Diastereoselectivities Associated with the 1,2-Addition of Chiral (Racemic) Cyclopentenyl Organometallics to Bicyclo[2.2.2]octenones

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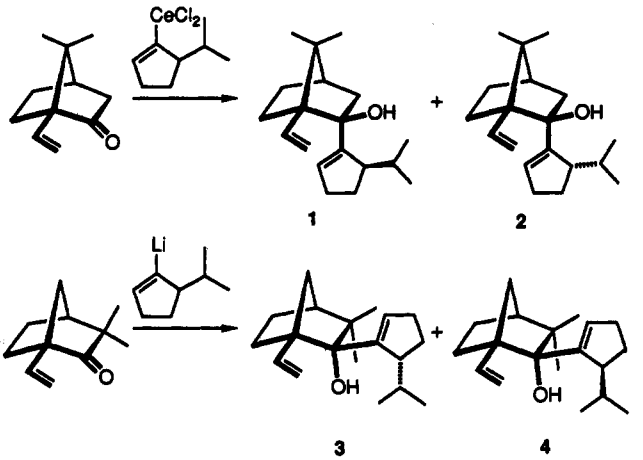
The levels of diastereoselection attainable during condensation of the bicyclo[2.2.2]octenones **5–7** with organometallics derived from a selection of the vinyl bromides **8–12** have been determined. The 1,2-additions involving **6** exhibit excellent molecular recognition (>98:2) during syn (endo) addition to the carbonyl group. The diastereoselectivities associated with the capture of **5** and **7** are lower and more variable, although still respectable in several examples. In all cases, the dominant product is the alcohol in which the C-5 substituent on the nucleophilic subunit is β-oriented. The structural assignments to the numerous alcohols follow from correlations of olefinic carbon chemical shifts, X-ray crystallography in selected examples, and anionic oxy-Cope rearrangement to generate polycyclic ketones whose stereochemical features were defined by NMR methods. The findings provide insight into the transition state geometries adopted in the course of these reactions. The model which has been formulated is consistent with the greater discriminatory power of **6** and conforms closely to earlier proposals for related reactions.

In connection with our successful total synthesis of (+)-ikarugamycin,[1] it was necessary to elucidate the extent and direction of double diastereoselectivity attainable upon 1,2-addition of chiral cyclopentenyl organometallics to 7,7-disubstituted norbornenones.[2] The heightened levels of molecular recognition realized with these systems subsequently prompted a broader examination of the structural interrelationships involved.[3] This chemistry has since formed the basis of synthetic approaches to germacranolides,[4] ophiobolins,[5] homologs of cerorubenic acid-III and crispolide,[6] and taxol.[7] Perhaps the most notable contrast in diastereoselective response is the superb control exercised when endo approach is forced upon an approaching nucleophile (**1:2** = 15.7:1) and the precipitous dropoff when exo capture operates (**3:4** = 1.2:1).[8]

In light of these findings, it was of interest to us to explore the ability with which variously substituted bicyclo[2.2.2]-octenones can deal with stereochemical information present in several cyclopentenyl anions. Past precedent suggested[9,10] that the facial selectivity of attack at the carbonyl group would not be as controlled as in the norbornyl and norbornenyl examples. Although the two systems appear superficially to be similar, geometrical differences were expected to lead to significantly different results. The consequences of these changes in structural geometry and their steric origins form the subject of this paper.



Results

Ketonic Substrates and Cyclopentenyl Nucleophiles. In our selection of bicyclo[2.2.2]octenones, we were guided by reasonable availability and the positioning of methyl groups at sites that might maximize the potential for diastereoselective interaction. Ketones **5–7** share a common rigid carbon framework yet differ in the direction

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(7) (a) Paquette, L. A.; Elmore, S. W.; Combrink, K. D.; Hickey, E. R.; Rogers, R. D. *Helv. Chim. Acta* **1992**, *75*, 1755. (b) Paquette, L. A.; Combrink, K. D.; Elmore, S. W.; Zhao, M. *Helv. Chim. Acta* **1992**, *75*, 1772 and relevant references cited therein.

(8) (a) Paquette, L. A.; Teleha, C. A.; Taylor, R. T.; Maynard, G. D.; Rogers, R. D.; Gallucci, J. C.; Springer, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 265. (b) Paquette, L. A.; Pegg, N. A.; Toops, D.; Maynard, G. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1990**, *112*, 277.

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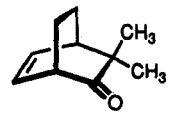
Table 1. Product Ratios Realized upon Addition of Vinyl Organometallics to Ketones 5–7

entry	ketone	vinyl bromide	endo adducts β	endo adducts α	exo adducts[a] 1st	exo adducts[a] 2nd	endo diastereoselectivity	endo:exo ratio	yield, %
1	5	8	19	–	1	–	>98:2	19	88
2		9	9.5	1.9	3.2	1	5:1	2.7	93
3		10	11.5	1	4.5	1.5	11.5:1	2.1	90
4		11	12	–	1	–	>98:2	12	70
5		12	5.8	3.0	1	1.1	1.9:1	4	93
6	6	8	7	–	1	–	>98:2	7	56
7		9	13.2	–	3.7	1	>98:2	2.8	81
8		11	14.8	–	1.8	1	>98:2	5.3	54
9	7	8	44	5.0	1	–	8.8:1	49	70
10		10	29.5	8.2	1	–	3.6:1	31.7	74
11		12	21.5	2.2	3.9	1.0	9.8:1	4.1	81

[a] The structures of the exo diastereomers were not differentiated.

and level of steric buttressing at positions α and β to the carbonyl group.

5



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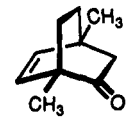

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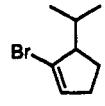
The parent system 5 was prepared by Diels–Alder addition of acrylonitrile to 1,3-cyclohexadiene, introduction of an α-chlorine atom by heating the adduct with phosphorus pentachloride and pyridine in $CHCl_3$, and hydrolysis with KOH in aqueous DMSO.[11] Gem-dialkylation of 5 with sodium hexamethyldisilazide and methyl iodide in THF gave the previously unknown 6. Ketone 7 was prepared from 4-methylanisole via 1,4-dimethyl-1,3-cyclohexadiene by the published procedure.[12]

The vinyl bromides 8–12, which have been utilized to probe the extent of diastereoselective discrimination attainable with the predescribed ketones, have been prepared by known methods.[2c,6b] These were selected because they are substituted at a minimum with an alkyl group at C-5. The proximity of such stereogenecity to the



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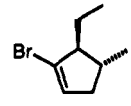

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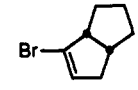

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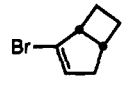

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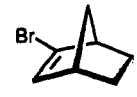

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nucleophilic seat of reaction has previously been recognized to provide a respectable capacity for molecular recognition. Beyond that, 9–11 possess a second alkyl substituent at C-4 oriented either trans or cis to that at C-5. The cis-annulated derivatives are strained to quite different degrees and are characterized by distinctively different internal bond angles and the like. Finally, the 3,5-ethano bridge in 12 forces adoption by its five-membered ring of a conformation uniquely different from the other four.

Condensation Reactions. For the purpose of achieving internal consistency, special care was given to conducting all of the coupling experiments in as similar a manner as possible. This attention to detail spanned the gamut from the desiccation of the cerium trichloride heptahydrate to the concentration of reagents, and even to the manner of quenching the reaction mixtures. A generalized procedure is given in the Experimental Section.

Since it was necessary to guard against the tendency of 5 and 7 simply to enolize in the presence of vinyllithium reagents, recourse was made to the less basic cerium reagents.[13] This metal–metal exchange was not necessary for 6, which was reacted directly with the first-formed lithium reagents since no appreciable diastereoselectivity differences were noted previously in condensations involving the lithium and cerium reagents of otherwise identical structure.[2,4,6] Control experiments performed in the course of this investigation also indicated that the nature of the specific counter ion had little effect on product distribution.

The possible influence of organometallic concentration was also briefly examined. In a series of experiments involving the coupling of 5 with 10, a greater than 20-fold increase (from 0.003 to 0.07 M) did result in a modest change in stereoselectivity from 2.9:1 at high dilution to 2.1:1. Temperature differences gave rise to more modest changes in product distribution. Notwithstanding the relatively minor impact of these variables, standardization of reaction conditions was implemented in all experiments.

An optimal reagent ratio for maximizing the level of diastereoselection was shown previously by DeRussy[4] to involve a 3:1 ratio of organometallic to ketone and this stoichiometry was employed herein.

Crude product mixtures were analyzed directly by analytical HPLC methods to determine the product distributions. Where unresolved peaks were seen, these measurements were complemented by high-field ^1H NMR analysis.

Table 1 provides an overview of the numerous experiments that were undertaken. The great majority of them were performed in duplicate. In no case was effort directed to distinguishing the stereochemistry of exo isomers when these were formed.

