

3-Methoxy-3-aryl-3H-1-oxacyclopenta[l]phenanthren-2-ones: Synthesis and Photochemistry

2.1. Abstract

A number of 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ols were synthesised by Claisen-Schmidt condensation reaction between phenanthrenequinone and 4-substituted acetophenones in methanol. Under the influence of heat, these furanols are readily converted to stable 3-methoxy-3-aryl-3H-1-oxacyclopenta[l]phenanthren-2-ones. Irradiation of these 2(3H)-furanone derivatives resulted in decarbonylation leading to phenanthrene derivatives. Here our endeavours on the synthesis and photochemistry of 3-methoxy-3-aryl-3H-1-oxacyclopenta[l]phenanthren-2-ones to assess the role of the methoxy substituents in facilitating light-induced acyl-oxygen bond cleavage are depicted.

2.2. Introduction

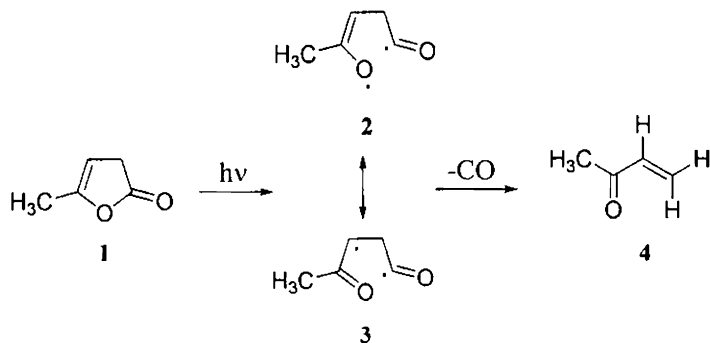
2(3H)-Furanones represent an important type of five membered heterocycles of synthetic and biological importance.¹⁻⁴ These ring systems serve as important moieties or precursors of several natural products⁵⁻⁸ (e.g., avenaciolide, plumieride, digitoxin, patulin) and a series of pharmacologically active compounds (digoxin, rofecoxib, protoanemonin, incrustoporine). In light of enormous interest in the versatile utility of these classes of heterocyclic compounds, numerous synthetic efforts have been directed towards these substances. The synthesis of these lactones can be achieved by Baeyer–Villiger oxidation, lactonisation of hydroxy acids, insertion of a

carbonyl group by transition metals, intramolecular cyclisation of 1,4-diones, etc.⁹ The methodology that we adopted for the synthesis of 2(3*H*)-furanones involved the Claisen-Schmidt condensation followed by thermal rearrangement.

Claisen-Schmidt condensation¹⁰⁻¹⁶ provides a simple and facile approach for the synthesis of α,β -unsaturated ketones. The reaction involves the nucleophilic addition of enolate ion onto a carbonyl group giving rise to the corresponding aldol which undergoes dehydration to yield the desired α,β -unsaturated carbonyl compound. The base-catalysed reaction between benzil and acetophenone, for example, yields dibenzoylstyrene in excellent yield. We surmised that the reaction between phenanthrenequinone and acetophenones should hence yield the corresponding phenanthrenone-9-ylidene ketones. However, condensation of phenanthrenequinone with acetophenones in the presence of a base in methanol yielded 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols³² arising through the intermediacy of phenanthrenone-9-ylidene ketones. When heated up to their respective melting points, these dihydrofuranols undergo facile thermal rearrangement to the required 2(3*H*) furanones.

Light induced transformations of β,γ -unsaturated lactones have been the subject of intensive study.¹⁷⁻²² Depending on the conditions applied, these lactones undergo several phototransformations including decarbonylation,¹ decarboxylation,²³ solvent addition to the double bond,²⁴ migration of aryl substituents²⁵ and dimerisation.²⁶ It has been established that decarbonylation is a singlet-mediated reaction while aryl group migration, dimerisation and solvent addition reactions are triplet mediated.^{27,28} Chapman and McIntosh have noted that a critical requirement for clean photochemical cleavage of the acyl-oxygen bond is

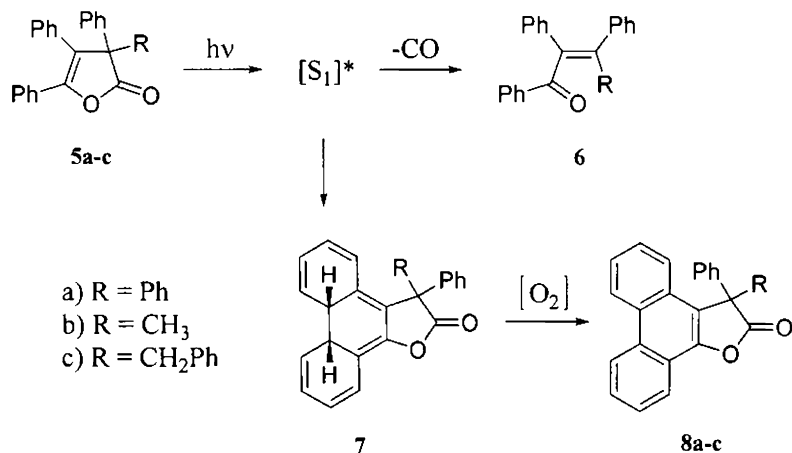
the presence of a double bond adjacent to the ether oxygen.²¹ Stabilisation of the incipient oxy radical was considered to be a determining factor in the photocleavage of the bond.



Scheme 1

While 2(3*H*)-furanones possessing this structural requirement undergo facile decarbonylation reaction, 2(5*H*)-furanones are reluctant to undergo decarbonylation. In principle, it should be possible to further enhance the propensity of 2(3*H*)-furanones to undergo decarbonylation by introducing radical-stabilizing groups at appropriate position on the furanone ring. In this chapter, we describe a successful validation of this hypothesis.

Though 3,3,5-triarylfuranones undergo phototransformations characteristic of 2(3*H*)-furanones, related phenanthrofuranones are isolated as photostable end products in certain photochemical transformations.¹⁸⁻²⁰ Lohray *et al.*²⁷ found that the photolysis of 3,3,4,5-tetraphenyl-2(3*H*)-furanone (**5a**), 3-methyl-3,4,5-triphenyl-2(3*H*)-furanone (**5b**), and 3-benzyl-3,4,5-triphenyl-2(3*H*)-furanone (**5c**) in the presence of oxygen, affords the corresponding phenanthrene derivatives **8a-c**.



