Cycloalkenylboranes as Highly Reactive and Selective Diels−Alder Dienophiles. A Simple Synthesis of Bridgehead Bicyclic Alcohols

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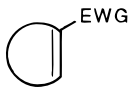
Possibly the simplest approach to the synthesis of bicyclics is the direct use of cycloalkenes as Diels−Alder dienophiles, but a long-standing limitation on this methodology is the recalcitrant dienophilicity of monoactivated cycloalkenes. The low reactivity of cyclohexenones is notorious, though many of the problems have been solved by employing Lewis acid catalysis.[1] Cycloalkenes of general structure **1** with the activating group exocyclic



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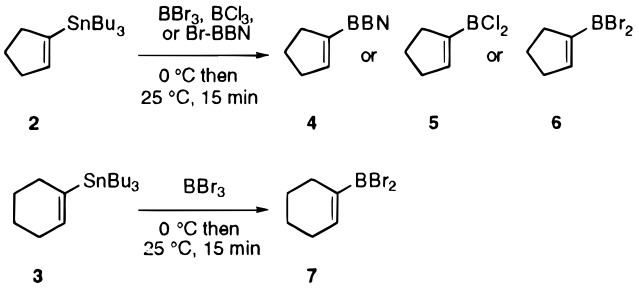
to the ring appear somewhat less reactive, and there is a history of these dienophiles either failing to react in Diels−Alder reactions or affording low yields after prolonged heating.[2,3] Cyclopentenes are more reactive than cyclohexenes,[4] and the best success has been obtained either with formyl as the activating group[3,5] or with highly reactive dienes such as Danishefsky's diene.[6−8]

Trivalent boron atoms are powerful activating substituents for dienophiles and impart a number of unusual and useful properties to the Diels−Alder reactions of vinylboranes and acetylenic boranes.[9,10] A special feature of these reactions is the potential to control their properties by variation of the boryl substituent.[11] In this paper, we make use of the dibromoboryl group, apparently the most powerful of neutral activating substituents, to carry out reactions of cyclopentenyl and cyclohexenyl dienophiles at room temperature. These reactions provide a simple, efficient, and highly regioselective synthesis of bridgehead bicyclic alcohols.

Results and Discussion

We had recently found that 2-alkenyl- and *cis*-1-alkenyldibromoboranes are highly reactive and selective dienophiles, in contrast to the low reactivity of some alkenyldi*alkyl*boranes.[12] Our initial efforts here were directed at determining if the powerful activating effect of the dibromoboryl group would allow the reaction of the more substituted cycloalkenylborane dienophiles.

The cycloalkenylboranes **4**−**7** were generated in situ from the boron−tin exchange reaction of cyclopentenyl- and cyclohexenyltributylstannanes **2** and **3**[16] with BBr_3, BCl_3, or 9-bromo-9-BBN (Br-9-BBN).[13] A slight excess of cycloalkenylstannane was generally used to remove adventitious protic acid that might be present in the stock haloborane solutions; this helped to provide consistent yields in the subsequent Diels−Alder reactions. The completion of boron−tin exchange reactions was judged from NMR spectra of the reaction mixtures taken immediately at room temperature, based on the disappearance in the ^{1}H NMR of the vinylic peak of the cycloalkenylstannanes **2** and **3** and appearance of vinylic peaks at δ 6.72, 7.21, 7.32, and 7.55 for **4**−**7**, respectively. No attempt was made to isolate **4**−**7**.



