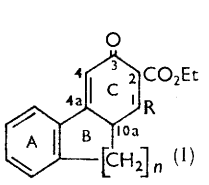
85. *Stereochemistry and Isomerisation of Some Hydrofluorene and Hydrophenanthrene β-Keto-esters.*

By D. M. W. Anderson and D. Leaver.

The constitutions of the cyclic keto-esters produced by base-catalysed reaction of ethyl acetoacetate with 2-benzylideneindan-1-one, 2-benzylidene-1-tetralone and 2-morpholinomethylindan-1-one methiodide have been elucidated. The course of acid- and base-catalysed double-bond migrations has been correlated with the stereochemistry of the compounds. Unusual aspects of the absorption spectra of certain of the compounds and their derivatives are also discussed.

In a previous paper [1] we reported that reaction of 2-benzylideneindan-1-one with ethyl acetoacetate in presence of sodium ethoxide (1 mol.) failed to yield the expected keto-ester (Ia) but gave instead an ester (m. p. 133—134°) which we now formulate as the enol form of its double-bond isomer (IIIa). 2-Benzylidene-1-tetralone yielded the analogous ester (IIIb). Peak, Robinson, and Walker [2] reported a similar reaction of 2-furfurylidene-1-tetralone but proposed structure (IVc) for the final, colourless product.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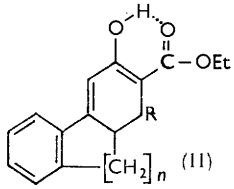
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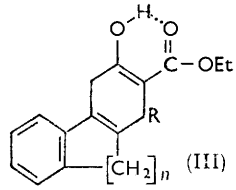
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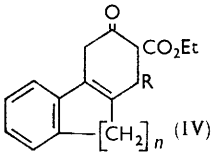
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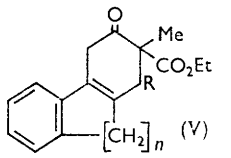
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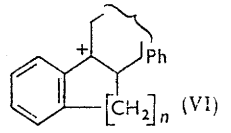
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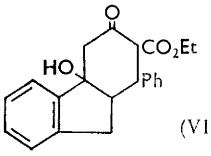
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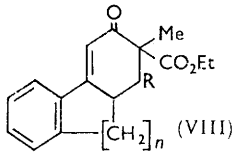

(VIII)

a : $n = 1$; R = Ph
b : $n = 2$; R = Ph
c : $n = 2$; R = 2-furyl
d : $n = 1$; R = H
e : $n = 2$; R = H

That our compounds possess the enolic, chelated structures illustrated is shown by their infrared carbonyl absorptions [single bands at 1665 and 1672 cm.$^{-1}$ in (IIIa) and and (IIIb), respectively, attributed to a chelated, αβ-unsaturated ester]. The presence of a double bond at the B/C ring junction was demonstrated by methylation of the sodium enolates in *NN*-dimethylformamide to yield *C*-methyl compounds (Va) and (Vb) having ultraviolet spectra similar to that of 1,2,3,4-tetrahydro-3-oxo-1-phenylfluorene [1] (IVa without CO_2Et). The colourless furyl compound prepared by Robinson and his co-workers was reported [2] to give a purple colour with ferric chloride, as do the esters (III); it seems probable, therefore, that this is also enolic (IIIc). The keto-ester (IVa) was obtained by another method and gave no immediate colour with ferric chloride.

Reaction between 2-benzylidene-1-tetralone and ethyl acetoacetate in presence of a smaller amount of sodium ethoxide (0·2 mol.) afforded two isomeric esters. The constitution of the colourless, major product (Ib) follows from the similarity of its ultraviolet spectrum (Fig. 1) to that of 1,2,3,9,10,10a-hexahydro-3-oxo-1-phenylphenanthrene [1]

[1] Anderson, Campbell, Leaver, and Stafford, *J.*, 1959, 3992.
[2] Peak, Robinson, and Walker, *J.*, 1936, 752.

(Ib without CO_2Et) and from infrared absorptions at 1744 (CO_2Et) and 1667 cm.$^{-1}$ (conjugated ketone). The other product (IIb) was yellow (ultraviolet spectrum in Fig. 2) with infrared absorption at 1645 cm.$^{-1}$ which is attributed to the chelated ester group. The first (yellow) product of the reaction between 2-furfurylidene-1-tetralone and ethyl acetoacetate (formulated [2] as Ic) was reported to give a colour (green) with ferric chloride similar to that given by ester (IIb) and, therefore, is probably also enolic (IIc). The keto-ester (Ib) gave no colour with ferric chloride.

