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A New Short Synthetic Approach to Cyclopentaphenanthrenones

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Abstract: The Diels-Alder reactions of 4-acetoxy-2-cyclopenten-1-one and 2-bromo-4-acetoxy-2-cyclopenten-1-one with vinylarenes are discussed. The aromatization of the reaction products opens a new two- step route for the synthesis of cyclopentaphenanthrenones. Structure analysis of reaction products by ^{1}H and ^{13}C-NMR spectroscopy is reported.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants produced in the incomplete combustion processes of fossil fuels and other organic matter. Members of PAHs have been shown to exhibit mutagenic and carcinogenic activity[1].In recent years much attention has been devoted to cyclopenta- and dicyclopenta-fused polycyclic aromatic hydrocarbons and their derivatives[2]. Synthetic methods, both to supply reference samples for environmental studies and model compounds to correlate structure and toxicity, are required.

We have devised a new synthetic approach based on the Diels-Alder cycloaddition of 4-acetoxy-2-cyclopenten-1-one **(1a)** with vinylarenes, that could open a new short and flexible route for the synthesis of cyclopenta- and dicyclopenta-fused polycyclic aromatic hydrocarbons. Diels-Alder reaction of 1-vinylhydronaphthalenes with cyclopentenones was used in earlier efforts to rapidly construct a steroid cyclopenta[a]hydrophenanthrene skeleton, i.e. AB+D-----> ABCD synthesis where C ring is formed[3].

Recently it was shown[4,5] that acetoxyketone **1a** can be utilized as a synthetic equivalent of cyclopentadienone in Diels-Alder reactions with cyclic and acyclic dienes; in the presence of a strong Lewis acid catalyst, the monocycloadducts underwent acid-induced β-elimination of acetic acid affording cyclic conjugated enones, which can undergo a second cycloaddition reaction, depending on the experimental conditions used[4].

We now report a new two-step synthetic methodology of cyclopenta-fused PAHs and the preparation of the 16,17-dihydrocyclopenta [a] phenanthren-15-one **(2)** and the 2,3-dihydrocyclopenta [c] phenanthren-1-one **(3)**, which are key intermediates for the synthesis of cyclopenta- and dicyclopenta-fused PAHs.

The starting points for the synthesis of the cyclopentaphenanthrenones **2** and **3** are 4-acetoxy-2-cyclopenten-1-one (**1a**)[6], 1-vinylnaphthalene (**4**)[7], 1-vinyl-3,4-dihydronaphthalene[3d,8] (**5**) and 2-vinylnaphthalene (**6**).

Since 2-cycloalkenones are poor dienophiles, the Diels-Alder reactions of **1** require Lewis acid catalysis[9] and/or high pressure[10].

The cycloadditions of the dienes **4-6** with acetoxyketone **1a** were executed in various diene-dienophile combinations under ethylaluminum dichloride catalysis and/or high pressure conditions in dichloromethane solution. The experimental conditions and yields are summarized in the Table.

Table. Diels-Alder Reactions of 4-Acetoxy-2-Cyclopenten-1-ones **1** with Dienes **4-6**[a]

	diene / ketone[b]	$EtAlCl_2$ / ketone[b,c]	Reaction temperature (°C)	Reaction time (h)	Pressure (Kbar)	Product(s)	yield (%)[d]
1a-4	5	0.9	0	6	-	**7**	75
1a-5	1.2	0.5	0	0.5	-	**8,9**	75
	2	-	35	16	10	**8,9**	68
1b-5	1.3	-	30	15	10	**10**	60
1a-6	2	0.2	35	14	10	**11**	42

[a]Complexation time, 40 min; complexation temperature, 20°C[11].

[b]Ratio of equivalents.

[c]Ketone concentration, 0.1 M.

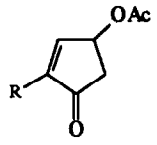
[d]The reaction yields refer to the isolated compounds.