Scheme 2

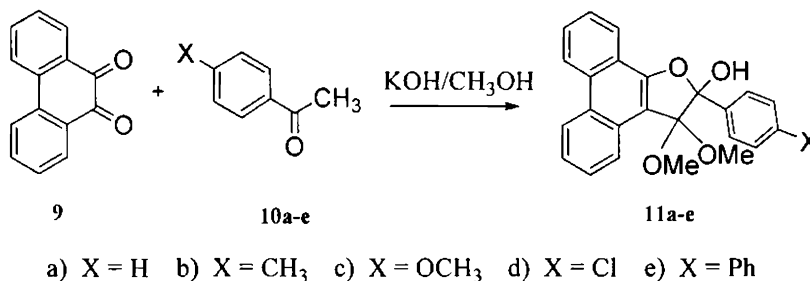
We reasoned that introduction of a radical stabilising methoxy group at the 3-position of phenanthrofuranes should enhance their propensity to undergo decarbonylation by stabilisation of the putative radical center at the 3-position. In the case of carbonyl compounds, Wagner has established that γ -alkoxy substituents enhance the rate of γ -hydrogen abstraction leading to Norrish Type II cleavage and appropriately positioned alkoxy substituents facilitate a rare δ -hydrogen abstraction reaction.^{30,31}

In the present study we have examined the photochemistry of a few phenanthro-2(3*H*)-furanones having a methoxy substituent at the 3-position. Required 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*I*]phenanthren-2-one derivatives **16a-e** were synthesised by the neat thermolysis of the corresponding 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*I*]phenanthren-2-ol derivatives **11a-e**, which in turn were generated by the condensation of phenanthrenequinone with acetophenones³²

2.3. Results and Discussion

2.3.1. Synthesis of 3,3-Dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ols 11a-e.

We employed Claisen-Schmidt condensation for the preparation of desired 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ols **11a-e**. The condensation of phenanthrenequinone (**9**) with acetophenone derivatives **10a-e** in the presence of potassium hydroxide in methanol gave products **11a-e** in 20–50% yield (Scheme 3). Aryl ketones of our choice were acetophenone (**10a**), 4-methylacetophenone (**10b**), 4-methoxyacetophenone (**10c**), 4-chloroacetophenone (**10d**) and 4-phenylacetophenone (**10e**). The structures of **11a-e** were established on the basis of analytical results and spectral data.



Scheme 3

UV spectra of all these compounds were dominated by absorption due to the phenanthrene residue present in them. The IR spectra of the products **11a-e** did not indicate the presence of carbonyl groups, but showed absorption at $\sim 3400\text{ cm}^{-1}$ indicating the presence of a hydroxy group in the molecule. ¹H NMR spectra of **11a-e** showed the presence of two methoxy groups.

^{13}C NMR spectra also indicated the absence of carbonyl groups in the molecule, but indicated the presence of two signals at $\sim\delta$ 51.24 and $\sim\delta$ 52.31 attributable to methoxy groups and another signal at $\sim\delta$ 108 attributable to a ketal group. The structure of these compounds was unequivocally determined by single crystal X-ray diffraction analysis (Figure 1) on a representative example **11d**. Crystals suitable for X-ray experiments were obtained by slow evaporation from methanol-dichloromethane mixture (3:2) at room temperature.

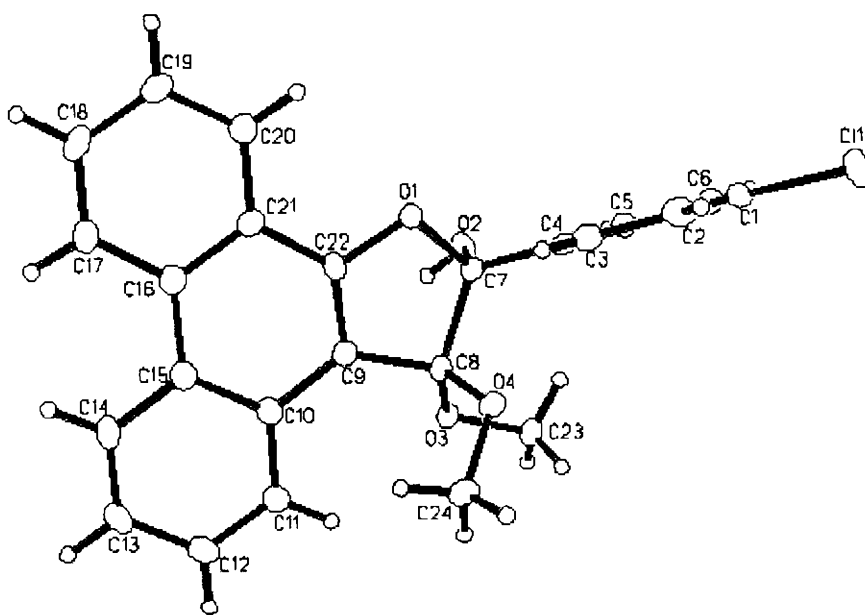
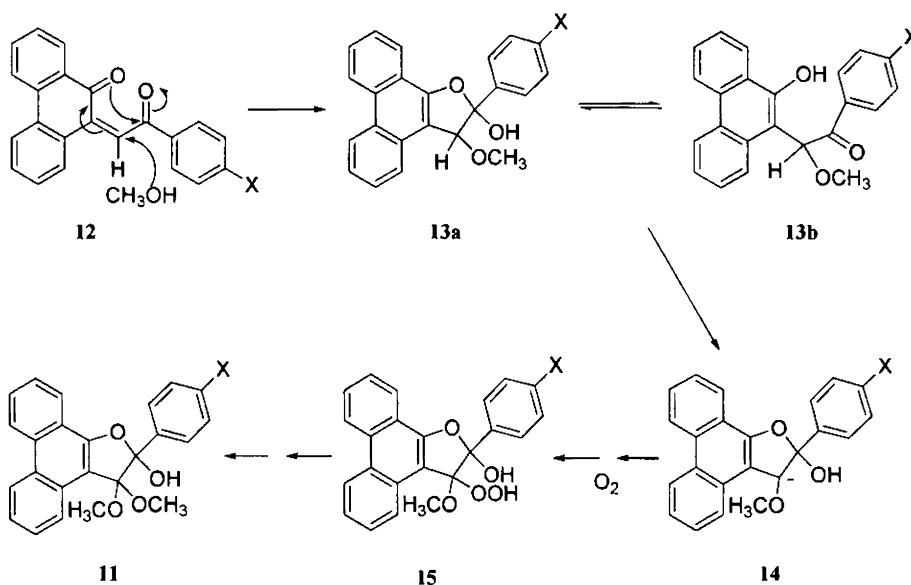


Figure 1. ORTEP diagram of molecular structure of **11d** in the crystal

A possible mechanism for the formation of dihydro-2-furanol **11** involving the intermediacy of phenanthrenone-9-ylidene ketones **12** is presented in Scheme 4. Nucleophilic addition of methanol to **12** leads to the formation of **11**. The carbanion intermediate **14** generated by abstraction of the moderately acidic proton at the 3-position of **13** undergoes oxidation by

the moderately acidic proton at the 3-position of **13** undergoes oxidation by single electron transfer to either oxygen³³ or phenanthrenequinone³⁴ followed by further transformations to give the hydroperoxide intermediate **15**.³⁵⁻³⁷ Under the conditions of work up, **15** is transformed to the dihydrofuranol **11**.³⁸⁻⁴⁰



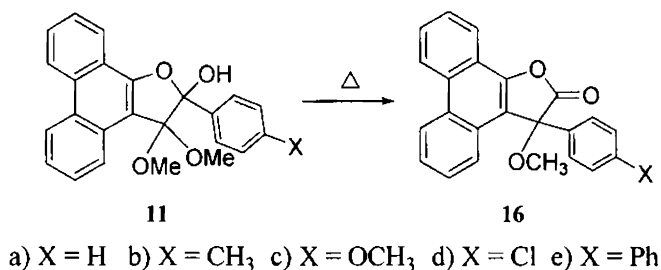
Scheme 4

2.3.2. Synthesis of 3-Methoxy-3-aryl-3H-1-oxacyclopenta[l]phenanthren-2-ones **16a-e**.

The dihydrofuranol derivatives **11a-e** underwent facile thermal rearrangement when heated up to their respective melting points. Neat thermolysis of **11a-e** in sealed tubes gave **16a-e** as colourless crystalline solids in high yield (83%).

