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High-Pressure Diels-Alder Reactions of Bicyclic Dienones. Short Syntheses of Hydrophenanthrenones

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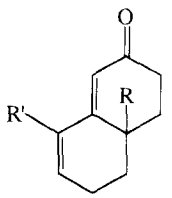
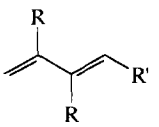
Abstract. Diels-Alder reactions of a heteroannular bicyclic dienone with acyclic dienes under Lewis acid catalysis at atmospheric and 7 Kbar pressure are presented. The pressure reactions are fast, high-yielding and highly diastereoselective en route to hydrophenanthrenones. As a consequence of some post-cycloaddition enolization, both cis and trans products are available.

The stereocontrolled construction of six-membered, polycarbocyclic compounds has been in the limelight for a long time chiefly due to the favorable, medicinal properties of many naturally occurring and unnatural representatives of this class of substances. In an attempt to develop short routes to synthesize these materials, based mainly on Diels-Alder reaction chemistry, recent studies were performed on the preparation of hydrophenanthrenones by cycloaddition of bicyclic, heteroannular dienones.[1,2] Whereas the latter were poor dienophiles[3], they afforded reasonable product yields on reaction with electron-rich dienes and on Lewis acid catalysis. In view of the known, strong acceleration of cycloadditions under high pressure[4] and the recent experience of the promotion of a Diels-Alder reaction of β-methyl-α,β-unsaturated cycloalkenones (dienophiles totally unreactive at atmospheric pressure) under Lewis acid catalysis and high pressure[5], an investigation of the pressurized and atmospheric cycloadditions of unsubstituted, bicyclic dienone **1a** with dienes **2a**, **b** and **c** was undertaken.



1a, R = R' = H
b, R = H, R' = Me
c, R = Me, R' = H



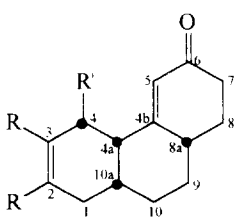
2a, R = Me, R' = H
b, R = H, R' = Me
c, R = R' = H

The dienone (**1a**)[6] needed for the study was prepared in the following manner. Treatment of $\Delta^{1,9}$-octal-2-one[7] with acetic anhydride and acetyl chloride in pyridine afforded its enol acetate, whose halogenation

with N-bromosuccinimide in dimethylformamide-water furnished a bromoketone. Exposure of the latter to a lithium bromide-carbonate mixture in the same medium produced dienone **1a** in a 75 % overall yield.[8]

RESULTS AND DISCUSSION

The cycloadditions were carried out in dry methylene chloride solutions of dienone **1a** under atmospheric or elevated (7 Kbar) pressure in the presence of ethylaluminum dichloride catalyst. The reaction with 2,3-dimethyl-1,3-butadiene (**2a**) at 7 Kbar led to a 9:1 mixture (70 % yield) of *anti-cis* and *syn-trans* tricyclic ketones, **3a** and **5a**, respectively, whereas at atmospheric pressure, the reaction produced the same product mixture (55 %) but in 1:9 ratio, respectively, a clear indication of the marked influence of pressure on the composition of the reaction mixture. When dienone **1a** was allowed to interact with (E)-piperylene (**2b**) at 7 Kbar, a 19:1 mixture (80 %) of *anti-endo-cis* and *syn-endo-trans* ketones **3b** and **5b**, respectively, was obtained. When the reaction was executed at atmospheric pressure, a 1:3 mixture (30 %) of the same ketones, respectively, was observed. As expected[9], both anti and syn additions were regioselective and *endo*-diastereoselective. Finally, the cycloaddition with 1,3-butadiene (**2c**) at 7 Kbar failed because of predominant diene polymerization, but at atmospheric pressure an 8:1 mixture (50 %) of *anti-cis* and *syn-cis* ketones, **3c** and **4c**, respectively, was produced. In this case, surprisingly, no *trans*-product was observed.