The Diels-Alder reaction of ketone **1a** with 1-vinylnaphthalene (**4**) at atmospheric pressure led regioselectively to tetracyclic conjugated ketone **7** in high yield. When ketone **1a** interacted with 1-vinyl-3,4-dihydronaphthalene (**5**), at atmospheric pressure, a 1:1 mixture of α,β-unsaturated ketones **8** and **9** was obtained. The reaction was endo-diastereoselective and unregioselective[3d]. A higher regioselectivity (**8/9** = 6) was observed when the reaction was accomplished under high pressure conditions[12].

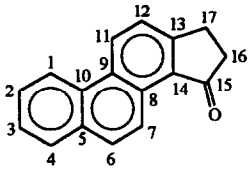
In order to have a higher regioselectivity we also studied the cycloaddition reaction of diene **5** with 2-bromo-4-acetoxy-2-cyclopenten-1-one (**1b**). The replacement of a hydrogen atom at the α-carbon of the double bond of ketone **1a** with a bromine atom could allow a better regiochemical control of the reaction due to both the electronic nature and size of bromine. $EtAlCl_2$-catalyzed cycloaddition of bromo-acetoxy-ketone **1b** with diene **5** in dry toluene at 90°C led regioselectively to tetracyclic ketone **10** in low yield (13%); better results (60%) were obtained when the reaction was accomplished under high pressure conditions (10 Kbar) in dichloromethane.

2-Vinylnaphthalene (**6**) is less reactive[13] than 1-vinylnaphthalene (**4**) and underwent Diels-Alder reaction with acetoxyketone **1a** only when high pressure was applied in combination with $EtAlCl_2$ to afford, regioselectively, tetracyclic conjugated ketone **11** in reasonable yield (40%). On the contrary a very low yielding reaction (3-5%) was observed when diene **6** interacted with bromo-acetoxy-ketone **1b** probably

because of the strong repulsive steric interaction between bromine and the peri hydrogen atom in both endo and exo transition states.



1 a, R=H
b, R=Br



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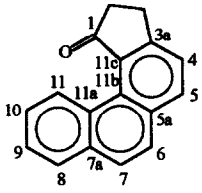

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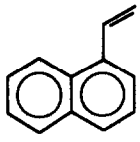

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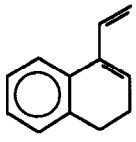

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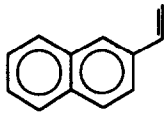

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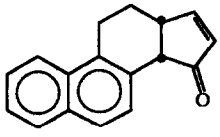

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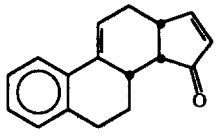

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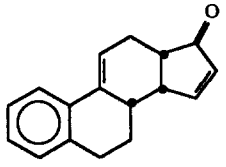

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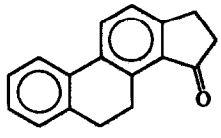

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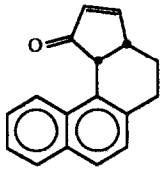

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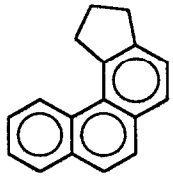

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The examination of the structures of the tetracyclic ketones **7-9** and **11** showed that *i*) the primary cycloadducts underwent β-elimination of acetic acid induced by Lewis acid catalyst[4,5] and/or high pressure, *ii*) the aromatic naphthalene moiety of enones **7** and **11** was derived from the rapid double bond isomerization of the cycloadducts, and iii) the product(s) of the reaction of the diene **5** with bromo-acetoxy-ketone **1b** also underwent β-elimination of both acetic acid and hydrogen bromide under reaction conditions followed by the rapid shift of double bond to afford the 5,6-dihydrocyclopenta[a]phenanthren-15-one (**1 0**).

Treatment of the tetracyclic enones **7,8,10** and **11** over a Pd/charcoal catalyst[14] allowed a one-step conversion to the fully aromatized cyclopentaphenanthrenones **2** and **3**[15], respectively, in high yield (75-85%) by combining a dehydrogenation process with the isomerization of the cyclopentene ring carbon-carbon

double bond. The dehydrogenation of ketone **10** can also be easily accomplished by DDQ. Finally tetracyclic ketone **11** was converted to the corresponding polycyclic hydrocarbon **12** by the usual procedure.