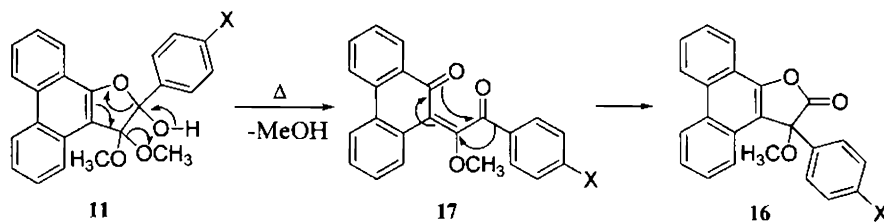
The structures of **16a-e** were arrived at on the basis of spectral and analytical data. All the thermolysis products **16a-e** showed strong IR

absorptions at $\sim 1813\text{ cm}^{-1}$ 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 **16a–e** showed a singlet at $\sim \delta 3.4$ 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 ($\text{C}=\text{O}$). The structures were further confirmed by elemental analysis, which gave acceptable data. Based on these data, the compounds were assigned the 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenathren-2-one **16a–e** structures



Scheme 5

It is interesting to note that the thermal transformation of **11** to **16** may proceed through two distinct pathways. One of mechanisms for the formation of 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenathren-2-one **16a–e** is given in Scheme 6. Upon heating, loss of a molecule of methanol from **11** and consequent bond reorganizations lead to the formation of methoxy-dibenzoylalkene **17**. Subsequently **17** undergoes thermal transformation analogous to that reported for other dibenzoylalkenes to yield the corresponding 2(3*H*)-furanone **16**.^{41,42}

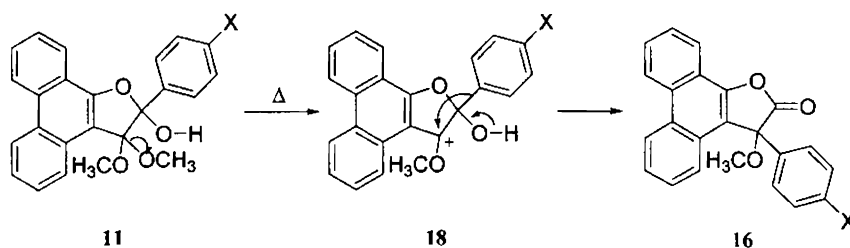


Scheme 6

To support the above proposed mechanism we attempted trapping experiment using dimethyl acetylenedicarboxylate by cycloaddition reaction. The proposed intermediate **17** here is an *o*-quinonemethide and hence may be intercepted by Diels-Alder reaction with a reactive dienophile such as DMAD. But our attempts to trap the intermediate **17** were unsuccessful and an intractable mixture resulted. Furthermore, dibenzoylalkenes rearrange to the corresponding 2(3*H*)-furanones at relatively high temperature. But the rearrangement of furanols **11** to furanones **16** proceeded under mild conditions. These observations cast doubt on the involvement of **17** as an intermediate in the observed transformation.

Alternately a pinacol-pinacolone type mechanism (Scheme 7) can also be suggested for the above formed product **16a-e**. It may be noted that the observed furanol-furanone transformation involves a 1,2-aryl migration step. If the pinacol-pinacolone-type mechanism as depicted in Scheme 7 is operating, the migration step involves 1,2-aryl migration to an electron deficient center and hence a substantial substituent effect is expected. We observed that **11c** having a 4-anisyl substituent is quite unstable and readily rearranges to yield the furanone **16c** whereas **11d** having a 4-chlorophenyl substituent is relatively more stable. These results suggest that 4-anisyl group migrates much faster than a 4-chlorophenyl group and hence a

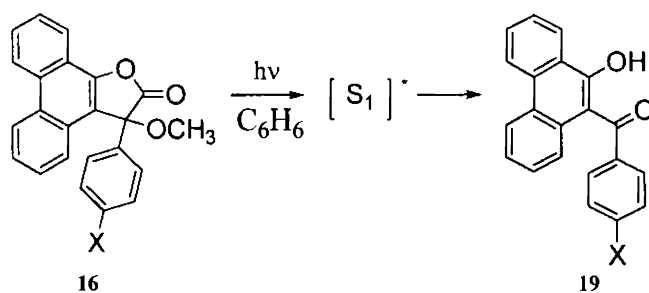
mechanism involving 1,2-aryl migration to an electron deficient center as depicted in Scheme 7 is more satisfactory. So under the reaction condition applied by us, a pinacol-pinacolone type mechanism is a better choice.



Scheme 7

2.3.3. Irradiation of 3-Methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones 16a-e.

The photolysis ($\lambda = 300$ nm) of 2(3*H*)-furanones **16a-e** in benzene gave 10-hydroxy-phenanthren-9-yl methanone derivatives **19a-e** as yellow crystalline compounds in good yields (64-68%). Structures of these compounds were arrived at on the basis of spectral and analytical data.



a) X = H b) X = CH₃ c) X = OCH₃ d) X = Cl e) X = Ph

Scheme 8

IR spectrum of **19a-e** showed the presence of hydroxyl and carbonyl group in the molecule. ^{13}C NMR spectrum also showed a peak at $\sim \delta$ 199 confirming the presence of a carbonyl carbon. The structure of these compounds was unequivocally determined by single crystal X-ray diffraction analysis of a representative example such as **19c**. The crystal of this compound was grown in a mixture (3:2) of chloroform and hexane. The crystal data and structural refinement parameters are given in Table 1 at the end of the chapter.

The unusually low carbonyl stretching frequency observed (1620 cm^{-1}) is attributable to strong intramolecular hydrogen bonding interaction between hydroxyl and carbonyl groups present in the molecule. This was further corroborated by the D-H...A distances and angle around H atoms ($\text{O1-H1}\dots\text{O2}=1.731\text{ \AA}$, 145.9° ; $\text{O1}'\text{-H1}'\dots\text{O2}'=1.745\text{ \AA}$, 148.9°) as determined from the X-ray structure.

