Registry No. (±)-**1a**, 121009-51-6; (±)-**1b**, 121009-48-1; (±)-**2**, 134486-02-5; **3**, 69514-47-2; **4**, 134486-03-6; (*E*)-**6a**, 134486-04-7; (*Z*)-**6a**, 134486-17-2; **6b**, 134486-11-6; **6c**, 134486-13-8; (±)-(*E*)-**7**, 134486-05-8; (±)-(*Z*)-**7**, 134486-18-3; (±)-(*E*)-**8**, 134486-06-9; (±)-(*Z*)-**8**, 134566-46-4; (±)-**9a**, 134486-07-0; (±)-**9b**, 134486-12-7; **10**, 918-86-5; **11**, 124177-30-6; (*E*)-**12**, 134486-08-1; (*Z*)-**12**, 134486-14-9; (*E*)-**13**, 134486-09-2; (*Z*)-**13**, 134486-15-0; (*E*)-**14**, 7643-60-9; (*Z*)-**14**, 7643-59-6; (±)-**15** (isomer 1), 134486-10-5; (±)-**15** (isomer 2), 134486-16-1; (±)-(*E*)-**16**, 134528-79-3; (±)-(*Z*)-**16**, 134486-19-4; $(CH_3)_2C{=}CHCHO$, 107-86-8.

Diels-Alder Reactions of a Bicyclic, Cross-Conjugated Dienone[1]

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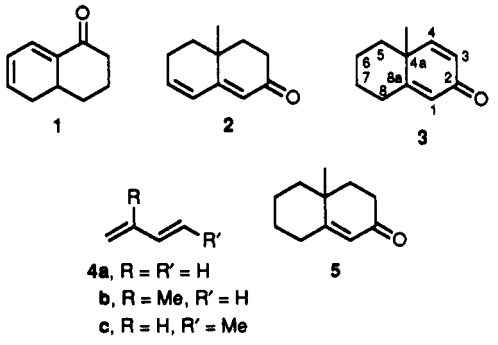
Aluminum chloride catalyzed Diels-Alder reactions of a bicyclic dienone of the 2,5-cyclohexadienone type with 1,3-butadiene, isoprene, and (*E*)-piperylene are described. Structure analysis of the adducts by NMR spectroscopy is presented. The site selectivity and face diastereoselectivity of the reactions are discussed.

Whereas acyclic and cyclic conjugated dienones constitute a class of dienophiles[2] interesting from the points of view of both theory and synthesis, little attention has been devoted to these substances thus far. To overcome in part this information void, the Diels-Alder reactions of simple, acyclic dienes with dienones of the hexalin type, bicycles **1**[3] and **2**,[4] have been investigated recently and



followed by the present study of the cycloaddition behavior of the cross-conjugated hydronaphthalenone **3**. As in the earlier studies, the principal goal of the present investigation was the discovery of the site selectivity, regioselectivity, and diastereoselectivity of the Diels-Alder reaction. In this connection, reactions with 1,3-butadiene (**4a**), isoprene (**4b**), and (*E*)-piperylene (**4c**) were undertaken.

The cycloadditions of hexalone **3**, prepared by oxidation of octalone **5**[5] with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[6] were carried out at 55 °C in toluene solution under aluminum chloride catalysis, the dienes and dienophile being employed in a variety of combinations. Interaction of hexalone **3** with 1,3-butadiene (**4a**) led to tricyclic ketones **8a**, **9a**, **6a**, and **7a** in 3.8:2.2:1.2:1 ratio and 68% yield and to tetracyclic ketone **10** in 8% yield. Exposure of dienone **3** to isoprene (**4b**) afforded tricyclic ketones **8b**, **9b**, **6b**, and **7b** in 10.4:2.9:2.3:1 ratio and 40% yield. Finally, mixing of ketone **3** with (*E*)-piperylene (**4c**) furnished an 8.6:2.4:1.8:1 mixture of tricyclic ketones **8c**, **6c**, **9c**, and **7c** in 68% yield. The Diels-Alder adducts **6** and **8** had been isomerized partly into tricycles **7** and **9**, respectively, in the acidic environment of the reaction conditions. The true equilibria, established by treatment of each isomer with ethanolic sodium ethoxide,[7] corresponded to 1.2, 1.2, and 0.036 for the **6a**/**7a**, **6b**/**7b**, and **6c**/**7c** epimer pairs, respectively, and 4.6, 3.5, and 0.25 for the **8a**/**9a**, **8b**/**9b**, and **8c**/**9c** bridgehead isomer couples, respectively. The Diels-Alder products were kinetically based, as shown by the constancy of the (**8** + **9**)/(**6** + **7**) product ratios through the course of each reaction and the absence of any cross-over reaction from **8** or **9** to **6** or **7** occurring on exposure of any adduct to the reaction conditions of the cycloaddition process.