In conclusion, we have described a new two-step synthesis of cyclopentaphenanthrenones based on the Diels-Alder reaction of 4-acetoxy-2-cyclopenten-1-one **1a** and 2-bromo-4-acetoxy-2-cyclopenten-1-one **1b**.This short methodology is potentially adaptable to the preparation of a variety of cyclopenta-fused-PAHs substituted in biologically interesting regions, starting from easily available precursors of vinylnaphthalenes **4-6.**

STRUCTURE ANALYSIS

The structure and stereochemistry of the reaction products were inferred from the analysis of their high field ^1H and ^{13}C NMR spectra recorded in $CDCl_3$ and/or C_6D_6 solutions. The ^1H and ^{13}C chemical shift assignments follow from 2D ^1H-^1H, ^1H-^{13}C connectivities (COSY and HETCOR experiments). The pertinent data are collected in the Experimental Section.

Tetracyclic Ketones 7 and 11. The regiochemistry of the carbonyl function of Ketone **7** is supported by ^1H-^1H NOE experiments. Selective preirradiation of the resonance due to H(13) resulted in signal enhancement of the resonance attributed to H(12) and H(17), while saturation of H(14) enhanced the signal of aromatic proton H(7). In the case of ketone **11** mutual enhancement observed between resonances of H(3), H(4) and H(3a) and between H(11) and H(11c) indicated the regiochemistry of the carbonyl function, which was further corroborated by the long-range heterocorrelations inferred from the FLOCK spectrum. Both H(11) and H(11c) showed cross-peaks with C(11a) and C(11b). Finally the *cis* junction between the cyclohexane and cyclopentane rings for both ketones **7** and **11** was assured by interproton coupling constant values ($^3J_{13,14}$= 6.2 Hz and $^3J_{3a,11c}$= 6.1 Hz) and the observed mutual dipolar contacts between bridgehead hydrogens.

Tetracyclic Ketones 8 and 9. Comparison of the chemical shifts of the axial H(7) for ketone **8** (2.40 ppm) and ketone **9** (1.68 ppm) showed H(7) to be deshielded strongly in the former compound, thus indicating the regiochemistry depicted in the formulas. The all-*cis* arrangement of protons H(8), H(13) and H(14) in both ketones follows from the vicinal couplings ($^3J_{8,14}$=$^3J_{13,14}$= 6.5 Hz). Further support for this stereochemical assignment is given by the NOE effects observed between H(8) and H(14), as well as between H(13) and H(14).

Tetracyclic Ketone 10. The carbon and proton spectra excluded the presence of methine protons. Selective 2D INEPT experiments showed that H(7) (3.60ppm) is separated from C(5), C(9) and C(14) by three chemical bonds. Further support for this regiochemical assignment is given by the 1 ppm difference between the chemical shifts of C(6) and C(7) methylene protons. The origin of the downfield shift can also be associated with the anisotropy effect exerted by the carbonyl group on the H(7) proton.

The structures of the cyclopentaphenanthrenones **2** and **3** and of the hydrocarbon **12** were based on the analysis of their ^1H and ^{13}C NMR spectra which evidenced unambiguously the presence of three condensed

aromatic rings. Further support is also given by the known outcome of the dehydrogenation reactions used to prepare them.

EXPERIMENTAL SECTION[16]

All operations for preparing mixtures of the Diels-Alder reactions were executed in a dry box. Melting points were determined on a Buchi 510 melting point apparatus and are uncorrected. Infrared spectra of $CHCl_3$ solutions were recorded on a Perkin-Elmer 983 spectrometer. GC analyses were performed on a Carlo Erba HRGC-5160 and Hewlett-Packard 5880A chromatographs. Absorption chromatography was carried out on a Merck Lichoprep Si 60 pre-packed column. All compounds gave correct elemental analyses. ^1H and ^{13}C NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument in $CDCl_3$ solution except for ketone **10** (C_6D_6). Commercially available (Aldrich Company) 2-vinylnaphthalene and 1M hexane solution of ethylaluminum dichloride were used; methylene chloride was distilled from CaH_2.