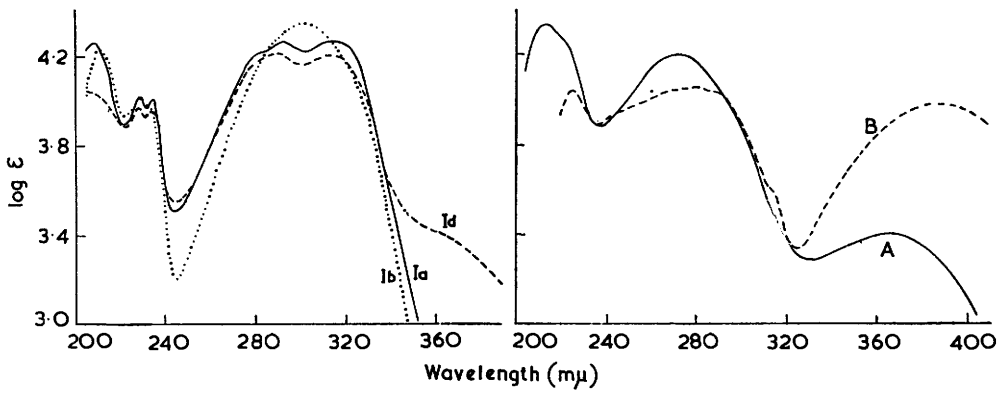


FIG. 1. FIG. 2.

FIG. 1. Ultraviolet absorption spectra, in ethanol, of the keto-esters (Ia), (Ib), and (Id).

FIG. 2. Ultraviolet absorption spectra of the ester (IIb): (A) in ethanol; (B) in 0·02M-ethanolic sodium ethoxide.

That the esters (Ib) and (IIb) are not tautomers was shown by the different behaviour of their respective enolate anions. Both esters dissolved in 0·02M-ethanolic sodium ethoxide to give yellow solutions with similar absorption spectra (*e.g.*, Fig. 2) but only (IIb) was stable in alkaline solution; (Ib) isomerised during several hours to the ester (IIIb). The two anions, therefore, are *cis–trans*-isomers about $C_{(1)}$ and $C_{(10a)}$.

Mixtures of the esters (Ib) and (IIb) were also obtained when a solution of the ester (IIIb) in concentrated sulphuric acid was diluted with water. Longer reaction times (in sulphuric acid) gave rise to a greater proportion of the keto-ester (Ib), suggesting that the isomer (IIb) is kinetically favoured. The latter compound was converted into its isomer (Ib) together with traces of the ester (IIIb) by boiling it in ethanol saturated with hydrogen chloride. Such isomeric changes are consistent with the existence, in strong acid, of the diastereoisomeric species represented by partial formula (VI; $n = 2$) and formed by protonation of ester (IIIb) at $C_{(10a)}$ or of its isomers (Ib) and (IIb) at $C_{(4)}$. (The oxygen-containing groups at $C_{(2)}$ and $C_{(3)}$ may also be protonated.) All three isomers (Ib), (IIb), and (IIIb) yielded the same 1,2,3,9,10,10a-hexahydro-3-oxo-1-phenylphenanthrene [1] (m. p. 99°) on hydrolysis and decarboxylation in acid or alkali.

The reaction between 2-benzylideneindan-1-one and ethyl acetoacetate did not yield the esters (Ia) and (IIa) under any conditions. Progressive reduction of the concentration of sodium ethoxide led to mixtures of the ester (IIIa) and the hydroxy-keto-ester (VII) which is analogous to a product from chalcone and ethyl acetoacetate.[1,3] It seems probable that the hydroxy-compound loses water to give the ester (IIIa) directly. However, dilution of a solution of the ester (IIIa) in concentrated sulphuric acid afforded the isomers (Ia) and (IIa) together with the ester (IVa), the keto-tautomer of (IIIa). The constitution (IVa) follows from the similarity of its ultraviolet spectrum to that of 1,2,3,4-tetrahydro-3-oxo-1-phenylfluorene [1] and from infrared absorptions at 1748 (unconjugated

[3] Dieckmann and von Fischer, *Ber.*, 1911, **44**, 966.

ester) and 1722 cm.$^{-1}$ (unconjugated ketone). The ester gave no immediate colour with ferric chloride but a purple colour (as given by IIIa) slowly developed. On treatment with alkali the compound immediately developed the ultraviolet spectrum characteristic of the enolate anion from the ester (IIIa) (Fig. 3) and after several weeks a neutral solution yielded the isomer (IIIa) on evaporation.