Product Structures. The tricyclic Diels-Alder adducts can be divided into two classes of structurally distinct α,β-unsaturated ketones, those containing a trisubstituted, conjugated double bond (i.e., ketones **8** and **9**) and those with a disubstituted equivalent function (i.e., ketones **6** and **7**). These two groups of cycloaddition products were recognized readily by NMR spectroscopy. Furthermore, the base-induced equilibrations revealed each group being made up of two epimer pairs (**6**-**7** and **8**-**9**). The structures

(1) (a) Based on the doctoral dissertation of Patrizia Pasciuti. (b) Diels-Alder Reactions of Cycloalkenones. 20. For part 19, see: Minuti, L.; Radics, L.; Taticchi, A.; Venturini, L.; Wenkert, E. *J. Org. Chem.* **1990**, *55*, 4261.

(2) Inter alia: (a) Adams, D. R.; Bhatnagar, S. P.; Cookson, R. C.; Inddenham, R. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1741. (b) Liu, H. J.; Browne, E. N. C. *Tetrahedron Lett.* **1977**, 2919. (c) Liu, H. J.; Browne, E. N. C. *Can. J. Chem.* **1979**, *57*, 377. (d) Liu, H. J.; Browne, E. N. C. *Can. J. Chem.* **1981**, *59*, 601. (e) Liotta, D.; Saindane, M.; Barnum, C. *J. Am. Chem. Soc.* **1981**, *103*, 3234. (f) Fringuelli, F.; Minuti, L.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 1810. (g) Schweizer, B. Structural Chemistry of Enones. Zalewski, R. I. Acid-Base Behaviour of Enones. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Part 1. (h) Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1990**, *55*, 1366.

(3) Fringuelli, F.; Minuti, L.; Radics, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1988**, *53*, 4607.

(4) Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1989**, *54*, 6138.

(5) Heathcock, C. H.; Ellis, J. E.; McMurry, J. E.; Coppolino, A. *Tetrahedron Lett.* **1971**, 4995.

(6) Caine, D.; Boucugnani, A. A.; Pennington, W. R. *J. Org. Chem.* **1976**, *41*, 3632.

(7) Angell, E. C.; Fringuelli, F.; Minuti, L.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1985**, *50*, 4686.

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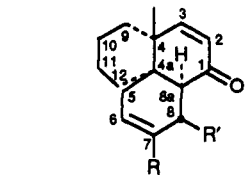

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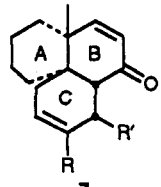
a, R = R′ = H
b, R = Me, R′ = H
c, R = H, R′ = Me



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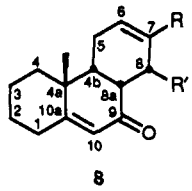

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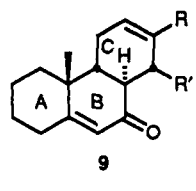

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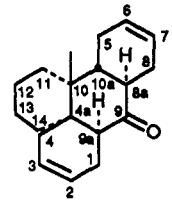

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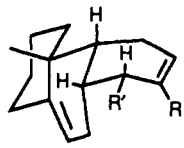
of the cycloadducts and their epimers were determined by ^{13}C NMR spectroscopy, and their carbon shifts are listed in the Experimental Section.

Comparison of the carbon shifts of the angular methyl group and the ring A, nonbridgehead carbons of butadiene adduct **8a** with those of the equivalent sites in model **5** shows C(4) to be shielded strongly (γ-shift), neither the methyl group nor other centers being affected. This fact favors C(5) to be axial and α to ring B. The observation of a nuclear Overhauser effect on H(8a) by irradiation of the angular methyl group indicates their cis relationship and a low J value (3 Hz) of the two methine hydrogens reveals a cis H(4b)–H(8a) relationship. These results limit ketone **8a** to a syn–cis hydrophenanthrone system, represented conformationally by structure **11a**. Being an



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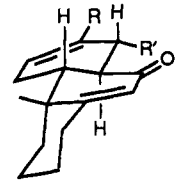

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a, R = R′ = H; b, R = Me, R′ = H; c, R = H, R′ = Me

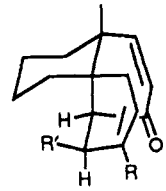
8a-epimer of tricycle **8a**, ketone **9a** is a syn–trans hydrophenanthrone, depicted conformationally by formula **12a**. The strong deshielding of C(5) in ketone **9a** vs its epimer **8a** is in accord with this picture in view of the loss of two γ-shifts from C(9) and C(10a) in the B–C cis compound.

COSY and carbon–hydrogen correlation experiments permitted the differentiation of carbons 5 and 8 in ketones **8a** and **9a**. Strong deshielding of C(8) in ketones **8b** and **9b** shows the Diels–Alder adducts derived from isoprene to have their olefinic methyl group at C(7). Conversion of C(8) into a methine places the piperylene methyl group at this site in ketones **8c** and **9c** and the absence of a γ-shift of the new C_1 unit on C(4b) indicates the lack of H(4b)–8(Me) 1,3-diaxial interaction and thus the methyl group being equatorial in tricycles **8c** (**11c**) and **9c** (**12c**).