Ketone 5 was reacted with all five vinyl bromides. When condensed with 8, only two alcohols were produced in good yield (88%), and these were amenable to separation by analytical HPLC (ratio 19:1). Previous observations have

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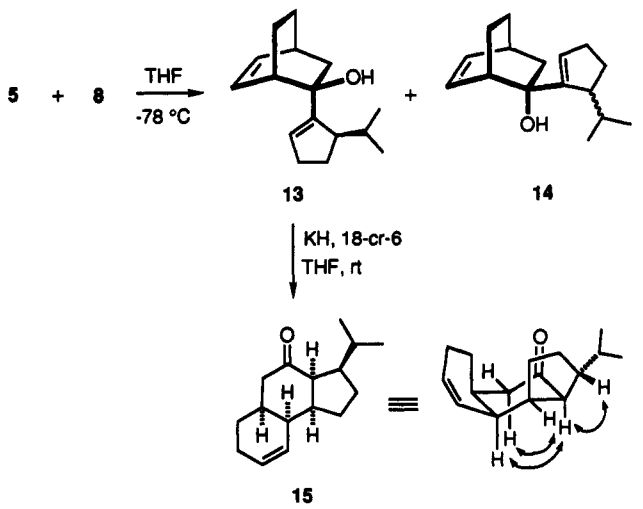
Table 2. Comparative ^{13}C Chemical Shift Data for the Olefinic Carbons in the Carbinol Adducts (all values in ppm)

ketone	vinyl bromide	β isomer/first isomer[a] bicyclooctene ring	Δ ppm	cyclopentene ring	Δ ppm	α isomer/second isomer[b] bicyclooctene ring	Δ ppm	cyclopentene ring	Δ ppm
				A. Endo Series					
5	8	152.4, 126.7	25.7	133.7, 132.8	0.9				
	9	152.6, 123.7	28.9	133.7, 132.5	1.2	152.3, 124.3	28.0	133.6, 133.1	0.5
	10	152.9, 124.2	28.7	133.5, 132.8	0.7	153.0, 124.5	28.5	133.5, 133.2	0.3
	11	153.8, 125.2	28.6	133.3, 133.0	0.3				
	12	155.2, 128.4	26.8	133.1, 133.0	0.1	156.2, 127.2	29.0	133.5, 133.1	0.4
6	8	150.9, 126.4	24.5	133.5, 132.3	1.2				
	9	150.4, 124.6	25.8	133.7, 132.2	1.5				
	11	152.5, 124.9	27.6	134.2, 132.0	2.2				
7	8	152.6, 126.4	26.2	137.9, 137.4	0.5	150.2, 127.7	22.5	139.9, 139.1	0.8
	9	152.1, 123.5	28.8	137.5, 137.3	0.2	153.5, 121.1	30.4	138.5, 138.0	0.5
	10	153.2, 123.7	29.5	138.5, 137.5	1.0	150.3, 126.5	23.8	139.9, 138.8	1.1
	12	156.2, 127.7	28.5	138.5, 138.1	0.4	156.3, 128.9	27.4	138.1, 137.4	0.7
				B. Exo Series					
5	8	148.4, 127.4	21.0	136.6, 131.8	4.8				
	9	148.6, 125.0	23.6	136.3, 131.9	4.4	148.7, 126.1	22.6	136.5, 131.1	5.4
	10	149.0, 125.8	23.2	136.4, 131.7	4.7	149.2, 126.4	22.8	136.3, 131.1	5.2
	12	152.7, 129.7	23.0	136.4, 131.2	5.2	150.2, 129.6	22.4	136.4, 131.1	5.1
6	8	146.7, 127.0	19.7	139.0, 131.1	7.9				
	9	146.5, 125.2	21.3	138.9, 131.0	7.9	148.5, 127.3	21.2	138.9, 131.1	7.8
	11	148.8, 126.0	22.8	138.7, 131.0	7.7	154.2, 126.1	28.1	135.8, 131.4	4.4
7	8	154.8, 125.4	29.4	139.1, 136.5	2.6				
	9	149.4, 123.4	26.0	140.3, 137.8	2.5	149.0, 126.3	22.7	140.2, 138.3	1.9
	12	152.0, 130.8	21.2	140.2, 137.8	2.4	153.3, 129.3	24.0	140.2, 137.3	2.9

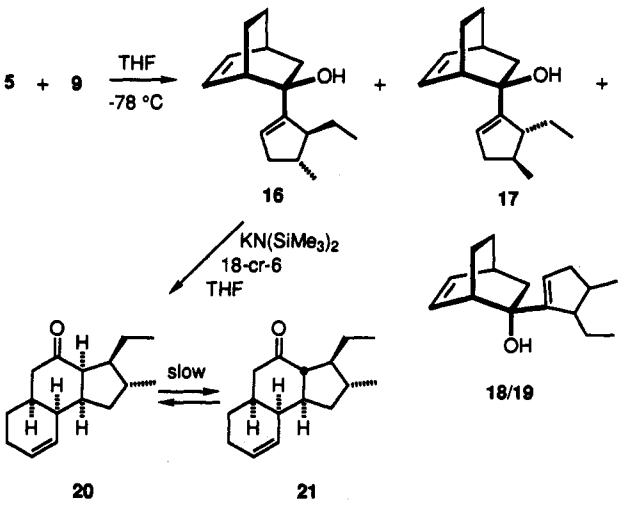
[a] β Isomer corresponds to endo series. [b] α Isomer corresponds to exo series.

indicated that the chemical shifts exhibited by structurally related isomer pairs can be relied upon to assign rigid bicyclic alcohols such as **13** and **14** to the endo or exo series.[2,4,6] Presently, this is also the case. Thus, as seen in Table 2, the Δppm values for the cyclopentenyl carbons



often fall well below 2 for the endo isomers and are generally significantly greater in the exo series. This trend is internally consistent and readily recognized in every example generated here. That the structural assignments have validity will be corroborated later by X-ray crystallographic analysis of select crystalline products. Further proof was available from the fact that **13** responds to charge-accelerated oxy-Cope rearrangement[14] while **14** does not. Furthermore, the spectral features of **15** conform fully to those anticipated for this tricyclic ketone based on homo- and heteronuclear shift correlations and the application of 2D methods (key NOE interactions shown).

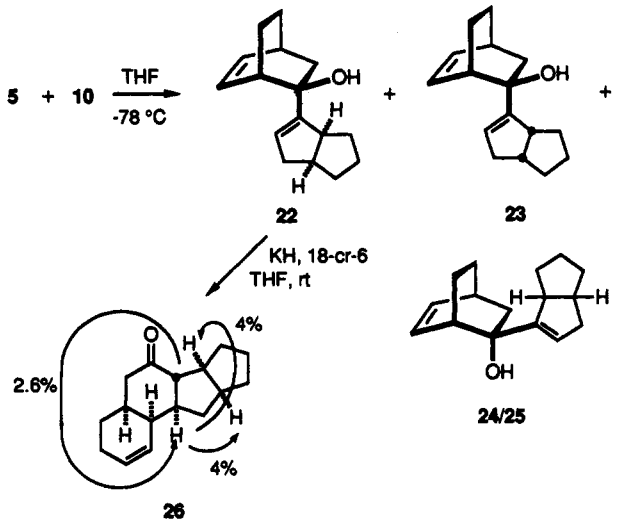
Combining **5** with **9** provided all four possible diastereomers. Thus, the pattern set by **8** is not followed when a 5-isopropyl group is replaced by a *trans*-5-ethyl-4-methyl substitution plan. Anionic oxy-Cope rearrangement performed directly on the mixture gave **20** and confirmed the stereochemistry of major product **16** to be as shown. On standing, **20** was seen to isomerize to the thermodynamically more stable trans B/C ketone **21**. The assignment

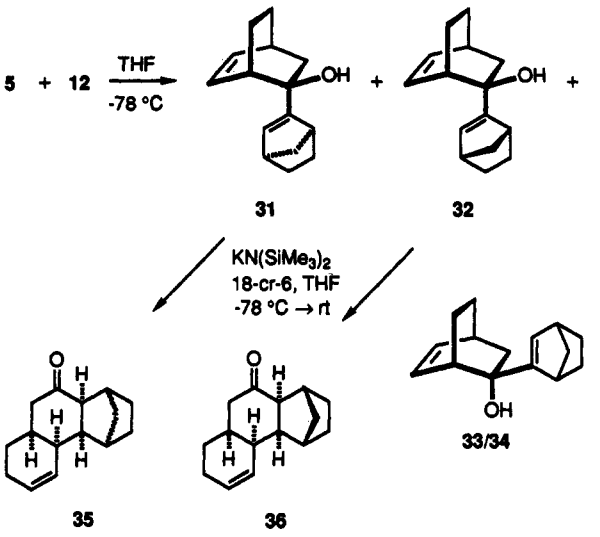


to **17** is based solely on ^{13}C NMR shift data (Table 2) since neither it nor its [3.3] sigmatropic counterpart could be isolated in pure condition.