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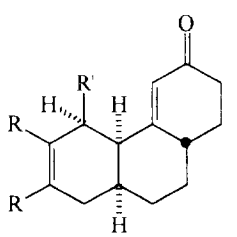

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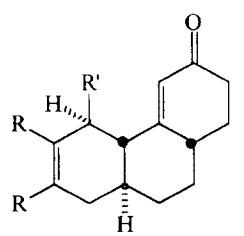
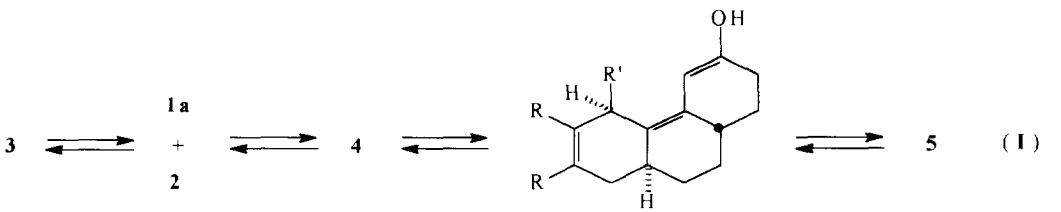


5

a, R = Me, R' = H; **b**, R = H, R' = Me; **c**, R = R' = H

The formation of unusual trans adducts (**5a** and **b**) in two of the three cycloadditions prompted a more detailed study of the Diels-Alder reaction between dienone **1a** and diene **2a**. Careful glc monitoring of the reaction at atmospheric pressure showed adduct **3a** to be an early product and the **3a/5a** product ratio to change throughout the course of the reaction. Furthermore, exposure of pure adduct **3a** to the **1a-2a** reaction conditions yielded the identical product mixture observed in the initial Diels-Alder reaction.[10] These results indicate that both the Diels-Alder reactions of 2,3-dimethyl-1,3-butadiene (**2a**) and (E)-piperylene (**2b**)[10] under atmospheric pressure are thermodynamically controlled and suggest that the formation of *trans*-compounds **5** is probably due to i) the conversion of the *anti-endo-cis* cycloadducts **3** into the short-lived *syn-endo-cis* adducts **4**, and ii) the tautomerization (via a dienol or its aluminum complexes) of the elusive *sin-cis* cycloadducts **4** (cf. equations I).

It seems reasonable that this explanation may be extended to the cycloadditions performed under high pressure conditions, with the different positions of equilibria depending on the effects of pressure[4].



In principle, the *trans*-products **5** could also be ascribed to non-concertedness of the cycloaddition; this hypothesis, however, seems to be untenable in view of i) the observed *cis*-bridgehead products obtained in the cycloaddition of methylated dienone **1b**[2] where the angular methyl group precluded any post-cycloaddition tautomerization, and ii) the vast array of data on thermal and Lewis acid-catalyzed Diels-Alder reactions of conjugated cycloalkenones, none of which required interpretation in terms of a two-step mechanism[3,5,11].

Whereas the formation of *trans*-adduct in the Diels-Alder reactions of dienes **2a** and **2b** has been reasonably justified, the different behaviour of 1,3-butadiene (**2c**) is still not understood.

Finally the observed marked effect of pressure on the Diels-Alder reactions of hexalone **1a** induced us to re-examine at 7 Kbar the cycloadditions of hexalones **1b** and **1c** with dienes **2a** and **2b**, previously studied at atmospheric pressure[1,2].

The **1b-2b** cycloaddition (70% yield) exhibited a 1.5 : 1 *anti-endo/syn-exo* product ratio (vs. at atmospheric pressure[2]: 45%, 1 : 1 ratio); the **1c-2b** reaction (80%) gave only the *anti-endo* product (vs. 62%, 9 : 1 ratio[2]) and the **1c-2a** Diels-Alder process (80%) afforded exclusively the *anti-endo* product (vs. 35%, the same compound[1]).

