Some Reactions of β-Ketoesters derived from 9,10-Phenanthraquinone with Ammonia, Hydrazine, and Substituted Hydrazines

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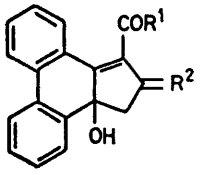
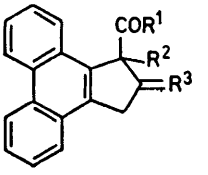
A number of β-ketoesters based on cyclopentanone, with and without additional αβ'-unsaturation, have been prepared from 9,10-phenanthraquinone and ethyl or methyl acetoacetate. Reactions of these with ammonia, hydrazine, and substituted hydrazines involve variously attack at the ester, the keto-group, and/or the olefinic group; ring-opening sometimes occurs, as does new ring-closure. Several novel compounds are described, including a 1,2-diazatriphenylene which is readily converted into a dibenzocinnolone.

CONDENSATION of 9,10-phenanthraquinone with ethyl acetoacetate was first reported by Japp *et al.*,[1,2] and the reaction and the chemistry of the product was subsequently investigated by Cope *et al.*,[3,4] when many structures were correctly established, the later workers having the advantage afforded by i.r. and u.v. spectroscopy.

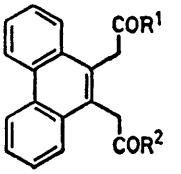
The condensation product is ethyl 3,3a-dihydro-3a-hydroxy-2-oxo-2*H*-cyclopenta[*l*]phenanthrene-1-carboxylate (1a); when this is boiled with aqueous sulphuric acid it isomerises to ethyl 2,3-dihydro-1-hydroxy-2-oxo-1*H*-cyclopenta[*l*]phenanthrene-1-carboxylate (2a), and when reduced with hydriodic acid it yields ethyl 2,3-dihydro-2-oxo-1*H*-cyclopenta[*l*]-phenanthrene-1-carboxylate (3a). The possible competing reactions of nitrogen nucleophiles with the various β-ketoester moieties in these compounds have now been investigated, and a wide variation is apparent.



(1a) R^1 = OEt, R^2 = O
(1b) R^1 = OMe, R^2 = O
(29) R^1 = NH_2, R^2 = O
(30) R^1 = NH_2, R^2 = NNH_2



(2a) R^1 = OEt, R^2 = OH, R^3 = O
(2b) R^1 = OMe, R^2 = OH, R^3 = O
(3a) R^1 = OEt, R^2 = H, R^3 = O
(3b) R^1 = OMe, R^2 = H, R^3 = O
(4) R^1 = OEt, R^2 = H, R^3 = NNHCOMe
(5) R^1 = OMe, R^2 = H, R^3 = $NNHCO_2Et$
(8) R^1 = OEt, R^2 = OH, R^3 = NNHCOMe
(9) R^1 = OEt, R^2 = OH, R^3 = $NNHCO_2Et$
(10) R^1 = OEt, R^2 = OH, R^3 = NNH_2
(11) R^1 = $NHNH_2$, R^2 = OH, R^3 = NNH_2
(12) R^1 = OEt, R^2 = OH, R^3 = NNHPh
(17) R^1 = R^2 = OMe, R^3 = $NNHCO_2Et$
(18) R^1 = R^2 = OMe, R^3 = NNHCOMe
(31) R^1 = OEt, R^2 = Cl, R^3 = O



(6a) R^1 = OEt, R^2 = $NHNH_2$
(6b) R^1 = OMe, R^2 = $NHNH_2$
(7) R^1 = OMe, R^2 = NH_2

RESULTS AND DISCUSSION

The compounds and the corresponding methyl esters were prepared according to the method [3] of Cope *et al.*; the i.r. absorptions were found to be at wavelengths appreciably lower than those recorded.[4] However, the ^1H n.m.r. spectra for deuteriochloroform solutions were as expected, except that although the ring-methylene proton signals from compounds (3) showed geminal coupling, the corresponding signals from compounds (2) were singlets.

The saturated ethyl β-ketoester (3a) gives the acetylhydrazone (4), and the methyl ester (3b) gives the ethoxycarbonylhydrazone (5) with the appropriate reagents. With hydrazine, the cyclopentenone ring of the esters (3) opens to give the ester–hydrazides (6), and with ammonia, the ester (3a) gives the ester–amide (7). With the analogous ester, ethyl 2-oxocyclopentane-1-carboxylate, it is reported [5] that the major product with ammonia is 2-aminocyclopent-1-enecarboxylate (the product expected [6]), and that a minor product is the diamide of butanedioic acid. The reported product [5] with hydrazine may be polymeric.

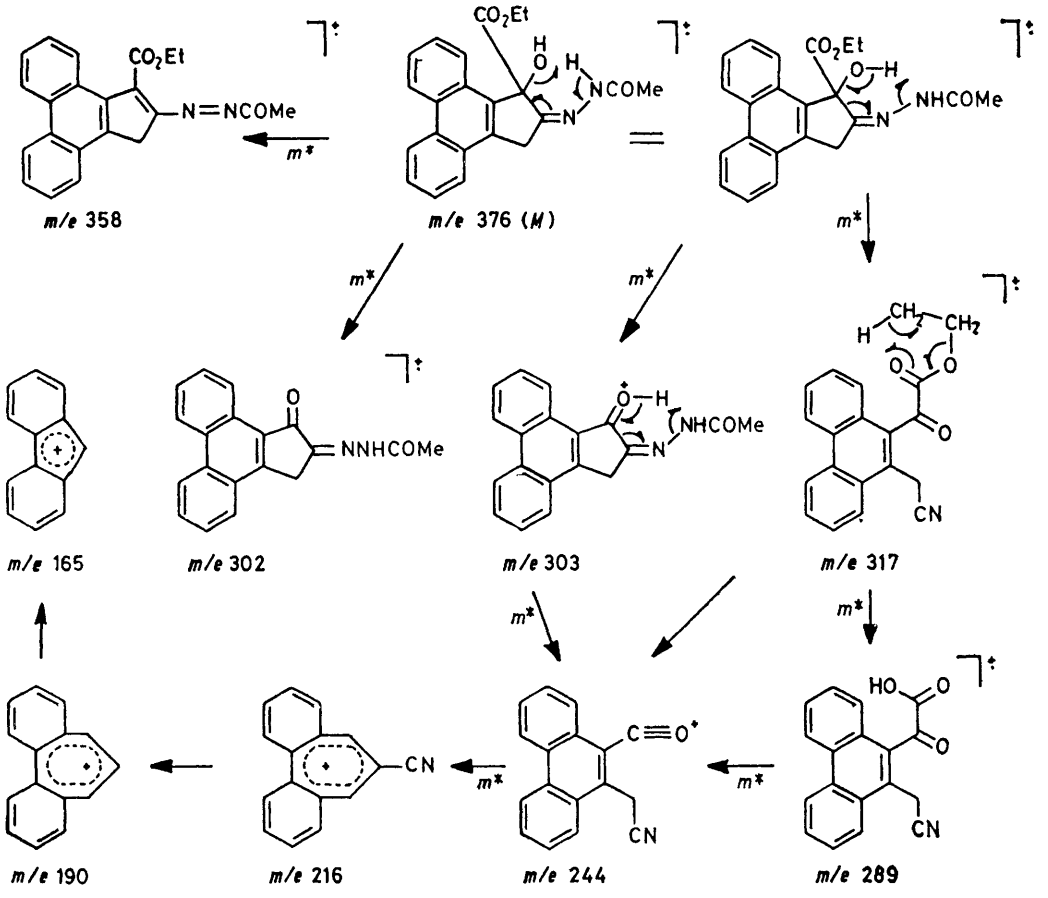
When the α-position of the β-ketoester carries an OH group (2a), the acetylhydrazone (8) is readily obtained. In the mass spectrometer, the molecular and fragment ions were found to undergo a number of rearrangements in which six-membered-ring transition states were favoured; Scheme 1 rationalises the appearance of the major ions. Similarly, the ethoxycarbonylhydrazone (9) is obtained, but a reaction time (*ca.* 7 h) is required that is much longer than that for others in this series. However, when hydrazine itself is used, not only can the simple hydrazone (10) be obtained, but in the presence of excess of reagent the simple hydrazone–hydrazide (11) is formed; there is no ring-opening.

Reaction of compound (2a) (before its structure had been determined) with phenylhydrazine was described [2] by Japp and Klingemann. From the spectra of the product it is clear that it is the simple phenylhydrazone (12).

The most remarkable reaction of compound (2b) is with methanolic ammonia. The product, $C_{18}H_{13}NO_3$, is 2,3-dihydro-2-hydroxy-3-oxo-1*H*-cyclopenta[*l*]phenanthrene-1-carboxamide (13a). Insolubility rendered recrystallisation impossible, but the molecular formula was established by isotope-abundance analysis using the low-resolution electron-impact mass spectrum (*M*, 291). The i.r. spectrum confirms the OH and amide-NH_2 groups ($\nu_{max.}$ 3 390, 3 210, 3 080, and 1 610 cm^{-1}), and also the C=O of αβ-unsaturated cyclic five-membered ketone and saturated amide (1 690 and 1 665 cm^{-1}). The u.v. spectrum (qualitative only, $\lambda_{max.}$ at 246 nm) is unlike those of (1b), (2b), or (7), but bears a strong resemblance to that [7] of 9-acetophenanthrene. Confirmation of structure (13a) was provided by the ^1H n.m.r. spectrum of a $(CD_3)_2SO$ solution (1 600 scans were necessary). Signals from 13 protons were observed, of which three singlets were exchangeable with D_2O. The pattern from the eight aromatic protons was like that from (2b), except that the chemical shift for one proton had changed from δ 7.8 to 9.0; this is expected because of the effect at the *peri*-position of the keto-group. The remaining two protons were coupled (*J* 6.1 Hz), and one of them was also coupled to the OH proton (*J* 6.7 Hz). Further confirmation is provided by the mass spectrum, where a metastable ion indicates the fragmentation *m/e* 291→230 (base peak), and this can be explained by a six-membered-ring transition state (13b) of the molecular ion, with simultaneous loss of H_2O and HN=C=O; this sequence requires a β-hydroxyamide structure. Other metastable ions show that the (stable) substituted cyclopentadiene ion also arises by other pathways. The absence of a metastable ion for the fragmentation *m/e* 291→273 suggests that loss of H_2O alone may be a purely thermal degradation.