The fact of ketones **6** being isomerizable into ketones **7** limits the cycloaddition process to one taking place on the angularly methylated face of cyclohexadienone **3**. Otherwise, the resultant *cis*-hexalone would not be able to undergo C(8a)-epimerization. The ^1H NMR spectral observation of low H(8a) coupling (br d, J = 4 Hz) of conformationally flexible ketone **6a** and large H(8a) coupling (dd, J = 11, 6 Hz) of rigid ketone **7a** fixes the configurations depicted in their formulas. The regiochemistry of the isoprene and piperylene adducts (**6b** and **6c**) and their epimers (**7b** and **7c**) is based on the same NMR experiments as those of hydrophenanthrones **8b**, **8c**, **9b**, and **9c** (vide supra). The simplification of the H(8a) doublet of ketones **6a** and **6b** to a singlet for ketone **6c** reveals an H(8a)–C(8a)–C(8)–H(8β) dihedral angle of nearly 90°, indicative of the stereochemistry of the methyl group as portrayed in formula **6a** (limiting this group to the same configuration in formula **7c**).

The ^{13}C NMR spectrum of dienone **10** reveals the olefinic carbons to be associated with isolated double bonds, implying that both unsaturated centers of cyclohexadienone **3** had participated in the two cycloaddition steps. The similarities of the chemical shifts of carbons 1–3 and 12–14 of ketone **10** and those of like carbons of tricycle **6a** as well as the similarity of the coupling characteristics of H(9a) of ketone **10** and the like bridgehead hydrogen of ketone **6a** reveals a common stereochemistry of three rings of tetracycle **10** with those of tricycle **6a**. The shielding of C(4) of ketone **10** vs the corresponding carbon of ketone **6a** reveals a 1,3-diaxial interaction between C(4) and H(10a) of ketone **10**, indicative of an H(10aβ) orientation. Moreover, the 10-Hz coupling between bridgehead hydrogens 8a and 10a supports a trans relationship of these hydrogens and hence a H(8aα) orientation.

It is worthy of note from the above equilibration studies that the energy content of the B–C *cis*-(**6a**, **6b**) and B–C *trans*-butadiene- and isoprene-derived (**7a**, **7b**) tricyclic ketones are essentially equal, whereas the introduction of an 8α-methyl group (the piperylene-derived ketones **6c**, **7c**) alters the stability pattern strongly in favor of the trans isomer **7c**. This dramatic change can be explained on inspection of the conformations of the two sets of spirocyclic substances. The B–C cis compounds **6** can be portrayed conformationally either by formula **13** or **14** and the B–C trans compounds **7** by **15**. Furthermore, the



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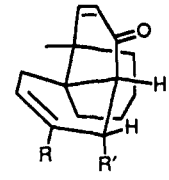

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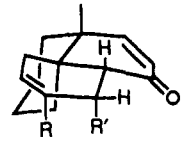

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presence of four 1,3-diaxial alkyl–hydrogen nonbonded interactions in **13a** (or **13b**) vs five like interactions and one 1,3-diaxial alkyl–alkyl interaction in **14a** (or **14b**) suggests **13a** (or **13b**) is the preferred conformer for B–C cis ketone **6a** (or **6b**). Introduction of the piperylene-based methyl group introduces one more 1,3-diaxial alkyl–alkyl nonbonded interaction, destabilizing conformer **13c** sufficiently for it to undergo configurational transformation into B–C trans ketone **7c** (**15c**). This overall conformational analysis favoring conformer **13** as representing ketones **6** is in accord with the ca. 90° H(8a)–C(8a)–C(8)–H(8β) dihedral angle in these compounds (vide supra).

Equilibration of the hydrophenanthrones **8** (**11**) with **9** (**12**) shows the B–C *cis*- (**8a**, **8b**) butadiene- and isoprene-emanating ketones to be somewhat (ca. 4:1) more stable than their B–C trans isomers (**9a**, **9b**). The inverted ratio for the piperylene-derived ketone **8c** implies the trans compound **9c** being preferred at equilibrium. One factor contributing to the greater stability of **12c** over **11c** is the destabilizing influence of the nonbonded, peri interaction of the carbonyl oxygen with the R′ = Me group present in the cis compound **11c** and absent in *trans*-**12c**.