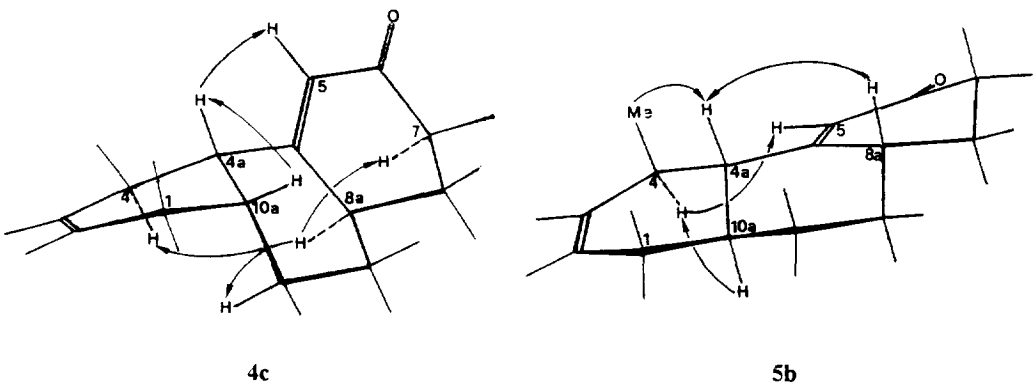
In conclusion, several interesting facts emerge from the present study. Diels-Alder reactions of hexalones **1** under pressure are fast, high-yielding, and highly diastereoselective. The cycloadditions of hexalones **1** with acyclic dienes (**2**) constitute facile, one-step syntheses of hydrophenanthrenones from readily available starting materials. Hence they have the potential for yielding ready access to natural products of especially the di- and tri-terpenic or steroid types. The formation of trans compounds (**5**) by acid-induced post-cycloaddition isomerization makes the method more flexible and thus more useful in organic synthesis.

Demonstration of the utility of this synthetic strategy will be reported in due course.

STRUCTURE ANALYSIS

The structure and stereochemistry of the tricyclic ketones were inferred from the analysis of their high-field ^1H and ^{13}C NMR spectra recorded in $CHCl_3$. Some of the ^1H spectra were repeated in C_6D_6 and/or in CD_3COOD to avoid overlapping of some proton resonances. The full assignment of the proton and carbon spectra followed from the examination of ^1H-^1H and ^1H-^{13}C connectivities (COSY, HETCOR and INEPT spectra). Stereochemical and regiochemical assignments were based on the values of the $J_{H,H}$ coupling constants and selective ^1H-^1H NOE experiments. The pertinent data are collected in the Experimental Section.

The *cis*-stereochemical relationship of H(4a), H(8a) and H(10a) for ketones **3a**, **3b** and **3c** followed from NOE effects observed on the resonances of H(8a) and H(10a) upon irradiation of the resonance attributed to the H(4a) proton. The $^3J_{4a,10a}$ value of 5 Hz for these ketones confirmed a *cis*-stereochemistry at the C(4a)-C(10a) ring junction; by contrast, the same vicinal coupling ($^3J_{4a,10a}$) in ketones **5a** and **5b** assumed the value of 11 Hz, indicating a *trans*-stereochemistry at C(4a)-C(10a) ring junction for both compounds. Furthermore the *cis* relationship between hydrogens H(4a) and H(8a) in both ketones **5a** and **5b** was revealed by ^{1}H-^{1}H NOE experiments. Selective pre-irradiation of the resonance due to H(8a) resulted in signal enhancement of the resonance attributed to H(4a), while no NOE effect was observed on H(4a) and H(8a) by selective pre-irradiation of H(10a). This stereochemical assignment was further supported by the similarity of the chemical shifts of carbon C(4a) and C(8a) of ketones **3a** and **3c** with those of the same carbon atoms of compound **5a**. The regiochemistry and stereochemistry of the methyl group for ketones **3b** and **5b** followed from selective NOE experiments, as well as from the $^3J_{4,4a}$ value of 4.5 and 9.5 Hz, respectively. Selective pre-irradiation of the H(4) resonance of **3b** resulted in signal enhancement of the resonances attributed to H-3, H(4a), and H(10a), revealing spatial proximity of these hydrogens. In the case of ketone **5b** (see figure), saturation of the methyl group resonance gave rise to signal enhancement of H(4a); in a similar manner, saturation of the H(10a) resonance resulted in signal enhancement of H(4) signal. This indicated the position of the C(4) methyl group and the stereochemistry depicted in the figure for ketone **5b**.



4c **5b**

Figure. Minimized energy conformations of products **4c** and **5b**; the arrows indicate observed n.O.e's.