In the exploratory studies, no reaction of **4** with isoprene could be observed by NMR at 55 °C. However, the reactivity of cycloalkenyldihaloboranes was striking. In contrast to the high temperatures required with the other activating groups,[6,7] both **5** and **6** reacted with isoprene at 25 °C. The reaction of isoprene with the dichloroborane **5** appeared ≈90% complete after 20 h, and the reaction with the dibromoborane **6** proceeded to completion in less than 3 h! For comparison, most Diels−Alder reactions of $AlCl_3$-complexed cycloalkenones still require prolonged heating at 40−70 °C,[1] and the reaction of 1-nitrocyclohexene with Danishefsky's diene involved heating for 13 h in refluxing xylene.[7]

Our studies were focused on the reactions of the dibromoboranes **6** and **7** because of their high reactivities. The Diels−Alder reactions of **6** and **7** with several dienes were characterized by an oxidative workup of the intermediate borane adducts to afford the corresponding alcohols. Our initial attempts at oxidative workups afforded discouragingly large amounts of products apparently derived from protodeboronation of the presumed bicyclic borane intermediates. However, addition of 7 equiv of triethylamine before proceeding with a standard H_2O_2/NaOH workup eliminated the protodeboronation side reaction and afforded alcohols in good to excellent yields. Our results are summarized in Table 1.

The assignment of the regiochemistry of **10**−**19** was complicated by the coupling of the vinylic protons to both CH_2's of the cyclohexenyl ring. In addition, the relatively small vicinal coupling constants between the vinylic

(1) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056−65. Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802−8.
(2) Idelson, M.; Becker, E. J. *J. Am. Chem. Soc.* **1958**, *80*, 908.
(3) Bergmann, E. D.; Becker, A. *J. Am. Chem. Soc.* **1959**, *81*, 221.
(4) Kronenthal, R. L.; Becker, E. I. *J. Am. Chem. Soc.* **1957**, *79*, 1095.
(5) Szmuszkovicz, J.; Bergmann, E. D. *Bull. Res. Counc. Isr.* **1953**, *3*, 93.
(6) Danishefsky, S.; Kitahra, T. *J. Org. Chem.* **1975**, *40*, 538−9. Danishefsky, S.; Schuda, P. F.; Kitahara, T.; Etheredge, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 6066−75. Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653.
(7) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, *100*, 6294−5.
(8) One might expect that use of Lewis acids would help with these dienophiles. Surprisingly, we were unable to find any examples.
(9) Singleton, D. A.; Martinez, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7423. Singleton, D. A.; Martinez, J. P.; Watson, J. V. *Tetrahedron Lett.* **1992**, *33*, 1017.
(10) Singleton, D. A.; Leung, S.-W. *J. Org. Chem.* **1992**, *57*, 4796.
(11) Singleton, D. A.; Martinez, J. P.; Watson, J. V.; Ndip, G. M. *Tetrahedron* **1992**, *48*, 5831.
(12) Singleton, D. A.; Kim, K.; Martinez, J. P. *Tetrahedron Lett.* **1993**, *34*, 3071.
(13) Singleton, D. A.; Martinez, J. P.; Ndip, G. M. *J. Org. Chem.* **1992**, *57*, 5768.

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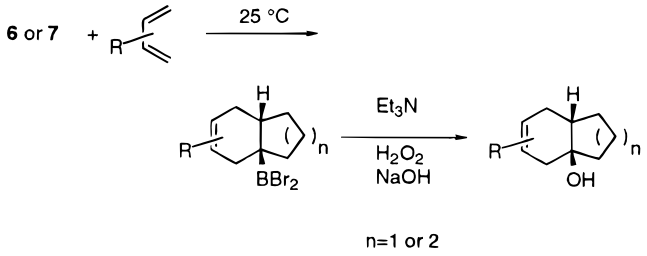


