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Synthesis of 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxa-cyclopenta[*l*]phenanthren-2-ols and their conversion to 2(3*H*)- and 3(2*H*)-furanones

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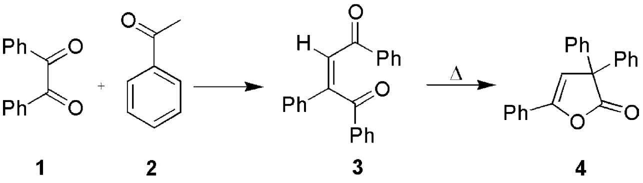
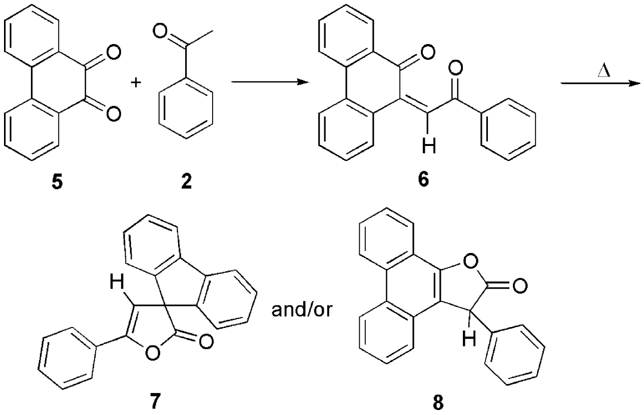
Abstract—A number of new 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols were synthesized by the base-catalyzed reaction between phenanthrenequinone and 4-substituted acetophenones in methanol. These furanols are unstable and are easily converted to stable 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenathren-2-ones in excellent yields. The furanols are converted to 2-aryl-1-oxacyclopenta[*l*]phenanthren-3-ones on treatment with acids. Plausible mechanisms for some of these new transformations are proposed.

1. Introduction

α,β-Unsaturated ketones are conveniently prepared by Aldol condensation.[1–4] Dibenzoylstyrene (**3**), for example, is synthesized by the base-catalyzed condensation between benzil (**1**) and acetophenone (**2**). Thermolysis of **3** and related systems leads to 2(3*H*)-furanones **4**, which exhibit rich photochemistry (Scheme 1).[5,6] Furthermore, due to their common occurrence in nature, oxygen containing heterocycles are frequent and important targets for synthesis either as final products or as useful synthetic intermediates. The synthesis of lactones can be achieved by the lactonization of hydroxy acids, Baeyer–Villiger oxidation, the insertion of a carbonyl group by transition metals, intramolecular cyclization of 1,4-diones, etc.[7] We reasoned that the condensation between phenanthrenequinone (**5**) and acetophenone (**2**) should lead to phenanthrenone-9-ylidene ketones **6**, which may be regarded as novel analogues of dibenzoylalkenes. Accordingly, these ketones, in principle, should undergo thermal rearrangement to give 2(3*H*)-furanone derivatives **7** and/or **8** (Scheme 2).



Scheme 1.



Scheme 2.

Close examination of the structural features of **6** reveals that it can be considered as a quinonemethide as well. Hence, **6** and its derivatives are expected to undergo transformations typical of other quinonemethides including Diels–Alder reactions, nucleophilic additions, etc. The reported procedure for the preparation of **6** involves the Wittig reaction between phenanthrenequinone and the triphenylphosphonium ylide prepared from phenacyl bromide.[8] Dimerization of **6** through a hetero Diels–Alder pathway is a major side reaction here making this procedure synthetically unviable. So, we explored the possibility of synthesizing **6** through the base-catalyzed reaction between phenanthrenequinone and acetophenones. In this article, we report our findings on the

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Keywords: Furanol; Furanone; Phenanthrenequinone; Rearrangement.

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base-catalyzed reaction between phenanthrenequinone and acetophenones.