2-Bromo-4-acetoxy-2-cyclopenten-1-one (1b)[17]

This compound was prepared starting from 4-acetoxy-2-cyclopenten-1-one (**1a**) in 50-55% overall yield according to a previously reported procedure to convert 2-cyclopentenone to 2-bromo-2-cyclopentenone[18]: b.p. 100-101°C/0.35 mmHg; ^1H NMR δ 2.10 (s, 3H, OAc), 2.50 (dd, 1H, J=17.0, 2.2 Hz, H-5), 3.00 (dd, 1H, J=17.0, 6.2 Hz, H-5), 5.82 (m, 1H, H-4), 7.73 (d, 1H, J=4.7 Hz, H-3).

Diels-Alder reactions of 4-acetoxy-2-cyclopentenones (1)

The mixtures of the starting materials were prepared in dry box by adding the hexane solution of $EtAlCl_2$ to the ketone in dry dichloromethane and kept at 25°C for 40 min.[11]; the diene was then added. The ratios of the reagents, as well as the reaction conditions used, are reported in the Table. Catalyzed and uncatalyzed cycloadditions under high pressure conditions were performed according to a previously described method[10b]. At the end of the reaction, the mixtures were worked up as usual and the products were purified by column chromatography.

1a-4 Reaction. Chromatography of the crude product and elution with gradient hexane to hexane/ethyl acetate - 7/3 furnished pure ketone **7**.

11,12,13,14-Tetrahydrocyclopenta[a]phenanthren-15-one (7): colorless liquid; IR 1705 (s, C=O), 1660 (w, C=C) cm^{-1}; ^1H NMR δ 2.04 (m, 2H, Hs-12), 2.69 (m, 1H, J= 15.8, 10.0, 5.0 Hz, H-11), 3.25 (m, 1H, J= 15.8, 5.0, 4.0 Hz, H-11), 3.53 (m, 1H, J= 6.2, 6.2, 5.0,2.5, 2.0 Hz, H-13), 3.75 (d, 1H, $J_{13,14}$= 6.2 Hz, H-14), 6.34 (dd, 1H, J= 5.5, 2.0 Hz, H-16), 7.44 (ddd, 1H, J= 7.9, 7.5, 1.0 Hz, H-3), 7.49 (ddd, 1H, J= 8.1, 7.5, 1.4 Hz, H-2), 7.70 (d, 1H, $J_{6,7}$= 8.5 Hz, H-7), 7.74 (dd, 1H, J= 5.5, 2.5 Hz, H-17), 7.76 (d, 1H, $J_{6,7}$= 8.5 Hz, H-6), 7.82 (dd, 1H, J= 7.9, 1.4 Hz, H-4), 7.97 (dd, 1H, J= 8.1, 1.0Hz, H-1); ^{13}C NMR δ 21.53 (C-11), 26.81 (C-12), 41.00 (C-13), 49.66 (C-14), 123.00 (C-1), 125.18* and 125.88* (C-2, C-3), 126.74* and 128.15* (C-6, C-7), 128.57 (C-4), 129.51*, 131.41*, 132.37* and 132.79* (C-9, C-10, C-5, C-8), 135.04 (C-16), 166.90 (C-17), 207.20 (C-15).

1a-5 Reaction. Chromatography of the crude product and gradient elution (9/1 to 7/1 - hexane/ethyl acetate) led to ketones **8** and **9**.