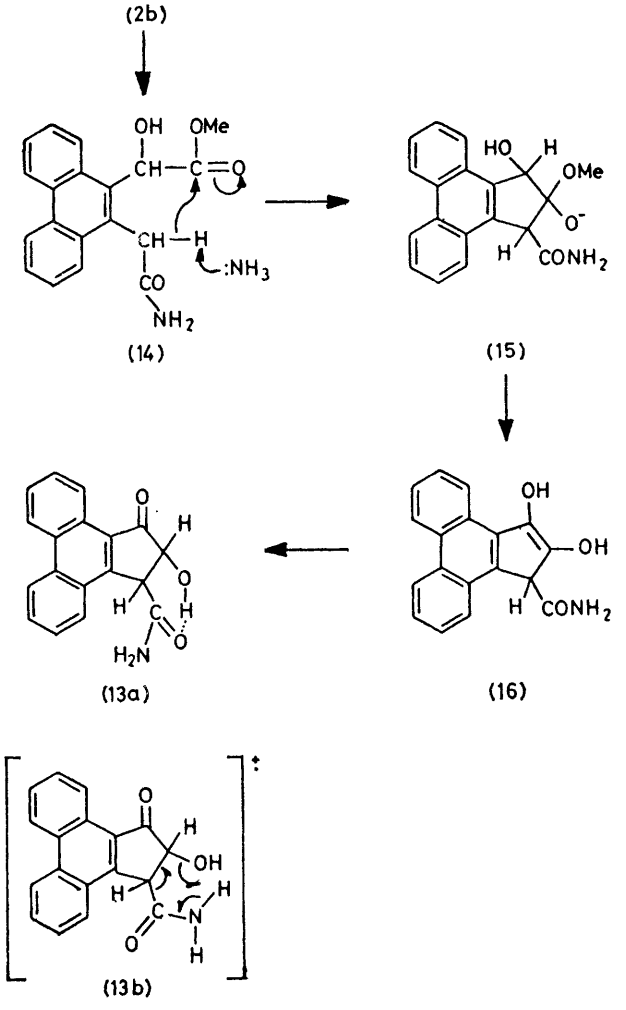
The formation of compound (13a) would appear to involve formation of amide (14) by ring-opening, followed by a new ring-closure (by an internal Claisen condensation) to give (15). Instead of elimination of MeO^-, there is acquisition of a proton, followed by elimination of MeOH to give (16), which then tautomerises to (13a). In the last step, it would be expected that the tautomeric addition would be from the less-hindered side, dictating a *cis*-configuration for the CH–CH moiety, and this is in accord with the n.m.r. evidence; for the CH_2–CH_2 grouping in cyclopent-2-enone itself, J_{cis} is 7.2 and J_{trans} 2.2 Hz.[8]

In reaction of the αβ′-unsaturated β-ketoester (1b) with ethyl carbazate or acetylhydrazine, the solvent (methanol) was treated with a trace of hydrochloric



SCHEME 1 Major fragmentations of the molecular ion from ethyl 2-acetylhydrazono-2,3-dihydro-1-hydroxy-1*H*-cyclopenta[*l*]-phenanthrene-1-carboxylate (8) (*m** signifies that the appropriate metastable ion was observed)

acid. The product in each case, (17) and (18) respectively, was the hydrazone derivative of methyl 2,3-dihydro-1-methoxy-2-oxo-1*H*-cyclopenta[*l*]phenanthrene-1-carboxylate. Probably the acid catalyses

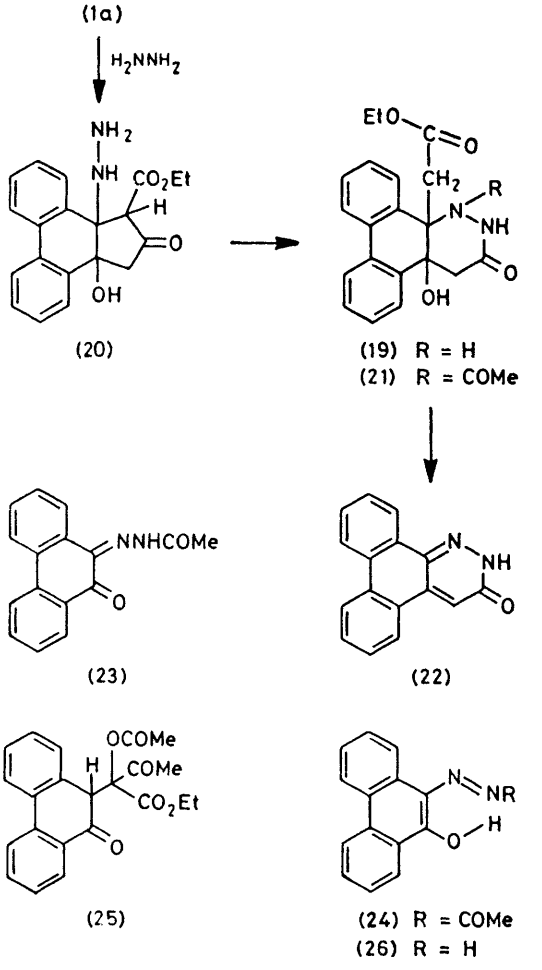


attack by solvent at position 1, with migration of the double bond as in the isomerisation [4] of (1a) to (2a), and the product then reacts as a saturated β-ketoester.

Structural assignments follow readily from the changes in the u.v. spectra. In the mass spectrometer, there are two consecutive losses of MeOH from the molecular ion of compound (17) (supported by *m**), and although it is easy to accommodate the first *via* a six-membered-ring transition state involving the hydrazino-hydrogen, it is not easy to account for the second. It may be noted that for all the hydrazone derivatives prepared, the ring methylene protons each had different chemical shifts in the n.m.r. spectra, except for compounds (4), (17), and (18).

Reaction between the ethyl ester (1a) and hydrazine itself occurs readily without any acid catalyst. The product, $C_{20}H_{20}N_2O_4$, is ethyl (1,2,3,4,4a,12b-hexahydro-4a-hydroxy-3-oxo-1,2-diazatriphenylen-12b-yl)-acetate (19). This reaction probably starts with addition of hydrazine at the olefinic bond to give (20), which is then transformed into (19) by a reaction analogous to the formation of (6) above. [Ring-opening of (1a) as a first step seems less likely.] This product has a u.v. spectrum ($\lambda_{max.}$ 274 nm) characteristic [9] of a 9,10-dihydrophenanthrene, and shows i.r. absorptions due to cyclic hydrazide CO (1 640), saturated ester CO (1 732 and 1 723), and OH and hydrazide-NH groups (3 300, 3 250, and 3 177 cm^{-1}). In the ^1H n.m.r. spectrum, the signal pattern from the aromatic protons most resembled that of 9,10-dihydrophenanthrenes; other signals are as expected, geminal coupling was observed for the protons of the newly created methylene group, and H-1 was chelated to the ester CO (exchange with D_2O took two weeks). Long-range coupling (J 1.8 Hz) was apparent between H-1 and one of the protons of the exocyclic methylene group. Acetylation of (19) gives the 1-acetyl derivative (21), in which the long-range coupling no longer exists.

The melting behaviour of compound (19) was especially interesting. Under the microscope, as the temperature was raised, the small rhombs melted at 215 °C; the melt then effervesced and gradually resolidified to needles that finally melted at 312 °C. The higher-melting product is readily identified as 1,2-diazatri-



phenylen-3(2*H*)-one (22) (a dibenzocinnolone). It had a u.v. spectrum like that of 9,10-phenanthraquinone; the n.m.r. spectrum was also similar, but with the addition of two singlets, one of which was exchangeable with D_2O. The reaction was performed on a preparative scale [from 2 g of (19)], and the evolved gases had an i.r. spectrum expected of a mixture of ethyl acetate and water. Compound (21) similarly gives (22).

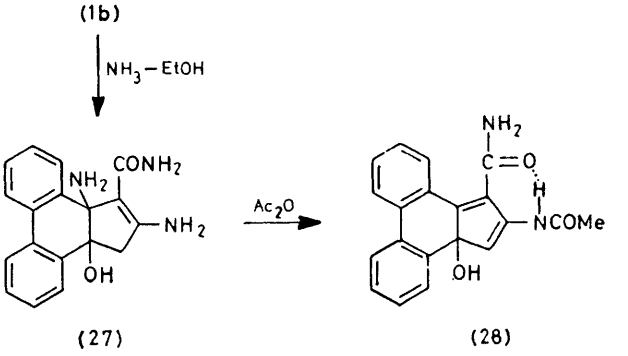
Alternative attempts to synthesise the cinnolone were unsuccessful. Reaction of 9,10-phenanthraquinone with acetylhydrazine gave a product, $C_{16}H_{12}N_2O_2$, which on the basis of its spectra must be formulated as the monoacetylhydrazone (23) of the *o*-quinone (*cf.* monohydrazones [10] of *ortho*-quinones). It was not light-sensitive, and the u.v. spectrum was unchanged by dilute acid although it underwent a marked change in alkali, presumably because a phenolic anion can be formed from the tautomeric form (24). However, the acetylhydrazone could not be made to yield the heterocycle (22) by treatment with acetic anhydride, concentrated sulphuric acid, or polyphosphoric acid.