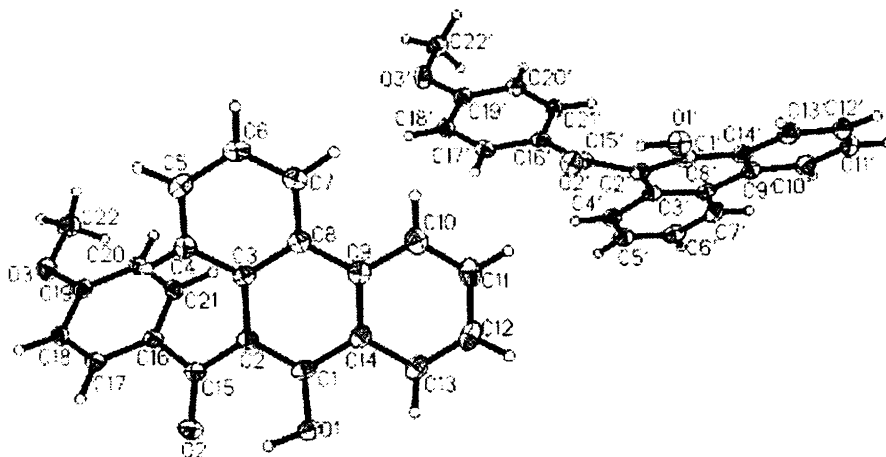


Figure 2. ORTEP diagram of molecular structure of **19c** in the crystal

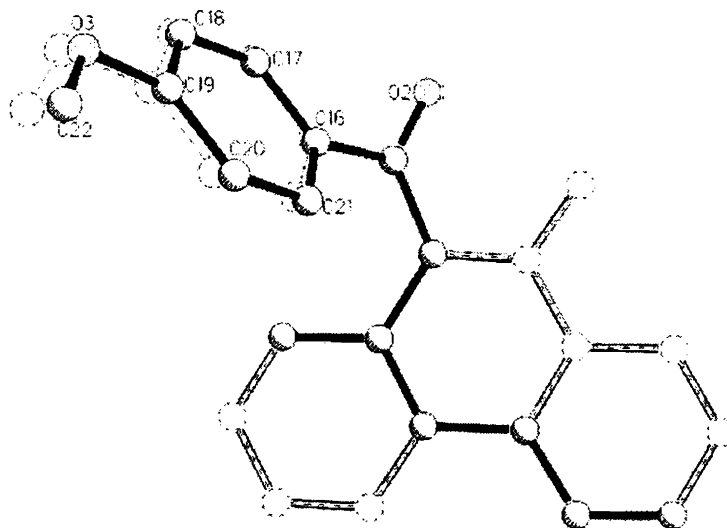


Figure 3. *Overlay of the two unique molecules in 19c*

(Solid bonds show the molecule 1 and dotted line bonds represent the 2nd molecule)

The compound crystallises in monoclinic space group $P2_1$ with two unique molecules in the asymmetric unit. As $Z' > 1$, molecular overlay was used to look for differences in the two unique molecules. The overlay (OFIT, Shelxtl) shows that the phenanthrene rings match very well (weighted RMS deviation = 0.0174). The molecules start to diverge after the carbonyl group ($c16-c16' = 0.143 \text{ \AA}$, $c19-c19' = 0.415 \text{ \AA}$). The two unique molecules in the asymmetric unit use the methoxy oxygen and a H atom of the phenanthrene ring to form 1-D chain mediated through C-H...O contacts. These chains are interconnected to form square-like network (Figure 4). Each square is formed by two different symmetry independent molecules and hence the square is not symmetrical [$O3' \cdots H11'(x, y-1, z) = 2.465$, $O3 \cdots H12(x, y-1, z) = 2.688$, $O2' \cdots H22b(x, y+1, z) = 2.595$, $O2 \cdots$

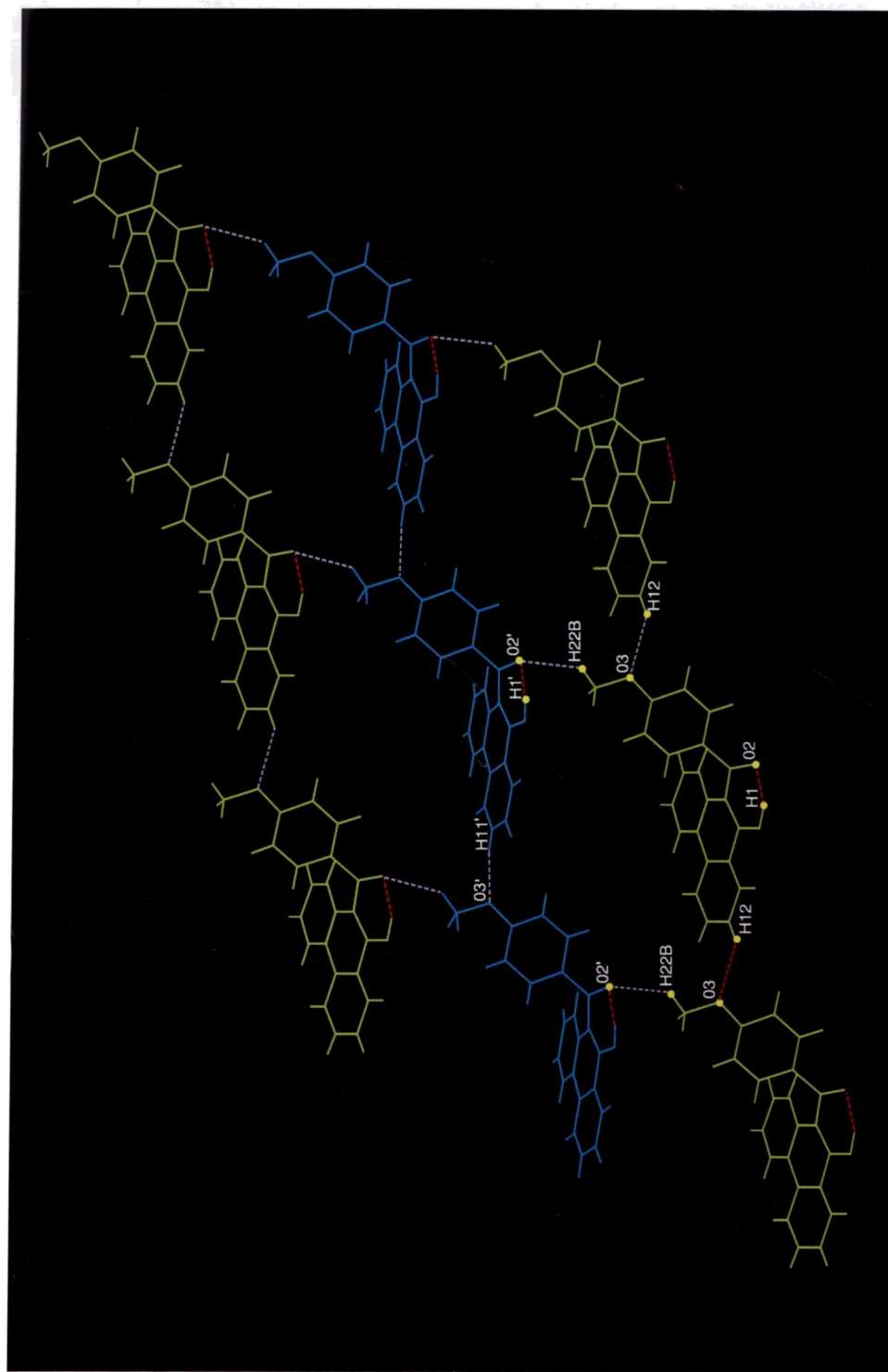
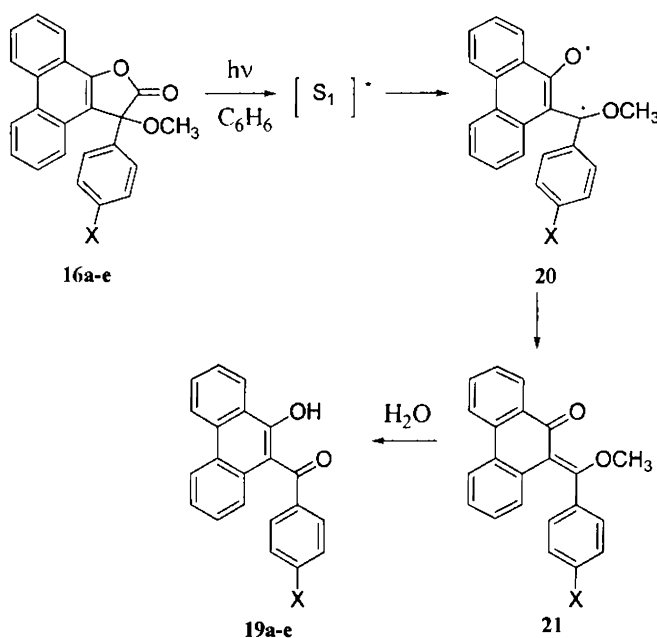