In contrast to the corresponding hydrophenanthrene compounds, both hydrofluorene esters (Ia) and (IIa) rearranged readily to (IIIa) in alkaline solution, although ester (Ia) changed more rapidly than its isomer (IIa). The greater ease of rearrangement in the hydrofluorene series is probably a consequence of the additional strain introduced by the five-membered ring and, in accord with this view, the hydrofluorene ester (Id), from which the 1-phenyl group is absent, rearranged to the isomer (IIId) in alkaline solution. The ester (Id) was prepared in low yield by the method of Harradence and Lions [4] but the major product (m. p. 156—157°), to which these authors assigned the structure (Id), was

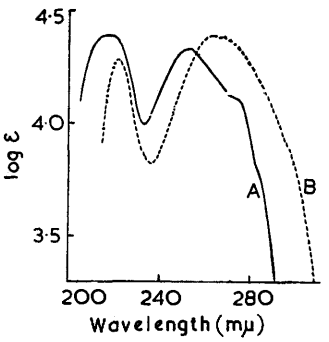


FIG. 3. Ultraviolet absorption spectra of the ester (IIIa): (A) in ethanol; (B) in 0·02M-ethanolic sodium ethoxide.

the isomer (IIId) as shown by its ultraviolet and infrared absorption spectra and those of its 2-methyl derivative. The ultraviolet (Fig. 1) and infrared (Table) absorptions of the ester (Id) indicate that it exists largely in the keto-form but the shoulder at *ca.* 370 mμ (solution faintly yellow) and reduced intensity of the main ultraviolet maxima show the presence of a small proportion of enol (IId). Attempts to prepare the hydrophenanthrene compound (Ie) resulted only in the isolation of the ketone, 1,2,3,9,10,10a-hexahydro-3-oxophenanthrene, as reported previously.[1]

Infrared C=O stretching frequencies (cm.$^{-1}$) of β-keto-esters in carbon tetrachloride.

(Ia)	1744	—	1665	(IVa)	1748	1722
(Ib)	1744	—	1667	(VII)	1749	1723
(Id)	1741	—	1667	(Va)	(1736)	1721
(VIIIa: *trans*)	—	1725	1662	(Vb)	—	1721
(VIIIa: *cis*)	1738	1710	1659			(1712)
(VIIIb: *trans*)	(1745)	1722	1662	(Vd)	(1735)	1721
(VIIIb: *cis*)	1740	1715	1661			

Parentheses denote a shoulder or inflection.

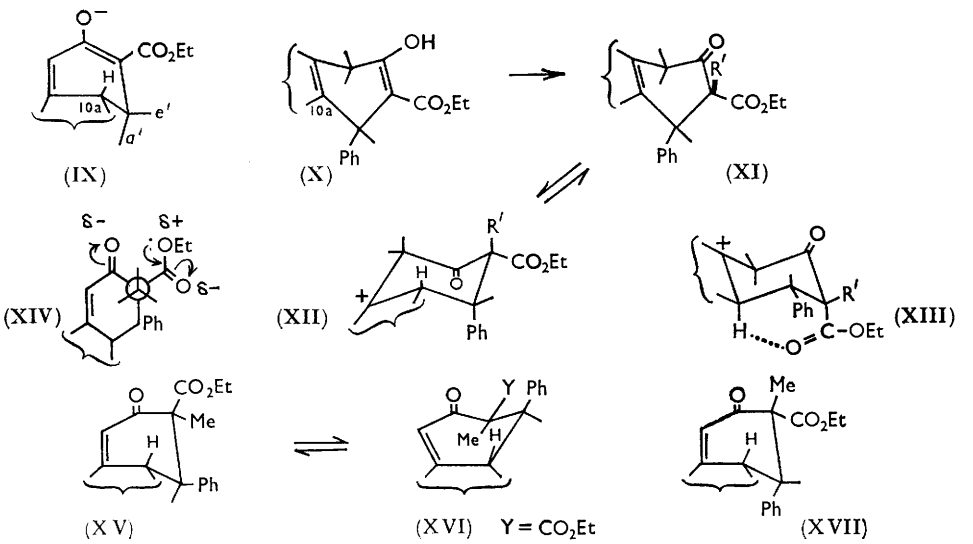
The sodium enolates derived from esters of types (I), (II), and (III) reacted with methyl iodide in *NN*-dimethylformamide to give *C*-methyl compounds. Corresponding esters of types (I) and (II) gave stereoisomeric methyl compounds (VIII). The methyl compounds (Va) and (Vb) and those (VIII) derived from esters (II), when boiled with saturated ethanolic hydrogen chloride, were converted quantitatively into their isomers (VIII) identical with those obtained by methylation of the keto-esters (I). These acid-catalysed transformations must proceed *via* intermediate cations (VI) which permit configurational inversions only at $C_{(10a)}$; therefore all the methyl compounds must have the same relative configurations at $C_{(1)}$ and $C_{(2)}$.