One product [11] of the acetic anhydride–sulphuric acid-induced condensation of ethyl acetoacetate and 9,10-phenanthraquinone is ethyl α-acetyl-α-acetoxy-α-(9-oxo-10*H*-phenanthren-10-yl)acetate (25). Reaction of this with hydrazine gave, surprisingly, hydrogenazo-9-phenanthren-10-ol [12] (26); this was light-sensitive and displayed i.r. absorptions (at 3 330, and at 2 110 and 2 090 cm^{-1}) characteristic of phenolic OH and of zwitterions of azophenols [10] respectively. Failure of this reaction to yield a heterocycle is unexpected because the spectra show that compound (25) is the tautomer depicted (*e.g.* there is no OH absorption in the i.r., neither are there any protons exchangeable with D_2O). The same hydrogenazo-product was obtained by the action of hydrazine on the monoacetylhydrazone (23).

Reaction of ammonia with the ethyl ester (1a) has been investigated [2] and a product of composition $C_{40}H_{38-40}N_4O_5$ reported. The rather drastic conditions employed (sealed tube, 100 °C) prompted us to try the reaction using the methyl ester (1b). A solution of (1b) in ethanol saturated with ammonia, when set aside for 136 d, yielded a product that decomposed at *ca.* 200 °C without melting and which had very low solubility. Elemental analysis (of a sample boiled in ethanol) indicated an empirical formula of $C_{18}H_{17}N_3O_2$, which was confirmed as the molecular formula by recognition of the molecular ion at *m/e* 307 in the mass spectrum (obtained with difficulty), and isotope-abundance analysis.

This product is identified as 2,3a-diamino-3a,11b-dihydro-11b-hydroxy-1*H*-cyclopenta[*l*]phenanthrene-3-carboxamide (27). The u.v. spectrum (qualitative only) is characteristic [9] of a 9,10-dihydrophenanthrene; it is quite unlike those of (1b) or (2b). The i.r. spectrum shows OH, NH_2, and amide-NH_2 groups (3 458, 3 368, 3 340, 3 270, 3 125, and 1 617 cm^{-1}), and CO and C=C of an αβ-unsaturated amide group (1 670, 1 648, and 1 635 cm^{-1}).

In the n.m.r. spectrum [1 024 scans, $(CD_3)_2SO$ solution], the expected signals from 17 protons were observed. The chemical shift for the methylene protons indicates that these are not adjacent to C=O or C=N. The signals



(27) (28)

from the αβ-unsaturated amino-group (δ 7.1 and 7.7) were very broad and coincident with the aromatic proton signals (for this solvent, the corresponding signals from methyl 3-aminobut-2-enoate are also very broad, at δ 7.0 and 7.6). The OH proton exchanged with D_2O immediately, those on nitrogen exchanged slowly over four weeks.

In the mass spectrometer, the presence of the appropriate metastable ions enabled the principal fragmentations of the molecular ion to be rationalised (Scheme 2). The base-peak ion arises by two successive losses of 17 a.m.u.; the first of these is probably OH·, because the *m/e* 290 ion can then lose either 17 or 1 a.m.u., and the latter is also readily accounted for. The loss of 27 a.m.u. from *m/e* 291 and from *m/e* 289 is probably HNC: in each case.

The formation of compound (27) parallels the non-ring-opening reaction [5] of ethyl 2-oxocyclopentan-1-carboxylate with ammonia, and further confirmation of the structure is found in its reactions. Treatment with acetic anhydride led to a product, $C_{20}H_{16}N_2O_3$, which is readily formulated as the acetamide (28). Mass spectrometry confirms the molecular ion as *m/e* 332. The u.v. spectrum most clearly resembles that of the starting material (1b), and the i.r. spectrum (several bands in the 3 500—3 100 cm^{-1} region) suggests OH and amide-NH, as well as (1 665 and 1 630 cm^{-1}) C=O of unsaturated amide and olefinic groups. The n.m.r. spectra are as expected; with D_2O the olefinic proton did not exchange, the OH proton exchanged immediately, the $CONH_2$ protons exchanged slowly, and the chelated CONH proton exchanged very slowly [for a $(CD_3)_2SO$ solution, exchange was still incomplete after three months].

Another reaction undergone by compound (27) occurred when it was added to warm aqueous sulphuric acid. The compound rapidly dissolved and a solid then separated, for which elemental analysis suggested the composition $C_{18}H_{13}NO_3$. This compound decomposed on heating, but a mass spectrum was eventually obtained that confirmed the molecular weight as 291. A minor impurity, which could not be removed, was

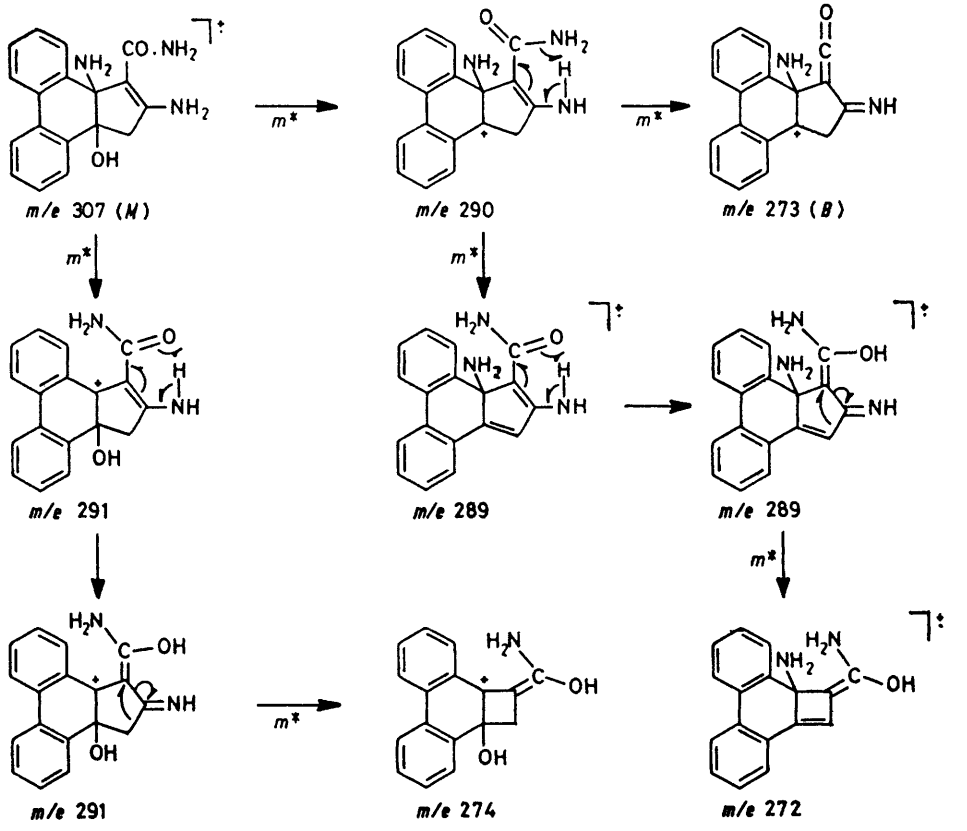
present with a molecular weight of 306, which evidently arises from the starting material (1b) [or from its acid-isomerised product (2b)]. In the mass spectrometer, the fragmentations of the product, *m/e* 291→274→246, supported by the presence of the appropriate metastable ions, would normally suggest a carboxylic acid (loss of OH·, then of CO), but the compound neither effervesces with sodium hydrogencarbonate, nor does it give an ester with diazomethane.

The close resemblance of the n.m.r. spectrum to that of the starting material (1b) and the i.r. band at 1 630 cm^{-1} [*cf.* 1 627 cm^{-1} for the olefinic bond in (1b)] leads to formulation of this product as 3,3a-dihydro-3a-hydroxy-2-oxo-2*H*-cyclopenta[*l*]phenanthrene-1-carboxamide (29), the amide corresponding to (1b). It is surprising that the acid-induced isomerisation does not occur, as in the preparation of (2b) from (1b).

Hydrazine reacted with (29) to give a very small amount of a derivative which resisted purification. This decomposed on heating and the carbon analysis was low, but u.v. and n.m.r. spectra were obtained. These were sufficient to identify the derivative as the hydrazone (30); in particular the aromatic signals in the n.m.r. spectrum are practically superimposable on those of (29), and the slight changes in chemical shifts and coupling constant for the methylene protons are consistent with the change C=O→C=NNH_2.

The different reactions with hydrazine of the ester (1b) and the corresponding amide (29) may be due to the chelation of the keto-group in the amide.

Alcoholic hydrogen chloride reacts with (1a), and the product was formulated [2] as $C_{20}H_{15}ClO_3$ on the basis of C and H analyses. The spectra now show that this is ethyl 1-chloro-2,3-dihyro-2-oxo-1*H*-cyclopenta[*l*]-phenanthrene-1-carboxylate (31). It is reported [2] that this reacts with ethanolic ammonia to give a product, $C_{40}H_{31}NO_6$, but we were unable to isolate this; with both ammonia and hydrazine we obtained complex mixtures.



SCHEME 2 Major fragmentations of the molecular ion from compound (27) (*m** signifies that the appropriate metastable ion was observed)

EXPERIMENTAL

Unless otherwise stated, u.v. spectra were recorded for solutions in 96% ethanol; i.r. spectra were recorded on Nujol mulls; ^1H n.m.r. spectra were recorded for deuteriochloroform solutions, using a Bruker WH-90 MHz (pulsed Fourier-transform) spectrometer; mass spectra were obtained on an A.E.I. MA 12 spectrometer using a direct inlet system and a beam energy of 70 eV; significant ions only are reported. Melting points were determined with a Kofler hot stage apparatus.

9,10-Phenanthraquinone (m.p. 208.5—210 °C) was prepared by oxidation of commercially available phenanthrene, and it was necessary to remove the last traces of anthraquinone by treatment with sodium hydrogensulphite. Acetylhydrazine had m.p. 66—67 °C; δ[$(CD_3)_2$-SO] 1.70 (s, Me), 4.16 (s, NH_2), and 8.95 (s, br, NH); $\nu_{max.}$

3 470(sh), 3 260vs, br, 3 043s, and 1 650vs, br cm^{-1}; the unrecrystallised material did not require further purification.