A *cis* relationship between H(4a) and H(10a) for ketone **4c** was assured by mutual dipolar contact observed between the two hydrogens, as well as their coupling value of 5.5 Hz. Furthermore, selective pre-irradiation of the H(8a) resonance gave no NOE effect on the signal attributed to H(4a) and H(10a), while strong enhancement occurred at the resonances attributed to axial protons on carbon atoms C(4), C(7) and C(10). This indicated a *trans*-relationship between H(10a), H(4a) and H(8a). Two further facts are in consonance with the stereochemistry depicted in the figure for ketone **4c**: i) the NOE effect observed between H(5) and H(4a), showing that proton H(4a) is in the plane of the C(4b)-C(5) double bond, and ii) the coupling constants of the hydrogens at C(4a) ($^3J_{4a,4\alpha}$ = 11.5, $^3J4_{a,10a}$ = 5.5, $^3J_{4a,4\beta}$ = 4.5 Hz) and at

C(8a) ($^3J_{8a,8\beta}$ = 9, $^3J_{8a,8\alpha}$ = 5, $^3J_{8a,9\beta}$ = 13, $^3J_{8a,9\alpha}$ = 6 Hz) indicating a conformation as depicted in the figure [e.g. H(4a) assumes a *trans*-axial orientation with respect to H(4)].

EXPERIMENTAL SECTION[12]

4,4a,5,6-Tetrahydro-2(3H)-naphthalenone (1a). Acetyl chloride (7 mL) was added under nitrogen to a solution of $\Delta^{1,9}$-octal-2-one[7] and then refluxed in an atmosphere of nitrogen for 3 h. The reaction mixture was cooled, diluted with water and worked up as usual, to afford 6 g of enol acetate.

A solution of the enol acetate in dimethylformamide (32 mL) and water (0.8 mL) was treated with NBS (6 g) at 0°C and under nitrogen. The addition of NBS was complete within 0.5 h. The reaction mixture was stirred at 0°C for 0.5 h. Then LiBr (2.7 g) and Li_2CO_3 (5.4 g) were added and the reaction mixture was heated at 70°C for 2.5 h under stirring. It was cooled, poured into ice-water (150 mL) and acetic acid (10 mL) and extracted with ether. After the usual workup a residual oil was obtained, which was purified by column chromatography. Elution with 4:1 hexane-ether gave 2.6 g of pure dienone **1a** in 75% overall yield.

Colorless oil; IR 1653 (s, C=O), 1617 (m, C=C) cm^{-1}; ^1H NMR δ 1.20-2.60 (m, 9H), 5.68 (s, 1H, H-1), 6.20 (m, 2H, H-7, H-8); ^{13}C NMR δ 26.11 (C-6), 29.14 (C-4 or C-5), 30.12 (C-5 or C4), 35.43 (C-4a), 37.81 (C-3), 123.76 (C-1), 128.27 (C-8), 139.21(C-7), 158.21 (C-8a), 199.96 (C-2).

Diels-Alder Reactions of Dienone 1a. General Procedure.

The mixture of the starting materials was prepared in a dry-box by adding the hexane solution of $EtAlCl_2$ to a dichloromethane solution of dienone. The mixture was kept at 25°C for 40 min.[13] and then the diene was added. Thereafter (in the case of the Diels-Alder reaction being carried out at atmospheric pressure) the mixture was heated in an oil bath and then worked up by following a previously reported set procedure[3a]. In the case of the Diels-Alder cycloadditions being performed under pressure, all operations were executed according to the recently described procedure[5].

Table I. Conditions of the Diels-Alder Reactions of Hexalone 1a with Dienes 2a

Diene	Diene/ Ketone[b]	Reaction Time (h)	Pressure (Kbar)	Products	Product Yield (%)[c]
2a	3	22	7	9:1 **3a/5a**	70
2a	5	240	-	1:9 **3a/5a**	55[d]
2b	3	65	7	19:1 **3b/5b**	80
2b	3	90	-	1:3 **3b/5b**	30[d]
2c	10	90	-	8:1 **3c/4c**	50[d]

[a]Complexation time[13]: 40 min; complexation temperature[13]: 25° C; reaction temperature: 35° C; ketone concentration: 0.2 M; catalyst/ketone equiv. ratio: 0.5. [b]Ratio of equivs. [c]Based on isolated compounds. [d]Plus product(s) (up to 3 %) of unknown constitution.

1a-2a Reactions. Tricyclic ketone **3a** was isolated from the reaction mixture of the cycloaddition performed under pressure (elution with 7:3 petroleum ether-ether). Tricyclic ketone **5a** was isolated from the reaction mixture of the cycloaddition accomplished at atmospheric pressure (same elution).