The reaction of **5** with **10** was next examined. Relevantly, four alcohols were again formed and their distribution compared relatively closely to that observed for **16–19** (Table 1). By means of MPLC on silica gel, it proved possible to acquire pure **22** and a mixture of **23–25** from which ^{13}C data could be extracted. The assignment of configuration to **22** was confirmed, as before, by treatment with potassium hydride and 18-crown-6 in THF at rt to give **26**. The conformational features peculiar to

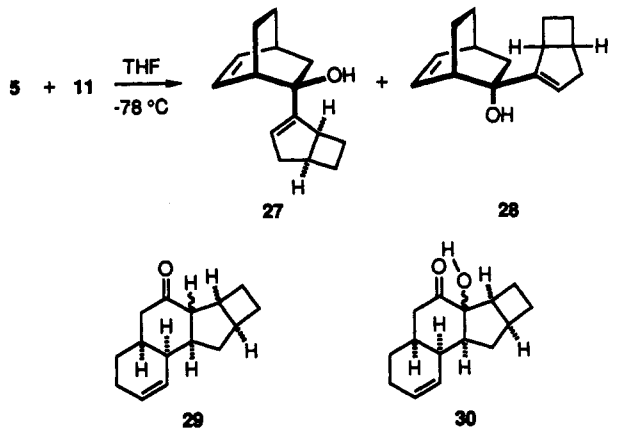
(14) Reviews: (a) Wilson, S. R. *Org. React.* **1993**, *43*, 93. (b) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 609. (c) Hill, R. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Volume 5, Chapter 7.1.





this tetracyclic framework were seen to result in protonation exclusively on the β-face of the enolate anion.

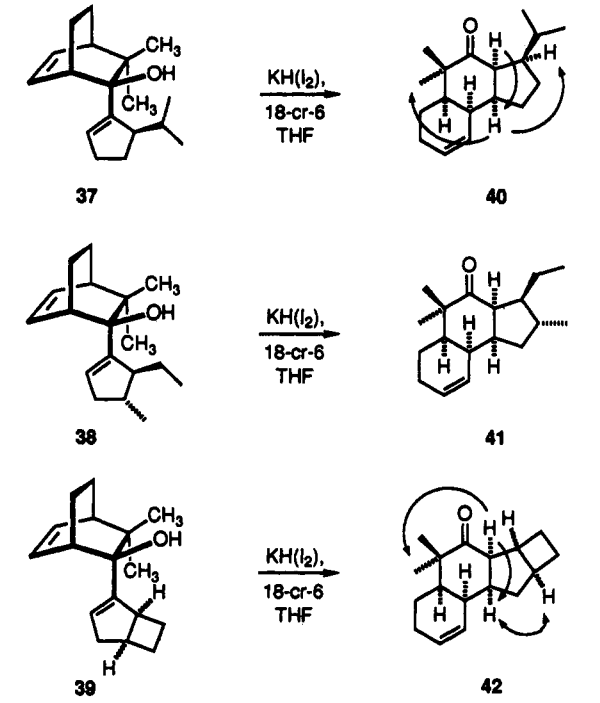
The addition of **11** to **5** gave a 12:1 mixture of alcohols **27** and **28**. The pronounced preference for formation of a



single endo diastereomer is obviously reinstated to a level greater than that previously observed with **8**. It was particularly striking to find that anionic oxy-Cope rearrangement of **27** gave not only **29** (as a 1:1 epimer mixture) but also **30**, the product of adventitious enolate oxygenation.[15] The enolate anion formed in the course of this isomerization is maximally strained for the series, a property that is evidently reflected in its heightened reactivity.

The four products generated upon condensation of **5** with **12** proved not to be separable by MPLC, but fully resolved under HPLC conditions. By repeated sample injection, it was possible to obtain small quantities of **31**–**34** in pure condition. The two endo adducts proved to be crystalline. Exposure of mixtures of **31** and **32** to potassium hexamethyldisilazide and 18-crown-6 resulted in conversion to ketones **35** and **36**, respectively. Very characteristic W-couplings were instrumental in leading to these assignments.

The consequences of α,α-dimethylation as in **6** were to heighten the general pattern of discrimination exhibited by **5**. The placement of additional steric barriers in that sector of the bicyclo[2.2.2]octenone further promotes kinetically-controlled formation of the β-stereoisomeric alcohols. When **8**, **9**, and **11** were added to **6**, the only endo products that were detected were **37**, **38**, and **39**, respectively. In agreement with these relative configura-



tional assignments, all three carbinols were found to be amenable to [3.3] sigmatropic rearrangement. In these examples, KH pretreated with iodine[16a] and admixed with 18-crown-6 in THF was found to be the reagent of choice. Once again, it could be quickly recognized that **40**–**42** were otherwise of identical stereochemistry in ring C. None of these examples were expected to have a reason for traversing a different rearrangement transition-state trajectory and this was not seen. However, the transition state for **38** is undoubtedly the most sterically congested. As a result, the yield of **41** was the most compromised (20%).

(15) (a) Paquette, L. A.; DeRussy, D. T.; Pegg, N. A.; Taylor, R. T.; Zydowsky, T. M. *J. Org. Chem.* **1989**, *54*, 4576. (b) Paquette, L. A.; Huber, S. K.; Thompson, R. C. *J. Org. Chem.* **1993**, *58*, 6874.

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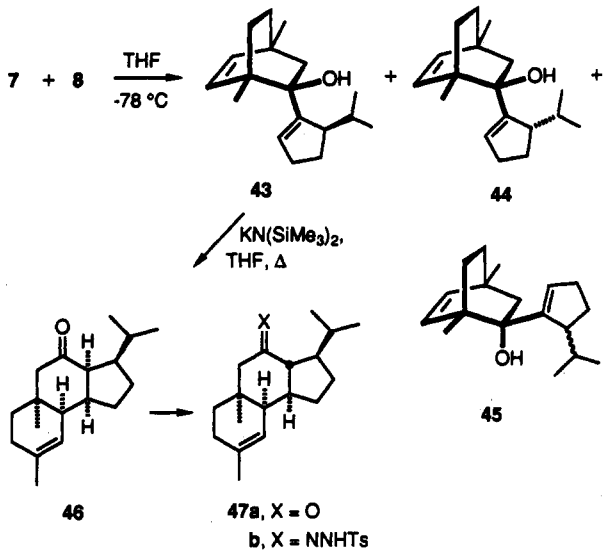
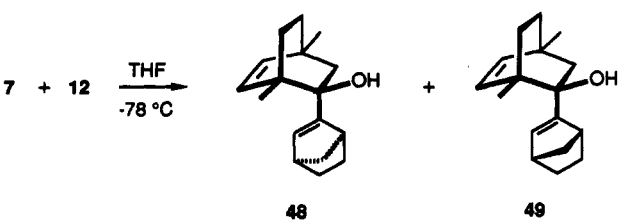
The discriminatory impact realized by positioning methyl groups at the pair of bridgehead sites as in 7 was little changed from that determined with the parent ketone 5. A respectable preference for production of β-endo diastereomeric alcohols continued to be demonstrated, indicating that increased steric bulk at C-1 of the ketone does not force alteration of the matched pairing reflected in other examples. A benefit of the structural features provided by 7 is the heightened crystallinity of the carbinols derived from it. The condensation of 8 with 7 afforded a four-component mixture rich in 43 (Table 1). The high quality crystallinity of pure 43 permitted the application of X-ray analysis[16b] to confirm that the isopropyl group was β-oriented as shown and that steric biases at play in the competing transition states did not effect a scrambling of the kinetic ordering observed earlier. The special sensitivity of the olefinic carbons to structure which was seen also in 43 and 44 (Table 2) is believed to stem from a particular conformation adopted by the

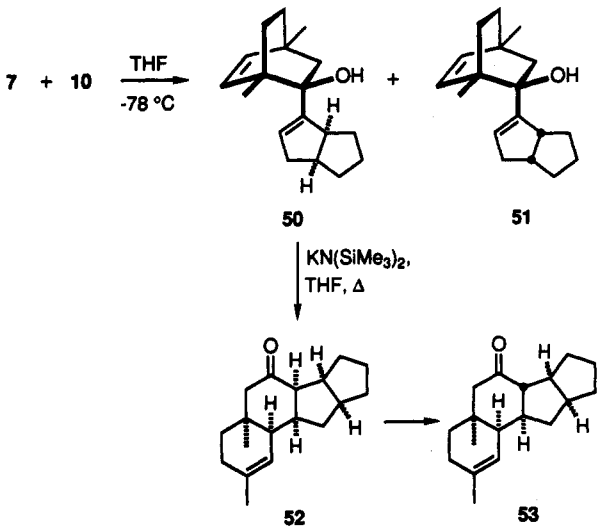


cyclopentenyl ring which differs within the diastereomer pair because of the specific stereochemical orientation demanded by stereoreversal of the isopropyl groups. When 43 was heated with potassium hexamethyldisilazide in THF in the absence of 18-crown-6 for 2 h, 46 was produced exclusively. When the reaction time was extended to 2 days, ketone 47a resulted instead. That the relative configurational assignments shown in the formulas are indeed correct was established by 2D-COSY and NOE measurements in the case of 46 and X-ray crystallographic analysis of the tosylhydrazone derivative 47b.[16b]

An additional point of reference was acquired by reaction of 7 with 12. The distribution of the resultant endo alcohols 48 and 49 (9.8:1) was seen to compare closely to the β:α ratio defined by 43 and 44 (8.8:1). Stereochemical distinction between these two diastereomers rests soundly on X-ray crystallographic evidence obtained for 48.[16b] As with 5, the two possible exo isomers were also generated in lesser amounts.