Ethyl 3,3a-Dihydro-3a-hydroxy-2-oxo-2H-cyclopenta[l]*phenanthrene-1-carboxylate* (1a), *and the Methyl Ester* (1b).—The ethyl ester (1a) was obtained by the procedure [4] described by Cope *et al.* It had m.p. 188—190 °C [Found: $M^{+\cdot}$, 320; $M : (M + 1) : (M + 2) = 100 : 22.0 : 3.1$. Calc. for $C_{20}H_{16}O_4$: M, 320; $M : (M + 1) : (M + 2) = 100 : 22.0 : 3.1$]; δ (at 60 MHz) 1.29 (t, J 7.0 Hz, CH_2CH_3), 2.58 (s, OH), 3.13 (d, J −18 Hz, CHHCO), 3.24 (d, J −18 Hz, CHHCO), 4.34 (q, J 7.0 Hz, CH_2CH_3), 7.5 (m, 4 H), and 7.8 (m, 4 H); $\lambda_{max.}$ 257 (log ε 4.46), 264 (4.56), 300 (4.03), and 352 nm (3.68); $\nu_{max.}$ 3 452vs, 1 725vs, 1 696vs (lit.,[4] 3 350, 1 715, and 1 680), and 1 630s cm^{-1}; *m/e* 320 (*M*, 52%), 303 (22), 292 (8), 291 (19), 275 (23), 274 (41), 247 (23), 231 (47), 230 (55), and 202 (base peak) with *m** 286.9 (320→303), 249.6 (303→275), 234.6 (320→274), 221.8 (275→247), and 194.0 (275→231).

The *methyl ester* (1b) was prepared similarly (83 g from 60 g quinone), m.p. 202—204 °C (Found: C, 74.6; H, 4.5. $C_{19}H_{14}O_4$ requires C, 74.5; H, 4.6%); δ 2.6 (s, OH), 3.14 (d, J −17.6 Hz, CHHCO), 3.26 (d, J −17.6 Hz, CHHCO), 3.87 (s, Me), 7.5 (m, 4 H), 7.7 (m, 1 H), and 7.9 (m, 3 H); δ[$(CD_3)_2SO$] 3.00 (d, J −17.6 Hz), 3.38 (d, J −17.6 Hz), 3.83 (s, Me), 6.31 (s, OH), 7.5 (m, 6 H), and 8.1 (m, 2 H); $\lambda_{max.}$ 257 (log ε 4.56), 264 (4.65), 300 (4.02), and 352 nm (3.90); $\nu_{max.}$ 3 448vs, 1 742vs, 1 689vs, and 1 627s cm^{-1}.

Ethyl 2,3-Dihydro-1-hydroxy-2-oxo-1H-cyclopenta[l]*phenanthrene-1-carboxylate* (2a), *and the Methyl Ester* (2b).—The ethyl ester (2a) was obtained [4] from (1a) by the action of aqueous sulphuric acid, m.p. 175—177 °C; δ (at 60 MHz) 1.00 (t, J 7.0 Hz, CH_2CH_3), 3.95 (s, CH_2CO), 4.19 (m, J 7.0 Hz, CH_2CH_3), 4.52 (s, OH, exchangeable with D_2O), 7.7 (m, 4 H), 8.1 (m, 2 H), and 8.7 (m, 2 H); $\lambda_{max.}$ 249sh (log ε 4.60), 257 (4.74), 279 (4.07), 290 (4.04), 301 (4.03), 334 (3.84), and 349 nm (3.84); $\nu_{max.}$ 3 400s, br, 1 765vs, and 1 737 cm^{-1} (*cf.* ref. 4).

The *methyl ester* (2b), prepared similarly from compound (1b), had m.p. 178—179 °C (Found: C, 74.4; H, 4.5. $C_{19}H_{14}O_4$ requires C, 74.5; H, 4.6%); δ 3.70 (s, OMe), 4.08 (s, CH_2), 4.45 (s, OH, exchangeable with D_2O), 7.8 (m, 5 H), 8.1 (m, 1 H), and 8.8 (m, 2 H); δ[$(CCD_3)_2SO$] 3.56 (s, OMe), 4.14 (s, CH_2), 7.20 (s, OH), 7.8 (m, 4 H), 7.9 (m, 1 H), 8.2 (m, 1 H), and 8.9 (m, 2 H); $\lambda_{max.}$ 257 (log ε 4.76), 279 (4.08), 290 (4.00), 301 (4.00), 334 (3.84), and 350 nm (3.84); $\nu_{max.}$ 3 438s, 3 068w, 1 762vs, and 1 739vs cm^{-1}.

Ethyl 2,3-Dihydro-2-oxo-1H-cyclopenta[l]*phenanthrene-1-carboxylate* (3a), *and the Methyl Ester* (3b).—Compound (3a) was obtained [4] by warming compound (1a) in hydriodic acid. It had m.p. 122—124 °C; δ 1.20 (t, 7.0 Hz, CH_2CH_3), 3.81 (d, J −22 Hz, CHHCO), 4.07 (d, J −22 Hz, CHHCO), 4.19 (dq, J 7.0 and 1.0 Hz, CH_2CH_3), 4.78 (s, CH), 7.7 (m, 6 H), and 8.7 (m, 2 H); $\lambda_{max.}$ 249 (log ε 4.67), 257 (4.83), 278 (4.19), 289 (4.08), 300 (4.13), 335 (3.86), and 350 nm (3.86); $\nu_{max.}$ 3 055w, 1 760vs, and 1 710vs cm^{-1}.

Similarly, (1b) (5 g) gave the *methyl ester* (3b) (3.9 g), m.p. 159—161 °C after two recrystallisations from methyl acetate (Found: C, 78.4; H, 4.8. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.9%); δ 3.72 (s, Me), 3.88 (d, J −22 Hz, CHHCO), 4.12 (d, J −22 Hz, CHHCO), 4.87 (s, CH); 7.7 (m, 6 H), and 8.8 (m, 2 H); $\lambda_{max.}$ 249 (log ε 4.70), 257 (4.94), 278 (4.18), 288 (4.07), 300 (4.12), 335 (3.97), and 350 nm (3.97); $\nu_{max.}$ 3 060w, 1 760vs, and 1 715vs cm^{-1}.

Ethyl 2-Acetylhydrazono-2,3-dihydro-1H-cyclopenta[l]*phenanthrene-1-carboxylate* (4).—Compound (3a) (1.5 g) and acetylhydrazine (0.4 g) in hot absolute ethanol (30 ml) yielded the *ester* (4) (1.5 g) after 10 min, pale green rhombs, m.p. 221—222 °C (from dioxan) [Found: C, 72.5; H, 5.6; N, 7.7; $M^{+\cdot}$, 360; $M : (M + 1) : (M + 2) = 100 : 25.8 : 3.2$. $C_{22}H_{20}N_2O_3$ requires C, 73.3; H, 5.6; N, 7.8%; M, 360; $M : (M + 1) : (M + 2) = 100 : 25.0 : 3.6$]; δ 1.22 (t, J 7.0 Hz, CH_2CH_3), 2.42 (s, COMe), 4.09 (s, br, $CH_2C{=}N$), 4.23 (q, J 7.0 Hz, CH_2CH_3), 5.22 (s, CH), 7.7 (m, 5 H), 7.9 (m, H), 8.7 (m, 2 H), and 8.8 (s, NH, exchangeable with D_2O); $\lambda_{max.}$ 248 (log ε 4.73), 256 (4.82), 278 (4.06), 288 (4.00), 300 (4.01), 335 (3.31), and 350 nm (3.31); $\nu_{max.}$ 3 182w, br, 3 095w, br, 3 064m, 1 757w, 1 727vs, 1 677vs, 1 670(sh), and 1 648m cm^{-1}; *m/e* 360 (*M*, 10%), 315 (4), 288 (8), 287 (2), 245 (12), 230 (80), and 202 (base peak).

Methyl 2-Ethoxycarbonylhydrazono-2,3-dihydro-1H-cyclopenta[l]*phenanthrene-1-carboxylate* (5).—An acidified (concentrated hydrochloric acid, 1 drop) solution of compound (3b) (1.5 g) and ethyl carbazate (0.6 g) in methanol (70 ml) was refluxed for 1 h. The cold mixture yielded the *ester* (5) (0.7 g), prisms, m.p. 215—216 °C (decomp.) after two recrystallisations from toluene [Found: C, 71.1; H, 5.4; N, 7.3; $M^{+\cdot}$, 376; $M : (M + 1) : (M + 2) = 100 : 24.4 : 4.2$. $C_{22}H_{20}N_2O_4$ requires C, 70.2; H, 5.4; N, 7.4%; M, 376; $M : (M + 1) : (M + 2) = 100 : 25.0 : 3.8$]; δ 1.38 (t, J 7.0 Hz, CH_2CH_3), 3.70 (s, OMe), 4.0 (d, J −20.5 Hz, CHHC=N), 4.1 (d, J −20.5 Hz, CHHC=N), 4.37 (q, J 7.0 Hz, CH_2CH_3), 5.33 (s, CH), 7.7 (m, NH + 5 H), 8.1 (m, 1 H), and 8.8 (m, 2 H); $\lambda_{max.}$ 249, 257, 279, 289, 301, 335, and 351 nm; $\nu_{max.}$ 3 240w, 3 150w, 3 065w, 1 741vs, 1 705vs, br, 1 690(sh), and 1 650 cm^{-1}; *m/e* 376 (*M*, 39%), 344 (26), 330 (6), 317 (7), 298 (18), 287 (7), 272 (27), 271 (31), 256 (24), 242 (16), and 215 (base peak), with *m** 314.7 (376→344), 289.7 (376→330), and 258.1 (344→298).

