acetoxy-5,6,7,8-tetrahydro-1-phenylphenanthrene-2-carboxylate (IIa) and ethyl 4-acetoxy-1-(6-tetralyl)-2-naphthoate (VIIIa). The derived phenolic acids (IIb) and (VIIIb) were converted into methyl 4-methoxy-1-phenylphenanthrene-2-carboxylate (VIc), and 4-methoxy-1-(2-naphthyl)-2-naphthoic acid (XIId), respectively. The latter was decarboxylated to 4-methoxy-1,2'-binaphthyl (XIIe). The anhydrides of *cis*- and *trans*-3-carboxy-4-(6-tetralyl)-4-phenylbut-3-enoic acid were isomerised with aluminium chloride to the corresponding indenylacetic acids (V) and (XI), which were cyclised with sodium acetate in acetic anhydride; then hydrolysis and methylation gave the corresponding fluorenones (IIIc) and (IXc), identical with those obtained by cyclisation of the methyl ethers of (IIb) and (VIIIb). Cyclisation of *cis*(Ph/CO_2Et)-3-ethoxycarbonyl-4-(2-naphthyl)-4-phenylbut-3-enoic acid (XIII; R = Et) by a similar series of reactions gave rise to (VIc).

It was reported previously [2] that 1-benzoylnaphthalene condensed with diethyl succinate to give *cis*(Ph/CO_2Et)-3-ethoxycarbonyl-4-(1-naphthyl)-4-phenylbut-3-enoic acid. Now 6-benzoyltetralin has been condensed with diethyl succinate in the presence of potassium t-butoxide, to give a mixture of *cis*- (I) and *trans*-(Ph/CO_2Et)-3-ethoxycarbonyl-4-phenyl-4-(6-tetralyl)but-3-enoic acid (VII), from which the crystalline *cis*-form (I) was isolated. This was achieved by cyclisation to 5,6,7,8-tetrahydro-4-methoxy-1-phenylphenanthrene-2-carboxylic acid (IId). The mixture of isomers (I) and (VII) was directly cyclised with sodium acetate in acetic anhydride to give a viscous oil which failed to solidify. Distillation in a vacuum gave two fractions, which from infrared spectra (Table 2) appeared to be, respectively, the esters (IIa) and (VIIIa) since the former shows a strong band at 702 $cm.^{-1}$, characteristic of 5 adjacent aromatic H atoms (cf. Table 2), which does not appear for the latter. Their structures were established as described below.

The derived phenolic acids (IIb) and (VIIIb) were methylated with alkaline dimethyl sulphate to give (IIc) and (VIIIc), which were hydrolysed to (IId) and (VIIId), respectively. The structure of (IId) was established by dehydrogenation with selenium, then methylation to give (VIc). Two pieces of evidence which confirmed structure (VIc) were the fact that the compound had an electronic spectrum (Table 1) very similar to that of 4-phenylphenanthrene,[3] with the expected bathochromic shift and hyperchromic effect for the presence of the methoxy- and alkoxy-carbonyl groups, and it was identical with the product obtained from 2-benzoylnaphthalene by a similar series of reactions.

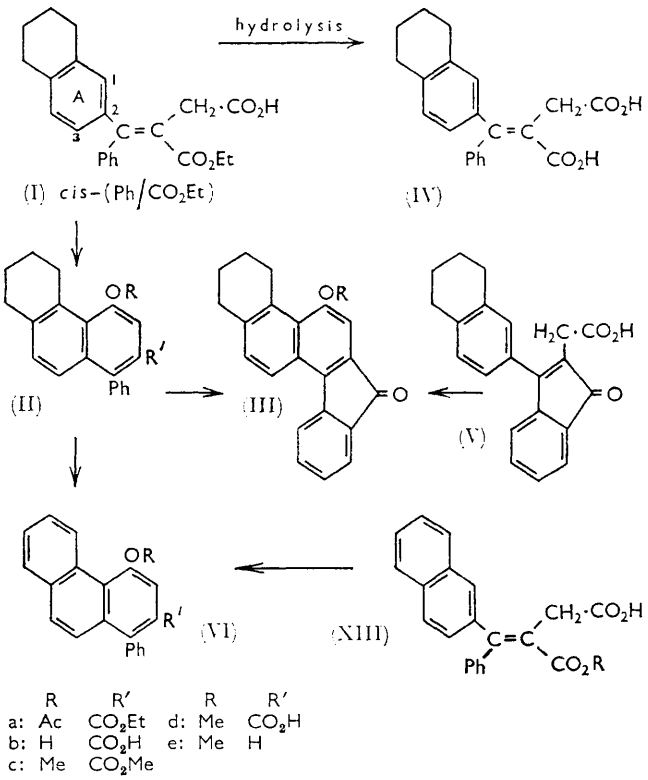
The formation of a phenanthrene derivative (IIa) and not the isomeric anthracene derivative by the cyclisation of (I) is indicative of the higher contribution of the Kekulé structure of ring-A to the actual state of the molecule,[4] *i.e.*, the bond between carbon atoms 1 and 2 has more double-bond character than that between atoms 2 and 3.