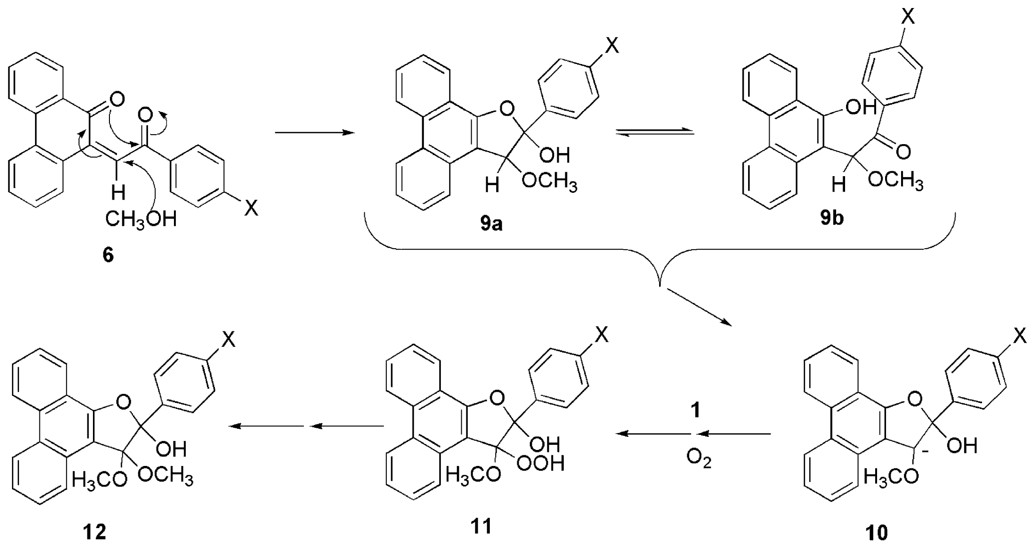
2. Results and discussion

We proposed to synthesize phenanthrenone-9-ylidene ketones **6a–f** by the condensation of phenanthrenequinone (**5**) with selected acetophenones **2a–f** in methanol in the presence of potassium hydroxide as catalyst (Scheme 2). Aryl ketones of our choice were acetophenone (**2a**), 4-methylacetophenone (**2b**), 4-methoxyacetophenone (**2c**), 4-bromoacetophenone (**2d**), 4-chloroacetophenone (**2e**), and 4-phenylacetophenone (**2f**).

The condensation of phenanthrenequinone with acetophenones in the presence of potassium hydroxide in methanol gave a product in 20–50% yield. These compounds were unstable and underwent slow degradation in solution. However, we obtained reliable elemental analysis and mass spectral data on freshly prepared samples. The UV spectra of all these compounds were dominated by absorption due to the phenanthrene residue present in them. Surprisingly, the IR spectra of the products did not indicate the presence of carbonyl groups, but showed absorption at 3400 cm^{-1} indicating the presence of a hydroxy group in the molecule. ^1H NMR spectra of **12a–f** showed the presence of two methoxy groups.[9] ^{13}C NMR spectra (noise decoupled) of two representative examples such as **12b**,**d** also indicated the absence of carbonyl groups in the molecule, but indicated the presence of two signals attributable to methoxy groups and another signal at $\sim\delta$ 108 attributable to a ketal group. Based on spectral and analytical data, the structure of the products was assigned as dihydrofuranols **12a–f**.

A possible mechanism for the formation of dihydro-2-furanol **12** involving the intermediacy of phenanthrenone-9-ylidene ketones **6** is presented in Scheme 3. Nucleophilic addition of methanol to **6** leads to the formation of **9**. The carbanion intermediate **10** generated by abstraction of the moderately acidic proton at the 3-position of **9** undergoes oxidation by single electron transfer to either oxygen[10] or phenanthrenequinone[11] followed by further transformations to give the hydroperoxide intermediate **11**.[12–14] Under the conditions of work up, **11** is transformed to the dihydrofuranol **12**.[15–18] The effect of oxygen on this reaction was studied by bubbling oxygen through the reaction mixture. No increase in the yield of **12** was observed by this method. When the reaction was repeated in degassed methanol, no noticeable change in yield or product distribution was observed. However, when the reaction was repeated with phenanthrenequinone and acetophenone taken in a 2:1 ratio, the yield of **12** improved moderately (35% vs 30%) suggesting a possible additional role for phenanthrenequinone on the course of the reaction. The poor solubility of phenanthrenequinone in other solvents such as ethanol, and *t*-butanol prevented us from carrying out the reaction in these solvents.

The dihydrofuranol derivatives **12a–f** underwent facile thermal rearrangement when heated up to their respective melting points. Neat thermolysis of **12a–f** in sealed tubes gave **14a–f** as colorless crystalline solids in high yield (>80%). The structures of **14a–f** were arrived at on the basis of spectral and analytical data. All the thermolysis products **14a–f** showed strong IR absorptions at ~1813 cm^{-1} indicating the presence of a γ-lactone component in the molecule. UV absorption spectra of these compounds are similar to that of phenanthrene indicating the presence of phenanthrene components. ^1H NMR spectra of **14a–f** showed a singlet at $\sim\delta$ 3.4 (3H) indicating the presence of a single methoxy group. In the ^{13}C NMR spectra, signals were observed at $\sim\delta$ 54 (OCH_3), 85, 114–150 (aromatic) and 175 (C=O). Mass spectral data suggested the loss of elements of methanol from the furanol precursors. Based on these data, the compounds were assigned the phenanthro-2(3*H*)-furanone structures **14a–f**. The structures of these compounds were unequivocally determined by single crystal X-ray diffraction analysis of a representative example such as **14a** (Fig. 1).[19] The mechanism for the formation of phenanthro-2(3*H*)-furanones is given in Scheme 4. Upon heating, loss of a molecule of methanol from **12** and consequent bond



Scheme 3. X = (a) H, (b) CH_3, (c) OCH_3, (d) Br, (e) Cl, (f) Ph.