Ethyl (10-Carbazoylmethyl-9-phenanthryl)acetate (6a), *and the Methyl Ester* (6b).—Hydrazine hydrate (100%, 0.5 ml) and compound (3a) (1.5 g) boiled in 96% ethanol (50 ml) for 15 min gave the *product* (6a) (1.3 g), m.p. 220 °C (preheated block) after two recrystallisations from ethanol [Found: C, 71.3; H, 5.8; N, 8.4; $M^{+\cdot}$, 336; $M : (M + 1) : (M + 2) = 100 : 23.5 : 3.3$. $C_{20}H_{20}N_2O_3$ requires C, 71.4; H, 6.0; N, 8.3; M, 336; $M : (M + 1) : (M + 2) = 100 : 22.8 : 3.1$]; δ 1.29 (t, J 7.0 Hz, CH_2CH_3), 3.7 (br s, NH_2), 4.25 (q, J 7.0 Hz, CH_2CH_3), 4.26 (s, 2 × CH_2), 7.7 (m, NH + 4 H), 8.1 (m, 2 H), and 8.8 (m, 2 H); $\lambda_{max.}$ 225 (log ε 4.45), 250 (4.69), 257 (4.79), 279 (4.08), 289 (3.98), and 3.01 nm (3.99); $\nu_{max.}$ 3 310vs, br, 3 200w, br, 3 075w, 1 730vs, 1 655vs, 1 650vs, and 1 640(sh) cm^{-1}; *m/e* 336 (*M*, 19%), 318 (1), 305 (7), 304 (24), 290 (24), 277 (27), 263 (6), 262 (9), 258 (22), 249 (9), 248 (8), 231 (57), and 203 (base peak); with *m** 275.0 (336→304), 250.2 (336→290), 229.5 (290→258), 223.8 (277→249), 205.4 (262→232), 184.5 (336→249), and 146.5 (249→191).

Compound (3b) similarly yielded the *product* (6b), m.p. 232 °C (preheated block), after recrystallisation from methanol (Found: C, 70.7; H, 5.6; N, 8.8. $C_{19}H_{18}N_2O_3$ requires C, 70.8; H, 5.6; N, 8.7%); δ 3.8 (br, s, NH_2), 3.79 (s, Me), 4.27 (s, CH_2CONH), 4.31 (s, CH_2COO), 7.5 (br s, CONH), 7.7 (m, 4 H), 8.1 (m, 2 H), and 8.8 (m, 2 H) (after shaking the solution with D_2O all the NH signals disappeared); $\lambda_{max.}$ 225 (log ε 4.41), 249 (4.67), 257 (4.76), 278 (4.03), 289 (3.95), and 301 nm (4.00); $\nu_{max.}$ 3 300vs, br, 3 190w, br, 3 075w, 1 728vs, 1 658vs, and 1 625s cm^{-1}.

Methyl (10-Carbamoylmethyl-9-phenanthryl)acetate (7).—A suspension of compound (3b) (1.0 g) in methanol

(100 ml) was stirred for 1 h whilst ammonia was passed into the mixture. After 18 h evaporation of solvent afforded the *ester* (7) (0.8 g), m.p. 256—257 °C after two recrystallisations from methanol [Found: C, 74.0; H, 5.5; N, 5.0; $M^{+\cdot}$, 307; $M : (M + 1) : (M + 2) = 100 : 21.2 : 2.7$. $C_{19}H_{17}NO_3$ requires C, 74.2; H, 5.6; N, 4.7%; M, 307; $M : (M + 1) : (M + 2) = 100 : 21.3 : 2.8$]; δ 3.78 (s, Me), 4.22 (s, CH_2CONH_2), 4.32 (s, CH_2COO), 5.2(br, s, N*H*H), 6.3(br s, NH*H*), 7.7 (m, 4 H), 8.1 (m, 1 H), 8.2 (m, 1 H), and 8.7 (m, 2 H) (after shaking the solution with D_2O the NH_2 signals disappeared); $\lambda_{max.}$ 225 (log ε 4.36), 249 (4.69), 256 (4.80), 279 (4.09), 288 (3.98), and 300 nm (4.02); $\nu_{max.}$ 3 398s, 3 310m, br, 3 205s, 1 710vs, 1 665vs, and 1 628m cm^{-1}; *m/e* 307 (*M*, 19%) 290 (10), 275 (14), 264 (7), 263 (3), 262 (3), 258 (3), 247 (20), 232 (16), 231 (33), 230 (40), 204 (41), 203 (base peak), with *m** 273.4 (307→290), 260.7 (290→275), 246.3 (307→275), 221.8 (275→247), 194.1 (275→231), 184.0 (290→231), 179.3 (232→204), 178.3 (231→203), and 166.8 (247→203).

Ethyl 2-*Acetylhydrazono*-2,3-*dihydro*-1-*hydroxy*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (8).—The ester (2a) (1.6 g) was boiled in absolute ethanol (75 ml) with acetylhydrazine (0.4 ml) for 2 h, to yield the *acetylhydrazone* (8) (1.0 g) which on crystallisation from ethanol, then chloroform, gave needles, m.p. 240—241 °C [Found: C, 70.4; H, 5.3; N, 7.4; $M^{+\cdot}$, 376; $M : (M + 1) : (M + 2) = 100 : 25.0 : 4.4$. $C_{22}H_{20}N_2O_4$ requires C, 70.2; H, 5.4; N, 7.4%; M, 376; $M : (M + 1) : (M + 2) = 100 : 25.0 : 3.8$]; δ 1.04 (t, *J* 7.0 Hz, CH_2CH_3), 2.40 (s, COMe), 4.03 (d, *J* −21 Hz, C*H*HC=N), 4.20 (dq, *J* 7.0 and 2 Hz, CH_2CH_3), 4.22 (d, *J* −21 Hz, CH*H*C=N), 4.56 (s, OH), 7.7 (m, 4 H), 7.9 (m, 1 H), 8.1 (m, 1 H), 8.8 (m, 2 H), and 9.1(br, s, NH) (after shaking the solution with D_2O the OH and NH signals disappeared); δ[$(CD_3)_2SO$] 0.96 (t, *J* 7.0 Hz, CH_2CH_3), 2.20 (s, COMe), 4.04 (q, *J* 7.0 Hz, CH_2CH_3), 4.06 (d, *J* −22 Hz, C*H*HC=N), 4.24 (d, *J* −22 Hz, CH*H*C=N), 6.71 (s, OH), 7.9 (m, 5 H), 8.1 (m, H), 8.9 (m, 2 H), and 10.5(br, NH) (addition of D_2O caused the OH and NH signals to disappear); $\lambda_{max.}$ 249 (log ε 4.71), 256 (4.74), 265sh (4.42), 278 (4.18), 288 (4.06), and 301 nm (4.07); $\nu_{max.}$ 3 522m, 3 138w, 3.088w, 1 730vs, 1 681vs, 1 657m, and 1 620w cm^{-1}; *m/e* 376 (*M*, 5%), 358 (2), 318 (30), 317 (37), 303 (30), 302 (10), 289 (3), 244 (base peak), 216 (59), and 190 (34), with *m** 340.9 (376→358), 267.3 (376→317), 263.5 (317→289), 242.5 (376→302), 196.5 (303→244), 191.2 (244→216), and 187.8 (317→244).

Ethyl 2-*Ethoxycarbonylhydrazono*-2,3-*dihydro*-1-*hydroxy*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (9).—To a hot stirred solution of compound (3a) (3.2 g) in absolute ethanol (85 ml) was added ethyl carbazate (1.04 g), and the mixture boiled for 7 h and then filtered. The solid that separated (2.8 g) was recrystallised from ethyl acetate to give plates, m.p. 199—200 °C, of the *product* (9) [Found: C, 68.1; H, 5.5; N, 7.0; $M^{+\cdot}$, 406; $M : (M + 1) : (M + 2) = 100 : 26.1 : 4.7$. $C_{23}H_{22}N_2O_5$ requires C, 68.0; H, 5.5; N, 6.9%; M, 406; $M : (M + 1) : (M + 2) = 100 : 26.2 : 4.3$]; δ 1.03 (t, *J* 7.0 Hz, CH_2CH_3), 1.38 (t, *J* 7.0 Hz, $NCO_2CH_2CH_3$), 3.95 (d, *J* −21 Hz, C*H*HC=N), 4.14 (d, *J* −21 Hz, CH*H*-C=N), 4.16 (dq, *J* 7.0 and 2 Hz, CH_2CH_3), 4.35 (q, *J* 7.0 Hz, $NCO_2CH_2CH_3$), 4.63 (s, OH), 7.7 (m, 5 H), 7.9(br, s, NH), 8.1 (m, 1 H), and 8.7 (m, 2 H) (after shaking the solution with D_2O the OH and NH signals disappeared); $\lambda_{max.}$ 249 (log ε 4.90), 257 (4.98), 278 (4.06), 288 (4.03), 300 (4.05), 335 (3.95), and 350 nm (3.96); $\nu_{max.}$ 3 575w, 3 504s, 3 230w, 3 125w, 3 075w, 1 735(sh), 1 727vs, 1 695vs, and 1 655m cm^{-1}; *m/e* 406 (*M*, 23%), 388 (1), 360 (3), 333 (36), 317 (52), 287 (41), 244 (base peak), 216 (48), 190 (26), and 165 (5.5), with *m** 370.8 (406→388), 247.4 (406→317), 247.3 (333→287), 207.4 (287→244), 191.3 (244→216), 178.8 (333→244), 125.8 (287→190), and 167.1 (216→190).