Finally, the condensation of 7 with 10 led predominantly to the formation of alcohols 50 and 51. These diastereomers proved to be inseparable by MPLC, analytical HPLC, and preparative VPC methods. It was possible, however, to establish their distribution as 3.6:1 by GC-MS. Fortuitously, the oily mixture of these alcohols crystallized upon standing at rt for 1 week. The crystalline solid proved to be almost exclusively 50, while the remaining oil contained 50 and 51 in a 1.3:1 ratio. Heating 50 with potassium hexamethyldisilazide in THF afforded ketone 52 as expected after a short reaction period. Longer reaction times gave rise to the epimer 53.



Discussion

Transition-State Model for 1,2-Addition to the Ketone Carbonyl. The results of this investigation show clearly that the structural features contained in bicyclo[2.2.2]octenones are conducive to good diastereoselectivity in condensation reactions and that useful amounts of a stereoisomerically defined product can be obtained in select cases. Although proper calculation of reaction trajectories in systems as large as the present examples remains problematical,[17] existing approximations[18] coupled with adaptation of the Bürgi–Dunitz model for the directionality of nucleophilic capture by the carbonyl group[19] provide for reasonable transition-state structural possibilities. A key warranted assumption is that these coupling reactions proceed irreversibly under kinetic control with mutual alignment of the reaction partners in a stacked mode that allows for operation of a somewhat obtuse trajectory of attack[20] following complexation of the oxygen to the metal.[21]

(17) For recent calculations of reaction trajectories involving simpler molecules, see: (a) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y.-D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108. (b) Liotta, C. L.; Burgess, E. M.; Eberhardt, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 4849. (c) Menger, F. M. *Tetrahedron* **1983**, *39*, 1013.

(18) (a) Bürgi, H. B.; Dunitz, J. D.; Lehn, J.-M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563. (b) Scheiner, S.; Lipscomb, W. N.; Kleier, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4770. (c) Eisenstein, O.; Schlegel, H. B.; Kayser, M. M. *J. Org. Chem.* **1982**, *47*, 2886.

(19) (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153 and relevant references cited therein.

(20) (a) Klopman, G. In *Chemical Reactivity and Reaction Paths*; Klopman, G., Ed.; Wiley-Interscience: New York, 1974; Chapter 4, pp 55–166. (b) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162.

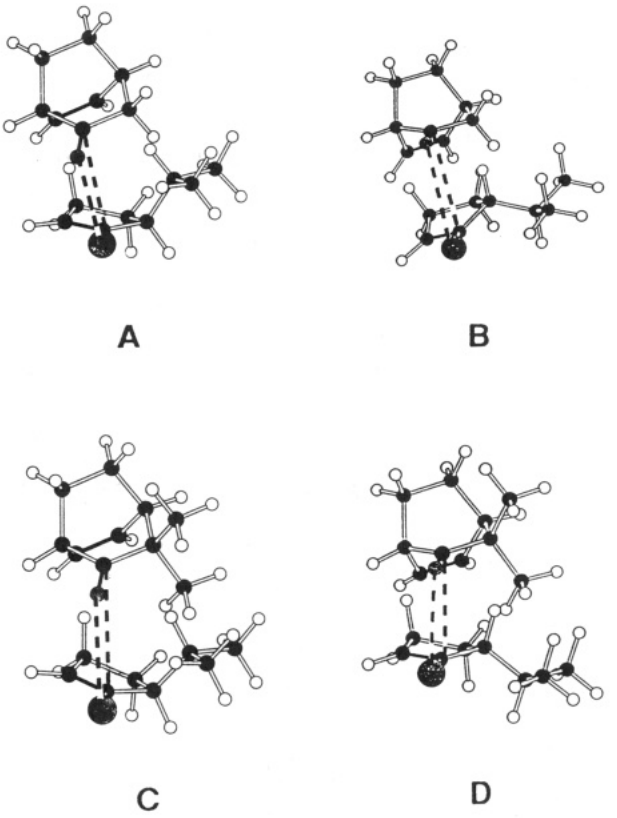


Figure 1. Stacked diastereomeric transition-state combinations for the condensation of **5** with **8** (**A**, **B**) and of **6** with **8** (**C**, **D**). The intermolecular distances have been arbitrarily selected.

The data reveal that an isopropyl fragment positioned at C-5 is a respectable controller of diastereoselectivity relative to the parent ketone **5**. The discrimination remains good when **10** is involved and improves dramatically when the nucleophile is bicyclo[3.2.0]hepten-2-yl in nature. Also of significance is the major advantage that accrues when the ketone is α,α-dimethylated as in **6**. Since substitution as in **7** does not have comparable consequences, the methyl group in **6** that is projected endo must play a significant role in dictating the preferred course of diastereoselection.

As seen in Figure 1, the principal difference distinguishing the bonding pathways associated with the endo approach of **8** to **5** (see **A** and **B**) and **6** (see **C** and **D**) is the appreciably heightened nonbonded steric compression that arises in **A** and **C** relative to the others. We believe this to be the underlying reason why bonding via the matched pairs **B** and **D** leads to the major and only products, respectively.

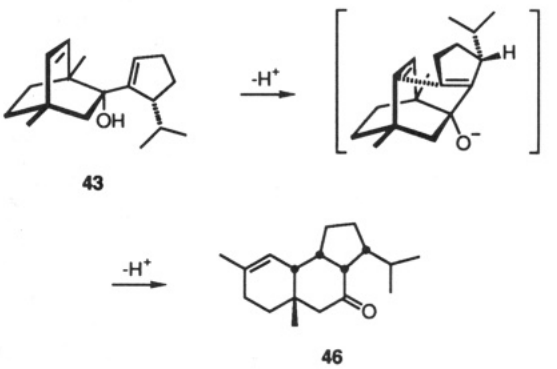
It is noteworthy that an *increase* in endo diastereoselectivity is accompanied by a *decrease* in the endo/exo product ratio. This trend is made apparent when comparing entry 9 with entries 6 and 1, entry 10 versus 3, or more globally, entries 1–5 with 6–8 and 9–11. The consistency with which this reactivity pattern surfaces would seem to indicate that when discrimination for the endo face is greatest, the rate of 1,2-addition has slowed sufficiently to provide enhanced opportunity for exo attack. A structural feature common to the vinyl anions derived from **9** and **12** is the positioning of pendant substituents on both surfaces of the nucleophile. When these steric barriers need to be accommodated, the endo/exo ratio is consistently low and only modestly affected by the placement of methyl groups on the bicyclic ketone (entries 2, 5, 7, and 11). The stacked transition state models depicted in Figure 1 satisfactorily and concisely address the full range of diastereoselectivities observed.

The considerable positive impact on endo selectivity resulting from introduction of *gem*-methyl groups at C_α as in **6**, and the relatively minor influence of methyl substitution at the bridgehead sites in **7** are likely manifested because of conformational twisting enforced on **6** with net alteration in the angle of approach required for 1,2-addition from either face of the carbonyl. The drop in endo selectivity can be relatively precipitous (compare entries 6 and 7).

This sensitivity to modest topographical changes surfaces in other ways. For example, on going from vinyl system **10** to **11** diastereoselectivity decreases for the [2.2.1] system studied earlier, but increases for the [2.2.2] system (entries 3 and 4). This behavior is accounted for by the proposed model. The point needs to be made that progressive reduction in the size of the ring adjoining the cyclopentenyl anions in **10** and **11** is also accompanied by major alterations in dihedral angles. The increased outward splaying of the C–H bonds at the ring junction is particularly telling in more crowded environments. As a consequence, the diastereomeric transition states associated with 2-norbornenones exhibit the greatest sensitivity to these changes.

The consistency with which conceptually related paradigms have served to lend predictability to the preferred course of diastereoselective condensations in a wide variety of contexts[2,4,6] suggests that they fulfill a convenient and reliable function. They are of course simplistic since solvation, the possibility of electron transfer, and stereoelectronic effects, and the like are not given explicit consideration.

Stereochemical Course of the Anionic Oxy-Cope Rearrangements. The number of stereogenic centers present in the product alcohols, the conformational rigidity of the bicyclo[2.2.2]octenyl subunits in these molecules, and the requirement that concerted [3.3] sigmatropy proceed via a boat-like transition state combine to allow operation of efficient chirality transfer with enhancement of the level of stereochemical content. As illustrated for the conversion of **43** to **46**, this phenomenon is made possible by the highly-ordered intramolecularity of the oxyanionic Cope process which does not allow the various stereochemical elements to function as independent variables.



(21) (a) Houk, K. N.; Rondan, N. G.; Schleyer, P. von R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821. (b) Kaufmann, E.; Schleyer, P. von R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560.

As a consequence of this superb stereocontrol, polycyclic ketones having well-defined relative configurations are accessible through implementation of two simple laboratory operations. Prior resolution of either chiral reactant would result in kinetic resolution and deliver products of known absolute configuration. The serviceability of this chemistry would thereby be expanded.