Discussion

Several significant facts emerge from the results of the cycloaddition processes. The reactions lead to reasonable

product yields and, while not highly site-selective, predominate at the site of the least-substituted double bond of the dienone dienophile 3. This fact is in accord with earlier observations on Diels–Alder reactions of 2,4,4-trimethyl-2,5-cyclohexadienone.[2f] The cycloadditions appear to be independent of the nature of the diene or catalyst[8] and those of isoprene (4b) and (*E*)-piperylene (4c) were totaly regioselective, a fact in agreement with results of previous Diels–Alder reactions of 2,5-cyclohexadienones.[2f]

Perhaps the most intriguing feature of the above cycloadditions is the complete dissimilarity of diene behavior at the two dienophile reaction sites in terms of both face selectivity and endo–exo diastereoselectivity. If it be assumed that the cycloaddition takes place in a concerted mechanism involving an unsymmetrical, nonsynchronous transition state (in which σ-bond formation with the dienophile's β-carbon is in advance of that with its α-carbon)[9] and, all factors being equal, diene attack on a β-carbon of dienophile 3 prefers to be axial, antiparallel to the angular methyl group in endo fashion, the reactions producing hydrophenanthrones 8 can be viewed as normal and expected. Whereas the Diels–Alder reactions en route to adducts 8 must have felt some steric interference from H(5α) of dienone 3, strong steric repulsion of incoming diene by H(5α) and H(7α) of the dienophile apparently precluded bond formation at the latter's C(8a) and C(1) in the same stereochemical sense as in the formation of hydrophenanthrones 8. Hence diene attack occurred cis to the angular methyl group in the production of spiro compounds 6, making the face-selectivity of the reactions at the dienophile's two reaction sites dissimilar. Finally, since steric interference between the diene and the angular methyl group is lower in a transition state leading to exo product than one directed toward endo adduct, the exo product (e.g., 6c) is obtained.

Experimental Section

Melting points are uncorrected. IR spectra were recorded in $CHCl_3$. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained at 300 and 75.5 MHz, respectively. The ^1H NMR spectra of ketone 10 in $CDCl_3$ were observed at 500 Mz. GC–MS analyses were calibrated with perfluorotributylamine for 70-eV operations. Analytical GC was performed with 30-m, 0.32-mm diameter SP-2340 fused silica capillary or 30-m, 0.25-mm diameter SPB-5 capillary columns with an "on column" injection system (internal standards: *m*- and *p*-methoxyacetophenone). Absorption chromatography was executed on Merck silica gel (230–400 mesh ASTM). On workup all extracts were washed with brine and dried over anhydrous Na_2SO_4.

4a-Methyl-5,6,7,8-tetrahydro-2(4a*H*)-naphthalenone (3). A mixture of 20.0 g (0.12 mol) of octalone 5 and 39.0 g (17.2 mmol) of DDQ in 1.28 L of dry toluene was refluxed for 4 h. It then was worked up in the usual manner.[6] Chromatography of the crude, oily product and elution with 20:1–2:1 hexane–ethyl acetate yielded 8.50 g (43%) of liquid dienone 3: IR C=O 1660 (s), C=C 1620 (m), 1605 (w) cm^{-1}; ^1H NMR δ 1.25 (s, 3, Me), 6.08 (br s, 1, H-1), 6.20 (dd, 1, J = 10, 2 Hz, H-3), 6.75 (d, 1, J = 10 Hz, H-4); ^{13}C NMR δ 20.5 (C-6), 22.5 (Me), 27.7 (C-7), 32.3 (C-8), 37.8 (C-5), 40.4 (C-4a), 123.7 (C-1), 126.2 (C-3), 156.9 (C-4), 167.1 (C-8a), 186.3 (C-2); MS *m/e* (rel intensity) 162 (M^+, 43), 119 (41), 106 (29), 105 (34), 91 (base), 77 (27). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.69. Found: C, 81.90; H, 8.73.

General Procedure for the Diels–Alder Reactions. The mixtures of the starting materials were prepared in a drybox, and the cycloadditions were carried out in degassed solutions. Table I delineates the conditions of Diels–Alder reactions, with the following discussion describing the 3–4a reaction in greater detail.

Table I. Reaction Conditions of the Diels–Alder Reactions of Dienes 4 with Dienone 3[a]

diene	$AlCl_3$/ ketone[b]	diene/ ketone[b]	reaction time (h)	products yield[c] (%)
4a	0.9	9	120	76
4b	0.25	12	260	40
4c	0.25	6	95	68[d]

[a] Key: complexation time,[10] 50 min; complexation temperature,[10] 22 °C; ketone concentration, 0.2 M; reaction temperature, 55 °C. [b] Ratio of equivalents. [c] GC-based yields (those of isolated products being 10–15% lower). [d] One other product, accounting for 3.5% of the reaction mixture, was not isolated.

A solution of 1.94 g (12.0 mmol) of ketone 3 in 6 mL of dry toluene was added slowly to 10.8 mL of a stirring 1.0 M solution of $AlCl_3$ in nitrobenzene at rt, and stirring was continued for 50 min. A 4.8 M solution (22.5 mL) of 1,3-butadiene (4a) in dry toluene and thereafter 20.7 mL of dry toluene were added and the ampule was sealed under vacuum and heated. The ampule was cooled and opened and the contents poured into ice–water. The mixture was extracted with ether, and the extract was washed with 10% $NaHCO_3$ solution and treated further in the usual manner. Nitrobenzene was removed by vacuum distillation, and the residue was chromatographed.