Ethyl 2-*Hydrazono*-2,3-*dihydro*-1-*hydroxy*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (10).—This was prepared from compound (2a) (1.6 g) and hydrazine hydrate (0.3 ml) in boiling 96% ethanol (35 ml) containing concentrated hydrochloric acid (1 drop). After 1 h the crystals (1.4 g) were isolated from the cold mixture, and one recrystallisation from absolute ethanol afforded the *hydrazone*, m.p. 189.5—190.5 °C [Found: C, 71.7; H, 5.4; N, 8.1; $M^{+\cdot}$, 334; $M : (M + 1) : (M + 2) = 100 : 23.8 : 2.7$. $C_{20}H_{18}N_2O_3$ requires C, 71.8; H, 5.4; N, 8.4%; M, 334; $M : (M + 1) : (M + 2) = 100 : 22.8 : 3.1$]; δ 1.00 (t, *J* 7.0 Hz, CH_2CH_3), 3.89 (d, *J* −21 Hz, C*H*HCO), 4.08 (d, *J* −21 Hz, CH*H*CO), 4.16 (q, *J* 7.0 Hz, CH_2CH_3), 4.55 (s, OH), 5.46 (s, NH_2), 7.7 (m, 4 H), 7.9 (m, 1 H), 8.1 (m, 1 H), and 8.8 (m, 2 H); δ[$(CD_3)_2SO$] 0.91 (t, *J* 7.0 Hz, CH_2CH_3), 3.98 (s, CH_2CO), 4.02 (q, *J* 7.0 Hz, CH_2CH_3), 6.29 (s, OH), 6.4 (br s, NH_2), 7.7 (m, 4 H), 8.0 (m, 2 H), and 8.9 (m, 2 H) (addition of D_2O caused the OH and NH_2 signals to disappear); $\lambda_{max.}$ 249 (log ε 4.76), 256 (4.84), 278 (4.14), 288 (4.04), 300 (4.08), 333 (3.68), and 349 nm (3.71); $\nu_{max.}$ 3 410s, 3 330(sh), 3 260s, br, 3 080w, 1 765m, 1 740vs, 1 675m, and 1 635m cm^{-1}; *m/e* 334 (*M*, 3%), 302 (69), 288 (32), 261 (91), and 244 (base peak), with *m** 285.0 (320→302) and 228.1 (261→244).

2-*Hydrazono*-2,3-*dihydro*-1-*hydroxy*-1H-*cyclopenta*[l]-*phenanthrene*-1-*carbohydrazide* (11).—Repetition of the preceding experiment using twice the quantity of hydrazine hydrate, with recrystallisation from acetonitrile, gave the *hydrazone-hydrazide* which decomposed at *ca.* 225°C [Found: C, 67.4; H, 4.9; N, 17.6; $M^{+\cdot}$, 320; $M : (M + 1) : (M + 2) = 100 : 20.5 : 3.0$. $C_{18}H_{16}N_4O_2$ requires C, 67.5; H, 5.0; N, 17.5%; M, 320; $M : (M + 1) : (M + 2) = 100 : 21.3 : 2.6$]; δ[$(CD_3)_2SO$] 3.82 (d, *J* −21 Hz, C*H*HC=N), 3.93 (d, *J* −21 Hz, CH*H*C=N), 4.3(br s, =N*N*H$_2$), 6.3(br s, CONH*N*H$_2$), 6.37 (s, OH), 7.7 (m, 4 H), 7.9 (m, 1 H), 8.2 (m, 1 H), 8.8 (m, 2 H), and 9.2(br s, CONH) (addition of D_2O caused all the NH and OH signals to disappear); $\lambda_{max.}$ 249(sh), 256, 277, 287, 300, 333, and 348 nm; $\nu_{max.}$ 3 440vs, 3 375s, 3 320w, 3 160m, br, 1 695w, 1 660vs, 1 650(sh), 1 642w, and 1 592w cm^{-1}. The same product was obtained almost quantitatively from the methyl ester.

Ethyl 2,3-*Dihydro*-1-*hydroxy*-2-*phenylhydrazono*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (12).—The phenylhydrazone was obtained by the procedure described [2] by Japp and Klingemann. It had m.p. 208—209 °C (decomp.) (lit.,[2] 210—212 °C) (Found: C, 76.2; H, 5.5; N, 6.7. Calc. for $C_{26}H_{22}N_2O_3$: C, 76.1; H, 5.4; N, 6.8%); δ 1.03 (t, *J* 7.0 Hz, CH_2CH_3), 4.01 (d, *J* −20 Hz, C*H*HC=N), 4.19 (d, *J* −20 Hz, CH*H*C=N), 4.19 (dq, *J* 7.0 and 1.8 Hz, CH_2CH_3), 4.5(br s, OH), 6.9 (m, 2 H), 7.3 (m, 4 H), 7.33 (s, NH), 7.7 (m, 3 H), 8.1 (m, 1 H), and 8.8 (m, 2 H) (after shaking the solution with D_2O the OH and NH signals disappeared); $\lambda_{max.}$ 249(sh) (log ε 4.83), 256 (4.94), 279 (4.61), 287 (4.58), 300 (4.55), 333(sh) (3.85), and 349 nm (3.71); $\nu_{max.}$ 3 525m, br, 3 315m, 3 050w, 1 732(sh), 1 721vs, 1 714(sh), 1 705(sh), 1 680(sh), 1 637w, and 1 598vs cm^{-1}.

2,3-*Dihydro*-2-*hydroxy*-2-*oxo*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxamide* (13a).—A suspension of compound (2b) (1.0 g) in methanol (200 ml) was stirred as ammonia was passed through it during 3 h. After a further 6 h stirring, the solid was filtered off and boiled in methanol to afford pale green needles of the *amide* (13a) (0.2 g), m.p.

252—255 °C [Found: $M^{+\cdot}$, 291; $M:(M+1):(M+2)$ = 100 : 20.8 : 2.8. $C_{18}H_{13}NO_3$ requires M, 291; $M:(M+1):(M+2)$ = 100 : 20.2 : 2.5]; δ[$(CD_3)_2SO$] 4.67 (t, J_{AX} 6.7, J_{AB} 6.1 Hz, C*H*OH), 4.96 (d, J_{AB} 6.1 Hz, CH), 5.91 (d, J_{AX} 6.7 Hz, CHO*H*), 7.3(br, s, CON*H*H), 7.8 (m, 4 H), 8.1(br s, CONH*H*), 8.4 (m, H), and 9.0 (m, 3 H); after irradiating at δ 5.91 the signal at δ 4.67 collapsed to a doublet (J 6.1 Hz), and on adding D_2O the OH and both NH signals disappeared and the signal at δ 4.67 collapsed to a doublet; $\lambda_{max.}$ 246, 264, 283, 315, 342(sh), and 358 nm; $\nu_{max.}$ 3 390vs, br, 3 210vs, br, 3 080w, 1 720(sh), 1 690vs, 1 665vs, and 1 610s cm^{-1}; *m/e* 291 (*M*, 60%), 275 (6), 274 (28), 273 (6), 247 (18), 246 (69), 231 (51), 230 (base peak), 218 (33), 202 (33), 189 (97), 176 (17), 165 (39), and 163 (19), with *m** 258.0 (291→274), 259.9 (291→275), 214.2 (247→230), 208.0 (291→246), 193.0 (274→230), 181.8 (291→230), and 177.4 (230→202).

Methyl 2-*Ethoxycarbonylhydrazono*-2,3-*dihydro*-1-*methoxy*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (17).—Treated as for the preparation of compound (5), compound (1b) (1.53 g) gave a crude product (0.6 g) after precipitation with water, which after repeated crystallisation from benzene yielded the pale yellow *ethoxycarbonylhydrazone* (17), m.p. 218—219 °C [Found: C, 67.8; H, 5.5; N, 7.1; $M^{+\cdot}$, 406; $M:(M+1):(M+2)$ = 100 : 27.1 : 4.5. $C_{23}H_{22}N_2O_5$ requires C, 68.0; H, 5.5; N, 6.9%; M, 406; $M:(M+1):(M+2)$ = 100 : 26.1 : 4.3]; δ 1.39 (t, J 7.0 Hz, CH_2CH_3), 3.19 (s, OMe), 3.65 (s, CO_2Me), 4.06 (s, $CH_2C{=}N$), 4.59 (q, J 7.0 Hz, CH_2CH_3), 7.7 (m, 4 H), 7.9 (m, 1 H), 8.1 (br, s, NH), 8.3 (m, 1 H), and 8.7 (m, 2 H) (after shaking the solution with D_2O the NH signal disappeared); $\lambda_{max.}$ 249 (log ε 5.07), 257 (5.13), 278 (4.42), 289 (4.13), 301 (4.34), 333 (3.28), and 348 nm (3.30); $\nu_{max.}$ 3 256s, 3 180m, 3 080w, 1 745vs, 1 723vs, 1 648m, and 1 612w cm^{-1}; *m/e* 406 (*M*, 29%), 374 (5), 347 (base peak), 342 (3), 333 (9), 301 (7), 269 (5), 241 (9), 216 (6), and 176 (2), with *m** 344.6 (406→374), 312.6 374→342), 296.6 (406→347), 261.0 (347→301), and 211.5 (342→269).

Methyl 2-*Acetylhydrazono*-2,3-*dihydro*-1-*methoxy*-2-*oxo*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (18).—A mixture of compound (1b) (3.06 g) and acetylhydrazine (0.42 g), in methanol (150 ml) containing concentrated hydrochloric acid (1 drop), was shaken at room temperature for 135 h and then filtered. The residue (2.3 g), twice recrystallised from methanol, afforded needles of the *acetylhydrazone* (18), m.p. 226—228.5 °C (decomp.) [Found: C, 70.2; H, 5.2; N, 7.5; $M^{+\cdot}$, 376; $M:(M+1):(M+2)$ = 100 : 24.2 : 3.7. $C_{22}H_{20}N_2O_4$ requires C, 70.2; H, 5.4; N, 7.4%; M, 376; $M:(M+1):(M+2)$ = 100 : 25.0 : 3.8]; δ 2.46 (s, NH-COC*H*$_3$), 3.16 (s, OMe), 3.64 (s, CO_2Me), 4.18 (s, $CH_2C{=}N$), 7.7 (m, 4 H), 7.9 (m, 1 H), 8.3 (m, 1 H), 8.8 (m, 2 H), and 9.11 (s, NH, exchangeable with D_2O); $\lambda_{max.}$ 249 (log ε 4.85), 257 (4.97), 278 (4.20), 289 (4.07), 301 (4.14), 333 (3.12), and 348 nm (3.13); $\nu_{max.}$ 3 235s, 3 080w, 1 748vs, 1 715s, 1 688vs, and 1 650m cm^{-1}; *m/e* 376 (*M*, 14%), 344 (13), 316 (36), 285 (4), 275 (21), 260 (18), 243 (24), 230 (25), 229 (13), and 43 (base peak), with *m** 314.7 (376→344).