Experimental Section

Melting points are uncorrected. ^{13}C NMR spectra were recorded at 75 or 62.5 MHz and ^1H NMR spectra at 300 or 500 MHz as recorded in the text. High resolution mass spectra were recorded at The Ohio State University Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. HPLC analyses were performed on a Perkin-Elmer Series 2 instrument fitted with a refractive index detector and a Fisher 10-μm Resolvex-Sil column (4.6 × 250 mm). Product distributions were obtained by HPLC analysis of the crude mixtures and complemented by ^1H NMR integration when necessary. All reactions were carried out under a dry, oxygen-free nitrogen atmosphere. Preparative-scale separations were achieved by MPLC on Merck LiChroprep (40–60 μm) columns or by flash chromatography on Merck silica gel HG_{254}. Solvents were dried before use.

3,3-Dimethylbicyclo[2.2.2]oct-5-en-2-one (6). To a magnetically stirred, N_2-blanketed THF solution of sodium hexamethyldisilazide (24.6 mmol, 6 equiv) was added dropwise a solution of ketone **5** (500 mg, 4.1 mmol) and methyl iodide (3.5 g, 24.6 mmol) in ether (15 mL). The reaction mixture was heated to the reflux temperature and left to stir overnight. When GC analysis showed a 4:6 mixture of mono- and dialkylated products to be present, another 3 equiv of sodium hexamethyldisilazide and 6 equiv of methyl iodide were introduced. The conversion to **6** was complete 1 h later. The reaction mixture was cooled, diluted with saturated NH_4Cl solution, and extracted with ether (3×). The combined organic phases were washed with 10% HCl, brine, saturated $NaHCO_3$ solution, and water prior to drying and solvent evaporation. Flash chromatography of the residue (silica gel, elution with hexanes–ether 4:1) gave **6** as a waxy solid (443 mg, 72%), mp ~23 °C; IR (neat, cm^{-1}) 1730, 1470, 1390, 1365, 1095, 720; ^1H NMR (300 MHz, $CDCl_3$) δ 6.47 (ddd, J = 1.5, 6.5, 7 Hz, 1 H), 6.03 (ddd, J = 2, 6.5, 7 Hz, 1 H), 3.05 (m, 1 H), 2.52 (m, 1 H), 1.94 (ddt, J = 10, 13, 3.5 Hz, 1 H), 1.75 (dddd, J = 2.5, 6, 13, 10 Hz, 1 H), 1.51 (ddt, J = 12, 13, 4 Hz, 1 H), 1.31 (ddd, J = 3, 6, 12.45 Hz, 1 H), 1.04 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 217.0, 138.7, 126.2, 48.7, 44.0, 43.6, 27.4, 24.2, 21.7, 20.6; MS m/z (M^+) calcd 150.1045, obsd 150.1059. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.03; H, 9.32.

General Procedure for Condensation with Organocerates. Cerium trichloride heptahydrate (1.00 g, 2.71 mmol) was dried overnight at 145–150 °C and 0.1–0.05 Torr and stirred at rt with dry THF (50 mL) for 3 h. To ensure dryness, this mixture was treated dropwise with 1.7 M *tert*-butyllithium in pentane until a bright orange color persisted. This slurry was cooled –78 °C, the vinyllithium reagent was introduced via cannula (2.46 mmol, prepared as described below), and stirring was maintained for 1 h prior to slow addition of the ketone (0.82 mmol) dissolved in dry THF (10 mL). After 3 h at –78 °C, the mixture was alowed to warm to rt, quenched with saturated NH_4Cl solution, and filtered through a pad of Celite. The cake was washed with brine (20 mL) and ether (2 × 20 mL), and the filtrate was extracted with ether. The combined organic phases were washed with brine (2 × 20 mL), dried, and evaporated in vacuo. The product mixture was analyzed by HPLC and the individual diastereomers were separated where possible by flash chromatography on preparative HPLC.

General Procedure for Condensation with Vinyllithium Reagents. A solution of the vinyl bromide (3.0 mmol) in dry THF (25 mL) was blanketed with N_2, cooled to –78 °C and treated dropwise with *tert*-butyllithium (6.0 mmol as 1.7 M solution in pentane) at such a rate as to maintain a colorless solution. Stirring was maintained for 75 min, at which point a solution of the ketone (150 mg, 1.0 mmol) in dry THF (3 mL) was added slowly. The colorless reaction mixture was stirred for 12 h at –78 °C, allowed to warm to rt, and processed in the predescribed manner.

Anionic Oxy-Cope Rearrangements. Procedure A. Potassium hydride (53 mg, 1.29 mmol) was placed in a dry flask under N_2, 10 mL of dry THF was added, and the suspension was stirred for 10 min at rt. A solution of the alcohol (0.43 mmol) and 18-crown-6 (343 mg, 1.29 mmol) in dry THF (10 mL) was slowly introduced. After completion of the addition, the mixture was stirred for 12 h, quenched with saturated NH_4Cl solution before being poured into a mixture of ether (20 mL) and NH_4Cl solution (20 mL). The separated organic phase was washed with brine, dried, and evaporated. The product was purified by flash chromatography on silica gel.

Procedure B. As above, but the suspension of KH was pretreated with a few drops of a 0.1 M solution of iodine in THF.

Procedure C. 18-Crown-6 (162 mg, 0.615 mmol) and the alcohol (0.216 mmol) was taken up in 1 mL of dry THF, cooled to –78 °C, and treated slowly with potassium hexamethyldisilazide solution (0.615 mmol, Aldrich). The reaction mixture was allowed to warm to rt overnight, quenched with saturated NH_4Cl solution, and worked up in the predescribed manner.

Procedure D. As in procedure C, but without the 18-crown-6 added. The reaction mixture was heated at the reflux temperature for varying periods of time as noted elsewhere.

Organocerate Additions to 5. A. Bromide 8: 88% yield of a 19:1 mixture of **13** and **14**. These were separated by a combination of MPLC and HPLC techniques.

For **13**: IR (neat, cm^{-1}) 2695, 1470, 1440, 1385, 1370, 1310, 1285; ^1H NMR (300 MHz, $CDCl_3$) δ 6.19–6.10 (m, 2 H), 5.57–5.55 (dt, J = 2.3, 1.6 Hz, 1 H), 2.74–2.71 (m, 2 H), 2.59–2.56 (m, 2 H), 2.23–2.11 (m, 4 H), 1.80–1.69 (m, 2 H), 1.65 (dddd, J = 2.4, 5.0, 9.6, 12.1 Hz, 1 H), 1.52 (dd, J = 2.5, 13.4 Hz, 1 H), 1.34–1.23 (tq, J = 3.3, 12 Hz, 1 H), 1.32 (br s, 1 H), 1.11–1.02 (ddt, J = 5.0, 3.0, 12.2 Hz, 1 H), 0.93 (d, J = 6.9 Hz, 3 H), 0.73 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) ppm 152.4, 133.7, 132.8, 126.7, 75.3, 51.3, 41.9, 41.4, 31.9, 30.8, 29.8, 24.3, 23.4, 22.3, 19.9, 15.4; FAB MS (M^+) calcd 232.40, obsd 232.22.

For **14**: IR ($CHCl_3$, cm^{-1}) 3600; ^1H NMR (300 MHz, $CDCl_3$) δ 6.46 (dd, J = 8, 8 Hz, 1 H), 6.25 (dd, J = 8, 8 Hz, 1 H), 5.68 (dd, J = 2, 4 Hz, 1 H), 2.92 (m, 1 H), 2.81 (m, 1 H), 2.63 (m, 1 H), 2.29 (m, 2 H), 2.19 (d of heptets, J = 3, 7 Hz, 1 H), 1.70 (dd, J = 2.5, 14 Hz, 1 H), 1.90–1.65 (m, 3 H), 1.60–1.35 (m, 2 H), 1.28 (s, 1 H), 1.24–1.08 (m, 2 H), 0.94 (d, J = 7 Hz, 3 H), 0.74 (d, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.4, 136.6, 131.8, 127.4, 52.0, 45.5, 41.4, 32.3, 31.0, 29.8, 24.9, 23.5, 22.4 (2 C), 20.3, 15.5; MS m/z (M^+ – 1) calcd 231.1748, obsd 231.1745.

B. Bromide 9: 93% yield of a 9.5:1.9:3.2:1.0 mixture of endo and exo alcohols. Flash chromatography (silica gel, elution with hexane–ether 4:1) afforded pure **16**.

For **16**: IR (neat, cm^{-1}) 3500, 1090; ^1H NMR (300 MHz, $CDCl_3$) δ 6.20–6.13 (ddd, J = 1.5, 7, 7.5 Hz, 1 H), 6.13–6.06 (ddd, J = 1, 7, 7.5 Hz, 1 H), 5.46–5.42 (m, 1 H), 2.73–2.68 (ddt, J = 1, 7, 3.5 Hz, 1 H), 2.60–2.53 (m, 1 H), 2.57–2.45 (ddt, J = 2, 7.5, 16.5 Hz, 1 H), 2.25–1.90 (m, 3 H), 1.80–1.59 (m, 4 H), 1.50 (dd, J = 2.5, 13 Hz, 1 H), 1.34–1.20 (m, 3 H), 1.15–1.00 (tdd, J = 3, 5, 12 Hz, 1 H), 0.92 (d, J = 7 Hz, 3 H), 0.88 (t, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.6, 133.7, 132.5, 123.7, 75.2, 55.0, 41.6, 41.1, 39.1, 36.7, 30.8, 26.9, 24.4, 22.5, 20.0, 11.7; MS m/z (M^+) calcd 232.1753, obsd 232.1790.