3–4a Reaction. Elution with 33:1 hexane–ethyl acetate led to ketones 6a, 7a, and 10. The fractions containing 8a–9a mixtures were combined and evaporated under vacuum. Crystallization of the residue from hexane gave ketone 8a, while HPLC (elution with 2:1 acetonitrile–water on a C-18 column) of the mother liquor afforded ketone 9a.

4β-Methyl-4$a\alpha$,4aα-tetramethylene-4,4a,5,8-tetrahydro-1-(8aα*H*)-naphthalenone (6a): colorless liquid; IR C=O 1670 (s) cm^{-1}; ^1H NMR δ 1.03 (s, 3, Me), 1.2–1.9 (m, 10, methylenes), 2.16 (br d, 1, J = 17 Hz, H-5), 2.77 (br d, 1, J = 17 Hz, H-8), 2.89 (br d, 1, J = 4 Hz, H-8a), 5.38 (dm, 1, J = 10 Hz, H-6), 5.52 (dm, 1, J = 10 Hz, H-7), 5.76 (d, 1, J = 10 Hz, H-2), 6.30 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 19.5 (4-Me), 20.2 (C-8), 20.8 (C-10 or C-11), 20.9 (C-11 or C-10), 29.7 (C-12), 31.5 (C-5), 33.9 (C-9), 39.1 (C-4), 40.0 (C-4a), 43.1 (C-8a), 124.1 (C-6), 124.5 (C-7), 125.0 (C-2), 157.0 (C-3), 200.4 (C-1); MS *m/e* (rel intensity) 216 (M^+, 60), 201 (64), 162 (53), 159 (base), 91 (92), 77 (59). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.20; H, 9.30.

4β-Methyl-4$a\alpha$,4aα-tetramethylene-4,4a,5,8-tetrahydro-1-(8aβ*H*)-naphthalenone (7a): colorless liquid; IR C=O 1670 (s), C=C 1658 (s) cm^{-1}; ^1H NMR δ 1.02 (s, 3, Me), 1.1–1.6 (m, 8, methylenes), 1.9–2.1 (m, 1, H-8), 2.16 (br s, 2, C-5 Hs), 2.35 (ddd, 1, J = 18, 6, 5 Hz, H-8), 2.66 (dd, 1, J = 11, 6 Hz, H-8a), 5.58 (dm, 1, J = 10 Hz, H-6), 5.65 (dm, 1, J = 10 Hz, H-7), 5.87 (d, 1, J = 10 Hz, H-2), 6.44 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 21.1 (C-10), 21.9 (C-8), 22.5 (4-Me), 23.1 (C-11), 23.9 (C-12), 27.3 (C-5), 36.1 (C-9), 39.2 (C-4), 40.1 (C-4a), 45.5 (C-8a), 124.4 (C-7 or C-6), 124.6 (C-6 or C-7), 126.8 (C-2), 159.0 (C-3), 200.7 (C-1); MS *m/e* (rel intensity) 216 (M^+, 46), 201 (65), 162 (58), 159 (base), 91 (79), 77 (55). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.35; H, 9.30.

10β-Methyl-4aα,10α-tetramethylene-1,4,4a,5,8,8aα,9aα,-10aβ-octahydro-9-anthrone (10): colorless, crystalline solid; mp 72–73 °C; IR C=O 1705 (s), C=C 1658 (w) cm^{-1}; ^1H NMR δ 1.05 (s, 3, Me), 1.3–2.4 (m, 16, methylenes, H-10), 2.38 (ddd, 1, J = 10, 10, 5 Hz, H-8a), 2.54 (dm, 1, J = 18 Hz, H-1), 3.08 (d, 1, J = 5 Hz, H-9a), 5.4–5.5 (m, 1, H-3), 5.6–5.7 (m, 3, H-2, H-6, H-7); ^{13}C NMR δ 19.6 (Me), 20.8 (C-12), 21.3 (C-1), 21.7 (C-13), 25.5 (C-5), 25.7 (C-8), 27.5 (C-4), 29.7 (C-14), 30.4 (C-11), 37.7 (C-10), 43.7 (C-4a), 44.7 (C-9a), 44.9 (C-8a), 45.9 (C-10a), 123.5 (C-3), 123.9 (C-2), 125.0 (C-7), 125.7 (C-6), 212.0 (C-9); MS *m/e* (rel intensity) 270 (M^+, base), 148 (39), 108 (46), 105 (42), 91 (84), 79 (79), 77 (53). Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.50; H, 9.70.

4aβ-Methyl-1,2,3,4,4a,4bβ,5,8-octahydro-9(8aβ*H*)-phenanthrenone (8a): colorless crystalline solid; mp 88–89 °C; IR C=O 1668 (s), C=C (w) cm^{-1}; ^1H NMR δ 1.3–1.4 (m, 2, CH_2), 1.39 (s, 3, Me), 1.6–1.9 (m, 4, methylenes), 1.9–2.2 (m, 4, H-4b,

(8) Replacement of $AlCl_3$ in reactions of (*E*)-piperylene (4c) with $Et_2O{\cdot}BF_3$, $SnCl_4$, or Yb(fod)$_3$ showed no change, except for the boron trifluoride inducing a slight decrease in site selectivity.