Ethyl (1,2,3,4,4a,12b-*Hexahydro*-4a-*hydroxy*-3-*oxo*-1,2-*diazatriphenylen*-12b-*yl*)*acetate* (19).—The ester (1a) (6.4 g) was dissolved in hot 96% ethanol (100 ml). Hydrazine hydrate (100%, 1.0 ml) was added and the mixture boiled for 10 min. Filtration in the cold gave the *diazatriphenylene* (19) (4.5 g), m.p. 214—215 °C, after two crystallisations from absolute ethanol (Found: C, 68.2; H, 5.6; N, 8.0. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 8.0%); δ 0.98 (t, J 7.0 Hz, CH_2CH_3), 2.40 (s, OH), 2.41 (dd, J −13.0 and 1.8 Hz, C*H*HCO$_2$), 2.70 (d, J −13.0 Hz, CH*H*CO$_2$), 3.06 (d, J −17.0 Hz, C*H*HCO), 3.22 (d, J −17.0 Hz, CH*H*CO), 3.76 (dq, J 7.0 and 2 Hz, CH_2CH_3), 5.3 (br s, chelated NH), 7.2 (br s, CONH), 7.4 (m, 5 H), 7.6 (m, H), and 7.9 (m, 2 H) (after shaking with D_2O the OH and NH signals disappeared and the signal at δ 2.41 collapsed to a doublet, J −13.0 Hz); also δ[$(CD_3)_2SO$] 0.89 (t, J 7.0 Hz, CH_2CH_3), 2.12 (d, J −13.0 Hz, C*H*HCO$_2$), 2.66 (d, J −13.0 Hz, CH*H*CO$_2$), 3.0 (s, CH_2CONH), 3.62 (q, J 7.0 Hz, CH_2CH_3), 5.39 (s, OH), 5.7 (br s, chelated NH), 7.4 (m, 6 H), 7.9 (m, 2 H), and 9.21 (s, CONH); long-range coupling was evident in the broadened signal at δ 2.12; $\lambda_{max.}$ 274 (log ε 4.14), and 293(sh) nm (3.90); $\nu_{max.}$ 3 300(sh), 3 250s, 3 177s, br (in $CHCl_3$ 3 580, 3 407, and 3 265), 3 040w, 1 732s, 1 723s, 1 657(sh), 1 640vs, br, and 1 608(sh) cm^{-1}.

The diazatriphenylene (19) (0.4 g) was dissolved in boiling acetic anhydride (1.0 ml) and the hot (50—60 °C) solution evaporated to dryness under reduced pressure. One recrystallisation from carbon tetrachloride afforded *ethyl* (1-*acetyl*-1,2,3,4,4a,12b-*hexahydro*-4a-*hydroxy*-3-*oxo*-1,2-*diazatriphenylen*-12b-*yl*)*acetate* (21) (0.35 g), m.p. 156—157 °C [Found: C, 66.7; H, 5.6; N, 7.3; $M^{+\cdot}$, 394; $M:(M+1):(M+2)$ = 100 : 25.7 : 4.0. $C_{22}H_{22}N_2O_5$ requires C, 67.0; H, 5.6; N, 7.1%; M, 394; $M:(M+1):(M+2)$ = 100 : 25.1 : 4.0]; δ 0.95 (t, J 7.0 Hz, CH_2CH_3), 2.35 (d, J −13.8 Hz, C*H*HCO$_2$), 2.61 (d, J −13.8 Hz, CH*H*CO$_2$), 2.64 (s, MeCO), 3.02 (s, OH), 3.27 (d, J −17.1 Hz, C*H*H-CONH), 3.37 (d, J −17.1 Hz, CH*H*CONH), 3.82 (q, J 7.0 Hz, CH_2CH_3), 6.62 (s, NH), 7.5 (m, 5 H), 7.6 (m, 1 H), and 7.9 (m, 2 H) (after shaking the solution with D_2O the OH signal disappeared immediately and the NH signal disappeared after some hours); $\lambda_{max.}$ 274 (log ε 4.12) and 293(sh) nm (3.89); $\nu_{max.}$ 3 332s, 3 250m, 3 060w, 1 734vs, 1 709vs, 1 685(sh), and 1 667w cm^{-1}; *m/e* 394 (*M*, 5%), 376 (13), 352 (20), 335 (20), 334 (11), 333 (7), 307 (8), 304 (3), 289 (82), 265 (45), 248 (77), 247 (90), 246 (61), and 43 (base peak), with *m** 314.5 (394→352), and 211.1 (289→247).

2,3-*Dihydro*-3-*oxo*-1,2-*diazatriphenylene* (22).—(*a*) Compound (19) (2.2 g) was placed in an oil-bath preheated to 250—260 °C. Five minutes after the compound had melted it was cooled to room temperature. After two recrystallisations, from dioxan (charcoal) followed by pyridine, this afforded pale green needles (300 mg), m.p. 310—312 °C (decomp.), of the *product* (22) [Found: C, 78.0; H, 4.1; N, 11.4; $M^{+\cdot}$, 246; $M:(M+1):(M+2)$ = 100 : 18.5 : 1.8. $C_{16}H_{10}N_2O$ requires C, 78.0; H, 4.1; N, 11.4%; M 246; $M:(M+1):(M+2)$ = 100 : 18.5 : 1.8]; δ 7.6 (m, 4 H), 7.83 (s, CHCO), 8.4 (m, 3 H), 8.8 (m, 1H), and 11.1 (br s, NH, exchangeable with D_2O); δ[$(CD_3)_2$-SO] 7.7 (m, 4 H), 8.00 (s, CHCO), 8.6 (m, 4 H), and 12.1 (br, NH); $\lambda_{max.}$ 236 (log ε 4.51), 255(sh) (4.59), 267 (4.67), 279 (4.54), 328 (3.40), and 377 nm (3.40); $\nu_{max.}$ 3 300w, 3 100w, 3 070w, 1 700(sh), 1 685(sh), 1 665vs, 1 645(sh), and 1 606s cm^{-1}; *m/e* 246 (*M*, 97%), 218 (80), 217 (3), 190 (77), 189 (base peak), and 163 (17), with *m** 193.3 (246→218), 166.3 (217→190), 165.5 (218→190), 164.6 (217→189), 163.8 (217→189), and 140.6 (189→163).

(*b*) The same product (20 mg) was obtained by a similar procedure (bath at 200—210 °C) from compound (21) (183 mg).

The Monoacetylhydrazone (23) *of* 9,10-*Phenanthraquinone*.—From acetylhydrazine (0.74 g) and the quinone (2.0 g) in absolute ethanol (25 ml), boiled for 1.5 h, there was obtained the *monoacetylhydrazone* (23) (2.41 g), orange needles from carbon tetrachloride, m.p. 164—164.5 °C

[Found: C, 72.7; H, 4.4; N, 10.6; $M^{+\cdot}$, 264; M : (M + 1) : (M + 2) = 100 : 18.6 : 2.0. $C_{16}H_{12}N_2O_2$ requires C, 72.7; H, 4.6; N, 10.6%; M, 264; M : (M + 1) : (M + 2) = 100 : 18.3 : 2.0]; δ 2.42 (s, Me), 7.5 (m, 3 H), 7.8 (m, 1 H), 8.2 (m, 2 H), 8.3 (m, 2 H), and 14.2 (br s, NH, which disappeared only after the solution had stood in contact with D_2O for 3 weeks); $\lambda_{max.}$ 242 (log ε 4.44), 249 (4.44), 270 (4.51), 293 (3.99), 303 (4.07), and 372 nm (4.08); the spectrum was unchanged on addition of dilute acid, but changed on addition of alkali to $\lambda_{max.}$ 247, 253, 262(sh), 276(sh), 370, and 390 nm; $\nu_{max.}$ 3 090w, 1 720(sh), 1 710(sh), 1 690vs, 1 665s, 1 620s, and 1 595s cm^{-1}, no absorption in the region 2 700—1 750 cm^{-1}; *m/e* 264 (*M*, 23%), 236 (2), 221 (86), 193 (64), 178 (5), and 165 (base peak). Solutions in ethanol, chloroform, and acid were yellow, solutions in alkali were colourless.

Ethyl α-Acetyl-α-acetoxy-α-(9-oxo-10H-phenanthren-10-yl)-acetate (25).—This was prepared as directed,[11] and had m.p. 151—152 °C (lit.,[11] m.p. 148 °C) [Found: $M^{+\cdot}$, 380; M : (M + 1) : (M + 2) = 100 : 24.4 : 4.1. Calc. for $C_{22}H_{20}O_6$: *M*, 380; M : (M + 1) : (M + 2) = 100 : 24.3 : 4.0]; δ 0.72 (t, 7.0 Hz, CH_2CH_3), 2.11 (s, COMe), 2.59 (s, OCOMe), 3.72 (m, CH_2CH_3), 4.31 (s, CH), 7.4 (m, 4 H), 7.7 (m, 1 H), and 8.1 (m, 3 H); no signal disappeared after the solution had stood in contact with D_2O for one week; $\lambda_{max.}$ 237(sh) (log ε 4.33), 246 (4.53), 254 (4.52), 279 (3.89), and 340 nm (3.48); $\nu_{max.}$ 3 060w, 1 750(sh), 1 743vs, 1 700s, 1 680s, and 1 598s cm^{-1}; *m/e* 380 (*M*, 22%), 338 (2), 337 (0.5), 320 (33), 251 (13), 193 (3), and 43 (base peak), with *m** 300.6 (380→338).