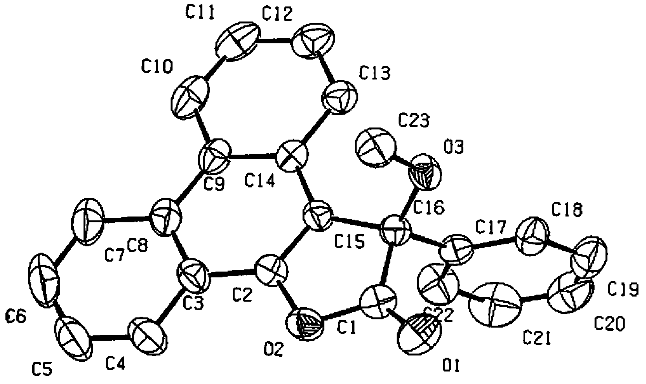
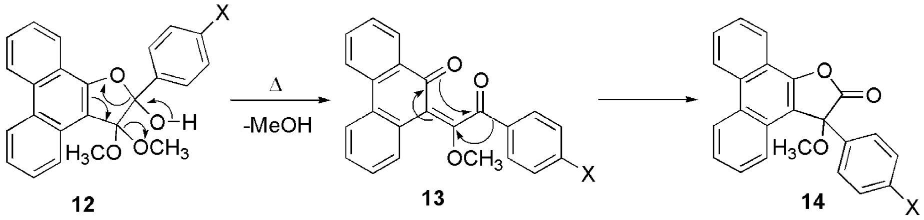


Figure 1. ORTEP diagram of molecular structure of **14a** in the crystal.

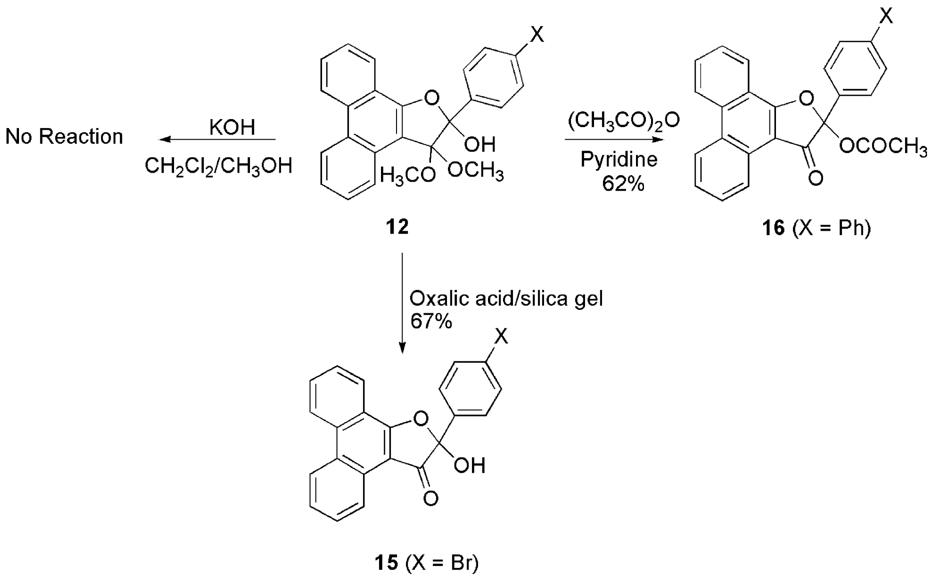
reorganizations lead to the formation of methoxydibenzoylalkene **13**. Subsequently **13** undergoes thermal transformation analogous to that reported for other dibenzoylalkenes to yield the corresponding 2(3*H*)-furanone **14**.[5,6] Our attempts to isolate **13** were not successful.

The thermolysis of **12** in refluxing *o*-dichlorobenzene also yielded **14** in comparable yields. In continuation, we carried out the neat thermolysis of **12** in an open vessel and obtained the furanones **14** in near quantitative amounts. Thermogravimetric analysis of **12a** indicated that its decomposition is completed in the narrow temperature range between 130 and 140 °C. The observed transformation appears to be a three-stage process.[20] The unstable nature of **12a–f** was further illustrated by a simple NMR experiment: ^{1}H NMR spectra of **12a–f** were collected over a period of 0–120 h. Freshly prepared samples of **12a–f** in $CDCl_3$ gave acceptable ^{1}H NMR spectra. However, ^{1}H NMR spectra of these samples recorded after storing at room temperature for 48–120 h indicated complete transformation of **12a–f** to **14a–f**. While this experiment gave no evidence in support of the formation of the dibenzoylalkene-type intermediate **13**, it indicated that the nature of the substituents on the 2-aryl group has a remarkable effect on the relative stability of these furanols. Bromo (**12d**), chloro (**12e**), and phenyl (**12f**) substituents at the fourth position of the 2-aryl moiety seem to impart higher stability to these furanols. On the other hand, compounds **12a**,**b** were particularly unstable and underwent fast conversion to **14a**,**b**.