(9) Angell, E. C.; Fringuelli, F.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1986**, *51*, 2642 and references cited therein.

(10) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802.

H-8, C-5 Hs), 2.25 (dm, 1, J = 13 Hz, H-1), 2.35 (dddd, 1, J = 13, 13, 5, 2 Hz, H-1), 2.85 (dd, 1, J = 18, 4 Hz, H-8), 3.02 (br t, 1, J = 4 Hz, H-8a), 5.58 (dm, 1, J = 10 Hz, H-6), 5.68 (dd, 1, J = 10, 5 Hz, H-7), 5.69 (br s, 1, H-10); ^{13}C NMR δ 21.3 (C-3), 23.0 (4a-Me), 23.8 (C-5), 23.8 (C-8), 26.6 (C-2), 32.3 (C-1), 35.0 (C-4), 39.6 (C-4a), 41.5 (C-8a), 43.5 (C-4b), 123.0 (C-10), 125.1 (C-6 or C-7), 125.3 (C-7 or C-6), 165.4 (C-10a), 199.5 (C-9); MS m/e (rel intensity) 216 (M^+, base), 201 (34), 162 (90), 147 (49), 91 (31), 79 (36), 77 (37). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.27; H, 9.27.

4aβ-Methyl-1,2,3,4,4a,4bβ,5,8-octahydro-9(8aαH)-phenanthrenone (9a): colorless liquid; IR C=O 1660 (s) cm^{-1}; ^{1}H NMR δ 1.18 (s, 3, Me), 1.2–2.6 (m, 13, methylenes, methines), 2.50 (ddd, 1, J = 13, 13, 5 Hz, H-1), 5.62 (br s, 2, H-6, H-7), 5.77 (s, 1, H-10); ^{13}C NMR δ 21.4 (C-3), 22.9 (4a-Me), 24.8 (C-8), 26.0 (C-2), 30.4 (C-5), 33.4 (C-1), 33.7 (C-4), 39.3 (C-4a), 40.4 (C-8a), 43.4 (C-4b), 122.2 (C-10), 125.0 (C-6 or C-7), 125.2 (C-7 or C-6), 171.9 (C-10a), 200.2 (C-9); MS m/e (rel intensity) 216 (M^+, 57), 201 (24), 162 (base), 147 (53), 134 (29), 91 (47), 79 (47), 77 (47). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.10; H, 9.33.

3–4b Reaction. Elution with 25:1 hexane–ethyl acetate gave mixtures of ketones **6b**, **7b**, **8b**, and **9b**. Rechromatography of combined **6b–7b** fractions and elution with 50:1 hexane–ethyl acetate separated pure ketones **6b** and **7b**. Evaporation of the combined **8b–9b** fractions and crystallization of the residue from hexane at −20 °C gave pure ketones **8b** and **9b**.

4β,7-Dimethyl-4α,4aα-tetramethylene-4,4a,5,8-tetrahydro-1(8aαH)-naphthalenone (6b): colorless liquid; IR C=O 1662 (s) cm^{-1}; ^{1}H NMR δ 1.11 (s, 3, Me), 1.2–2.1 (m, 10, methylenes), 1.66 (br s, 3, 7-Me), 2.22 (br d, 1, J = 17 Hz, H-5), 2.72 (br d, 1, J = 17 Hz, H-8), 2.96 (br, d, 1, J = 4 Hz, H-8a), 5.16 (br s, 1, H-6), 5.84 (d, 1, J = 10 Hz, H-2), 6.37 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 19.9 (4-Me), 21.0 (C-10 or C-11), 21.1 (C-11 or C-10), 23.0 (7-Me), 25.0 (C-8), 29.8 (C-12), 31.8 (C-5), 34.2 (C-9), 39.1 (C-4), 39.5 (C-4a), 43.6 (C-8a), 118.5 (C-6), 125.1 (C-2), 131.1 (C-7), 157.2 (C-3), 200.6 (C-1); MS m/e (rel intensity) 230 (M^+, 41), 215 (38), 173 (53), 121 (base), 105 (32), 91 (49), 77 (30). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.55; H, 9.70.