The structure (VIIId) was established by dehydrogenation, then decarboxylation to 4-methoxy-1,2'-dinaphthyl (XIIe) which was identical with a sample prepared by condensing 1-iodo-4-methoxynaphthalene [5] with ethyl 3-bromo-2-naphthoate [6] and decarboxylating the resulting acid. Its electronic absorption spectrum (Table 1) is nearly identical with that of 1,1'-binaphthyl.[7]

2-Benzoylnaphthalene was condensed with diethyl succinate to compare the steric effect of the 2-naphthyl

[1] Part III, F. G. Baddar, V. B. Baghos, and A. Habashi, *J. Chem. Soc.* (*C*), 1966, 603.
[2] W. I. Awad, F. G. Baddar, and M. I. B. Selim, *J. Chem. Soc.*, 1962, 1854.
[3] A. D. Campbell, *J. Chem. Soc.*, 1954, 3659.
[4] A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 169.
[5] C. Sear and K. Ehrenreich, *Monatsh.*, 1913, **34**, 631.
[6] H. E. Fierz and R. Tobler, *Helv. Chim. Acta*, 1922, **5**, 557.
[7] A. E. Gillam and E. S. Stern, 'An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry,' Arnold, London, 1955, p. 245.

group with that of the 1-naphthyl and 6-tetralyl groups, especially since Hewett [8] reported the isolation of one



dibasic acid (XIII; R = H) from such a condensation, but did not investigate its stereochemistry. The condensation gave rise to one half-ester, *cis*Ph(CO_2Et)-3-ethoxycarbonyl-4-(2-naphthyl)-4-phenylbut-3-enoic acid (XIII; R = Et); this was cyclised to the acetoxy-derivative (VIa), and hydrolysis and methylation gave (VIc), which was hydrolysed to (VId) then decarboxylated to (VIe). The structure assigned to (VIe) was inferred from its ultraviolet spectrum (Table 1), which was nearly identical with that of 4-phenylphenanthrene,[3] and from the band at 707 $cm.^{-1}$ characteristic of 5 aromatic H atoms (Table 2).