Stereochemistry and Absorption Spectra.—In all the compounds or intermediates studied, the 3- and the 4a-position are occupied by trigonal carbon atoms and it is probable,

[4] Harradence and Lions, *J. Proc. Roy. Soc. New South Wales*, 1939, **72**, 284.

therefore, that compounds (or conformations) with quasi-axial 1-phenyl groups are more stable than their quasi-equatorial epimers since the 1,3-interactions, which normally destabilise axial, relatively to equatorial, configurations in cyclohexane derivatives, are absent and 1,2-interactions will dominate the energy relations.

Molecular models indicate that ring C, in the esters (II) and in the anions (IX) derived from esters (I) and (II), possesses a rigid conformation such that the 10a-hydrogen atom is always quasi-axial; hence the 1-phenyl group is quasi-equatorial in the *cis*- and quasi-axial in the *trans*-isomers.* It is then possible to account for the greater ease of rearrangement in the anions derived from the esters (I) if these have a *cis*-configuration whilst the anions from esters (II) are the *trans*-isomers. Steric repulsion between the quasi-equatorial phenyl group and the ethoxycarbonyl group in the *cis*-anions then provides the driving force for rearrangement, but when the phenyl group is quasi-axial (*trans*-isomers) this steric effect is absent and the esters (II), which exist in the enolic form under neutral conditions, rearrange more slowly (if at all) in alkali. This assignment of configuration to the esters (I) and (II) is also in accord with the course of acid-catalysed isomerisation of the esters (III). Ketonisation seems to be the most probable first stage in these transformations [a view which is supported by the isolation of the keto-tautomer (IVa) from a solution of the ester (IIIa) in sulphuric acid] and may be represented by the conformational diagrams (X) ⟶ (XI; R′ = H) if we assume that the conformation of ring C is such that the phenyl group occupies a sterically favourable [5] quasi-axial position. Approach



of a solvated proton towards $C_{(10a)}$ from the less hindered side of the ring will then give the *trans*-cation (XII; R′ = H), a prediction which is in accord with the isolation of the ester (IIb) as the kinetically favoured product. However, the predominant formation of the (presumed less stable) *cis*-product (Ib) after longer reaction times requires that the *cis*-cation be more stable than its *trans*-isomer. We tentatively suggest that stabilisation of the *cis*-cation is achieved by hydrogen bonding of an acidic 4- or 10a-hydrogen atom to the quasi-axial ethoxycarbonyl group as shown in diagram (XIII). The acid-catalysed transformations of the methyl compounds (V) and (VIII) can be accommodated in the same scheme (XI—XIII; R′ = Me).

The esters (I) show normal infrared carbonyl absorptions at 1665—1667 (αβ-unsaturated

* In this discussion the terms *cis* and *trans* refer to the relation between the 10a-hydrogen atom and the 1-phenyl group.

[5] Beckett and Mulley, *Chem. and Ind.*, 1955, 146; *J.*, 1955, 4159.