4β,7-Dimethyl-4α,4aα-tetramethylene-4,4a,5,8-tetrahydro-1-(8aβH)-naphthalenone (7b): colorless liquid; IR C=O 1665 (s) cm^{-1}; ^{1}H NMR δ 1.08 (s, 3, Me), 1.1–1.8 (m, 8, methylenes), 1.9–2.1 (m, 1, H-8), 1.69 (br s, 3, 7-Me), 2.21 (br s, 2, C-5 Hs), 2.29 (dd, 1, J = 18, 6 Hz, H-8), 2.76 (dd, 1, J = 11, 6 Hz, H-8a), 5.31 (br s, 1, H-6), 5.95 (d, 1, J = 10 Hz, H-2), 6.52 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 21.2 (C-10), 22.6 (4-Me), 23.0 (7-Me), 23.2 (C-11), 24.1 (C-12), 26.7 (C-8), 27.7 (C-5), 36.3 (C-9), 39.1 (C-4), 40.3 (C-4a), 46.0 (C-8a), 118.5 (C-6), 127.0 (C-2), 131.6 (C-7), 159.3 (C-3), 201.3 (C-1); MS m/e (rel intensity) 230 (M^+, 74), 215 (82), 201 (53), 173 (base), 159 (41), 91 (62), 77 (41). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43, H, 9.63. Found: C, 83.40; H, 9.63.

4aβ,7-Dimethyl-1,2,3,4,4a,4bβ,5,8-octahydro-9(8aβH)-phenanthrenone (8b): colorless, crystalline solid; mp 90–91 °C; IR C=O 1660 (s), C=C 1615 (w) cm^{-1}; ^{1}H NMR δ 1.3–1.5 (m, 2, CH_2), 1.38 (s, 3, Me), 1.6–1.8 (m, 3, CH_2, H), 1.68 (br s, 3, 7-Me), 1.8–2.1 (m, 5, H-2, H-4b, H-8, C-5 Hs), 2.25 (dm, 1, J = 13 Hz, H-1), 2.34 (dddd, 1, J = 13, 13, 5, 2 Hz, H-1), 2.73 (br d, 1, J = 16 Hz, H-8), 3.00 (dd, 1, J = 5, 3 Hz, H-8a), 5.25 (br d, 1, J = 2 Hz, H-6), 5.69 (br s, 1, H-10); ^{13}C NMR δ 21.4 (C-3), 23.1 (7-Me), 23.2 (4a-Me), 24.1 (C-5), 26.6 (C-2), 28.5 (C-8), 32.4 (C-1), 35.2 (C-4), 39.6 (C-4a), 42.0 (C-8a), 43.5 (C-4b), 119.2 (C-6), 123.2 (C-10), 132.5 (C-7), 165.5 (C-10a), 199.6 (C-9); MS m/e (rel intensity) 230 (M^+, 64), 162 (31), 147 (35), 137 (34), 136 (base), 93 (37), 91 (39). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.60; H, 9.55.

4aβ,7-Dimethyl-1,2,3,4,4a,4bβ,5,8-octahydro-9(8aαH)-phenanthrenone (9b): colorless, crystalline solid; mp 94–95 °C; IR C=O 1654 (s), C=C 1622 (w) cm^{-1}; ^{1}H NMR δ 1.1–2.5 (m, 13, methylenes, methines), 1.25 (s, 3, Me), 1.69 (br s, 3, 7-Me), 2.58 (ddd, 1, J = 13, 13, 5 Hz, H-1), 5.41 (br s, 1, H-6), 5.86 (s, 1, H-10); ^{13}C NMR δ 21.6 (C-3), 23.0 (4a-Me), 23.1 (7-Me), 25.2 (C-2), 30.6 (C-8), 30.9 (C-5), 33.6 (C-1), 33.9 (C-4), 39.5 (C-4a), 41.0 (C-8a), 43.5 (C-4b), 119.4 (C-6), 122.4 (C-10), 132.4 (C-7), 172.3 (C-10a), 200.8 (C-9); MS m/e (rel intensity) 230 (M^+, base), 215 (68), 201 (69), 162 (90), 147 (69), 91 (57). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.40; H, 9.58.

3–4c Reaction. Elution with 33:1 hexane–ethyl acetate yielded ketones **6c** and **7c** and **8c–9c** mixtures. The combined **8c–9c** fractions were evaporated and the residue chromatographed on silica gel impregnated with 20% silver nitrate. Elution with 50:1 hexane–ethyl acetate furnished ketones **8c** and **9c**.

4β,8α-Dimethyl-4α,4aα-tetramethylene-4,4a,5,8-tetrahydro-1(8aαH)-naphthalenone (6c): colorless, crystalline solid; mp 68–69 °C; IR C=O 1672 (s) cm^{-1}; ^{1}H NMR δ 1.09 (s, 3, Me), 1.1–1.9 (m, 9, H, methylenes), 1.42 (d, 3, J = 7 Hz, 8-Me), 2.22 (dddd, 1, J = 18, 4, 2, 2, Hz, H-5), 2.3–2.6 (m, 1, H-8), 2.94 (br s, 1, H-8a), 5.42 (dm, 1, J = 10 Hz, H-6), 5.56 (br d, 1, J = 10 Hz, H-7), 5.68 (d, 1, J = 10 Hz, H-2), 6.21 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 18.7 (8-Me), 18.9 (4-Me), 20.9 (C-10), 21.3 (C-11), 28.2 (C-8), 29.9 (C-12), 32.1 (C-5), 33.8 (C-9), 39.5 (C-4), 42.4 (C-4a), 48.6 (C-8a), 123.2 (C-6), 125.2 (C-2), 130.6 (C-7), 154.8 (C-3), 202.0 (C-1); MS m/e (rel intensity) 230 (M^+, 12), 121 (base), 105 (36), 91 (76), 77 (46), 67 (45), 55 (37), 53 (36). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.20; H, 9.70.