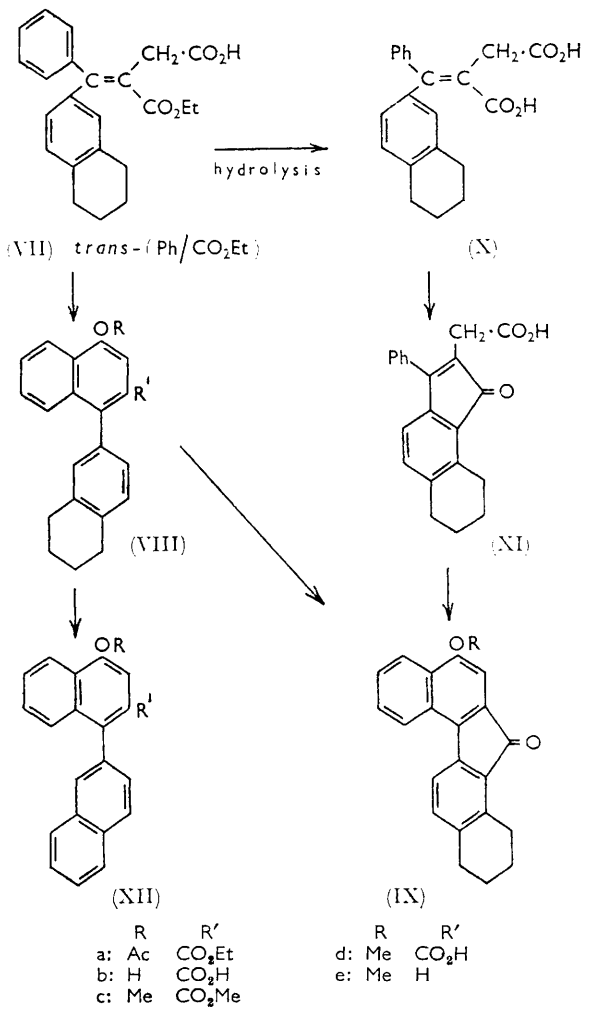
TABLE 1

Electronic spectra

Compound	Solvent	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$
(VIc)	Methanol	260	85,000
		350	3300
		365	3300
(VIe)	Cyclohexane	254	64,900
		274	32,000
		298	14,700
		306	15,500
		341	3400
		358	3100
(XIIe)	Ethanol	222	56,230
		297	14,450

The formation of one isomer in the case of 2-benzoyl-

[8] C. L. Hewett, *J. Chem. Soc.*, 1942, 585.



naphthalene and two isomers in the case of 6-benzoyltetralin cannot be attributed to steric interference only, since the 2-naphthyl and the 6-tetralyl group exert

TABLE 2

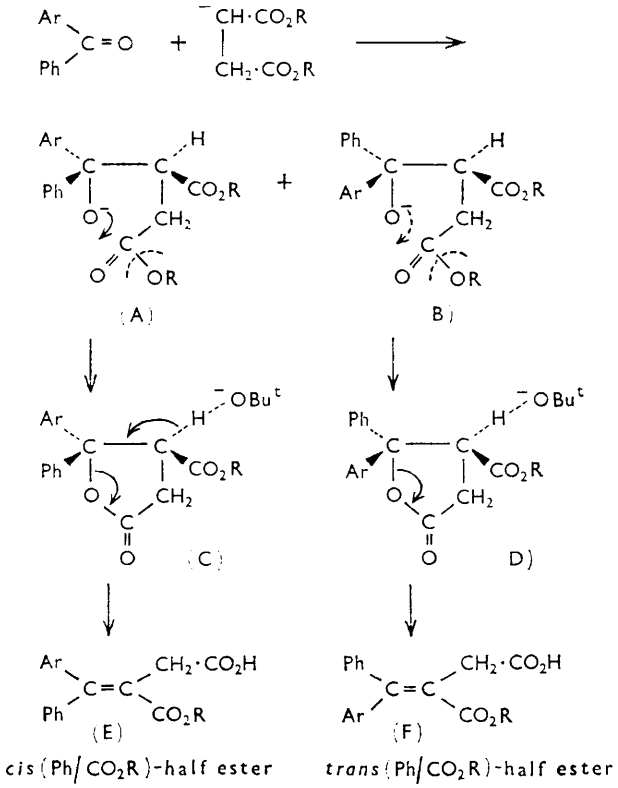
Infrared spectra ($cm.^{-1}$) (KBr disc)

	ν(C=O)			
	Ar acids [a] and esters [b]	Aryl acetates [b]	5-Cyclic Ar ketones [c]	γ(C–H) 5 Ar H [d]
(IIa)	1695	1760		702
(IIb)	1695			702
(IIc)	1730			707
(IId)	1690			698
(VIa)	1724	1785		709
(VIb)	1700			709
(VIc)	1718			712
(VId)	1704			702
(VIe)				707
(V) and (XI)			1695 *	
(IIIa) and (IXa)		1765	1700 †	
(IIIb) and (IXb)			1700	
(IIIc) and (IXc)			1700	

L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1959, (*a*) p. 162, (*b*) p. 179, (*c*) p. 132, (*d*) p. 65.