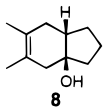
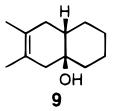
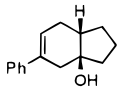
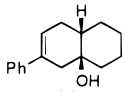
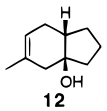
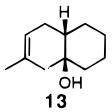
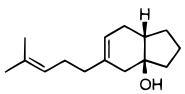
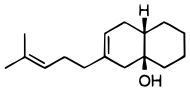
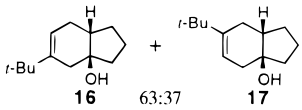
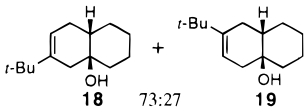
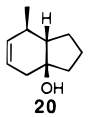
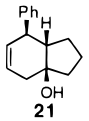
protons and the adjacent CH_2 could not be clearly distinguished from the allylic coupling of the vinylic protons with the other CH_2. Instead, the CH_2's of the cyclohexenyl rings were distinguished by phase-sensitive NOESY experiments. The regiochemistry was finalized by DQCOSY or selective homonuclear decoupling experiments to determine which CH_2 was coupled to the bridgehead proton. Figure 1 shows the key coupling and NOE observations used in the regiochemical assignments of **10**−**13**, **16**, and **18**. In the cases of **13** and **18** no definitive NOE was observed between the vinylic protons and the adjacent CH_2, but the regiochemistry could still be assigned on the basis of an NOE between the methyl or *tert*-butyl groups and the other CH_2 group of the cyclohexene ring. The regiochemistry of **14** and **15** assigned by analogy with **12** and **13**. These analogies were supported by the observation of very similar chemical shifts and coupling patterns for the cyclohexenyl ring CH_2's for **12** and **14** and for **13** and **15**, respectively. The stereochemistry of **20** was assigned on the basis of NOEs between the methine proton of the cyclohexenyl ring and three protons on the cyclopentyl ring. There was also observed an NOE between the −OH and the bridgehead proton, indicative of a *cis* ring fusion. In all other cases a *cis* ring fusion was assumed. The stereochemistry of **21** was assigned on the basis of an 8.2 Hz coupling between the bridgehead proton and the methine proton on the cyclohexenyl ring.

Aside from the high reactivity of **6** and **7**, the regioselectivity and endo-stereoselectivity exhibited in these reactions was striking. With the exception of the 2-*tert*-butyl-1,3-butadiene reactions, only a single regioisomeric or stereoisomeric product alcohol could be detected in the crude product mixtures for each reaction. For comparison, uncatalyzed Diels−Alder reactions of carbonyl-activated dienophiles are normally neither very regioselective with isoprene nor very stereoselective with *trans*-piperylene, while Lewis acid-catalyzed reactions afford fairly high (though usually not complete) selectivity.[14] Regular cycloalkenyl dienophiles appear to follow the same trend, though product epimerization has often been a problem under Lewis acid-catalyzed conditions.[1]

In the reactions of **6** and **7** with both 1- and 2-substituted dienes the major or exclusive product is derived from a 1,3-orientation of diene substituent and dibromoboryl group. This electronic preference for the "meta" product is a unique property of some but not all boron-activated dienophiles. Along with **6** and **7**, simple 2-alkenyl- and *cis*-1-alkenyldihaloboranes and alkynylboranes favor the meta product, while vinyldialkylboranes, vinyldihaloboranes, and *trans*-1-alkenyldihaloboranes favor a normal regioselectivity.[10,12]

In keeping with the proposed explanation for the unusual regiochemistry with alkynylboranes (based on ab initio calculations),[10] the unusual regiochemistry with **6** and **7** could be the result of a [4 + 3] transition state that looks something like **22**, in which there is advanced bonding of B to C_1 relative to the bonding of C_5 to C_4. This would result in a partial positive charge buildup on

Table 1. Reaction Conditions, Products and Yields for Diels−Alder Reactions of 6 and 7[a]

Diene	Borane	Reaction Time	Yield	Product(s)
	**6**	8.5 h	80%	 **8**
	7	8 h	81%	 **9**
	**6**	3.5 h	58%	 **10**
	7	8 h	58%	 **11**
	**6**	8.5 h	66%	 **12**
	7	8 h	76%	 **13**
	**6**	8.5 h	50%	 **14**
	7	8.5 h	41%	 **15**
	**6**	8.5 h	80%	 **16** 63:37 **17**
	7	8 h	81%	 **18** 73:27 **19**
	**6**	6 h[b]	50%	 **20**
	**6**	3.5 h	42%	 **21**

[a] All reactions were carried out at 25 °C in hexanes solvent using limiting diene unless otherwise noted. [b] Excess diene was used in this experiment.