2,3-Dimethyl-1,4,4aβ,8,8aβ,9,10,10aβ-octahydro-6(7H)-phenanthrenone (3a): m.p. 67-68°C; IR 1658 (s, C=O), 1615 (w, C=C) cm^{-1}; ^1H NMR δ 1.54 (br.s, 3H, 3-Me), 1.64 (br.s, 3H, 2-Me), 1.65 (m, 3H, H-8, H-9, H-10), 1.75-1.85 (m, 4H, Hs-1, H-9, H-10), 2.06 (d, 1H, J = 18.0, 1.5 Hz, H-4), 2.14 (ddd, 1H, J = 13.5, 8.5, 5.5 Hz, H-8), 2.24 (m, 1H, J = 9.0, 7.0, 5.0, 4.5, 2.6 Hz, H-10a), 2.26 (m, 1H, H-4), 2.28 (m, 2H, J = 16.0, 11.0, 9.0, 5.0, 1.5 Hz, H-7, H-8a), 2.39 (ddd, 1H, J = 16.0, 8.5, 5.0 Hz, H-7), 2.53 (m, 1H, J = 5.0, 5.0, 1.5, 1.0 Hz, H-4a), 5.63 (dd, 1H, J = 1.5, 1.0 Hz, H-5); ^{13}C NMR δ 18.58 (C-2 Me), 28.38 (C-8), 29.51 (C-9), 30.17 (C-1 or C-10), 32.20 (C-1 or C-10), 33.67 (C-4), 35.33 (C-7), 35.67 (C-10a), 38.34 (C-8a), 42.20 (C-4a), 122.15 (C-2 or C-3), 122.74 (C-5), 124.33 (C-2 or C-3), 168.02 (C-4b), 200.35 (C-6); MS, m/e (rel intensity) 230 (M^+, 30), 157 (10), 150 (11), 149 (base), 120 (62), 119 (24). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.49; H, 9.61.

2,3-Dimethyl-1,4,4aβ,8,8aβ,9,10,10aα-octahydro-6(7H)-phenanthrenone (5a): m.p. 100-101°C; IR 1662 (s, C=O), 1617 (w, C=C) cm^{-1}; ^1H NMR δ 1.24 (m, 1H, J = 13.0, 12.5, 11.0, 4.0 Hz, H-10), 1.30 (m, 1H, j = 13.5, 12.5, 12.0, 4.0 Hz, H-9), 1.43 (m, 1H, J = 11.5, 11.0, 11.0, 4.0, 4.0 Hz, H-10a), 1.62 (br.s, 3H, 3-Me), 1.66 (br.s, 3H, 2-Me), 1.67 (m, 1H, J = 13.5, 12.0, 8.5, 5.0 Hz, H-7), 1.83-1.86 (m, 2H, H-9, H-10), 1.96 (m, 1H, J = 11.0, 7.5, 7.5, 1.4 Hz, H-4a), 1.98 - 2.06 (m, 4H, Hs-1, Hs-4), 2.08 (ddd, 1H, J = 13.5, 5.5, 5.0 Hz, H-8), 2.27 (ddd, 1H, J = 16.0, 12.0, 5.0 Hz, H-7), 2.28 (m, 1H, J = 12.0, 8.5, 5.0, 5.0, 1.5 Hz, H-8a), 2.37 (ddd, 1H, J = 16.0, 5.5, 5.0 Hz, H-7), 5.88 (br.s, 1H, H-5); ^{13}C NMR δ 18.57 (C-3 Me), 19.04 (C-2 Me), 29.06 (C-8), 32.72 (C-10), 33.73 (C-9), 34.22 (C-4), 36.05 (C-7), 38.47 (C-8a), 39.78 (C-10a), 40.64 (C-1), 43.37 (C-4a), 122.10 (C-5), 124.17 (C-2), 124.61 (C-3), 169.00 (C-4b), 200.27 (C-6); MS, m/e (rel. intensity) 230 (M^+, base), 202 (20), 187 (17), 159 (17), 157 (18), 132 (17). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.54; H, 9.59.

1a-2b Reactions. Tricyclic ketones **3b** and **5b** were purified by column chromatography of the crude mixtures of reactions performed at atmospheric and elevated pressure, eluting with gradient petroleum ether to 7:3 petroleum ether-ether.