* The infrared spectra show also ν(C=O) at 1715 $cm.^{-1}$ of fatty acids. † ν(C=O) of 7*H*-benzo[*c*]fluoren-7-one at 1709 $cm.^{-1}$ [Baddar *et al.*, *J. Chem. Soc.* (*C*), 1967, 506].

nearly the same steric influence, but it may be attributed to a difference in electron density. The attack of the carbanion derived from the succinic ester on the carbonyl group leads to the formation of either or both of the condensate anions (A) and (B) in which the groups



attached to the central C–C σ-bond are forced to assume the eclipsed conformation in order to allow the formation of the cyclic paraconic esters (C) and (D), respectively, whose relative stabilities will determine the ratio in which they are converted, under the influence of t-butoxide ion, into the unsaturated half-esters (E) and (F), respectively. The stability of (A) and (B) depends on the non-bonded interaction of the eclipsed groups, which appears to be both steric and polar in origin.

Hydrolysis of the mixture of half-esters (I) and (VII) gave a mixture of two dibasic acids which was separated by fractional crystallisation into the *cis*-acid (IV), m. p. 196°, and the *trans*-acid (X), m. p. 186°. Hewett [8] reported m. p.s 188—189 and 183—185°, but did not investigate their stereochemistry.

The *cis*-acid (IV) was converted into its anhydride, which upon cyclisation with aluminium chloride in nitrobenzene gave the indenylacetic acid (V) whose infrared spectrum showed ν(C=O) corresponding to a fatty acid and an αβ-unsaturated cyclic aryl ketone (Table 2). This was further cyclised with sodium acetate in acetic anhydride to the indenophenanthrene (IIIa); its infrared spectrum (Table 2) shows ν(C=O) of a five-membered aryl cyclic ketone. Hydrolysis and methylation gave (IIIc), identical with a specimen obtained by cyclisation of (IId) with phosphoric oxide; its infrared spectrum (Table 2) shows ν(C=O) of a five-membered cyclic ketone.

The anhydride of (X) was subjected to the same series of reactions. With aluminium chloride in nitrobenzene it isomerised to give (XI). The structure assigned to this compound was based on the fixation of the double bond in the tetralin nucleus;[4] it was cyclised with sodium acetate in acetic anhydride to give (IXa) which shows two characteristic infrared bands in its infrared spectrum similar to those of (IIIa) (Table 2). This was hydrolysed, and methylation gave (IXc), identical with the product obtained by cyclisation of (VIIId) with phosphoric oxide. The infrared spectrum (Table 2) shows ν(C=O) of a five-membered cyclic ketone.

Hydrolysis of *cis*-3-ethoxycarbonyl-4-(2-naphthyl)-4-phenylbut-3-enoic acid (XIII; R = Et) gave a dibasic acid (XIII; R = H) which was apparently identical with that (m. p. 174·5—175·5°) isolated by Hewett.[8]

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer Infracord model 137 spectrophotometer using potassium bromide discs, and ultraviolet spectra on Perkin-Elmer Spectracord model 4000A spectrophotometer.

cis- *and* trans-(Ph/CO_2Et)-3-*Ethoxycarbonyl*-4-*phenyl*-4-(6-*tetralyl*)*but*-3-*enoic Acid* (I) *and* (VII).—A solution of potassium t-butoxide [from potassium (4 g.) and t-butyl alcohol (90 ml.)] was treated during 20 min. with a mixture of diethyl succinate (36 g.) and 6-benzoyltetralin (25 g) in t-butyl alcohol (30 ml.), heated for a further 55 min., and worked up as usual.[9,10] The product was a viscous oil (26 g.) from which a pure solid half-ester was isolated (1·2 g.). Crystallisation from light petroleum (b. p. 100—120°) gave the cis-*compound* (I), m. p. 138—139°, ν(C=O) 1710 $cm.^{-1}$ (Found: C, 76·0; H, 6·7. $C_{23}H_{24}O_4$ requires C, 75·8; H, 6·6%).

Cyclisation of the Half-esters (I) *and* (VII).—The crude mixture of half-esters (10 g.) was directly cyclised, by refluxing with sodium acetate (3 g.) in acetic anhydride (45 ml.), as previously described.[9] Distillation of the solvent left a brown oil, which was separated by vacuum-distillation into two fractions, (1) b. p. 240°/5 mm. (4 g.) and (2) 280°/5 mm. (6 g.). From infrared spectra it appears that the former was mainly ethyl 4-acetoxy-5,6,7,8-tetrahydro-1-phenylphenanthrene-2-carboxylate (IIa), and that the main constituent of the latter was ethyl 4-acetoxy-1-(6-tetralyl)-2-naphthoate (VIIIa).