(14) (a) Güner, O. F.; Ottenbrite, R. M.; Shillady, D. D.; Alston, P. V. *J. Org. Chem.* **1988**, *53*, 5348 and references therein. (b) Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 1121.

(15) We have recently observed examples of stepwise Diels−Alder reactions with alkynyldihaloboranes, although the favored mechanism started with a concerted [4 + 3] cycloaddition. Leung, S.-W.; Singleton, D. A. *J. Organomet. Chem.*, in press.

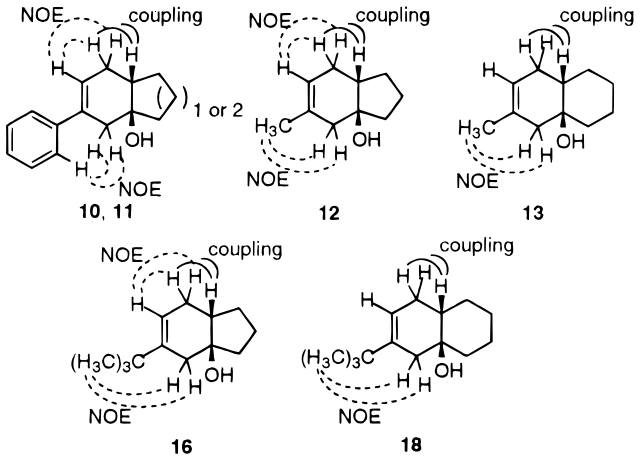
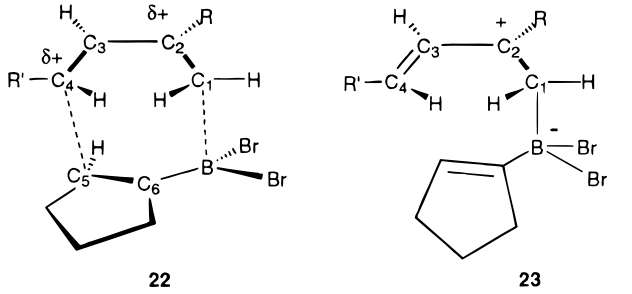


Figure 1. Structurally significant NOEs and couplings for **11**−**13**, **16**, and **17**.

C_2 and C_4 that would be stabilized by R or R′, favoring the observed regiochemistry. Alternatively, the unusual regiochemistry could be explained by a stepwise reaction involving the zwitterionic intermediate **23**.[15] However, this would not explain the high endo-stereoselectivity observed in these reactions.



Conclusion

The normally poor dienophilicity of cycloalkenes is overcome through the use of a dibromoboryl activating group. Cycloalkenyldibromoboranes are uniquely reactive with simple dienes at 25 °C and exhibit exceptional selectivity among Diels−Alder reactions. Combination of the high reactivity, regioselectivity, and endo-stereoselectivity of these reactions with the potential versatility of the product boranes should provide easy access to a variety of bicyclics not otherwise available from Diels−Alder reactions.

Experimental Section

All reactions were carried out in dry glassware under a nitrogen atmosphere using solvents dried by standard techniques. ^{1}H NMR spectra of reaction mixtures were taken in sealed glass capillaries within NMR tubes and were referenced approximately to the peaks of the solvent hexanes or CH_2Cl_2. Cyclopentenyltributylstannane (**2**) and cyclohexenyltributylstannane (**3**) were prepared by literature methods.[16]

General Procedure for the in Situ Formation and Diels−Alder Reactions of Cycloalkenyldibromoboranes. A solution of 1.00 mL of 1.0 M BBr_3 in hexanes was cooled to 0 °C, and 381 mg (1.1 mmol) of 1-(tributylstannyl)cyclohexene was added dropwise. The solution was then warmed to room temperature and stirred for 15 min. To the resulting mixture was added dropwise 0.5−0.6 mmol of diene (except for the reaction with *trans*-piperylene, which used 1.5 mmol of diene), and the resulting mixture was stirred at room temperature for the time listed in Table 1. The reaction mixture was cooled to 0 °C and treated successively with 1 mL of triethylamine, 3 mL of 3 N NaOH, 3 mL of THF, and dropwise, 3.0 mL of 30% H_2O_2. The mixture was then stirred at 25 °C for 16 h and extracted with three 10-mL portions of ether. The combined organic layers were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The residue was then chromatographed on an 8-in. × 10 mm silica gel column using 15% ethyl acetate in petroleum ether as eluent to afford the product alcohols.