Furanol **12** may be considered as the dimethylketal of 3(2*H*)-furanone **15**. 3(2*H*)-Furanone moiety is identified as a central structural unit in a growing number of natural products including simple compounds such as bullatenone[21] and geipavarin[22] and more complex compounds such as jatrophone, eremantholide,[23] and lychnophorolide.[24] Many of these natural products possess significant tumor-inhibiting properties. Therefore, the synthesis of 3(2*H*)-furanones has attracted considerable attention.[25–28] So, it was of interest to us to study the conversion of **12** to **15**. Treatment of **12** with base did not lead to any reaction. However, treatment of **12** with acid led to the transformation to 3(2*H*)-furanone **15**. Further, we acetylated a representative furanol derivatives, **12f** using acetic anhydride in



Scheme 4. X = (a) H, (b) CH_3, (c) OCH_3, (d) Br, (e) Cl, (f) Ph.



Scheme 5.

pyridine. Under these conditions, the acetylated phenanthro-3(2*H*)-furanone **16** was formed in 62% yield (Scheme 5).

3. Conclusions

In summary, we have synthesized several phenanthrofuranols by the base-catalyzed reaction between phenanthrenequinone and acetophenones. These phenanthrofuranols are converted to 2(3*H*)- or 3(2*H*)-furanones in near-quantitative yields under suitable reaction conditions. The furanone derivatives thus obtained have immense potential for further investigations.

4. Experimental section

4.1. General procedures

All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica gel or aluminum sheets coated with silica gel (Merck) were used for thin layer chromatography. Visualization was achieved by exposure to iodine vapor or UV radiation. Column chromatography was carried out with slurry-packed silica gel (Qualigens 60–120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Brucker 300 FT-NMR spectrometer with tetramethylsilane as internal standard.

4.2. Starting materials

Phenanthrenequinone (**1**) and acetophenone (**2**) were purchased from E. Merck and were used as obtained. Ketones **2b–f** were prepared using a known procedure.[29]

4.3. Preparation of 12a–f

12a–f were prepared by the condensation of phenanthrenequinone with appropriate acetophenone derivatives in the presence of potassium hydroxide in methanol. In a typical experiment, a mixture of phenanthrenequinone (0.025 mol), acetophenone (0.027 mol), and powdered potassium hydroxide (1 g) in methanol (30 mL) was stirred at 60 °C for 1 h and then kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallization from a mixture (2:1) of methanol and dichloromethane.

4.3.1. 3,3-Dimethoxy-2-phenyl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (12a). Light yellow solid (30%); mp 116–118 °C (dec.); IR ν_{max} (KBr) 3408 cm^{-1} (OH); UV λ_{max} (CH$_3$CN) 224 (ε 20,000), 248 (ε 30,000), 302 nm (ε 5100), 359 nm (ε 2400); ^{1}H NMR (CDCl$_3$) δ 3.3 (s, 3H, OCH$_3$), 3.5 (s, 3H, OCH$_3$), 5.6 (s, 1H, OH), 7.0–8.8 (m, 12H, aromatic); ESI-MS (*m/z*): calcd for $C_{24}H_{20}NaO_4$ $[M+Na]^{+}$ 395.1. Found 394.9; HRMS $(M-CH_3OH+Na)^{+}$ found 363.0995. $C_{23}H_{16}NaO_3$ requires 363.0997; Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.10; H, 5.04.

4.3.2. 3,3-Dimethoxy-2-*p*-tolyl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (12b). Light yellow solid (20%); mp 118–120 °C (dec.); IR ν_{max} (KBr) 3406 (OH), and 2941, 1633, 1500 cm^{-1}; UV λ_{max} (CH$_3$CN) 215 (ε 14,000), 251 (ε 5800), 341 nm (ε 1500); ^{1}H NMR (CDCl$_3$) δ 2.3 (s, 3H, CH$_3$); 3.2 (s, 3H, OCH$_3$), 3.5 (s, 3H, OCH$_3$), 5.6 (s,1H, OH), 7.0–8.6 (m, 12H, aromatic); ^{13}C NMR (CDCl$_3$) δ 21.1, 51.2, 52.2, 108.7, 110.5, 121.6, 122.8, 123, 123.1, 123.5, 123.9, 124.1, 125.7, 126.6, 126.9, 127.1, 128.3, 128.4, 129.3, 130.1, 132.7, 134.6, 138.6; MS (*m/z*) 354 $\{(M-CH_3OH)^{+}\}$, 326, 221, 119, 91, and other peaks; ESI-MS (*m/z*): calcd for $C_{25}H_{22}NaO_4$ $[M+Na]^{+}$: 409.14. Found 409.2; HRMS $(M-CH_3OH+Na)^{+}$ found 377.1156. $C_{24}H_{18}NaO_3$ requires 377.1154; Anal. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.98; H, 5.63.

4.3.3. 3,3-Dimethoxy-2-(4-methoxyphenyl)-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (12c). Light yellow solid (50%); mp 136–138 °C (dec.); IR ν_{max} (KBr) 3408, 2992, and 1635 cm^{-1}; UV λ_{max} (CH$_3$CN) 248 (ε 42,000), 302 (ε 8300), 359 nm (ε 2600); ^{1}H NMR (CDCl$_3$) δ 3.2 (s, 3H, OCH$_3$), 3.5 (s, 3H, OCH$_3$), 3.6 (s, 3H, OCH$_3$), 5.6 (s, 1H, OH), 6.9–8.7 (m, 12H, aromatic); MS (*m/z*) 370 $\{(M-CH_3OH)^{+}\}$, 342, 107, and other peaks; ESI-MS (*m/z*): calcd for $C_{25}H_{22}NaO_5$ $[M+Na]^{+}$: 425.14. Found 425.1; Anal. Calcd for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51. Found: C, 74.43; H, 5.28.