5,6,7,8-*Tetrahydro*-4-*hydroxy*-1-*phenylphenanthrene*-2-*carboxylic Acid* (IIb) *and* 4-*Hydroxy*-1-(2-*tetralyl*)-2-*naphthoic Acid* (VIIIb).—The acetoxy-derivative (IIa) (4 g.) (fraction 1) was hydrolysed with 10% alcoholic potassium hydroxide (40 ml.) as usual. The *acid* (2·5 g.) (IIb) had m. p. 135° (from glacial acetic acid) (Found: C, 79·9; H, 5·8. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%). The same acid was obtained when the pure *cis*-half-ester (I) was similarly treated. Fraction 2 (6 g.) was hydrolysed with 10% alcoholic potassium hydroxide (60 ml.). The *acid*

[9] F. G. Baddar, L. S. El-Assal, and V. B. Baghos, *J. Chem. Soc.*, 1955, 1714.

[10] W. S. Johnson and M. W. Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 511.

(VIIIb) (3·9 g.) had m. p. 196° (from glacial acetic acid) (Found: C, 78·9; H, 5·8%).

Methyl 5,6,7,8-Tetrahydro-4-methoxy-1-phenylphenanthrene-2-carboxylate (IIc) *and Methyl 4-Methoxy-1-(2-tetralyl)-2-naphthoate* (VIIIc).—The acid (IIb) (2·5 g.) was methylated with dimethyl sulphate (5 g.) in 20% aqueous sodium hydroxide (25 ml.). The *methoxy-ester* (IIc) (2·6 g.) had m. p. 110° (from methanol) (Found: C, 79·2; H, 6·4; OMe, 17·9. $C_{23}H_{22}O_3$ requires C, 79·7; H, 6·4; OMe, 17·9%). The acid (VIIIb) (4 g.) similarly gave the *methoxy-ester* (VIIIc) (4·2 g.), m. p. 112° (from methanol) (Found: C, 79·3; H, 6·4; OMe, 18·1%).

5,6,7,8-Tetrahydro-4-methoxy-1-phenylphenanthrene-2-carboxylic Acid (IId) *and 4-Methoxy-1-(6-tetralyl)-2-naphthoic Acid* (VIIId).—The methoxy-ester (IIc) (2 g.) was hydrolysed with 10% alcoholic potassium hydroxide (20 ml.) as usual to give the *acid* (IId) (1·5 g.), m. p. 230° (from glacial acetic acid) (Found: C, 79·2; H, 6·1. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·1%). The *acid* (VIIId) (2·5 g.), obtained by hydrolysis of (VIIIc) (3 g.) had m. p. 174° (from glacial acetic acid((Found: C, 79·2; H, 6·0%).

1,2,3,4-Tetrahydro-5-methoxy-7H-indeno[1,2-a]phenanthren-7-one (IIIc) *and 1,2,3,4-Tetrahydro-11-methoxy-13H-dibenzo[a,g]fluoren-13-one* (IXc).—The methoxy-acid (IId) (0·3 g.) was cyclised with phosphoric oxide (0·5 g.) in dry benzene and worked up as usual.[11] The product (0·25 g.) was crystallised from benzene to give (IIIc) as red *needles*, m. p. 215° (from benzene) (Found: C, 83·5; H, 5·7; OMe, 9·7. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7; OMe, 9·9%). Similarly (IXc) (0·4 g.) was obtained, by the cyclisation of (VIIId) (0·5 g.) with phosphoric oxide (0·6 g.) in dry benzene (25 ml.), as red *needles*, m. p. 209° (Found: C, 83·9; H, 5·6; OMe, 9·8%).

3-(4-Methoxy-1-naphthyl)-2-naphthoic Acid.—A mixture of 1-iodo-4-methoxynaphthalene [5] (1·5 g.), ethyl 3-bromo-2-naphthoate [6] (1·4 g.), and copper-bronze (2 g.) was heated for 6 hr. at 265—270° (ethyl cinnamate bath) with vigorous stirring, then worked up as usual.[9] The oily product was directly hydrolysed with 8% methanolic sodium hydroxide (100 ml.) to give the *acid* (0·5 g.), m. p. 184° (from benzene) (Found: C, 80·9; H, 5·05. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%).