4α-Methyl-1,4,4aβ,8,8aβ,9,10,10aβ-octahydro-6(7H)-phenanthrenone (3b): m.p. 77-78°C; IR 1660 (s, C=O), 1625 (m, C=C) cm^{-1}; ^1H NMR δ 0.99 (d, 3H, J = 7.3 Hz, 4-Me), 1.15-1.44 (m, 5H, H-8, Hs-9, Hs-10), 1.52 (ddd, 1H, J = 18.0, 5.5, 2.5 Hz, H-1), 1.60 (m, 1H, H-8a), 1.67 (ddd, 1H, J = 18.0, 11.5, 4.5 Hz, H-1), 1.73 (m, 1H, H-8), 1.91 (m, 1H, J = 11.5, 5.0, 4.5, 4.5, 2.5 Hz, H-10a), 2.01 (ddd, 1H, J = 4.5, 4.5, 1.0 Hz, H-4a), 2.14 (ddd, 1H, J = 16.0, 5.0, 5.0 Hz, H-7), 2.19 (ddd, 1H, J = 16.0, 11.0, 5.0 Hz, H-7), 2.31 (m, 1H, J = 7.3, 4.5, 4.5, 3.0 Hz, H-4), 5.36 (m, 1H, J = 10.0, 4.5, 3.0 Hz, H-2), 5.39 (ddd, 1H, J = 10.0, 4.5, 2.5 Hz, H-3), 6.16 (br.s, 1H, H-5); ^{13}C NMR δ 17.23 (C-4 Me), 26.36 (C-1), 27.72 (C-8), 30.41 (C-9), 30.55 (C-10), 33.92 (C-4), 33.96 (C-7), 39.03 (C-10a), 39.89 (C-8a), 48.96 (C-4a), 124.65 (C-5), 125.55 (C-2), 130.54 (C-3), 161.86 (C-4b), 197.06 (C-6); MS, m/e (rel. intensity) 216 (M^+, 39), 149 (base), 120 (61), 105 (29), 91 (79). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.40; H, 9.32.

4β-Methyl-1,4,4aβ,8,8aβ,9,10,10aα-octahydro-6(7H)-phenanthrenone (5b): m.p. 102-103°C; IR 1662 (s, C=O), 1621 (m, C=C) cm^{-1}; ^1H NMR δ 1.01 (d, 3H, J = 7.0 Hz, 4-Me), 1.34 (m, 1H, J = 13.5,

12.0, 11.0, 4.5 Hz, H-10), 1.51 (m, 1H, J = 11.0,11.0, 11.0, 4.5, 4.0 Hz, H-10a), 1.64 (m, 1H, J = 13.5, 12.5, 12.0, 4.0 Hz, H-9), 1.73 (ddd, 1H, J = 11.0, 9.5, 1.5 Hz, H-4a), 1.78, (m, 1H, H-8), 1.84 (ddd, 1H, J = 17.0, 11.0, 2.0 Hz, H-1) 1.90 (m, 2H, H-9, H-10), 2.13 (ddd, 1H, J = 17.0, 4.5, 2.0 Hz, H-1), 2.23 (m, 1H, J = 13.5, 12.0, 10.0, 5.0 Hz, H-8), 2.30 (m, 1H, J = 12.5, 10.0, 5.0, 5.0 Hz, H-8a), 2.34 (ddd, 1H, J = 16.0, 5.5, 5.0 Hz, H-7), 2.42 (ddd, 1H, J = 16.0, 12.0, 5.0 Hz, H-7), 2.44 (ddd, 1H, J = 9.5, 7.0, 2.5 Hz, H-4), 5.49 (m, 1H, J = 10.0, 2.5, 1.8, 1.5 Hz, H-3), 5.62 (m, 1H, J = 10.0, 4.5, 2.5, 2.0 Hz, H-2), 5.87 (dd, 1H, J = 1.5, 1.0 Hz, H-5); ^{13}C NMR δ 20.27 (C-4 Me), 27.87 (C-8), 29.97 (C-4), 33.30 (C-1), 33.54 (C-9), 33.66 (C-10), 34.24 (C-7), 39.87 (C-8a), 40.60 (C-10a), 52.17 (C-4a), 121.12 (C-5), 123.96 (C-2), 132.40 (C-3), 169.21 (C-4b), 200.04 (C-6); MS, m/e (rel. intensity) 216 (M^+, base), 201 (24), 149 (38), 145 (21), 120 (32), 91 (44). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.16; H, 9.30.