6,7,8,12,13,14-Hexahydrocyclopenta[a]phenanthren-15-one (8): colorless liquid; IR 1700 (s, C=O), 1660 (w, C=C) cm^{-1}; ^1H NMR δ 2.06 (m, 1H, J= 12.0, 6.0, 4.0, 3.5 Hz, H-7), 2.35 (m, 1H, J= 15.5, 6.5, 3.2, 3.0 Hz, H-12),

2.40 (m, 1H, J= 12.0, 12.0, 11.0, 3.8 Hz, H-7), 2.48 (ddd, 1H, J= 15.5, 7.0, 1.5 Hz, H-12), 2.66 (m, 2H, Hs-6), 2.68 (m, 1H, J= 12.0, 6.5, 4.0, 3.0 Hz, H-8), 2.73 (dd, 1H, J= 6.5, 6.5 Hz, H-14), 3.43 (m, 1H, J= 6.5, 6.5, 2.6 Hz, H-13), 6.12 (dd, 1H, J= 5.6, 2.0 Hz, H-16), 6.15 (m, 1H, J= 7.0, 3.2, 3.0 Hz, H-11), 7.08-7.11 (m, 3H, H-2, H-3, H-4), 7.39 (dd, 1H, J= 5.6, 2.6 Hz, H-17), 7.40 (dd, 1H, J= 8.0, 1.2 Hz, H-1); ^{13}C NMR δ 23.80 (C-7), 27.29 (C-12), 30.38 (C-6), 37.95 (C-8), 42.20 (C-13), 47.91 (C-14), 118.80 (C-11), 123.21 (C-1), 126.27*, 126.80* and 128.14* (C-2, C-3, C-4), 134.17 (C-10), 136.77 (C-16), 137.98* and 138.07* (C-9, C-5), 164.47 (C-17), 210.97 (C-15).

6,7,8,12,13,14,-Hexahydrocyclopenta[a]phenanthren-17-one (9): m.p. 108-109°C (diethyl ether); IR 1701 (s, C=O), 1658 (w, C=C) cm^{-1}; ^{1}H NMR δ 1.68 (m, 1H, J= 12.0, 12.0, 11.5, 4.0 Hz, H-7), 2.11 (m, 1H, J= 12.0, 6.0, 3.5, 3.5 Hz, H-7), 2.28 (m, 1H, J= 15.5, 7.0, 3.2, 3.0 Hz, H-12), 2.68 (m, 2H, Hs-6), 2.70 (ddd, 1H, J= 7.0, 6.5, 1.5 Hz, H-13), 2.74 (m, 1H, J= 12.0, 6.5, 3.5,3.0 Hz, H-8), 2.79 (m, 1H, J= 15.5, 7.5, 1.5 Hz, H-12), 3.45 (m, 1H, J= 6.5, 6.5, 2.5, 2.2 Hz, H-14), 6.21 (dd, 1H, J= 5.8, 2.2 Hz, H-16) 6.25 (ddd, 1H, J= 7.5, 3.2, 3.0 Hz, H-11), 7.08-7.12 (m, 3H, H-2, H-3, H-4), 7.42 (dd, 1H, J= 8.0, 1.2 Hz, H-1), 7.58 (dd, 1H, J= 5.8, 2.5 Hz, H-15); ^{13}C NMR δ 25.45 (C-7), 25.69 (C-12), 30.22 (C-6), 37.63 (C-8), 45.12 (C-13), 46.20 (C-14), 120.38 (C-11), 123.43 (C-1), 126.55*, 126.72* and 128.06* (C-2, C-3, C-4), 134.15 (C-10), 136.16 (C-9), 136.72 (C-16), 137.39 (C-5), 164.61 (C-15), 212.29 (C-17).

1b - 5 Reaction. Chromatography of the crude product and elution with 4/1 - hexane/ethyl acetate furnished pure ketone **10**.