ketone) and 1741—1744 cm.$^{-1}$ (unconjugated ester), but in the *C*-methyl esters (VIII) the second of these bands is partially or completely replaced by a band at 1710—1725 cm.$^{-1}$ and the frequency of the ketone absorption is very slightly reduced to 1659—1662 cm.$^{-1}$ (see Table). The low frequency of the ester carbonyl absorption is considered to be caused by the presence of a quasi-axial methyl group which tends to force the quasi-equatorial ethoxycarbonyl group to occupy a position (coplanar with the ring) in which electrostatic interaction with the ketone group is possible. If this interaction is of the form shown in diagram (XIV) it will tend to reduce the double-bond character and hence the stretching frequencies of the two carbonyl groups. The *cis*-compounds (VIII) which, in the conformation (XV) most free from angle strain, have quasi-axial ethoxycarbonyl groups, show two ester-carbonyl bands that are considered to be due to conformational isomerism rather than Fermi resonance because of the absence of splitting in very closely related compounds. The band of higher (normal) frequency is attributed to the conformation (XV) and the lower one to a conformation (XVI) in which an almost complete inversion of ring C has taken place. (A complete inversion is not possible since rigidity at the ring junction requires the 10a-hydrogen atom to remain quasi-axial.) The approximately equal intensities of the two bands indicate that the gain in energy due to angle strain in conformation (XVI) is balanced by the loss due to the phenyl group's becoming quasi-axial. Use of the more polar solvent chloroform leads to an increase in the intensity of the higher-frequency band, supporting its assignment to the more polar conformation (XV) and providing a further indication that the splitting is unlikely to be caused by Fermi resonance [6] which usually results in intensification of the lower-frequency band when a more polar solvent is used.[7] The *trans*-compounds (VIII), in which both methyl and phenyl groups are quasi-axial in the most strain-free conformation (XVII), show only a single (low-frequency) ester-carbonyl absorption with (in one instance) a shoulder on the high-frequency side. A similar lowering of the ester-carbonyl frequency is apparent in the infrared spectra of the *C*-methyl keto-esters (V).

All compounds containing the conjugated system (styryl ketone) shown in structures (I) and (VIII) absorb strongly in the 300 mμ region, but when ring B is five-membered ($n = 1$) this band is split into two maxima of slightly reduced intensity and in some of these instances the smaller maximum near 230 mμ is also split (Fig. 1). This phenomenon is similar to the fine-structure effect in the spectra of fluorene and related hydrocarbons and may be attributed to the rigidity imposed upon the system by the five-membered ring.[8]

Experimental

Solvent extracts were dried (Na_2SO_4) and then evaporated under reduced pressure. The light petroleum, unless otherwise stated, had b. p. 60—80°. Alumina (Peter Spence's type H) was treated with ethyl acetate for 24 hr., dried at 200°, and stored over saturated aqueous calcium chloride. Ultraviolet spectra were measured with a Unicam S.P. 500 quartz spectrophotometer. The infrared absorptions quoted were found for dilute solutions in carbon tetrachloride by using a Hilger H 800 double-beam spectrophotometer. For the 1650—1750 cm.$^{-1}$ region, calibration was checked with reference to a dilute solution of acetone in carbon tetrachloride (1719 cm.$^{-1}$) or to the 1603 cm.$^{-1}$ band of polystyrene. Wavenumbers quoted are believed accurate within ±2 cm.$^{-1}$. Absorptions due to the chelated hydroxyl groups in the enolic compounds could not be detected even in very dilute solution.

Methylation of Esters.—Each ester (0·5—1·0 g.) in *NN*-dimethylformamide (10 ml. per g. of ester) was treated with sodium ethoxide (1 mol.) in ethanol (1 ml.) followed immediately by methyl iodide (2 ml.) and left at room temperature for 12 hr. Dilution with water and extraction with ether yielded the crude methyl compound.

Ethyl 1,2,3,9,10,10a-*Hexahydro*-3-*oxo*- (Ib) *and Ethyl* 1,9,10,10a-*Tetrahydro*-3-*hydroxy*-1-*phenylphenanthrene*-2-*carboxylate* (IIb).—2-Benzylidene-1-tetralone (5 g.), ethyl acetoacetate

[6] Brooks, Eglinton, and Morman, *J.*, 1961, 106.
[7] Jones, Angell, Ito, and Smith, *Canad. J. Chem.*, 1959, **37**, 2007; Allen, Ellington, and Meakins, *J.*, 1960, 1909.
[8] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2130.