4-Methoxy-1,2′-binaphthyl (XIIe).—(*a*) 3-(4-Methoxy-1-naphthyl)-2-naphthoic acid (0·5 g.) was decarboxylated with copper-bronze (0·8 g.) and quinoline (5 ml.) at 205—210° (nitrobenzene bath). The product crystallised from light petroleum (b. p. 60—80°) to give the *product* (XIIe), m. p 166° (Found: C, 88·9; H, 5·7. $C_{21}H_{16}O$ requires C, 88·7; H, 5·7%).

(*b*) 4-Methoxy-1-(6-tetralyl)-2-naphthoic acid (VIIId) (1 g.) was dehydrogenated by heating with selenium (0·4 g.) at 300° (ethyl phthalate bath) for 8 hr. The product (0·8 g.) crystallised from benzene to give the *product* (XIId), m. p. 178° (Found: C, 80·55; H, 5·0. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). Decarboxylation of 0·6 g. with copper-bronze (1·2 g.) in quinoline (8 ml.) as usual [9] gave 4-methoxy-1,2′-binaphthyl (0·49 g.), m. p. 166° [from light petroleum (b. p. 30—50°)] undepressed on admixture with the above specimen.

4-Methoxy-1-phenylphenanthrene-2-carboxylic Acid (VId).—5,6,7,8-Tetrahydro-4-methoxy-1-phenylphenanthrene-2-carboxylic acid (IId) (0·5 g.) was heated with selenium (0·3 g.) at 300° for 12 hr., to give (VId) (0·4 g.), m. p. 226—227° (from glacial acetic acid). The methyl ester had m. p. 147° (from methanol) undepressed on admixture with the methyl ester obtained from 2-benzoylnaphthalene.

cis(Ph/CO$_2$Et)-3-Ethoxycarbonyl-4-(2-naphthyl)-4-phenylbut-3-enoic Acid (XIII).—2-Benzoylnaphthalene (24 g.) in benzene (30 ml.) was condensed as usual [9,10] with diethyl succinate (36 g.) in the presence of potassium t-butoxide [from potassium (4 g.) and t-butyl alcohol (90 ml.)], to give a viscous oil (26 g.) from which the solid pure half-ester (XIII) was isolated (2·3 g.), m. p. 142—143° [from light petroleum (b. p. 100—120°)], ν(C=O) 1710 cm.$^{-1}$ (Found: C, 76·85; H, 5·8. $C_{23}H_{20}O_4$ requires C, 76·65; H, 6·5%). On hydrolysis with 10% alcoholic potassium hydroxide it gave the dibasic acid (XIII; R = H), m. p. 174·5—175·5° (from benzene–toluene) (lit.,[8] same m. p.).

Ethyl 4-Acetoxy-1-phenylphenanthrene-2-carboxylate (VIa).—A mixture of the above crude half-ester (10 g.), sodium acetate (3 g.), and acetic anhydride (35 ml.) was refluxed for 6 hr. and worked up as previously described.[9] Crystallisation from light petroleum (b. p. 100—120°) gave the *ester* (VIa), m. p. 147—148° (11 g.) (Found: C, 77·9; H, 5·0. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%).

4-Hydroxy-1-phenylphenanthrene-2-carboxylic Acid (VIb).—The acetoxy-derivative (VIa) (4 g.) was hydrolysed with 10% alcoholic potassium hydroxide (40 ml.); crystallisation from benzene gave the *product* (VIb), m. p. 187—188° (2·5 g.) (Found: C, 80·0; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%).

Methyl 4-Methoxy-1-phenylphenanthrene-2-carboxylate (VIc).—The phenolic acid (VIb) (3·5 g.) was heated with dimethyl sulphate (6·5 g.), sodium hydroxide (6 g.), and water (30 ml.) on a boiling-water bath for 30 min. The precipitate crystallised from methanol to give the *product* (VIc) (3·8 g.), m. p. 147° (Found: C, 80·7; H, 5·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%).

4-Methoxy-1-phenylphenanthrene-2-carboxylic Acid (VId).—The methoxy-ester (VIc) (3·5 g.) was hydrolysed with 10% potassium hydroxide (40 ml.) and worked up as usual. The *acid* (2·5 g.) had m. p. 226—227° (from glacial acetic acid) (Found: C, 80·7; H, 4·9. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%).