6,7,16,17-Tetrahydrocyclopenta[a]phenanthren-15-one (10): crystalline solid; m.p. 141-142°C (methanol) [lit.[19]: 143-144°C]; IR 1705 (s, C=O) cm^{-1}; ^{1}H NMR δ 2.20 (dd, 2H, J= 6.5,6.5 Hz, Hs-16), 2.39 (dd, 2H, J= 6.5, 6.5 Hz, Hs-17), 2.60 (dd, 2H, J= 7.0, 7.5 Hz, Hs-6), 3.60 (dd, 2H, J= 7.0, 7.5 Hz, Hs-7), 6.91 (d, 1H, J= 8.1 Hz, H-12), 6.99 (dd, 1H, J= 7.0, 1.3 Hz, H-4), 7.09 (t, 1H, J= 7.0, 7.0 Hz, H-3), 7.16 (dd, 1H, J= 8.0, 7.0 Hz, H-2), 7.54 (d, 1H, J= 8.0 Hz, H-1); ^{13}C NMR δ 22.63 (C-7), 24.97 (C-17), 28.24 (C-6), 37.05 (C-16), 124.05 (C-1), 124.69 (C-12), 127.17 (C-2), 127.84 (C-3), 128.52 (C-4), 129.44 (C-11), 133.95 (C-10), 134.05 (C-14), 134.35 (C-8), 137.71 (C-5), 137.87 (C-9), 154.81 (C-13), 206.37 (C-15).

1a - 6 Reaction. Chromatography of the crude product and elution with 4/1 - hexane/diethyl ether led to pure ketone **11**.

3a,4,5,11c-Tetrahydrocyclopenta[c]phenanthren-1-one (11): crystalline solid; m.p. 132-133°C (methanol); IR 1711 (s, C=O) cm^{-1}; ^{1}H NMR δ 1.85 (m, 1H, J= 13.0, 13.0, 7.1, 3.8 Hz, H-4), 2.09 (m, 1H, J= 13.0, 3.9, 3.8, 2.0 Hz, H-4), 2.53 (ddd, 1H, J= 15.2, 13.0, 3.9 Hz, H-5), 2.67 (m, 1H, J= 15.2, 3.8, 3.8,1.0 Hz, H-5), 3.64 (m, 1H, J= 7.1, 6.1, 2.6, 2.0 Hz, H-3a), 4.53 (d, 1H, $J_{11c,3a}$= 6.1 Hz, H-11c), 6.44 (dd, 1H, J= 5.5, 2.0 Hz, H-2), 7.18 (d, 1H, J= 8.3 Hz, H-6), 7.45 (dd, 1H, J= 7.8, 7.5 Hz, H-9), 7.57 (ddd, 1H, J= 8.1, 7.5, 1.4 Hz, H-10), 7.65 (d, 1H, J= 8.3 Hz, H-7), 7.68 (dd, 1H, J= 5.5, 2.6 Hz, H-3), 7.80 (dd, 1H, J= 7.8, 1.4 Hz, H-8), 8.29 (dd, 1H, J= 8.1, 1.0 Hz, H-11); ^{13}C NMR δ 26.91 (C-5), 27.02 (C-4), 42.07 (C-3a), 45.35 (C-11c), 125.01 (C-11), 125.32 (C-9), 126.41 (C-10), 127.20 (C-6), 127.24 (C-7), 128.63 (C-8), 128.75 (C-11b), 133.17 (C-11a), 133.43 (C-7a), 136.26 (C-5a), 136.44 (C-2), 167.17 (C-3), 206.63 (C-1).

16,17-Dihydrocyclopenta[a]phenanthren-15-one (2) and 2,3-Dihydrocyclopenta[c]phenanthren-1-one (3).

Hydrocyclopentaphenanthrenones **7**, **8**, **10** and **11** were converted to the corresponding fully aromatized ketones **2** and **3** respectively, in high yield, (75-85%) by heating with 10% Pd/C in triglyme at reflux for 18h under nitrogen

according to previously reported procedures[20]. Overall yields (cycloaddition + dehydrogenation) higher than 70% were obtained by directly treating the crude mixtures of the **1a-4**, **1b-5** and **1a-6** Diels-Alder reactions.

Furthermore 6,7,16,17-tetrahydrocyclopenta[a]phenanthren-15-one (**10**) was also easily converted to ketone **2** by treatment with DDQ in benzene[21] under mild conditions.