C. Bromide 10: 90% yield of an 11.5:1.0:4.5:1.5 mixture of endo and exo alcohols. MPLC (silica gel, elution with hexane–ether 6:1) afforded pure **24** (or **25**) and somewhat less pure **22**.

For **22**: IR (neat, cm^{-1}) 3580, 3460, 1460, 1445, 1370, 1310, 1280, 1170, 1090; ^1H NMR (300 MHz, $CDCl_3$) δ 6.18–6.10 (m, 2 H), 5.39–5.37 (dt, J = 1.6, 2.2 Hz, 1 H), 3.10–3.00 (m, 1 H), 2.72–2.49 (m, 4 H), 2.22–2.13 (ddt, J = 3.1, 9.3, 12.3 Hz, 1 H), 2.01–1.92 (ddt, J = 7.0, 3.6, 16.7 Hz, 1 H), 1.85–1.20 (series of m, 11 H), 1.07 (ddt, J = 12.1, 4.9, 2.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.9, 133.5, 132.8, 124.2, 75.3, 50.8, 41.5, 41.4, 41.2, 39.6, 35.1, 33.3, 30.7, 26.7, 24.3, 19.9; MS m/z (M^+) calcd 230.1671, obsd 230.1658.

For **24** (or **25**): IR (neat, cm^{-1}) 3600, 1455, 1380, 1100; ^1H NMR (250 MHz, $CDCl_3$) δ 6.45 (t, J = 7 Hz, 1 H), 6.28 (td, J = 1.7 Hz, 1 H), 5.55 (br s, 1 H), 3.25–3.22 (m, 1 H), 2.85–2.55 (series of m, 4 H), 2.10–1.98 (dd, J = 2.5, 14 Hz, 2 H), 1.90–1.05 (series of m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 149.0, 136.4, 131.7, 125.8,

76.2, 51.5, 44.1, 41.8, 41.4, 40.0, 35.1, 33.0, 30.9, 26.7, 24.7, 20.5; MS *m/z* (M^+) calcd 230.1669, obsd 230.1670.

D. Bromide 11: 70% yield of a 12:1 mixture of **27** and **28** from which pure **27** was obtained by MPLC on silica gel (elution with 1 → 5% ethyl acetate in hexanes).

For **27**: IR (CCl_4, cm^{-1}) 3596, 3500, 1549, 1462, 1444, 1370, 1278, 1253, 1164, 1091, 1048; ^1H NMR (300 MHz, $CDCl_3$) δ 6.19–6.10 (m, 2 H), 5.55 (br s, 1 H), 3.35–3.23 (m, 1 H), 2.84 (br q, *J* = 8 Hz, 1 H), 2.63–2.43 (m, 3 H), 2.43–2.28 (m, 1 H), 2.23–2.08 (m, 3 H), 2.01–1.88 (m, 1 H), 1.75 (dt, *J* = 3.5, 13.5 Hz, 1 H), 1.69–1.57 (m, 2 H), 1.57 (br s, 1 H), 1.47 (dd, *J* = 2.5, 13.5 Hz, 1 H), 1.25 (tq, *J* = 3, 12 Hz, 1 H), 1.04 (tdd, *J* = 3, 5, 12.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 153.8, 133.3, 133.0, 125.2, 75.5, 45.5, 41.7, 41.6, 40.3, 36.0, 30.7, 28.4, 27.0, 24.1, 20.1; MS *m/z* (M^+) calcd 216.1514, obsd 216.1505.

E. Bromide 12: 93% yield of a 5.8:3.0:1.0:1.1 mixture of **31–34** from which **31/32**, **33**, and **34** were obtained by preparative HPLC methods.

For **31/32:** colorless solid, mp 79–80 °C; IR (KBr, cm^{-1}) 3500–3100, 1440, 1370, 1310, 1280; ^1H NMR (300 MHz, $CDCl_3$) δ 6.15–6.08 (m, 2 H), 6.08–6.0 (ddd, *J* = 1, 7.5, 7 Hz, 1 H), 5.63 and 5.53 (two d's, *J* = 3 Hz, total 2 H), 2.98 and 2.92 (two m's, total 1 H), 2.77 (m, 1 H), 2.60–2.51 (m, 1 H), 2.22–2.10 (m, 2 H), 1.80–1.3 (series of m, 7 H), 1.3–1.0 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm (major isomer) 155.2, 133.1, 133.0, 128.4, 75.1, 49.2, 42.3, 42.0, 40.4, 40.3, 30.5, 25.7, 25.4, 24.4, 19.6; (minor isomer) 156.2, 133.5, 133.1, 127.2, 74.8, 49.5, 42.7, 41.9, 40.5, 40.4, 30.6, 26.0, 25.5, 24.2, 19.9; MS *m/z* (M^+) calcd 216.1514, obsd 216.1517.

For **33**: IR ($CHCl_3$, cm^{-1}) 3600–3500, 1445, 1370, 1190, 1095, 1060, 1030; ^1H NMR (300 MHz, $CDCl_3$) δ 6.44 (t, *J* = 7 Hz, 1 H), 6.26 (ddd, *J* = 1, 6, 6 Hz, 1 H), 5.91 (d, *J* = 3 Hz, 1 H), 3.04 (m, 1 H), 2.85 (m, 2 H), 2.61 (m, 1 H), 2.02 (dd, *J* = 2, 14 Hz, 1 H), 1.75–1.00 (series of m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.7, 136.4, 131.2, 129.7, 75.6, 49.3, 42.6, 42.4, 41.8, 40.3, 30.9, 25.8 (2 C), 24.0, 21.1; MS *m/z* (M^+) calcd 216.1514, obsd 216.1492.

For **34**: IR ($CHCl_3$, cm^{-1}) 3560, 1445, 1370, 1190, 1175, 1095, 1055, 1030; ^1H NMR (300 MHz, $CDCl_3$) δ 6.44 (t, *J* = 7.5 Hz, 1 H), 6.24 (ddd, *J* = 1.5, 6, 8 Hz, 1 H), 5.87 (d, *J* = 3 Hz, 1 H), 3.11 (m, 1 H), 2.86 (m, 1 H), 2.67–2.59 (m, 2 H), 1.95 (dd, *J* = 2, 14 Hz, 1 H), 1.8 (br s, 1 H), 1.72–1.61 (m, 2 H), 1.60 (br s, 1 H), 1.5–1.0 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.0, 136.4, 131.3, 129.6, 76.5, 49.5, 42.6, 42.5, 42.4, 40.5, 30.6, 25.7, 24.9, 24.4, 20.6; MS *m/z* (M^+) calcd 216.1514, obsd 216.1539.

(3*R,3a*S**,5a*S**,9a*R**,9b*S**)-1,2,3,3a,5,5a,6,7,9a,9b-Decahydro-3-isopropyl-4*H*-benz[*e*]inden-4-one (15):** procedure A; 80% yield; colorless oil; IR (CCl_4, cm^{-1}) 1710; ^1H NMR (300 MHz, C_6D_6) δ 5.47 (dddd, *J* = 2, 2, 4, 10 Hz, 1 H), 2.58–2.46 (m, 2 H), 2.40–2.18 (m, 3 H), 2.03–1.89 (m, 2 H), 1.85–1.77 (m, 2 H), 1.66–1.18 (series of m, 8 H), 0.97 (d, *J* = 7 Hz, 3 H), 0.89 (d, *J* = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.8, 128.9, 127.1, 54,2, 52.6, 48.3, 47.8, 37.6, 35.1, 29.2, 27.3, 27.2, 27.1, 24.7, 22.5, 22.4; MS *m/z* (M^+) calcd 232.1827, obsd 232.1840. Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.66; H, 10.45.

(2*R,3*S**,3a*S**,5a*S**,9a*R**,9b*S**)-3-Ethyl-1,2,3,3a,5,5a,-6,7,9a,9b-decahydro-2-methyl-4*H*-benz[*e*]inden-4-one (20):** procedure A; 60% yield of **20** and 25% yield of **21**. For **20**: colorless oil; IR (CCl_4, cm^{-1}) 1711; ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (dddd, *J* = 2.5, 3, 5, 10 Hz, 1 H), 5.57 (dddd, *J* = 2, 3, 4, 10 Hz, 1 H), 2.84 (br t, *J* = 7.5 Hz, 1 H), 2.72–2.55 (m, 2 H), 2.58 (ddd, *J* = 2, 7, 13 Hz, 1 H), 2.29 (m, 1 H), 2.13 (dd, *J* = 7, 13 Hz, 1 H), 2.10–1.80 (m, 4 H), 1.70–1.20 (m, 5 H), 1.01–0.80 (m, 1 H), 0.94 (d, *J* = 7 Hz, 3 H), 0.91 (t, *J* = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 215.0, 129.0, 127.2, 55.0, 53.8, 47.1, 45.3, 36.8, 36.6, 36.4, 35.1, 27.4, 24.2, 22.5, 20.7, 13.4; MS *m/z* (M^+) calcd 232.1827, obsd 232.1821.