5,6-Dimethyl-2,3,3a,4,7,7a-hexahydro-(1*H*)-inden-3a-ol (**8**): ^{1}H NMR ($CDCl_3$) δ 2.26−2.10 (m, 2 H), 2.04 (d, J = 17 Hz, 1 H) 1.96−1.84 (m, 2 H) 1.79−1.54 (m, 11 H), 1.45 (s, 1 H), 1.27 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 124.3, 123.1, 79.9, 44.6, 42.3, 38.4, 35.1, 30.5, 20.6, 19.1, 18.7; HRMS (EI) calcd for $C_{11}H_{18}O$ 166.1358, found 166.1355.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.17; H, 10.74.

2,3-Dimethyl-1,4,4a,5,6,7,8,8a-octahydro-4a-naphthalenol (9): ^{1}H NMR ($CDCl_3$) δ 2.48−2.32 (m, 2 H), 1.74−1.53 (m, 13H), 1.50 (m, 1 H), 1.46−1.08 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 123.2, 121.2, 71.4, 41.4, 40.3, 38.0, 35.4, 30.2, 25.0, 24.0, 19.0, 18.8; HRMS (EI) calcd for $C_{12}H_{20}O$ 180.1514, found 180.1521.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.99; H, 10.94.

2,3,3a,4,7,7a-Hexahydro-5-phenyl-(1*H*)-inden-3a-ol (**10**): ^{1}H NMR ($CDCl_3$) δ 7.40−7.36 (m, 2 H), 7.34−1.28 (m, 2 H), 7.22 (tt, J = 7.3, 1.5 Hz, 1 H), 6.09 (m, 1 H), 2.70 (dm, J = 17.6 Hz, 1 H) 2.57 (dm, J = 17.6 Hz, 1 H), 2.48 (dm, J = 17.6 Hz, 1 H), 2.06−1.94 (m, 3 H), 1.83−1.68 (m, 4 H), 1.54 (s, 1 H), 1.38 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 141.6, 134.6, 128.3, 126.8, 125.1, 123.0, 80.0, 43.3, 38.2, 37.6, 30.4, 29.0, 20.3; HRMS (EI) calcd for $C_{15}H_{18}O$ 214.1358, found 214.1356.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.86; H, 8.21.

1,4,4a,5,6,7,8,8a-Octahydro-3-phenyl-4a-naphthalenol (**11**): ^{1}H NMR ($CDCl_3$) δ 7.42−7.37 (m, 2 H), 7.35−7.29 (m, 2H), 7.23 (tt, J = 7.2, 1.6 Hz, 1 H), 6.1 (m, 1 H), 2.82 (dm, J = 17.6, 1.8 Hz, 1 H), 2.69 (d of hextets, J = 19.0, 3.6 Hz, 1 H), 2.27 (d, J = 17.2 Hz, 1 H), 2.05 (dm, J = 17.2 Hz, 1 H), 1.87−1.58 (m, 6 H), 1.55−1.43 (m, 2 H), 1.41−1.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 141.6, 132.3, 128.2, 126.8, 125.0, 122.1, 71.4, 40.1, 38.4, 35.6, 30.0, 29.4, 25.0, 24.0; HRMS (EI) calcd for $C_{16}H_{20}O$ 228.1514, found 228.1521.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.89; H, 8.79.