4.3.4. 2-(4-Bromophenyl)-3,3-dimethoxy-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (12d). Light brown crystals (25%); mp 140–141 °C (dec.); IR ν_{max} (KBr) 3400, 2943, 1614, 1589, and 1520 cm^{-1}; UV λ_{max} (CH$_3$CN) 224 (ε 32,200), 248 (ε 37,000), 308 (ε 7100) 341 nm (ε 2000); ^{1}H NMR (CDCl$_3$) δ 3.2 (s, 3H, OCH$_3$), 3.5 (s, 3H, OCH$_3$), 5.6 (s, 1H, OH), 7.2–8.8 (m, 12H, aromatic); ^{13}C NMR δ 51.3, 52.2, 108.7, 109.9, 111.0, 122.9, 124.1, 124.2, 126.8, 127.2, 128.9, 130.8, 132.8, 136.9, 154.2; MS (*m/z*) 420 $\{(M-CH_3OH)^{+}\}$, 390, 221, 185, and other peaks; FABMS, *m/z* 453 $\{(M+H)^{+}\}$. ESI-MS (*m/z*): calcd for $C_{24}H_{20}BrO_4$ $[M+1]^{+}$: 451.9. Found: 451.1; Anal. Calcd for $C_{24}H_{19}O_4Br$: C, 63.87; H, 4.24. Found: C, 63.82; H, 4.17.

4.3.5. 2-(4-Chlorophenyl)-3,3-dimethoxy-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (12e). Light yellow crystals (20%); mp 142–143 °C (dec.); IR ν_{max} (KBr) 3419 (OH), 2949, 1637, 1603, 1506, 756 cm^{-1}; UV λ_{max} (CH$_3$CN) 209 (ε 55,000), 263 (ε 56,000), 320 (ε 8200), 410 nm (ε 3300); ^{1}H NMR (CDCl$_3$) δ 3.2 (s, 3H, OCH$_3$), 3.5 (s, 3H, OCH$_3$), 5.6 (s, 1H, OH), 6.5–8.5 (m, 13H, aromatic); MS (*m/z*) 374 $\{(M-CH_3OH)^{+}\}$, 346, 315, 139, 111, and other peaks; Anal. Calcd for $C_{24}H_{20}O_4$: C, 70.85; H, 4.71. Found: C, 71.03; H, 4.53.

4.3.6. 3-Biphenyl-4-yl-3,3-dimethoxy-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (12f). Light yellow solid (30%); mp 132–134 °C (dec.); IR ν_{max} (KBr), 3404 (OH), 1635, 1610 and 1506 cm^{-1}; UV λ_{max} (CH$_3$CN) 203 (ε 60,000), 257 (ε 59,000), 308 (ε 9200), 341 nm (ε 2400); ^{1}H NMR (CDCl$_3$) δ 3.3 (s, 3H, OCH$_3$), 3.5 (s, 3H, OCH$_3$), 5.6 (s, 1H, OH), 7.4–8.8 (m, 17H, aromatic); MS (*m*/*z*) 416 {$(M-CH_3OH)^+$}, 416, 388, 357, 181, and other peaks; ESI-MS (*m*/*z*) calcd for $C_{30}H_{25}O_4$ $[M+1]^{+}$: 449.1. Found: 448.0; HRMS $(M-CH_3OH+Na)^+$ Found: 439.1313. $C_{29}H_{20}NaO_3$ requires 439.1310; Anal. Calcd for $C_{30}H_{24}O_4$: C, 80.34; H, 5.39. Found: C, 80.30; H, 5.14.

4.4. Reaction of phenanthrenequinone and acetophenone under oxygen bubbling

A mixture of phenanthrenequinone (0.025 mol), acetophenone (0.027 mol), and powdered potassium hydroxide (1 g) in methanol (30 mL) was stirred at 60 °C, under oxygen bubbling for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **12a** (28%); mp 116–118 °C.

4.5. Reaction of phenanthrenequinone and 4-phenylacetophenone in degassed methanol

A mixture of phenanthrenequinone (0.025 mol), 4-phenylacetophenone (0.027 mol), and powdered potassium hydroxide (1 g) in degassed methanol (30 mL) was stirred at 60 °C, for 4 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **12f** (28%); mp 132–134 °C.

4.6. Reaction of 2 equiv of phenanthrenequinone with 1 equiv of acetophenone

A mixture of phenanthrenequinone (0.05 mol), acetophenone (0.025 mol), and powdered potassium hydroxide (1 g) in methanol (30 mL) was stirred at 60 °C for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **12a** (35%); mp 116–118 °C.