(4a*R,6a*S**,6b*R**,9a*R**,10a*R**,10b*S**)-3,4a,5,6a,6b,7,8,9,9a,-10,10a,10b-Dodecahydropentaleno[2,1-*a*]naphthalen-6(4*H*)-one (26):** procedure A; 70% yield; colorless oil; IR ($CHCl_3$, cm^{-1}) 1710; ^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (dddd, *J* = 3, 3, 3, 11 Hz, 1 H), 5.70 (br d, *J* = 11 Hz, 1 H), 2.69 (q, *J* = 9 Hz, 1 H), 2.56 (m, 1 H), 2.46 (m, 1 H), 2.42 (ddd, *J* = 13, 13, 1 Hz, 1 H), 2.28–2.22 (m, 1 H), 2.14–2.04 (m, 3 H), 2.06 (dd, *J* = 13, 4.5 Hz, 1 H), 2.01 (ddd, *J* = 13, 9, 1 Hz, 1 H), 1.94–1.80 (m, 3 H), 1.64–1.50 (m, 4 H), 1.46–1.34 (m, 2 H), 1.33–1.23 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 211.3, 129.0, 124.0, 57.3, 51.0, 41.9, 41.3, 40.0. 37.9, 36.5, 35.6, 33.1, 32.3, 26.5, 25.1, 21.0; MS *m/z* (M^+) calcd 230.1671, obsd 230.1683. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.45; H, 9.83.

(4a*R,6b*R**,8a*R**,9a*R**,9b*S**)-3,4,4a,5,6a,6b,7,8,8a,9,9a,9b-Dodecahydro-6*H*-cyclobuta[3,4]cyclopenta[1,2-*a*]naphthalen-6-one (29) and (4a*R**,6b*R**,8a*R**,9a*R**,9b*S**)-3,4,4a,5,6a,-6b,7,8,8a,9,9a,9b-dodecahydro-6a-hydroxy-6*H*-cyclobuta-[3,4]cyclopenta[1,2-*a*]naphthalen-6-one (30):** procedure A, 13% yield of one epimer of **29**, 11% yield of a second epimer of **29**, and 19% yield of **30**. For **29** (epimer A): colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (br d, *J* = 12 Hz, 1 H), 5.90 (br d, *J* = 12 Hz, 1 H), 3.00–2.90 (m, 1 H), 2.78–2.65 (m, 3 H), 2.63 (ddd, *J* = 1, 6.5, 11 Hz, 1 H), 2.51 (dd, *J* = 11, 11 Hz, 1 H), 2.35–2.25 (m, 3 H), 2.20–2.13 (m, 2 H), 2.11 (dd, *J* = 5, 13.5 Hz, 1 H), 2.05–1.85 (m, 2 H), 1.75–1.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 210.8, 129.0, 124.1, 58.7, 53.8, 41.9, 37.9, 36.9, 36.5, 36.2, 35.7, 27.0, 26.5, 24.6, 21.0; MS *m/z* (M^+) calcd 216.1514, obsd 216.1516.

For **29** (epimer B): colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 5.80 (br d, *J* = 12 Hz, 1H), 5.73 (br d, *J* = 12 Hz, 1 H), 3.05 (br ddd, *J* = 8.5, 9, 17 Hz, 1 H), 2.80–2.43 (m, 5 H), 2.40 (d, *J* = 7 Hz, 1 H), 2.38–2.25 (m, 1 H), 2.22–2.00 (m, 4 H), 1.88 (ddd, *J* = 3.5, 9, 18 Hz, 1 H), 1.81–1.68 (m, 2 H), 1.68–1.54 (m, 2 H), 1.50–1.40 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.1, 128.9, 127.2, 54.6, 48.3, 45.8, 41.8, 39.0, 38.2, 34.4, 34.3, 27.8, 24.0, 23.9, 23.7; MS *m/z* (M^+) calcd 216.1514, obsd 216.1510.

For **30**: colorless oil; IR (neat, cm^{-1}) 3484, 1710, 1461, 1168, 1088, 1064; ^1H NMR (300 MHz, $CDCl_3$) δ 5.89–5.82 (m, 1 H), 5.71–5.65 (br d, *J* = 10.5 Hz, 1 H), 3.40 (br s, 1 H), 2.90–2.45 (series of m, 6 H), 2.45–2.35 (m, 2 H), 2.35–1.75 (series of m, 7 H), 1.70–1.45 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 216.2, 128.7, 127.6, 87.7, 57.5, 51.7, 43.9, 38.3, 36.8, 35.1, 33.3, 29.2, 23.9, 23.5, 22.1; MS *m/z* (M^+) calcd 232.1463, obsd 232.1457.

(1*R,4*S**,4a*R**,4b*S**,8a*R**,10a*R**)-1,3,4,4a,4b,7,8,8a,9,10a-Decahydro-1,4-methanophenanthren-10(2*H*)-one (35):** procedure C; 62% yield; colorless oil; IR (neat, cm^{-1}) 1710; ^1H NMR (500 MHz, $CDCl_3$) δ 5.70 (ddd, *J* = 2, 4.5, 10 Hz, 1 H), 5.62 (ddd, *J* = 3, 6.5, 10 Hz, 1 H), 2.93–2.89 (m, 1 H), 2.68 (dddd, *J* = 2, 3.5, 10, 12 Hz, 1 H), 2.64 (m, 1 H), 2.51 (dd, *J* = 5, 12.5 Hz, 1 H), 2.39 (br s, 1 H), 2.30 (dd, *J* = 11, 17 Hz, 1 H), 2.28–2.20 (m, 2 H), 2.05–1.90 (m, 2 H), 1.72–1.57 (m, 2 H), 1.46–1.20 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 215.9, 129.2, 125.1, 49.1, 44.7, 42.9, 41.3, 40.5, 40.0, 33.8, 33.2, 25.8, 25.2, 23.6, 21.7; MS *m/z* (M^+) calcd 216.1514, obsd 216.1518.

(1*R,4*S**,4a*S**,4b*R**,8a*S**,10a*S**)-1,3,4,4a,4b,7,8,8a,9,10a-Decahydro-1,4-methanophenanthren-10(2*H*)-one (36):** procedure C; 83% yield; colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 5.58 (m, 2 H), 2.68 (m, 1 H), 2.65 (m, 1 H), 2.53–2.46 (m, 1 H), 2.37 (t, *J* = 11 Hz, 1 H), 2.29 (dd, *J* = 8, 18.5 Hz, 1 H), 2.26 (br s, 1 H), 2.21 (d, *J* = 11 Hz, 1 H), 2.13 (dd, *J* = 11, 18.5 Hz, 1 H), 2.12–2.05 (m, 1 H), 2.05–1.93 (m, 1 H), 1.80–1.70 (m, 1 H), 1.66–1.50 (m, 3 H), 1.30–1.00 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.0, 128.2, 125.9, 55.0, 47.6, 39.2, 38.9, 36.4, 35.9, 35.4, 31.6, 30.7, 27.9, 26.8, 20.9; MS *m/z* (M^+) calcd 216.1514, obsd 216.1501.

Organolithium Additions to 6. A. Bromide 8: 56% yield of an inseparable 7:1 mixture of **37** and an exo isomer. For **37**: IR (CCl_4, cm^{-1}) 3640, 1475, 1385, 1365, 1035; ^1H NMR (300 MHz, $CDCl_3$) δ 6.28 (ddd, *J* = 1, 7, 8 Hz, 1 H), 6.14 (ddd, *J* = 1, 7, 8 Hz, 1 H), 5.65 (br td, *J* = 1, 3 Hz, 1 H), 2.70 (m, 1 H), 2.58 (ddt, *J* = 3, 8, 3 Hz, 1 H), 2.38 (d of heptets, *J* = 3, 7 Hz, 1 H), 2.25–2.00 (m, 4 H), 1.95–1.65 (m, 2 H), 1.27 (br s, 1 H), 1.14 (s, 3 H), 1.15–0.96 (m, 3 H), 0.94 (d, *J* = 7 Hz, 3 H), 0.89 (s, 3 H), 0.74 (d, *J* = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 150.9, 133.5, 132.3, 126.4, 79.8, 54.0, 45.5, 44.5, 41.5, 31.3, 29.6, 24.6, 23.3, 22.5, 21.3, 19.0, 16.0 (1 C not observed); MS *m/z* (M^+) calcd 260.2140, obsd 260.2155.