4-Methoxy-1-phenylphenanthrene (VIe).—The acid (VId) (0·4 g.) was heated with copper-bronze (0·8 g.) in boiling quinoline for 4 hr. and worked up as usual,[9] to give the *product* (VIe) (0·3 g.), m. p. 110—111° [from light petroleum (b. p. 40—60°)] (Found: C, 88·95; H, 5·9. $C_{21}H_{16}O$ requires C, 88·7; H, 5·7%).

cis- (IV) *and trans-(Ph/CO$_2$H)-3-Carboxy-4-phenyl-4-(6-tetralyl)but-3-enoic Acid* (X).—The crude mixture of half-esters (I) and (VII) (8 g.) was hydrolysed with 5% alcoholic potassium hydroxide (80 ml.) for 2 hr. The semi-solid acid (*ca.* 7·0 g.) was triturated with ethyl acetate, and repeatedly crystallised from ethyl acetate–light petroleum (b. p. 30—50°), to give the *acid* (X) (4·0 g.), m. p. 186° (Found: C, 74·7; H, 6·1. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%). Hewett [8] gives m. p. 183—185°. No depression occurred on admixture with a specimen of the product obtained by Hewett's route. The ethyl acetate used for trituration was evaporated and the residue repeatedly crystallised from light petroleum (b. p. 100—120°), to give (IV) (3 g.), m. p. 196° (lit.,[8] 188—189°) (Found: C, 74·75; H, 6·1%).

1-Oxo-3-(6-tetralyl)inden-2-ylacetic Acid (V) *and (6,7,8,9-Tetrahydro-1-oxo-3-phenylbenz[e]inden-2-yl)acetic Acid* (XI).—The *cis*-acid (IV) (1·5 g.) was converted into the

[11] J. Lackett and W. F. Short, *J. Chem. Soc.*, 1939, 787.

anhydride by heating with acetyl chloride for 2 hr., and this was treated with aluminium chloride (1·5 g.) in nitrobenzene (15 ml.) and worked up as usual.[9] Crystallisation from ether gave the *product* (V) (1·3 g.), as yellow needles, m. p. 196° (Found: C, 78·8; H, 5·75. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%). The anhydride of the *trans*-acid (X) was similarly prepared, then treated in nitrobenzene (30 ml.) with aluminium chloride (2·5 g.) and worked up, to give the *acid* (XI) as orange fine needles, m. p. 166° (from benzene) (Found: C, 78·4; H, 5·7%).

5-*Acetoxy*-1,2,3,4-*tetrahydro*-7H-*indeno*[1,2-a]*phenanthren*-7-*one* (IIIa) *and* 11-*Acetoxy*-1,2,3,4-*tetrahydro*-13H-*dibenzo*[a,g]*fluoren*-13-*one* (IXa).—The indenylacetic acid (V) (1·2 g.) and sodium acetate (0·9 g.) in acetic anhydride (15 ml.) were refluxed for 5 hr., to give (IIIa) (1·2 g.), yellow *needles*, m. p. 201° [from benzene–light petroleum (b. p. 30—50°)] (Found: C, 80·65; H, 5·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%). On hydrolysis with N-sodium hydroxide (10 ml.) for 2 hr. it gave (IIIb) (0·9 g.), purple-black plates, m. p. 275° (from ethanol) (Found: C, 83·3; H, 5·5. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%). The indenylacetic acid (XI) (2·5 g.) and sodium acetate (1·5 g.) in acetic anhydride (25 ml.) were refluxed for 6 hr., to give (IXa), orange needles, m. p. 254° (from ethanol) (Found: C, 80·3; H, 5·3%). On hydrolysis with N-sodium hydroxide (20 ml.) for 2 hr., it gave the crude hydroxy-derivative (IXb) (1·7 g.), which failed to crystallise.

Compounds (IIIc) *and* (IXc) (*see earlier*).—Compound (IIIb) (5 g.) was methylated with dimethyl sulphate (0·9 g.), potassium carbonate (0·5 g.), and acetone (10 ml.) in the usual manner. Crystallisation from acetone gave (IIIc) as red needles, m. p. 215° undepressed on admixture with the product obtained by cyclisation of (IId). Methylation of crude (IXb) gave (IXc), red needles, m. p. 209° (from benzene), undepressed on admixture with the compound obtained by cyclisation of (VIIId).

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