2,3,3a,4,7,7a-Hexahydro-5-methyl-(1*H*)-inden-3a-ol (**12**): ^{1}H NMR ($CDCl_3$) δ 5.31 (m, 1 H), 2.25−2.14 (m, 2 H), 2.02 (d, J = 17 Hz, 1 H), 1.94−1.56 (m, 10 H), 1.52 (s, 1 H), 1.31 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.2, 119.0, 79.5, 42.7, 40.0, 37.7, 29.6, 28.1, 23.5, 19.8; HRMS (EI) calcd for $C_{10}H_{16}O$ 152.1201, found 152.1186.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.54; H, 10.54.

3-Methyl-1,4,4a,5,6,7,8,8a-octahydro-4a-naphthalenol (**13**): ^{1}H NMR ($CDCl_3$) δ 5.33 (m, 1 H), 2.44 (dm, J = 18 Hz, 1 H), 2.34 (d, J = 18 Hz, 1 H), 1.81−1.58 (m, 9 H), 1.58−1.44 (m, 2 H), 1.44−1.30 (m, 2 H), 1.30-1.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 129.7, 118.7, 71.3, 40.4, 38.8, 38.2, 30.0, 28.8, 25.0, 24.0, 23.4; HRMS (EI) calcd for $C_{11}H_{18}O$ 166.1358, found 166.1345.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.57; H, 11.22.

2,3,3a,4,7,7a-Hexahydro-5-(4-methyl-3-pentenyl)-(1*H*)-inden-3a-ol (**14**): ^{1}H NMR ($CDCl_3$) 5.34 (m, 1 H), 5.06 (t of quintets, J = 6.8, 1.4 Hz, 1 H), 2.28−2.15 (m, 2 H), 2.11−1.55 (m, 18 H), 1.48 (s, 1 H), 1.30 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 135.1, 131.5, 124.1, 119.0, 79.6, 43.1, 38.3, 37.7, 37.5, 29.9, 28.1, 26.3, 25.7, 20.0, 17.7; HRMS (EI) calcd for $C_{15}H_{24}O$ 220.1827, found 220.1813.

3-(4-Methyl-3-pentenyl)-1,4,4a,5,6,7,8,8a-octahydro-4a-naphthalenol (**15**): ^{1}H NMR ($CDCl_3$) δ 5.35 (m, 1 H), 5.06 (t-quintet, J = 6.9, 1.4 Hz, 1 H), 2.45 (dm, J = 20 Hz, 1 H), 2.36 (d, J = 19 Hz, 1 H), 2.12−2.03 (m, 2 H), 2.02−1.91 (m, 2 H), 1.78 (d, J = 19 Hz, 1 H), 1.73−1.45 (m, 13 H), 1.45−1.09 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 133.6, 131.4, 124.4, 118.6, 71.3, 40.6, 38.2, 37.6, 37.2, 30.1, 28.9, 26.5, 25.6, 25.0, 24.0, 17.7; HRMS (EI) calcd for $C_{16}H_{26}O$ 234.1984, found 234.1973.

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5-(1,1-Dimethylethyl)-2,3,3a,4,7,7a-hexahydro-(1*H*)-inden-3a-ol (**16**) **and 6-(1,1-dimethylethyl)-2,3,3a,4,7,7a-hexahydro-(1*H*)-inden-3a-ol** (**17**) were isolated as a 63:37 mixture of isomers from which samples of purified **16** could be obtained after a second chromatography: **(16)** ^{1}H NMR ($CDCl_3$) δ 5.44 (m, 1 H), 2.32−2.19 (m, 2 H), 2.13 (d, J = 16 Hz, 1 H), 1.94 (m, 1 H), 1.88−1.56 (m, 6 H), 1.45 (br s, 1 H), 1.25 (m, 1 H), 1.01 (s, 9 H); **(16 + 17)** ^{1}H NMR ($CDCl_3$) δ 5.44 (m), 5.40 (m), 2.34−2.08 (m, 3 H), 2.00−1.56 (m, 7 H), 1.50 (br s, 1 H), 1.25 (m, 1 H), 1.01 (s, 9 H); **(16)** ^{13}C NMR ($CDCl_3$) δ 144.1, 116.3, 80.8, 44.1, 38.3, 35.3, 35.0, 31.3, 28.7, 21.1; **(17)** ^{13}C NMR ($CDCl_3$) δ 146.3, 115.1, 80.2, 46.0, 39.2, 36.5, 31.1, 29.0, 28.2, 21.5; HRMS (EI, of mixture) calcd for $C_{13}H_{22}O$ 194.1671, found 194.1674.