4β,8α-Dimethyl-4α,4aα-tetramethylene-4,4a,5,8-tetrahydro-1(8aβH)-naphthalenone (7c): colorless, crystalline solid; mp 63–64 °C; IR C=O 1672 (s), C=C 1659 (s) cm^{-1}; ^{1}H NMR δ 1.1–1.7 (m, 8, methylenes), 1.11 (s, 3, Me), 1.16 (d, 3, J = 7 Hz, 8-Me), 2.1–2.3 (m, 2, C-5 Hs), 2.40 (d, 1, J = 9 Hz, H-8a), 2.4–2.5 (m, 1, H-8), 5.48 (br d, 1, J = 10 Hz, H-7), 5.53 (dm, 1, J = 10 Hz, H-6), 5.91 (d, 1, J = 10 Hz, H-2), 6.41 (d, 1, J = 10 Hz, H-3); ^{13}C NMR δ 21.2 (C-10), 22.1 (8-Me), 22.4 (4-Me), 23.1 (C-11), 24.5 (C-12), 27.0 (C-5), 27.4 (C-8), 36.2 (C-9), 40.4 (C-4), 41.4 (C-4a), 53.2 (C-8a), 121.8 (C-6), 127.5 (C-2), 132.0 (C-7), 157.6 (C-3), 201.3 (C-1); MS m/e (rel intensity) 230 (M^+, 30), 215 (base), 173 (51), 159 (59), 91 (82), 77 (53). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.43; H, 9.60.

4aβ,8α-Dimethyl-1,2,3,4,4a,4bβ,5,8-octahydro-9(8aβH)-phenanthrenone (8c): colorless liquid; IR C=O 1670 (s), C=C 1623 (m) cm^{-1}; ^{1}H NMR δ 1.2–1.5 (m, 2, CH_2), 1.38 (s, 3, Me), 1.40 (d, 3, J = 7 Hz, 8-Me), 1.6–1.8 (m, 3, H, CH_2), 1.85 (dm, 1, J = 13 Hz, H-2), 1.9–2.2 (m, 3, H-4, C-5 Hs), 2.22 (dm, 1, J = 13 Hz, H-1), 2.3–2.5 (m, 1, H-8), 2.32 (dddd, 1, J = 13, 13, 5, 2 Hz, H-1), 2.96 (br t, 1, J = 3 Hz, H-8a), 5.50 (dm, 1, J = 10 Hz, H-6), 5.56 (br s, 1, H-10), 5.62 (br d, 1, J = 10 Hz, H-7); ^{13}C NMR δ 18.9 (8-Me), 21.3 (C-3), 22.8 (4a-Me), 24.5 (C-5), 26.7 (C-2), 31.9 (C-1), 33.8 (C-8), 35.0 (C-4), 39.8 (C-4a), 47.0 (C-4b), 47.2 (C-8a), 123.4 (C-10 or C-6), 123.5 (C-6 or C-10), 131.8 (C-7), 162.9 (C-10a), 200.5 (C-9); MS m/e (rel intensity) 230 (M^+, 33), 163 (59), 121 (base), 109 (73), 91 (73), 79 (77), 77 (77). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.30; H, 9.59.

4aβ,8α-Dimethyl-1,2,3,4,4a,4bβ,5,8-octahydro-9(8aαH)-phenanthrenone (9c): colorless, crystalline solid; mp 50–51 °C; IR C=O 1670 (s), C=C 1655 (s) cm^{-1}; ^{1}H NMR δ 1.17 (d, 3, J = 7 Hz, 8-Me), 1.2–2.2 (m, 13, methylenes, methines), 1.24 (s, 3, Me), 2.54 (ddd, 1, J = 13, 13, 5 Hz, H-1), 5.49 (br d, 1, J = 10 Hz, H-7), 5.66 (dm, 1, J = 10 Hz, H-6), 5.80 (s, 1, H-10); ^{13}C NMR δ 21.5 (C-3), 22.9 (4a-Me), 23.1 (8-Me), 24.2 (C-2), 30.0 (C-5), 30.5 (C-8), 33.2 (C-1), 33.2 (C-4), 39.7 (C-4a), 43.9 (C-4b), 47.8 (C-8a), 122.4 (C-10), 123.0 (C-6), 132.3 (C-7), 170.0 (C-10a), 200.6 (C-9); MS m/e (rel intensity) 230 (M^+, 63), 215 (66), 162 (base), 147 (50), 91 (49), 77 (45). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.35; H, 9.61.

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