4.7. Thermolysis experiments

4.7.1. Neat thermolysis of 12a. The samples **12a–f** were heated in sealed tubes to give phenanthro-2(3*H*)-furanones **14a–f**. In a typical experiment, a sample of **12a** (100 mg, 0.27 mmol) was heated in a sealed tube at 150 °C for 4 h. The solid residue was chromatographed over silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **14a** (79 mg, 0.232 mmol).

4.7.2. -Methoxy-3-phenyl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one (14a). White solid (86%); mp 214–216 °C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 17,200), 222 (ε 13,000), 245 (ε 17,600), 257 (ε 14,100), 276 (ε 6300), 308 (ε 3000), 337 (ε 900), 355 nm (ε 800); ^1H NMR ($CDCl_3$) δ 3.4 (3H, s, OCH_3), 7.2–8.9 (13H, m, aromatic); MS (*m*/*z*) 340 (M^+), 312, 281, 239, 125, and other peaks; Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.22; H, 4.74.

Crystal data of (**14a**). $C_{23}H_{16}O_3$. $M=340.36$, triclinic, space group *P*1, $a=8.4695(7)$ Å, $b=10.2384(9)$ Å, $c=10.9698(5)$ Å, $\alpha=100.368(5)°$, $\beta=110.282(4)°$, $\gamma=102.529(7)°$, $U=836.51(11)$ Å^3, $Z=4$, $D_C=1.351$ g cm^{-3}, $\mu=0.715$ mm^{-1}, (Cu Kα, $\lambda=1.54180$ Å), $T=293$ K. Of 3402 reflections measured on an Enraf-Nonius CAD4 diffractometer and corrected by Psi scan for absorption, 3172 were unique ($R_{int}=0.0280$). The structure was solved by direct methods and refined on F^2 values. Hydrogen atoms were refined isotropically. $R=0.0537$ [F values, $I>2\sigma(I)$]. $wR2=0.1521$ (F^2 values, all data), goodness-of-fit = 1.141, final difference map extremes $+0.316$ and -0.225 eA^{-3}. Software: SHELXS-97, SHELXL-97.

4.7.3. 3-Methoxy-3-*p*-tolyl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one (14b). White solid (82%); mp 160–162 °C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 19,600), 223 (ε 14,000), 245 (ε 19,300), 256 (ε 15,900), 276 (ε 7100), 308 (ε 3400), 337 (ε 800), 355 nm (ε 700); ^1H NMR ($CDCl_3$) δ 2.3 (3H, s, methyl); δ 3.4 (3H, s, OCH_3); 7.0–8.9 (12H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.5, 54.3, 85.3, 114.0, 120.1, 122.6, 122.8, 123.4, 123.5, 123.7, 124.0, 124.2, 126.0, 127.5, 127.5, 127.7, 128.0, 128.3, 128.8, 128.9, 129.1, 132.6, 149.6, 175.3.; MS (*m*/*z*) 354 (M^+), 326, 91, and other peaks; Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.62; H, 5.34.

4.7.4. 3-Methoxy-3-(4-methoxyphenyl)-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one (14c). White solid (86%); mp 135–138 °C; IR ν_{max} (KBr) 1815 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 23,300), 225 (ε 20,000), 246 (ε 29,900), 257 (ε 22,000), 275 (ε 10,500), 304 (ε 5000), 339 (ε 2400), 355 nm (ε 2000); ^1H NMR ($CDCl_3$) δ 3.3 (3H, s, OCH_3), 3.8 (3H, s, OCH_3), 6.8–8.9 (12H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.2, 55.3, 85.1, 114.1, 120.0, 122.6, 122.9, 123.4, 123.5, 123.7, 124.0, 124.2, 126.0, 127.5, 127.5, 127.7, 128.0, 128.3, 128.8, 128.9, 129.2, 132.5, 149.6, 175.3.; MS (*m*/*z*) 371 (M^+), 341, 204, 135, and other peaks; Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.9. Found: C, 78.1; H, 4.94.

4.7.5. 3-(4-Bromophenyl)-3-methoxy-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one (14d). White solid (82%); mp 191–193 °C; IR ν_{max} (KBr) 1811 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 205 (ε 23,000), 226 (ε 19,500), 244 (ε 29,200), 257 (ε 21,000), 274 (ε 10,000), 304 (ε 4000), 339 (ε 2400), 355 nm (ε 2000); ^1H NMR ($CDCl_3$) δ 3.3 (3H, s, OCH_3), 7.2–8.9 (12H, m, aromatic); MS (*m*/*z*) 420 (M^+), 394, 361, 155, and other peaks; Anal. Calcd for $C_{23}H_{15}O_3Br$: C, 65.9; H, 3.61. Found: C, 65.56; H, 3.76.