Figure. 4. The Square like network and hydrogen bonding in the crystal lattice of 19c.

H22d (x, y-1, z) = 2.694 Å]. It may be noted that the supramolecular grid like pattern formation is controlled by the methoxy group present on the 9-aryl substituent.

The formation of photoproducts **19a-e** on irradiation in benzene or acetone can be understood in terms of the pathways shown in Scheme 9).^{21,27}



a) X = H b) X = CH₃ c) X = OCH₃ d) X = Cl e) X = Ph

Scheme 9

The initial excitation of the 2(3*H*)-furanones to the corresponding singlet excited state resulted in decarbonylation to the diradical intermediate **20** which undergoes bond reorganization to give the quinonemethide intermediate **21**. It appears that the methoxy group has a major role to play on the facile decarbonylation here *vis-à-vis* other

phenanthrofuranones. Hydrolytic elimination of methanol followed by tautomerisation will eventually lead to **19**. Since the phenanthrene-furanones **16a-e** absorbed strongly in the 220 – 400 nm range, it was not feasible to carry out sensitized irradiation of these compounds using common triplet sensitizers.

In order to generate further support for the involvement of intermediates such as **20** and **21**, we carried out trapping experiments. Our attempts to trap the quinonemethide intermediate **21** by a 4+2 cycloaddition reaction with DMAD, however, were not successful. We conclude that the hydrolysis of the vinyl ether component in **21** is much faster than the cycloaddition reaction under the reaction conditions applied by us. A good hydrogen atom donor such as 2-propanol was used to trap radical intermediate **20** by *H*-transfer. However, trapping experiment using 2-propanol was unsuccessful indicating the reactive nature of **20**. Though the proposed intermediates could not be intercepted, the photochemical transformation of **16a-e** involving acyl-oxygen bond cleavage appears to be analogous to that of other 2(3*H*)-furanones.^{21,22,24,25}

2.4. Conclusion

We have synthesised several 3-methoxy-3-aryl-3*H*-1-oxacyclopenta-*[l]*phenanthren-2-one derivatives and examined their photochemistry. We have demonstrated that the methoxy group in the lactone ring has a profound effect on the acyl-oxygen bond cleavage leading to decarbonylation reaction. Our attempts to trap the proposed intermediates by using DMAD and 2-propanol were unsuccessful presumably due to their reactive nature.

2.5. Experimental

2.5.1. 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 aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours 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 infra red spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. All steady state irradiations were carried out using Rayonet Photochemical Reactor (RPR). Solvents for photolysis were purified and distilled before use. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Bruker 300 FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane. Elemental analysis was performed using Elementar Systeme (Vario ELIII) at STIC, Kochi.

2.5.2. Starting Materials: Phenanthrenequinone, acetophenone, 4-methylacetophenone, 4-chloroacetophenone, 4-methoxyacetophenone, 4-chloroacetophenone and 4-phenylacetophenone were purchased from Sigma Aldrich and were used as obtained.

2.5.2.1. 3,3-Dimethoxy-2-phenyl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (11a): Prepared using a known procedure (30%, mp 116-118 $^{\circ}\text{C}$).³²

2.5.2.2. 3,3-Dimethoxy-2-(4'-methylphenyl)-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ol (11b): Prepared using a known procedure (20%, mp 118-120 °C).³²

2.5.2.3. 3,3-Dimethoxy-2-(4'-chlorophenyl)-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ol (11c): Prepared using a known procedure (25%, mp 142-143 °C).³²

2.5.2.4. 3,3-Dimethoxy-2-(4'-methoxyphenyl)-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ol (11d): Prepared using a known procedure (40%, mp 136-138 °C).³²

2.5.2.5. 3,3-Dimethoxy-2-(4'-phenylphenyl)-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ol (11e): Prepared using a known procedure (30%, mp 132-134 °C).³²

2.5.3. Synthesis of 3-Methoxy-3-aryl-3H-1-oxacyclopenta[l]phenanthren-2-ones (16a-e).

Phenanthrenefuranones **16a-e** were synthesised by neat thermolysis of the corresponding phenanthrofurans **11a-e**.

2.5.3.1. Thermolysis of 11a: A sample of **11a** (100 mg, 0.27 mmol) was thermolysed in a sealed tube at 180 °C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16a** as a white solid.

Compound 16a: (86%); mp 214-216 °C; IR ν_{\max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{\max} (CH₃CN) 208 (ϵ 17,200), 222 (ϵ 13,000), 245 (ϵ 17,600), 257 (ϵ 14,100), 276 (ϵ 6,300), 308 (ϵ 3,000), 337 (ϵ 900), 355 nm (ϵ 800); ¹H NMR (CDCl₃) δ 3.41 (3H, s, methoxy protons), 7.21-8.93 (13H, m, aromatic

protons) Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.22; H, 4.76.