(3·2 ml.), and ethanol (50 ml.) containing sodium ethoxide (from 0·1 g. of sodium) were boiled for 3 hr. and allowed to cool. During 12 hr. at room temperature, the solution deposited the *ester* (Ib) (3 g.), plates, m. p. 168—169° (from ethanol) (Found: C, 79·8; H, 6·6. $C_{23}H_{22}O_3$ requires C, 79·7; H, 6·4%), $\lambda_{max.}$ 229 and 301 mμ (log ε 4·01 and 4·34) in ethanol. In 0·02M-ethanolic sodium ethoxide the ester had an absorption band at 380—390 mμ but this disappeared during several hours and the spectrum became identical with that of the isomer (IIIb) in the same medium. Methylation of the ester (0·5 g.) yielded *ethyl* 1,2,3,9,10,10a-*hexahydro*-2-*methyl*-3-*oxo*-1-*phenylphenanthrene*-2-*carboxylate* (0·4 g.), prisms, m. p. 124—125° (from light petroleum–ethanol) (Found: C, 79·7; H, 6·7. $C_{24}H_{24}O_3$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 229 and 301—304 mμ (log ε 3·99 and 4·33) in ethanol.

Dilution of the mother liquors, after removal of the above keto-ester (Ib), with light petroleum (b. p. 40—60°) afforded the *ester* (IIb) (0·8 g.), yellow rhombs, m. p. 157—158° (from light petroleum–ethyl acetate) (Found: C, 79·3; H, 6·4%), $\lambda_{max.}$ 272 and 365 mμ (log ε 4·28 and 3·48) in ethanol, 281 and 387 mμ (log ε 4·14 and 4·06) in 0·02M-ethanolic sodium ethoxide. When boiled for 1 hr. in ethanol saturated with hydrogen chloride, the ester yielded a mixture separated by extraction with boiling light petroleum into plates (petroleum-insoluble; main product), m. p. 168—169°, not depressed when mixed with the isomer (Ib), and needles (petroleum-soluble; trace), m. p. 136—137°, mixed m. p. with isomer (IIIb) 136—139°. Methylation of the ester (IIb) (0·5 g.) yielded *ethyl* 1,2,3,9,10,10a-*hexahydro*-2-*methyl*-3-*oxo*-1-*phenylphenanthrene*-2-*carboxylate* (0·4 g.), prisms, m. p. 130—131° (from light petroleum–ethanol) (Found: C, 79·9; H, 6·7%), $\lambda_{max.}$ 231 and 309—310 mμ (log ε 4·08 and 4·34) in ethanol.

Ethyl 1,4,9,10-*Tetrahydro*-3-*hydroxy*-1-*phenylphenanthrene*-2-*carboxylate* (IIIb).—Ethanol (50 ml.) containing ethyl 1,2,3,9,10,10a-hexahydro-3-oxo-1-phenylphenanthrene-2-carboxylate (2 g.) and sodium ethoxide (from 0·4 g. of sodium) was set aside at room temperature for 12 hr. and poured into aqueous acetic acid. Extraction with ether and evaporation of the ether yielded the ester (IIIb) (1·9 g.), prisms, m. p. 141—142° (from light petroleum–ethyl acetate), $\lambda_{max.}$ 223, 269, and 276 mμ (log ε 4·38, 4·41, and 4·41) in 0·02M-ethanolic sodium ethoxide, identical with the ester prepared [1] directly from 2-benzylidene-1-tetralone and ethyl acetoacetate. Methylation of this ester (1 g.) yielded *ethyl* 1,2,3,4,9,10-*hexahydro*-2-*methyl*-3-*oxo*-1-*phenylphenanthrene*-2-*carboxylate* (0·9 g.), plates, m. p. 94—95° (from light petroleum–ethanol) (Found: C, 79·9; H, 7·2%), $\lambda_{max.}$ 267 and 275 mμ (log ε 4·09 and 4·10) in ethanol. The methyl compound (0·2 g.) was boiled for 1 hr. in ethanol (7 ml.) saturated with hydrogen chloride. Evaporation gave a 1,2,3,9,10,10a-hexahydro-compound (0·2 g.), m. p. 124—125°, identical (mixed m. p. and infrared spectrum) with that obtained by methylation of the ester (Ib).

Isomerisation of Ethyl 1,4,9,10-*Tetrahydro*-3-*hydroxy*-1-*phenylphenanthrene*-2-*carboxylate*.—(*a*) The ester (0·5 g.) was dissolved in cold concentrated sulphuric acid and, after 2 min., the solution was poured into water. Extraction with ethyl acetate and evaporation of the solvent afforded the ester (IIb) (0·3 g.), m. p. and mixed m. p. 157—158°.