(2): crystalline solid, (eluted with hexane/ethyl acetate-8/2); m.p. 188-189°C (hexane-ethyl acetate) [lit.[22]: 185-186°C]; IR 1702 (s, C=O) cm^{-1}; ^1H NMR δ 2.82 (dd, 2H, J= 6.5 6.5 Hz, Hs-16), 3.23 (dd, 2H, J= 6.5, 6.5 Hz, Hs-17), 7.63 (dd, 1H, J= 8.0, 7.0 Hz, H-3), 7.66 (d, 1H, J= 8.6 Hz, H-12), 7.67 (ddd, 1H, J= 8.0, 7.0, 1.3 Hz, H-2), 7.93 (dd, 1H, J= 8.0, 1.3Hz, H-4), 7.94 (d, 1H, J= 9.1 Hz, H-6), 8.65 (d, 1H, J= 8.0 Hz, H-1), 8.88 (d, 1H, J= 8.6 Hz, H-11), 9.17 (d, 1H, J= 9.1 Hz, H-7); ^{13}C NMR δ 24.66 (C-17), 36.18 (C-16), 120.86 (C-7), 121.60 (C-1), 123.29 (C-12), 125.69 (C-3), 125.98 (C-2), 127.78 (C-4), 128.07* (C-10), 128.15 (C-9), 128.55 (C-11), 128.75* (C-8), 129.02 (C-6), 130.30 (C-14), 130.90 (C-5), 156.22 (C-13), 206.87 (C-15).

(3): crystalline solid (eluted with hexane/ethyl acetate-9/1); m.p. 143-144°C (methanol); IR 1696 (s, C=O) cm-1; ^1H NMR δ 2.95 (t, 2H, J= 5.8 Hz, Hs-2), 3.30 (t, 2H, J= 5.8 Hz, Hs-3), 7.58 (d, 1H, J= 8.1 Hz, H-4), 7.66 (m, 2H, H-9 and H-10), 7.74 (d, 1H, J= 9.0 Hz, H-6), 7.83 (dd, 1H, J= 9.0, 1.0 Hz, H-7), 7.90 (m, 1H, H-8), 8.05 (d, 1H, J= 8.1 Hz, H-5), 9.43 (m, 1H, H-11); ^{13}C NMR δ 26.05 (C-3), 37.31 (C-2), 124.66 (C-4), 125.42 (C-10), 126.45 (C-6), 127.70 (C-9), 127.78 (C-8), 128.10 (C-7), 128.96 (C-11a), 129.53 (C-11b), 129.89 (C-11), 132.58 (C-5a), 133.64 (C-7a and C-11c), 136.17 (C-5), 158.19 (C-3a), 205.70 (C-1).

16,17-Dihydro-1H-cyclopenta[c]phenanthrene (12)

Prepared starting from Diels - Alder product **11** by reduction with $NaBH_4$ followed by concurrent dehydrogenation and dehydration over 10% Pd/charcoal catalyst[23]; m.p. 59-60°C (methanol) [lit1[3b]: 69-71°C]; ^1H NMR δ 2.28 (m, 2H, Hs-2), 3.13 (t, 2H, J= 7.6 Hz, Hs-3), 3.77 (t, 2H, J= 7.2 Hz, Hs-1), 7.53 (d, 1H, J= 8.1 Hz, H-5), 7.57 (m, 1H, H-9), 7.61 (m, 1H, H-10), 7.66 (dd, 1H, J= 8.9, 1.0 Hz, H-7), 7.74 (dd, 2H, J= 8.9, 8.1 Hz, H-6 and H-4), 7.89 (dd, 1H, J= 7.5, 1.8 Hz, H-8), 8.81 (dd, 1H, J= 8.5, 1.0 Hz, H-11); ^{13}C NMR δ 25.63 (C-2), 33.17 (C-3), 37.37 (C-1), 123.36 (C-5), 125.65 (C-9), 125.81 (C-10), 125.92 (C-7), 126.69 (C-11), 127.63 (C-4), 127.86 (C-6), 128.39 (C-8 and C-11b), 131.38 (C-11a), 131.84 (C-5a), 133.17 (C-7a), 139.61 (C-3a), 144.14 (C-11c).

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