2.5.3.2. Thermolysis of 11b: A sample of **11b** (100 mg, 0.26 mmol) was thermolysed in a sealed tube at 180 °C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16b** as a white solid

Compound 16b: (81%); mp 160-162 °C; IR ν_{\max} (KBr) 1815 cm^{-1} (lactone C=O); UV λ_{\max} (CH₃CN) 208 (ϵ 19,600), 223 (ϵ 14,000), 245 (ϵ 19,300), 256 (ϵ 15,900), 276 (ϵ 7,100), 308 (ϵ 3,400), 337 (ϵ 800), 355 nm (ϵ 700); ¹H NMR (CDCl₃) δ 2.31 (3H, s, methyl); δ 3.35 (3H, s, methoxy protons); 7.10-8.90 (12H, m, aromatic protons); Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.62; H, 5.34.

2.5.3.3. Thermolysis of 11c: A sample of **11c** (100 mg, 0.22 mmol) was thermolysed in a sealed tube at 180 °C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16c** as a white solid

Compound 16c: (82%); mp 193-194 °C; IR ν_{\max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{\max} (CH₃CN) 208 (ϵ 21,400), 245 (ϵ 21,500), 258 (ϵ 17,800), 276 (ϵ 7,900), 308 (ϵ 24,100), 338 (ϵ 1000), 354 nm (ϵ 900); ¹H NMR (CDCl₃) δ 3.22 (3H, s, methoxy protons), 7.24-8.87 (12H, m, aromatic protons); Anal. Calcd for $C_{23}H_{15}O_3Cl$: C, 73.85; H, 4.03. Found: C, 74.02; H, 4.05.

2.5.3.4. Thermolysis of 11d: A sample of **11d** (100 mg, 0.25 mmol) was thermolysed in a sealed tube at 180 °C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16d** as a white solid

Compound 16d: (86%); mp 135-138 °C; IR ν_{\max} (KBr) 1815 cm^{-1} (lactone C=O); UV λ_{\max} (CH₃CN) 208 (ϵ 23,300), 225 (ϵ 20,000), 246 (ϵ 29,900), 257 (ϵ 22,000), 275 (ϵ 10,500), 304 (ϵ 5,000), 339 (ϵ 2,400), 355 nm (ϵ 2,000); ¹H NMR (CDCl₃) δ 3.38 (3H, s, methoxy protons), 3.47 (3H, s, methoxy protons), 6.96-8.09 (12H, m, aromatic protons); ¹³C NMR (CDCl₃) δ 54.20, 55.26, 85.10, 114.09, 120.04, 122.55, 122.9, 123.38, 123.52, 123.74, 124.01, 124.19, 126.27, 127.49, 127.51, 127.69, 127.99, 128.32, 128.78, 128.91, 129.18, 132.54, 149.59, 175.28.; Anal. Calcd for C₂₄H₁₈O₄: C, 77.82; H, 4.9. Found: C, 78.1; H, 4.94.

2.5.3.5. Thermolysis of 11e: A sample of **11e** (100 mg, 0.27 mmol) was thermolysed in a sealed tube at 180 °C for 6 h. The solid was extracted with dichloromethane. Column chromatography by using a mixture (3:2) of hexane and dichloromethane gave (**16e**) as a white solid

Compound 16e: (81%); mp 152-154 °C; IR ν_{\max} (KBr), 1810 cm^{-1} (lactone C=O); UV λ_{\max} (CH₃CN) 207 (ϵ 41,000), 262 (ϵ 39,000), 306 (ϵ 8,000), 342 nm (ϵ 4,600) 338 (ϵ 2,800), 356 nm (ϵ 1,800); ¹H NMR (CDCl₃) δ 3.35 (3H, s, methoxy protons), 7.31-8.86 (17H, m, aromatic protons); Anal. Calcd for C₂₉H₂₀O₃: C, 83.64; H, 4.84. Found: C, 83.48; H, 4.86.

2.5.4. Irradiation of Phenanthrenefuranones 16a-e

Direct irradiation of **16a-e** resulted in the formation of the corresponding 10-hydroxy-phenanthren-9-yl-methanones **19a-e** in good yields.

2.5.4.1. Irradiation of 16a: A benzene solution of **16a** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel.

Compound 19c:(68%); mp 152-154°C; IR ν_{\max} (KBr) 3420 cm^{-1} (OH), 1618 cm^{-1} , and 1605 cm^{-1} ; UV λ_{\max} (CH_3CN) 245 (ϵ 21,500), 252 (ϵ 13,000), 290 (ϵ 4,600), 369 nm (ϵ 1700); ^1H NMR (300 MHz, CDCl_3) δ 7.06-8.80 (m, aromatic and hydroxy protons); Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{O}_2$: C, 75.80; H, 3.94. Found: C, 75.69; H, 4.01.

2.5.4.4. Irradiation of 16d: A benzene solution of **16d** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19d** as a yellow crystalline compound.

Compound 19d: (66%); mp 156-157°C; IR ν_{\max} (KBr) 3425 cm^{-1} (OH), 1615 cm^{-1} , and 1600 cm^{-1} ; UV λ_{\max} (CH_3CN) 251 (ϵ 21,000), 293 (ϵ 9,500), 375 nm (ϵ 1,500); ^1H NMR (CDCl_3) δ 3.76 (3H, s, methoxy), 6.80-8.54 (13H, m, aromatic and hydroxy protons); ^{13}C NMR (CDCl_3) δ 55.01, 104.40, 114.03, 122.41, 122.90, 124.46, 125.12, 126.25, 127.50, 127.66, 128.34, 129.43, 130.33, 132.53, 159.78, 199.94; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{O}_3$: C, 80.47; H, 4.9. Found: C, 80.18; H, 4.94.

2.5.4.5. Irradiation of 16e: A benzene solution of **16e** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19e** as a yellow crystalline compound.

Compound 19e: (65%); mp 153-155°C; IR ν_{\max} (KBr), 3420 (OH), 1615 cm^{-1} , and 1600 cm^{-1} ; UV λ_{\max} (CH_3CN) 217 (ϵ 55,000), 255 (ϵ 52,000), 302 (ϵ

8,500), 376 nm (ϵ 2,100); ^1H NMR (CDCl_3) δ 6.82-8.59 (m, aromatic and hydroxy protons); Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{O}_2$: C, 86.61; H, 4.85. Found: C, 86.38; H, 5.14.

2.5.5. Irradiation of 16a in the presence of Dimethyl acetylenedicarboxylate (DMAD)

A benzene solution of **16a** (0.73 mmol in 150 mL) containing DMAD (590 mg, 4.14 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19a** (64%).

2.5.6. Irradiation of 16a in the presence of 2-Propanol

A benzene solution of **16a** (0.73 mmol in 150 mL) containing 2-propanol (0.20 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19a** (60%).

Compound 19c:(68%); mp 152-154°C; IR ν_{\max} (KBr) 3420 cm^{-1} (OH), 1618 cm^{-1} , and 1605 cm^{-1} ; UV λ_{\max} (CH₃CN) 245 (ϵ 21,500), 252 (ϵ 13,000), 290 (ϵ 4,600), 369 nm (ϵ 1700); ¹H NMR (300 MHz, CDCl₃) δ 7.06-8.80 (m, aromatic and hydroxy protons); Anal. Calcd. for C₂₁H₁₃O₂: C, 75.80; H, 3.94. Found: C, 75.69; H, 4.01.