(*b*) The ester (2 g.) was dissolved in concentrated sulphuric acid and, after 10 min., the solution was poured into water. Working up as in (*a*) gave a yellow syrup which crystallised (1·3 g.) on trituration with ethanol. Fractional crystallisation from light petroleum–ethyl acetate aided by manual separation afforded the esters (Ib) (0·4 g.), m. p. and mixed m. p. 165—167°, and (IIb) (0·8 g.), m. p. and mixed m. p. 157—158°.

1,2,3,9,10,10a-*Hexahydro*-3-*oxo*-1-*phenylphenanthrene*.—Decarbethoxylation of esters in the hydrophenanthrene series was accomplished by boiling with (*a*) acetic acid–sulphuric acid–water (4 : 2 : 1 v/v) for 15 min. and (*b*) 6% (w/v) potassium hydroxide in 80% (v/v) ethanol for 6 hr. In both circumstances the ketone was isolated by dilution with water, extraction with ether, and chromatography on alumina in light petroleum (b. p. 40—60°)–benzene. The ketone was dimorphic, existing as needles (metastable at room temperature), m. p. 99° (as previously reported [1]), and prisms, m. p. 104—105°.

Ethyl 1,4-*Dihydro*-3-*hydroxy*-1-*phenylfluorene*-2-*carboxylate* (IIIa) *and Ethyl* 1,2,3,4,4a,9a-*Hexahydro*-4a-*hydroxy*-3-*oxo*-1-*phenylfluorene*-2-*carboxylate* (VIII).—2-Benzylideneindan-1-one (3 g.), ethyl acetoacetate (2·1 ml.), and ethanol (9 ml.) containing sodium ethoxide (from 0·01 g. of sodium) were boiled for 5 hr. and allowed to cool. During 12 hr. at room temperature the solution deposited the ester (IIIa) (1 g.), m. p. 133—134° (from light petroleum–ethyl acetate), $\lambda_{max.}$ 221, 263, and 268 mμ (log ε 4·29, 4·40, and 4·39) in 0·02M-ethanolic sodium ethoxide, identical with the ester prepared [1] previously. Methylation of the ester (1 g.) yielded *ethyl* 1,2,3,4-*tetrahydro*-2-*methyl*-3-*oxo*-1-*phenylfluorene*-2-*carboxylate* (0·8 g.), tablets, m. p. 107—108°

(from light petroleum–ethanol) (Found: C, 79·8; H, 6·6. $C_{23}H_{22}O_3$ requires C, 79·7; H, 6·4%), $\lambda_{max.}$ 261 mμ (log ε 4·12) in ethanol. The methyl compound (0·475 g.) in ethanol (10 ml.) saturated with hydrogen chloride was boiled for 1·5 hr. Evaporation gave a 1,2,3,9a-tetrahydro-compound (0·46 g.), m. p. 142—143°, identical (mixed m. p.) with that obtained by methylation of the ester (Ia).

Dilution of the mother liquors from ester (IIIa) with light petroleum (b. p. 40—60°) caused crystallisation of the *ester* (VII) (1·2 g.), m. p. 180° with previous softening (from ethyl acetate), (Found: C, 75·2; H, 6·2. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%), $\nu_{max.}$ 3560, 1749, and 1723 cm.$^{-1}$.

Isomerisation of Ethyl 1,4-*Dihydro*-3-*hydroxy*-1-*phenylfluorene*-2-*carboxylate*.—The ester (3 g.) and ethanol (3 ml.) were dissolved in concentrated sulphuric acid (20 ml.) and, after 5 min., the solution was poured into water (200 ml.). Crystallisation of the resulting semisolid mass from ethanol gave a yellow solid which, on crystallisation from carbon tetrachloride, yielded *ethyl* 1,2,3,4-*tetrahydro*-3-*oxo*-1-*phenylfluorene*-2-*carboxylate* (0·32 g.), plates, m. p. 149—150° (from ethanol–benzene) (Found: C, 80·0; H, 6·2. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·1%), $\lambda_{max.}$ 260 mμ (log ε 4·16) in ethanol.