4.7.6. 3-(4-Chlorophenyl)-3-methoxy-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one (14e). White solid (81%); mp 193–194 °C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O););
UV λ_{max} (CH_3CN) 208 (ε 21,400), 245 (ε 21,500), 258 (ε 17,800), 276 (ε 7900), 308 (ε 24,100), 338 (ε 1000), 354 nm (ε 900); ^1H NMR ($CDCl_3$) δ 3.3 (3H, s, OCH_3), 7.2–8.8 (12H, m, aromatic); MS (*m*/*z*) 374 (M^+), 346, 239, 163,111, and other peaks; Anal. Calcd for $C_{23}H_{15}O_3Cl$: C, 73.85; H, 4.03. Found: C, 74.02; H, 4.05.

4.7.7. 3-Biphenyl-4yl-3-methoxy-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one (14f). White solid (82%); mp 152–154 °C; IR ν_{max} (KBr), 1813 cm^{-1} (lactone C=O); UV

λ_{max} (CH_3CN) 207 (ε 41,000), 262 (ε 39,000), 306 (ε 8000), 342 nm (ε 4600) 338 (ε 2800), 356 nm (ε 1800); ^1H NMR ($CDCl_3$) δ 3.4 (3H, s, OCH_3), 7.3–8.8 (17H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.3, 85.4, 114.1, 120.1, 122.7, 123.5, 123.6, 124.2, 126.2, 126.7, 127.5, 127.6, 128.8, 128.9, 132.7, 136.2, 140.5, 142.0, 149.8, 175.1.; MS (*m*/*z*) 416 (M^+), 388, 357, 281, and other peaks; Anal. Calcd for $C_{29}H_{20}O_3$: C, 83.64; H, 4.84. Found: C, 83.48; H, 4.86.

4.8. Thermolysis in open vessel

The samples **12a–f** were thermolyzed in open vessels to give phenanthro-2(3*H*)-furanones. In a typical experiment, a sample of **12a** (100 mg, 0.27 mmol) was heated in conical flask at 150 °C for 4 h. The solid was extracted with dichloromethane. Column chromatography using a mixture (4:1) of hexane and dichloromethane gave **14a** as a white solid (75 mg, 83%).

4.9. Thermolysis in *o*-dichlorobenzene

The samples **12a–f** were refluxed in *o*-dichlorobenzene to give the corresponding phenanthro-2(3*H*)-furanones. In a typical experiment, a sample of **12a** (100 mg, 0.27 mmol) was dissolved in *o*-dichlorobenzene and refluxed for 4 h. Solvent was removed under reduced pressure. The solid was extracted with dichloromethane. Column chromatography by using a mixture of hexane and dichloromethane (4:1) gave **14a** as a white solid (71 mg, 79%).

4.10. Reaction of 12a with base

A sample of **12a** (100 mg, 0.27 mmol) was dissolved in dichloromethane (10 mL) and potassium hydroxide (0.5 g) in methanol (2 mL) was added and stirred for 12 h. The progress of the reaction was monitored by TLC. No change was observed. The solution was then refluxed for 6 h. and was monitored by TLC. The unchanged **12a** was recovered almost quantitatively (90 mg).

4.11. Reaction of 3b in acidic medium

A sample of **12d** (100 mg, 0.26 mmol) was dissolved in dichloromethane (10 mL) and oxalic acid adsorbed on silica gel was added. The mixture was stirred for 12 h. The progress of the reaction was monitored by TLC. The product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane to give **15d** as a white solid.

4.11.1. 2-(4-Bromophenyl)-2-hydroxy-2-hydroxy-1-oxacyclo-penta[l]phenanthren-3-one (15d). 67%. Mp 195–197 °C; IR ν_{max} (KBr), 3236 (OH), 1690 (C=O), 1618 and 1506 cm^{-1}; UV λ_{max} (CH_3CN) 202 (ε 40,000), 254 (ε 28,000), 306 (ε 5300), 338 nm (ε 1700); ^1H NMR ($CDCl_3$) δ 7.2–8.6 (m, aromatic and hydroxy). Anal. Calcd for $C_{22}H_{13}O_3Br$: C, 65.20; H, 3.23. Found: C, 65.30; H, 3.26.

4.12. Reaction of 12f with acetic anhydride

A sample of **12f** (100 mg, 0.22 mmol) was dissolved in dichloromethane (20 mL) and pyridine (5 mL) was added. Acetic anhydride was added dropwise to the mixture over 30 min and then refluxed for 2 h. The mixture was cooled and diluted with dichloromethane. Then it was washed with dil. H_2SO_4, sodium bicarbonate, and with water. The organic layer was separated, dried over anhydrous sodium sulfate, and solvent was evaporated to give **16f**. It was then recrystallised from a mixture (2:1) of dichloromethane and hexane.

4.12.1. 2-Biphenyl-4-yl-3-oxo-2,3-dihydro-1-oxacyclopenta-[*l*]phenanthren-2-yl acetate (16f). White solid (62%); mp 182–185 °C; IR ν_{max} (KBr), 1774, 1713, 1620, 1600 cm^{-1}; UV λ_{max} (CH_3CN) 202 (ε 45,000), 255 (ε 31,000), 306 (ε 8200), 340 nm (ε 2100); ^1H NMR ($CDCl_3$) δ 2.3 (3H, s, acetoxy), 7.2–8.8 (17H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.7, 102.0, 108.0, 109.0, 120.8, 122.9, 123.1, 123.7, 124.0, 126.1, 126.9, 127.1, 127.3, 127.5, 127.7, 128.8, 131.8, 132.0, 136.0, 140.3, 143.0, 168.3, 171.2, 194.2; MS (*m*/*z*) 444 (M^+), 386, 263, 181, and other peaks; Anal. Calcd for $C_{30}H_{20}O_4$: C, 81.07; H, 4.54. Found: C, 81.30; H, 4.14.