2.5.4.4. Irradiation of 16d: A benzene solution of **16d** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19d** as a yellow crystalline compound.

Compound 19d: (66%); mp 156-157°C; IR ν_{\max} (KBr) 3425 cm^{-1} (OH), 1615 cm^{-1} , and 1600 cm^{-1} ; UV λ_{\max} (CH₃CN) 251 (ϵ 21,000), 293 (ϵ 9,500), 375 nm (ϵ 1,500); ¹H NMR (CDCl₃) δ 3.76 (3H, s, methoxy), 6.80-8.54 (13H, m, aromatic and hydroxy protons); ¹³C NMR (CDCl₃) δ 55.01, 104.40, 114.03, 122.41, 122.90, 124.46, 125.12, 126.25, 127.50, 127.66, 128.34, 129.43, 130.33, 132.53, 159.78, 199.94; Anal. Calcd. for C₂₂H₁₆O₃: C, 80.47; H, 4.9. Found: C, 80.18; H, 4.94.

2.5.4.5. Irradiation of 16e: A benzene solution of **16e** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19e** as a yellow crystalline compound.

Compound 19e: (65%); mp 153-155°C; IR ν_{\max} (KBr), 3420 (OH), 1615 cm^{-1} , and 1600 cm^{-1} ; UV λ_{\max} (CH₃CN) 217 (ϵ 55,000), 255 (ϵ 52,000), 302 (ϵ

8,500), 376 nm (ϵ 2,100); ^1H NMR (CDCl_3) δ 6.82-8.59 (m, aromatic and hydroxy protons); Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{O}_2$: C, 86.61; H, 4.85. Found: C, 86.38; H, 5.14.

2.5.5. Irradiation of 16a in the presence of Dimethyl acetylenedicarboxylate (DMAD)

A benzene solution of **16a** (0.73 mmol in 150 mL) containing DMAD (590 mg, 4.14 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19a** (64%).

2.5.6. Irradiation of 16a in the presence of 2-Propanol

A benzene solution of **16a** (0.73 mmol in 150 mL) containing 2-propanol (0.20 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19a** (60%).

Table 1. Crystal data and structure refinement for compound 19c

Empirical formula	C ₂₂ H ₁₆ O ₃
Formula weight	328.35
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, P2 ₁
Unit cell dimensions	a = 7.2298(3) Å α = 90°. b = 13.7492(7) Å β = 92.621(2)°. c = 16.0107(8) Å γ = 90°.
Volume	1589.86(13) Å ³
Z, Density (calculated)	4, 1.372 Mg/m ³
Absorption coefficient	0.091 mm ⁻¹
F(000)	688
Crystal size	0.19 x 0.17 x 0.16 mm ³
Theta range for data collection	1.27 to 27.78°.
Index ranges	-9 ≤ h ≤ 9, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	27486
Independent reflections	7421 [R(int) = 0.0496]
Completeness to theta = 27.78°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9856 and 0.9830
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7421 / 1 / 579
Goodness-of-fit on F ²	1.023
Final R indices [I > 2σ(I)]	R1 = 0.0450, wR2 = 0.0897
R indices (all data)	R1 = 0.0626, wR2 = 0.0982
Absolute structure parameter	-1.7(8)
Largest diff. peak and hole	0.219 and -0.222 e.Å ⁻³

Table 2. Bond lengths (in angstroms) of compound 19c

O(1)-C(1)	1.346(2)	C(11)-C(12)	1.400(4)
O(1)-H(1)	0.97(4)	C(11)-H(11)	0.94(3)
O(2)-C(15)	1.245(2)	C(12)-C(13)	1.368(4)
O(3)-C(19)	1.360(3)	C(12)-H(12)	0.97(2)
O(3)-C(22)	1.431(3)	C(13)-C(14)	1.422(3)
O(1')-C(1')	1.345(3)	C(13)-H(13)	0.99(3)
O(1')-H(1')	0.90(4)	C(15)-C(16)	1.490(3)
O(2')-C(15')	1.243(2)	C(16)-C(17)	1.389(3)
O(3')-C(19')	1.371(3)	C(16)-C(21)	1.399(3)
O(3')-C(22')	1.435(3)	C(17)-C(18)	1.375(3)
C(1)-C(2)	1.381(3)	C(17)-H(17)	1.00(2)
C(1)-C(14)	1.439(3)	C(18)-C(19)	1.395(3)
C(2)-C(3)	1.445(3)	C(18)-H(18)	0.99(2)
C(2)-C(15)	1.471(3)	C(19)-C(20)	1.395(3)
C(3)-C(8)	1.412(3)	C(20)-C(21)	1.387(3)
C(3)-C(4)	1.416(3)	C(20)-H(20)	0.94(2)
C(4)-C(5)	1.371(3)	C(21)-H(21)	0.96(2)
C(4)-H(4)	0.93(3)	C(22)-H(22A)	1.00(3)
C(5)-C(6)	1.402(3)	C(22)-H(22B)	0.99(3)
C(5)-H(5)	0.97(2)	C(22)-H(22C)	0.96(3)
C(6)-C(7)	1.373(3)	C(1')-C(2')	1.385(3)
C(6)-H(6)	0.98(3)	C(1')-C(14')	1.438(3)
C(7)-C(8)	1.414(3)	C(2')-C(3')	1.456(3)
C(7)-H(7)	1.02(3)	C(2')-C(15')	1.475(3)
C(8)-C(9)	1.464(3)	C(3')-C(4')	1.411(3)
C(9)-C(14)	1.408(3)	C(3')-C(8')	1.417(3)
C(9)-C(10)	1.411(3)	C(4')-C(5')	1.373(3)
C(10)-C(11)	1.371(3)	C(4')-H(4')	0.97(2)
C(10)-H(10)	0.98(2)	C(5')-C(6')	1.396(3)

C(5')-H(5')	0.90(3)	C(13')-H(13')	0.99(3)
C(6')-C(7')	1.372(3)	C(15')-C(16')	1.479(3)
C(6')-H(6')	0.94(3)	C(16')-C(21')	1.397(3)
C(7')-C(8')	1.412(3)	C(16')-C(17')	1.398(3)
C(7')-H(7')	0.94(2)	C(17')-C(18')	1.377(3)
C(8')-C(9')	1.451(3)	C(17')-H(17')	0.97(2)
C(9')-C(14')	1.413(3)	C(18')-C(19')	1.395(3)
C(9')-C(10')	1.415(3)	C(18')-H(18')	0.95(2)
C(10')-C(11')	1.375(4)	C(19')-C(20')	1.385(3)
C(10')-H(10')	0.96(3)	C(20')-C(21')	1.393(3)
C(11')-C(12')	1.396(4)	C(20')-H(20')	0.92(2)
C(11')-H(11')	0.97(3)	C(21')-H(21')	0.95(3)
C(12')-C(13')	1.370(3)	C(22')-H(22D)	0.97(3)
C(12')-H(12')	0.96(3)	C(22')-H(22E)	1.04(3)
C(13')-C(14')	1.417(3)	C(22')-H(22F)	0.99(3)