Hydrogenazo-9-phenanthren-10-ol (26).—(*a*) Compound (25) (0.76 g), hydrazine hydrate (100%, 0.2 ml), and absolute ethanol (10 ml) were shaken together for 3 h and then filtered. The residue, twice recrystallised from cyclohexane, yielded light-sensitive green prisms of the hydrogenazophenanthrene (26) (0.22 g), m.p. 135 °C (decomp.) (*cf.* ref. 12) [Found: C, 76.0; H, 4.4; N, 12.7; $M^{+\cdot}$, 222. Calc. for $C_{14}H_{10}N_2O$: C, 75.7; H, 4.5; N, 12.6%; *M*, 222]; δ 7.5 (m, 2 H), 7.7 (m, 2 H), 8.2 (m, 3 H), 8.5 (m, 1 H), and 13.5(br) and 13.7(br) (NH and OH respectively); after standing in contact with D_2O for one week the OH proton only had partially exchanged; $\nu_{max.}$ 3 330s, br, 3 080w, 2 110m, 2 090m, 1 675w, 1 620(sh), 1 600s, and 1 575(sh) cm^{-1}; *m/e* 222 (*M*, 57%), 194 (66), and 165 (base peak).

(*b*) Compound (23) (0.13 g) and hydrazine hydrate (0.05 ml) were boiled in absolute ethanol for 1 h, and then chilled. Recrystallisation of the solid from cyclohexane yielded compound (26) (0.04 g), m.p. 135 °C (decomp.), with an identical i.r. spectrum to that above.

2,3a-*Diamino*-3a,11b-*dihydro*-11b-*hydroxy*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxamide* (27).—Compound (1b) (3 g, finely powdered) was added to absolute ethanol (800 ml) and ammonia was passed through the suspension for 7 h. The resulting mixture was set aside for 136 d. The solid (1.3 g), isolated by filtration, was boiled in absolute ethanol to give the *amide* (27) (decomp. at *ca.* 200 °C) [Found: C, 70.2; H, 5.5; N, 14.0; $M^{+\cdot}$, 307; M : (M + 1) : (M + 2) = 100 : 20.7 : 2.2. $C_{18}H_{17}N_3O_2$ requires C, 70.3; H, 5.6; N, 13.7%; *M*, 307; M : (M + 1) : (M + 2) = 100 : 20.9 : 2.5]; δ[$(CD_3)_2SO$] 1.89br (s, CNH_2), 2.08 (d, *J* −16.2 Hz, CHH), 2.34 (d, *J* −16.2 Hz, CHH), 5.56 (s, OH), 6.97(s, br, $CONH_2$), 7.1(br s, =CNHH), 7.3 (m, 4 H), 7.7 (br s, =CNHH), and 7.9 (m, 4 H); on addition of D_2O the OH signal disappeared immediately and all the NH signals disappeared after four weeks; $\lambda_{max.}$ 263, 281, and 350 nm; $\nu_{max.}$ 3 458s, 3 368(sh), 3 340vs, br, 3 270(sh), 3 125m, br, 3 068w, 1 670s, 1 648(sh), 1 635vs, 1 622(sh), and 1 617(sh) cm^{-1}; *m/e* 307 (*M*, 49%), 291 (18), 290 (19), 289 (17), 274 (35), 273 (base peak), 272 (14), 257 (13), 256 (10), 246 (29), 245 (19), 233 (18), 231 (14), 230 (18), and 202 (24), with *m** 288.0 (290→289), 275.9 (307→291), 273.9 (307→290), 271.0 (273→272), 257.0 (290→273), 256.0 (289→272), 241.0 (274→257), and 240.0 (273→256).

2-*Acetamido*-3a-*hydroxy*-3aH-*cyclopenta*[l]*phenanthrene*-1-*carboxamide* (28).—Compound (27) (300 mg) and acetic anhydride (2 ml) were warmed on a steam-bath until solid began to separate from the clear solution (5 min). The cold mixture was filtered and the solid recrystallised from acetone–light petroleum to yield the *acetamide* (28) (34 mg), m.p. 210—212.5 °C [Found: C, 72.2; H, 4.9; N, 8.4; $M^{+\cdot}$, 332; M : (M + 1) : (M + 2) = 100 : 22.4 : 3.4. $C_{20}H_{16}N_2O_3$ requires C, 72.3; H, 4.9; N, 8.4%; *M*, 332; M : (M + 1) : (M + 2) = 100 : 22.7 : 3.1]; δ 2.14 (s, OH), 2.18 (s, Me), 5.53(br s, CONHH), 6.11 (br s, CONHH), 7.14 (s, =CH), 7.5 (m, 4 H), 7.8 (m, 2 H), 8.0 (m, 2 H), and 9.8(br s, CONH); δ[$(CD_3)_2SO$]) 2.07 (s, Me), 5.56 (s, OH), 6.87 (s, =CH), 7.3 (m, 4 H), 7.5 (m, 2 H), 7.6 (br s, CONHH), 7.8 (m, 2 H), 8.25 (br s, CONHH), and 9.2 (br s, CONH); $\lambda_{max.}$ 248 (log ε 4.64), 291 (4.02), and 353 nm (3.50); $\nu_{max.}$ 3 410w, 3 360w, 3 320s, br, 3 275(sh), 3 210(sh), 1 760w, 1 690sh, 1 670(sh), 1 665vs, 1 655(sh), 1 630s, and 1 595m cm^{-1}; *m/e* 332 (*M*, 18%), 315 (17), 299 (6), 290 (8), 289 (6), 287 (18), 273 (9), 259 (11), 246 (23), 231 (11), 230 (11), 217 (35), 189 (27), and 43 (base peak), with *m** 298.9 (332→315), 283.8 (315→299), 261.5 (315→287), 253.3 (332→290), and 224.5 (332→273).

3,3a-*Dihydro*-3a-*hydroxy*-2-*oxo*-2H-*cyclopenta*[l]*phenanthrene*-1-*carboxamide* (29).—Compound (27) (0.5 g) was boiled with aqueous sulphuric acid (5%, 25 ml) for 10 min. The greenish-yellow solid was isolated and washed well with water. Crystallisation from 96% ethanol afforded the *amide* (29) (0.23 g) as yellow rhombs, m.p. 209—210 °C (decomp.) (preheated block) [Found: C, 72.7; H, 4.4; N, 4.5; $M^{+\cdot}$, 291; M : (M + 1) : (M + 2) = 100 : 19.6 : 2.2. $C_{18}H_{13}NO_3$ requires C, 74.2; H, 4.5; N, 4.8; *M*, 291; M : (M + 1) : (M + 2) = 100 : 20.2 : 2.5]; δ 2.60 (s, OH), 3.18 (d, *J* −18 Hz, CHH), 3.37 (d, *J* −18 Hz, CHH), 5.69 (br s, CONHH), 7.4 (m, CONHH + 4 H), 7.7 (m, 1 H), 7.9 (m, 2 H), and 8.1 (m, 1 H) (after shaking the solution with D_2O the OH and NH_2 signals disappeared); δ[$(CD_3)_2SO$] 2.93 (d, *J* −18 Hz, CHH), 3.21 (d, *J* −18 Hz, CHH), 6.04 (s, OH), 7.4 (m, CONHH + 5 H), 7.7 (br s, CONHH), 7.9 (m, 1 H), and 8.1 (m, 2 H); $\lambda_{max.}$ 220(sh) (log ε 4.11), 260 (4.50), 300 (4.0), and 353 nm (3.50); $\nu_{max.}$ 3 575w, br, 3 445s, 3 360s, br, 3 148w, 3 060w, 1 725(sh), 1 698vs, 1 676vs, 1 648m, and 1 625(sh) cm^{-1}; *m/e* 291 (*M*, 53%), 274 (65), 246 (59), 232 (23), 218 (64), 204 (45), 202 (92), 189 (base peak), 178 (53), 176 (46), 165 (35), 163 (19), 152 (11), 151 (19), and 150 (18), with *m** 258.0 (291→274) and 221.0 (274→246).

The Hydrazone (30) *of Compound* (29).—Using compound (29), the reaction conditions for the preparation of compound (19) (above) gave the yellow *hydrazone* (30), m.p. 190 °C (decomp.) (Found: C, 66.1; H, 4.8; N, 13.7. $C_{18}H_{15}N_3O_2$ requires C, 70.8; H, 5.0; N, 13.8%); δ[$(CD_3)_2SO$] 3.12 (d, *J* −20 Hz, CHH), 3.22 (d, *J* −20 Hz, CHH), 5.5 (s, OH), 7.4 (m, CONHH + 5 H), 7.7 (br s, CONHH), 7.9 (m, 1 H), and 8.1 (m, 2 H) (on addition of D_2O the OH and all the NH_2 signals disappeared); $\lambda_{max.}$ 254 (log ε 4.40), 277sh (4.22), 322 (4.14), and 402 nm (3.27).

Ethyl 1-*Chloro*-2,3-*dihydro*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (31).—Prepared by reaction of alcoholic hydrogen chloride with compound (1a) as described,[2] this ester had m.p. 140—141 °C (as reported) (Found: C, 71.0; H, 4.3; Cl, 10.9. Calc. for $C_{20}H_{15}ClO_3$: C, 70.9; H, 4.4; Cl, 10.5%); δ 1.11 (t, *J* 7.0 Hz, CH_2CH_3), 4.18 (s, $COCH_2$), 4.24 (m, CH_2CH_3), 7.8 (m, 5 H), 8.1 (m, 1 H), and 8.7 (m, 2 H); $\lambda_{max.}$ 219(sh) (log ε 4.27), 257 (4.65), 281(sh) (4.16), 295(sh) (4.13), 307 (4.07), 336 (3.19), and 352 nm (3.16); $\nu_{max.}$ 3 065w, 1 774vs, 1 745vs, and 1 710w cm^{-1}.

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