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References and notes

1. Nielsen, A. T.; Houliban, W. J. *Org. React.* **1968**, *16*, 1–438.
2. Claisen, L.; Claparede, A. *Ber.* **1881**, *14*, 2460–2468.
3. House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlopark, CA, 1972.
4. Perkin, W. *Ber.* **1882**, *15*, 2802–2811.
5. Lahiri, S.; Dabral, V.; George, M. V. *Tetrahedron Lett.* **1976**, *26*, 2259–2262.
6. Lahiri, S.; Dabral, V.; Mahajan, M. P.; George, M. V. *Tetrahedron* **1977**, *33*, 3247–3260.
7. Ogliaruso, M. A.; Wolfe, J. F. *Synthesis of Lactones and Lactams*; Wiley: New York, 1993.
8. Sullivan, W. W.; Ullman, D.; Shechter, H. *Tetrahedron Lett.* **1969**, *6*, 457–461.
9. ^1H NMR spectra of **12a–f** indicate the presence of varying amounts of **14a–f** as contaminants.
10. Burns, D. H.; Li, Y. H.; Shi, D. S.; Delaney, M. O. *Chem. Commun.* **1998**, 1677–1678.
11. Russel, G. A. *Am. Chem. Soc., Div. Petrol. Chem., Prepr.* **1968**, *13*(2), D56–D59. *Chem. Abstr.* **1969**, *71*, 123255.
12. Sosnovsky, G.; Zaret, E.H. Swern. **1970**, *1*, 517–560.
13. Barton, D. H. R.; Jones, D. W. *J. Chem. Soc.* **1965**, 3563–3570.
14. Russel, G. A.; Bemis, A. G. *J. Am. Chem. Soc.* **1966**, *88*, 5491–5497.
15. Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 4715–4720.
16. Sorensen, P. E.; Pedersen, K. J.; Pedersen, P. R.;

Kanagasabapathi, V. M.; Mc Clelland, K. A. *J. Am. Chem. Soc.* **1988**, *110*, 5118–5123.

17. Leussing, P. L. *J. Org. Chem.* **1990**, *55*, 666–673.
18. For the preparation of 2,3-dihydrofurans, see (a) Mawaziny, S.; Lakani, A. M. *Chim. Chron.* **1996**, *25*, 215–234. *Chem. Abstr.* **1998**, *127*, 34112. Cameroon, B.; Serge, L.; Peptiboon, P.; Zhaoyin, W.; Pierre, H.; Yongxin, H.; Gregory, H. US patent 9716,435, 1998; *Chem. Abstr.* **1998**, *127*, 34112. (c) Srogl, J. *Synthesis* **1975**, 717–724. (d) Parkanyi, C. *J. Org. Chem.* **1976**, *41*, 151–153.
19. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre. The CCDC no. 258913 has been assigned for the compound **14a**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: C44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).
20. Jose, B. Ph.D. Thesis, Cochin University of Science and Technology, Kerala, 2000.
21. Parker, W.; Aphael, R. A.; Wilkinson, D. I. *J. Chem. Soc.* **1958**, 3871–3879.
22. Dreyer, D. L.; Lee, A. *Phytochemistry* **1972**, *11*, 763–767.
23. LeQuesne, P. W.; Levery, S. B.; Menachery, M. D.; Brennan, T. F.; Onan, K. D.; Raffauf, R. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1572–1580.
24. LeQuesne, P. W.; Menachery, M. D.; Pastore, M. P.; Kelley, C. J.; Brennan, T. F.; Onan, K. D.; Raffauf, R. F. *J. Org. Chem.* **1982**, *47*, 1519–1521.
25. Smith, A. B., III; Levenberg, P. A.; Jerris, P. J.; Scarborough, R. M., Jr.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 1501–1513.
26. Smith, A. B., III; Jerris, P. J. *Tetrahedron Lett.* **1980**, *21*, 711–714.
27. Saimoto, H.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1981**, *103*, 4975–4977.
28. Shin, S. S.; Byun, Y.; Lim, K. M.; Choi, J. K.; Lee, K-W. ; Moh, J. H.; Kim, J. K.; Jeong, Y. S.; Kim, J. Y.; Choi, Y. H.; Koh, H.-J.; Park, Y.-H.; Oh, Y. I.; Noh, M.-S.; Chung, S. *J. Med. Chem.* **2004**, *47*, 792–804.
29. Vogel, A. I. *A Text Book of Practical Organic Chemistry*; English Language Book Society and Longman Group: London, 1996; pp 1012–1013.