Dilution of the carbon tetrachloride mother liquors with light petroleum (b. p. 40—60°) and concentration of the ethanol mother liquors afforded *ethyl* 1,2,3,9a-*tetrahydro*-3-*oxo*-1-*phenylfluorene*-2-*carboxylate* (0·74 g.), prisms, m. p. 118—119° (from ethanol) (Found: C, 79·3; H, 6·0%), $\lambda_{max.}$ 229, 235, 292, and 316 mμ (log ε 4·02, 4·01, 4·26, and 4·27) in ethanol. In 0·02M-ethanolic sodium ethoxide, the ester gave a yellow solution initially but the colour faded rapidly and the absorption spectrum became identical with that of the ester (IIIa) in the same medium. Methylation of the ester (0·5 g.) gave a syrup which, after chromatography on alumina in light petroleum (b. p. 40—60°)–benzene, yielded an *ethyl* 1,2,3,9a-*tetrahydro*-2-*methyl*-3-*oxo*-1-*phenylfluorene*-2-*carboxylate* (0·02 g.), plates, m. p. 141—142° (from light petroleum–ethanol) (Found: C, 80·3; H, 6·6%), $\lambda_{max.}$ 229, 293, and 316 mμ (log ε 4·00, 4·26, and 4·28) in ethanol.

Evaporation of the diluted mother liquors afforded *ethyl* 1,9a-*dihydro*-3-*hydroxy*-1-*phenylfluorene*-2-*carboxylate* (0·58 g.), yellow plates, m. p. 123—124° (from ethanol–ethyl acetate) (Found: C, 79·1; H, 6·1%), $\lambda_{max.}$ 253 and 368 mμ (log ε 4·22 and 4·00) in tetrahydrofuran, $\nu_{max.}$ 1660 cm.$^{-1}$. The behaviour in 0·02M-ethanolic sodium ethoxide was similar to that of the isomer (Ia) but the colour faded less rapidly. Methylation of the ester (0·5 g.) gave a solid (0·34 g.) which was separated by chromatography on alumina in light petroleum (b. p. 40—60°)–benzene into (a) the ester (Va), m. p. and mixed m. p. 107—108°, and (b) an *ethyl* 1,2,3,9a-*tetrahydro*-2-*methyl*-3-*oxo*-1-*phenylfluorene*-2-*carboxylate*, prisms, m. p. 143—144° (from light petroleum–ethanol), depressing the m. p. of the stereoisomer from ester (Ia) (Found: C, 79·7; H, 6·5%), $\lambda_{max.}$ 231, 297, and 319 mμ (log ε 3·94, 4·23, and 4·28) in ethanol.

Ethyl 1,4-*Dihydro*-3-*hydroxyfluorene*-2-*carboxylate* (IIId) *and Ethyl* 1,2,3,9a-*Tetrahydro*-3-*oxofluorene*-2-*carboxylate* (Id).—2-Morpholinomethylindan-1-one methiodide [4] (7·1 g.), ethyl acetoacetate (5 ml.), and ethanol (20 ml.) containing sodium ethoxide (from 0·6 g. of sodium) were boiled for 30 min. and poured into water (100 ml.) containing acetic acid (1·5 ml.). Extraction with ether and evaporation of the ether gave a syrup which was dissolved in ethanol (40 ml.) containing sodium ethoxide (from 1 g. of sodium) and set aside. Dilution with water then yielded a syrup which crystallised partially. Separation of the solid and crystallisation from ethyl acetate afforded the *ester* (IIId) (1·5 g.), pale yellow needles, m. p. 156—157° (lit.,[4] m. p. 157°), $\lambda_{max.}$ 210 and 252 mμ (log ε 4·34 and 4·35) in ethanol, 220 and 265 mμ (log ε 4·14 and 4·35) in 0·02M-ethanolic sodium ethoxide, $\nu_{max.}$ 1667 and 1640 cm.$^{-1}$, previously assigned an erroneous constitution.[4] Methylation of the ester (0·65 g.) yielded *ethyl* 1,2,3,4-*tetrahydro*-2-*methyl*-3-*oxofluorene*-2-*carboxylate* (0·3 g.), m. p. 77—79° (from light petroleum) (Found: C, 75·7; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%), $\lambda_{max.}$ 259 mμ (log ε 4·06) in ethanol.

Concentration of the ethyl acetate mother liquors yielded the *ester* (Id) (0·1 g.), plates, m. p. 80—81° (from light petroleum–carbon tetrachloride) (Found: C, 74·8; H, 6·4. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%), $\lambda_{max.}$ 228, 234, 290, and 314 mμ (log ε 3·97, 3·96, 4·22, and 4·21) in ethanol. A solution in 0·02M-ethanolic sodium ethoxide, yellow at first, slowly faded and the spectrum became identical with that of the isomer (IIId) in the same medium.

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