Anal. (of mixture) Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41. Found: C, 80.45; H, 11.21.

3-(1,1-Dimethylethyl)-1,4,4a,5,6,7,8,8a-octahydro-4a-naphthalenol (**18**) **and 2-(1,1-dimethylethyl)-1,4,4a,5,6,7,8,8a-octahydro-4a-naphthalenol** (**19**) were isolated as a 73:27 mixture of isomers from which samples of purified **18** could be obtained after a second chromatography: ^{1}H NMR ($CDCl_3$) δ 5.41 (m, 1 H), 2.43 (dm, J = 19 Hz, 1 H), 2.35 (dm, J = 18 Hz, 1 H), 1.90−1.78 (m, 2 H), 1.74−1.48 (m, 6 H), 1.47−1.34 (m, 2 H), 1.34−1.08 (m, 2 H), 1.01 (s, 9 H); (**18** + **19**) ^{1}H NMR ($CDCl_3$) δ 5.41 (m), 5.30 (m), 2.25−2.55 (m), 1.95−0.9 (m); **(18)** ^{13}C NMR ($CDCl_3$) δ 141.3, 115.1, 71.4, 39.9, 37.6, 35.1, 33.0, 30.1, 29.1, 28.9, 24.8, 23.7; **(19)** ^{13}C NMR ($CDCl_3$) δ 143.0, 113.0, 70.4, 41.4, 38.2, 33.9, 29.6, 29.3, 28.9, 27.5, 25.1, 24.1; HRMS (EI, of mixture) calcd for $C_{14}H_{24}O$ 208.1827, found 208.1832.

Anal. (of mixture) Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.16; H, 11.55.

2,3,3a,4,7,7a-Hexahydro-7-methyl-(1*H*)-inden-3a-ol (**20**): ^{1}H NMR ($CDCl_3$) δ 5.56 (m, 1 H), 5.47 (dq, J = 9.9, 2.2 Hz, 1 H), 2.30 (d-quintet, J = 17.1, 2.4 Hz, 1 H), 2.20 (dq, J = 17.1, 2.7 Hz , 1 H), 2.04 (m, 1 H), 1.84−1.56 (m, 5 H), 1.51−1.40 (m, 2 H), 1.33 (s, 1 H), 1.03 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 132.3, 123.3, 80.3, 51.9, 37.3, 35.6, 35.0, 29.2, 20.6, 20.5; HRMS (EI) calcd for $C_{10}H_{16}O$ 152.1201, found 152.1189.

2,3,3a,4,7,7a-Hexahydro-7-phenyl-(1*H*)-inden-3a-ol (**21**): ^{1}H NMR ($CDCl_3$) δ 7.34−7.27 (m, 2 H), 7.25−7.19 (m, 3 H), 5.78 (dm, J = 10.0 Hz, 1 H), 5.64 (dq, J = 10.0, 2.3 Hz, 1 H), 2.97 (m, 1 H), 2.49−2.34 (m, 2 H), 2.02−1.75 (m, 5 H), 1.70 (m, 1 H), 1.57 (m, 1 H), 1.39 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 145.2, 130.1, 128.4, 128.3, 126.3, 125.0, 80.1, 52.5, 47.3, 37.5, 35.7, 28.7, 20.2; HRMS (EI) calcd for $C_{15}H_{18}O$ 214.1358, found 214.1346.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.14; H, 8.39.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **10**, **12**−**15**, and **20** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm edition of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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