Table 3. Selected Bond angles (in degrees) of compound 19c

C(1)-O(1)-H(1)	107(2)	C(8)-C(3)-C(2)	120.4(2)
C(19)-O(3)-C(22)	117.66(18)	C(4)-C(3)-C(2)	121.4(2)
C(1')-O(1')-H(1')	106(2)	C(5)-C(4)-C(3)	121.8(2)
C(19')-O(3')-C(22')	117.31(17)	C(5)-C(4)-H(4)	118.2(16)
O(1)-C(1)-C(2)	122.9(2)	C(3)-C(4)-H(4)	120.0(16)
O(1)-C(1)-C(14)	115.75(19)	C(4)-C(5)-C(6)	120.0(2)
C(2)-C(1)-C(14)	121.24(19)	C(4)-C(5)-H(5)	116.9(12)
C(1)-C(2)-C(3)	118.9(2)	C(6)-C(5)-H(5)	122.9(12)
C(1)-C(2)-C(15)	117.26(18)	C(7)-C(6)-C(5)	119.6(2)
C(3)-C(2)-C(15)	123.78(19)	C(7)-C(6)-H(6)	118.9(17)
C(8)-C(3)-C(4)	117.99(19)	C(5)-C(6)-H(6)	121.2(17)

C(6)-C(7)-C(8)	121.3(2)	C(19)-C(20)-H(20)	121.0(14)
C(6)-C(7)-H(7)	116.7(14)	C(20)-C(21)-C(16)	120.9(2)
C(8)-C(7)-H(7)	122.0(14)	C(20)-C(21)-H(21)	118.9(14)
C(3)-C(8)-C(7)	119.2(2)	C(16)-C(21)-H(21)	120.2(14)
C(3)-C(8)-C(9)	119.09(19)	O(3)-C(22)-H(22A)	111.2(14)
C(7)-C(8)-C(9)	121.6(2)	O(3)-C(22)-H(22B)	109.3(17)
C(14)-C(9)-C(10)	117.8(2)	H(22A)-C(22)-H(22B)	107(2)
C(14)-C(9)-C(8)	119.1(2)	O(3)-C(22)-H(22C)	109.5(14)
C(10)-C(9)-C(8)	123.0(2)	H(22A)-C(22)-H(22C)	110(2)
C(11)-C(10)-C(9)	121.0(2)	H(22B)-C(22)-H(22C)	110(2)
C(11)-C(10)-H(10)	122.2(15)	O(1')-C(1')-C(2')	123.1(2)
C(9)-C(10)-H(10)	116.8(15)	O(1')-C(1')-C(14')	115.10(19)
C(10)-C(11)-C(12)	121.0(2)	C(2')-C(1')-C(14')	121.71(19)
C(10)-C(11)-H(11)	120.1(15)	C(1')-C(2')-C(3')	118.7(2)
C(12)-C(11)-H(11)	118.9(15)	C(1')-C(2')-C(15')	116.73(19)
C(13)-C(12)-H(12)	121.9(14)	C(3')-C(2')-C(15')	124.48(19)
C(12)-C(13)-C(14)	120.1(2)	C(4')-C(3')-C(8')	118.62(19)
C(14)-C(13)-H(13)	117.1(15)	C(4')-C(3')-C(2')	121.3(2)
C(9)-C(14)-C(1)	119.7(2)	C(8')-C(3')-C(2')	119.98(19)
O(2)-C(15)-C(2)	120.76(19)	C(5')-C(4')-C(3')	121.3(2)
C(2)-C(15)-C(16)	120.62(17)	C(5')-C(4')-H(4')	117.3(13)
C(17)-C(16)-C(15)	119.77(18)	C(3')-C(4')-H(4')	121.4(13)
C(18)-C(17)-C(16)	120.79(19)	C(4')-C(5')-H(5')	118.4(16)
C(16)-C(17)-H(17)	118.8(13)	C(6')-C(5')-H(5')	121.4(16)
C(17)-C(18)-H(18)	121.9(13)	C(7')-C(6')-C(5')	119.7(2)
O(3)-C(19)-C(20)	124.30(19)	C(5')-C(6')-H(6')	120.4(16)
O(3)-C(19)-C(18)	115.76(19)	C(6')-C(7')-C(8')	121.6(2)
C(20)-C(19)-C(18)	119.9(2)	C(6')-C(7')-H(7')	119.4(14)
C(21)-C(20)-C(19)	119.28(19)	C(8')-C(7')-H(7')	118.9(14)
C(21)-C(20)-H(20)	119.7(14)	C(7')-C(8')-C(3')	118.5(2)

3-Methoxy-3-aryl-3H-1-oxacyclopenta[1]phenanthren-2-ones

C(7')-C(8')-C(9')	122.0(2)	C(21')-C(16')-C(15')	121.2(2)
C(3')-C(8')-C(9')	119.48(18)	C(17')-C(16')-C(15')	119.70(18)
C(14')-C(9')-C(10')	117.4(2)	C(18')-C(17')-C(16')	120.7(2)
C(10')-C(9')-C(8')	122.8(2)	C(18')-C(17')-H(17')	121.9(13)
C(11')-C(10')-C(9')	121.4(2)	C(16')-C(17')-H(17')	117.3(13)
C(9')-C(10')-H(10')	120.9(16)	C(17')-C(18')-C(19')	119.7(2)
C(10')-C(11')-C(12')	120.5(2)	C(17')-C(18')-H(18')	123.1(13)
C(10')-C(11')-H(11')	121.9(15)	C(19')-C(18')-H(18')	117.1(13)
C(12')-C(11')-H(11')	117.6(15)	O(3')-C(19')-C(18')	115.3(2)
C(13')-C(12')-C(11')	120.1(2)	C(20')-C(19')-C(18')	120.8(2)
C(11')-C(12')-H(12')	117.4(15)	C(19')-C(20')-C(21')	119.07(19)
C(12')-C(13')-C(14')	120.2(2)	C(21')-C(20')-H(20')	123.2(14)
C(12')-C(13')-H(13')	123.1(14)	C(20')-C(21')-C(16')	120.8(2)
C(9')-C(14')-C(13')	120.4(2)	C(16')-C(21')-H(21')	119.6(15)
C(9')-C(14')-C(1')	119.20(19)	O(3')-C(22')-H(22D)	105.4(14)
C(13')-C(14')-C(1')	120.4(2)	O(3')-C(22')-H(22E)	109.6(14)
O(2')-C(15')-C(2')	120.3(2)	H(22D)-C(22')-H(22E)	109(2)
O(2')-C(15')-C(16')	118.1(2)	O(3')-C(22')-H(22F)	109.6(16)
C(2')-C(15')-C(16')	121.23(18)	H(22D)-C(22')-H(22F)	114(2)
C(21')-C(16')-C(17')	118.8(2)	H(22E)-C(22')-H(22F)	109(2)

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