1a-2c Reaction. The crude mixture was chromatographed on a column and elution with gradient petroleum ether to 7:3 petroleum ether-ether led to pure ketones **3c** and **4c.**

1,4,4aβ,8,8aβ,9,10,10aβ-Octahydro-6(7H)-phenanthrenone (3c): m.p. 60-61°C; IR 1653 (s, C=O), 1613 (m, C=C) cm^{-1}; ^{1}H NMR δ 1.66 - 1.88 (m, 7H, Hs-1, H-8, Hs-9, Hs-10), 2.14 (m, 1H, J = 13.5 8.5, 5.2, 5.0 Hz, H-8), 2.21-2.27 (m, 2H, Hs-4), 2.28 (m, 1H, J = 9.0, 6.5, 5.0, 4.5, 3.0 Hz, H-10a), 2.29 (ddd, 1H, J = 16.0, 10.0, 4.5 Hz, H-7), 2.30 (m, 1H, J = 11.5, 11.0, 5.0, 4.0, 1.5 Hz, H-8a), 2.39 (ddd, 1H, J = 16.0, 8.5, 5.0 Hz, H-7), 2.58 (m, 1H, J = 5.5, 5.0, 1.4, 1.0 Hz, H-4a), 5.56 (m, 1H, J = 10.0, 4.0, 2.0, 2.0 Hz, H-2), 5.60 (m, 1H, J = 10.0, 4.0, 2.5, 1.5 Hz, H-3), 5.81 (dd, 1H, J = 1.5, 1.4 Hz, H-5); ^{13}C NMR δ 25.76 (C-1), 27.19 (C-4), 28.44 (C-8), 29.83 (C-9), 30.26 (C-10), 35.08 (C-10a), 35.31 (C-7), 38.43 (C-8a), 41.51 (C-4a), 122.78 (C-5), 123.78 (C-3), 126.02 (C-2), 167.16 (C-4b), 200.06 (C-6); MS, m/e (rel. intensity) 202 (M^+, 83), 148 (50), 120 (89), 91 (base), 79 (51), Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 9.01.

1,4,4aα,8,8aβ,9,10,10aα-Octahydro-6(7H)-phenanthrenone (4c): m.p. 80-81°C; IR 1662 (s, C=O), 1613 (m, C=C) cm^{-1}; ^{1}H NMR δ 1.24 (m, 1H, J = 13.5, 13.0, 4.0 Hz, H-9), 1.44 (m, 1H, H-10), 1.61 (m, 1H, J = 13.5, 13.0, 9.0, 4.0 Hz, H-8), 1.73 (m, 1H, J = 13.0, 12.5, 3.5 Hz, H-10), 1.86 (m, 1H, H-1), 1.92 (m, 1H, J = 12.5, 5.5, 3.5, 3.0, 3.0 Hz, H-10a), 1.95 (m, 1H, H-4), 2.01 (m, 1H, J = 13.5, 6.0, 3.5, 3.0 Hz, H-9), 2.10 (m, 1H, J = 13.5, 5.0, 4.5, 4.0 Hz, H-8), 2.18 (m, 1H, H-4), 2.30 (ddd, 1H, J = 16.5, 13.0, 4.5 Hz, H-7), 2.38 (m, 1H, H-1), 2.42 (ddd, 1H, J = 16.5, 4.0, 4.0 Hz, H-7), 2.54 (m, 1H, J = 13.0, 9.0, 6.0, 5.0, 2.0 Hz, H-8a), 2.64 (ddd, 1H, J = 11.5, 4.5, 4.5 Hz, H-4a), 5.63 (m, 1H, H-3), 5.64 (m, 1H, H-2), 5.87 (d, 1H, J = 2.0 Hz, H-5), ^{13}C NMR δ 26.33 (C-10), 27.26 (C-4), 29.59 (C-8), 30.59 (C-1), 33.43 (C-8a), 34.31 (C-9), 34.72 (C-10a), 37.01 (C-7), 42.26 (C-4a),124.01 (C-3), 124.69 (C-5), 125.04 (C-2), 170.62 (C-4b), 200.49 (C-6); MS, m/e (rel. intensity) 202 (M^+, 81), 160 (19), 148 (62), 120 (base), 91 (42); Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.11; H, 8.93.

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