B. Bromide 9: 81% yield of **38** and the two exo diastereomers in a ratio of 13.2:3.7:1.0. For **38**: colorless oil; IR (CCl_4, cm^{-1}) 3600; ^1H NMR (300 MHz, $CDCl_3$) δ 6.27 (ddd, *J* = 1.5, 7, 8 Hz, 1 H), 6.17 (ddd, *J* = 1.5, 7, 8 Hz, 1 H), 5.52 (br s, 1 H), 2.68 (dddd, *J* = 1.5, 3, 3, 7 Hz, 1 H), 2.51 (ddt, *J* = 2.5, 8, 17 Hz, 1 H), 2.22–2.06 (m, 2 H), 2.05–1.95 (m, 2 H), 1.95–1.75 (m, 2 H), 1.71 (ddd, *J* = 2, 3.5, 7 Hz, 1 H), 1.50–1.34 (m, 1 H), 1.13 (s, 3 H), 1.10–0.90 (m, 3 H), 0.94 (d, *J* = 8 Hz, 3 H), 0.86 (t, *J* = 8 Hz, 3 H), 0.84 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 150.4, 133.7, 132.2, 124.6,

79.5, 57.5, 45.7, 44.7, 41.9, 38.5, 37.9, 30.0, 28.2, 23.5, 23.1, 21.1, 19.0, 11:6; MS *m/z* (M^+) calcd 260.2140, obsd 260.2140.

For exo diastereomer A: colorless oil; IR (CCl_4, cm^{-1}) 3500; ^1H NMR (300 MHz, $CDCl_3$) δ 6.61 (br t, J = 7 Hz, 1 H), 6.13 (br t, J = 7 Hz, 1 H), 5.70 (br t, J = 2.5 Hz, 1 H), 3.09 (dd, J = 4.5, 6 Hz, 1 H), 2.55 (ddt, J = 7.5, 16 Hz, 1 H), 2.26 (br d, J = 9 Hz, 1 H), 2.11–1.82 (series of m, 5 H), 1.81–1.70 (m, 2 H), 1.45–1.15 (m, 3 H), 1.06 (s, 3 H), 0.98 (d, J = 7.5 Hz, 3 H), 0.97 (s, 3 H), 0.86 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.5, 138.9, 131.0, 125.2, 79.2, 57.7, 45.7, 44.3, 42.5, 38.2, 37.2, 28.1 (2 C), 27.3, 22.9, 22.5, 19.3, 12.2; MS *m/z* (M^+) calcd 260.2140, obsd 260.2147.

For exo diastereomer B: colorless oil; IR (CCl_4, cm^{-1}) 3580; ^1H NMR (300 MHz, $CDCl_3$) δ 6.60 (br t, J = 7 Hz, 1 H), 6.16 (br t, J = 7 Hz, 1 H), 5.70 (br t, J = 12.5 Hz, 1 H), 2.61 (ddt, J = 2, 7, 16.5 Hz, 1 H), 2.26 (br d, J = 10 Hz, 1 H), 2.12–2.03 (m, 1 H), 2.05 (t, J = 7 Hz, 1 H), 1.88–1.60 (m, 4 H), 1.53 (br s, 1 H), 1.30–1.03 (m, 4 H), 1.01 (s, 3 H), 1.00 (d, J = 7 Hz, 3 H), 0.97 (s, 3 H), 0.94 (t, J = 8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.5, 138.9, 131.1, 127.3, 78.8, 57.8, 45.4, 43.2, 42.9, 38.7, 36.0, 29.9, 27.6, 26.8, 22.9, 21.5, 19.0, 12.4; MS *m/z* (M^+) calcd 260.2140, obsd 260.2141.

C. Bromide 11: 54% yield of **39** and two exo diastereomers in a ratio of 14.8:1.8:1.0. For **39**: colorless oil; IR (CCl_4, cm^{-1}) 3500; ^1H NMR (300 MHz, $CDCl_3$) δ 6.28 (td, J = 6.5, 1 Hz, 1 H), 6.17 (td, J = 6.5, 1 Hz, 1 H), 5.59 (br t, J = 2 Hz, 1 H), 3.24 (m, 1 H), 2.85 (q, J = 8 Hz, 1 H), 2.70 (m, 1 H), 2.60–2.38 (m, 2 H), 2.27–2.10 (m, 3 H), 2.06–2.00 (m, 1 H), 2.00–1.83 (m, 2 H), 1.76–1.60 (m, 1 H), 1.25 (s, 1 H), 1.09 (s, 3 H), 1.06 (tt, J = 3, 10 Hz, 1 H), 0.94 (tdd, J = 9, 2, 3.5 Hz, 1 H), 0.70 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.5, 134.2, 132.0, 124.9, 79.7, 48.1, 45.3, 44.4, 41.6, 40.4, 35.7, 29.8 (2 C), 27.4, 23.6, 20.7, 19.2; MS *m/z* (M^+) calcd 244.1827, obsd 244.1826.

For exo diastereomer A: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 6.59 (ddd, J = 1, 7.5, 8 Hz, 1 H), 6.17 (ddd, J = 1, 7.5, 8 Hz, 1 H), 5.90 (br s, 1 H), 3.48 (br s, 1 H), 2.90 (m, 1 H), 2.86–2.82 (m, 1 H), 2.55 (ddt, J = 9, 17, 2 Hz, 1 H), 2.48–2.38 (m, 1 H), 2.22 (ddt, J = 17, 2.5, 3 Hz, 2 H), 2.17–1.95 (m, 3 H), 1.90–1.68 (m, 3 H), 1.30–0.83 (series of m, 2 H), 0.92 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.8, 138.7, 131.0, 126.0, 79.9, 48.6, 45.3, 44.2, 42.0, 40.4, 35.4, 29.7, 27.8 (2 C), 27.4, 22.2, 19.4; MS *m/z* (M^+) calcd 244.1827, obsd 244.1799.

For exo diastereomer B: white crystals, mp 52–54 °C; IR (CCl_4, cm^{-1}) 3600; ^1H NMR (300 MHz, $CDCl_3$) δ 6.26 (t, J = 7 Hz, 1 H), 6.13 (t, J = 7 Hz, 1 H), 5.72 (dt, J = 2 Hz, 1 H), 3.26–3.20 (m, 1 H), 2.83 (q, J = 8 Hz, 1 H), 2.58–2.38 (m, 3 H), 2.25–2.05 (m, 4 H), 2.05–1.85 (m, 2 H), 1.75–1.60 (m, 1 H), 1.45 (br s, 1 H), 1.07 (tt, J = 4, 12.5 Hz, 1 H), 1.04 (s, 3 H), 0.93 (tdd, J = 17, 3, 4.5 Hz, 1 H), 0.73 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 154.2, 135.8, 131.4, 126.1, 78.5, 47.6, 44.5, 43.3, 43.2, 39.8, 35.9, 30.3, 29.1, 26.9, 23.3, 20.0, 19.9; MS *m/z* (M^+) calcd 244.1827, obsd 244.1826.

(3*R,3a*S**,5a*R**,9a*R**,9b*S**)-1,2,3,3a,5,5a,6,7,9a,9b-Decahydro-3-isopropyl-5,5-dimethyl-4*H*-benz[*e*]inden-4-one (40):** procedure B; 53% yield; colorless oil; IR (CCl_4, cm^{-1}) 1706; ^1H NMR (300 MHz, $CDCl_3$) δ 5.72 (br d, J = 10 Hz, 1 H), 5.60 (dddd, J = 1.5, 3, 5.5, 10 Hz, 1 H), 3.22 (dd, J = 5, 8 Hz, 1 H), 3.08 (br s, 1 H), 2.62 (dddd, J = 1, 8, 11, 16 Hz, 1 H), 2.50 (dq, J = 7, 10 Hz, 1 H), 2.15–1.95 (m, 3 H), 1.90 (ddd, J = 14, 7, 4 Hz, 1 H), 1.80–1.40 (series of m, 5 H), 1.38 (s, 3 H), 1.30–1.12 (m, 1 H), 1.00 (s, 3 H), 0.85 (d, J = 7 Hz, 3 H), 0.80 (d, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 217.2, 128.8, 126.5, 52.5, 50.5, 49.1, 48.4, 48.3, 32.5, 28.7, 28.2, 27.2, 26.0, 25.5, 22.6 (2 C), 21.9, 21.5; MS *m/z* (M^+) calcd 260.2140, obsd 260.2142. Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.91, H, 10.99.

(4a*R,6a*S**,6b*S**,8a*S**,9a*S**,9b*R**)-3,4,4a,5,6a,6b,7,8,8a,9,-9a,9b-Dodecahydro-5,5-dimethyl-6*H*-cyclobuta[3,4]cyclopenta[1,2-*a*]naphthalen-6-one (42):** procedure B; 53% yield; colorless solid, mp 90–91 °C (from ether–hexanes); IR (CCl_4, cm^{-1}) 1710; ^1H NMR (500 MHz, $CDCl_3$) δ 5.80–5.65 (m, 2 H), 3.08–3.02 (m, 1 H), 2.98 (dd, J = 11, 8.5 Hz, 1 H), 2.98–2.92 (m, 1 H), 2.85–2.75 (m, 1 H), 2.25–2.23 (m, 2 H), 2.17 (dtt, J = 18, 6, 2 Hz, 1 H), 2.07 (dddd, J = 18, 9, 4, 2.5 Hz, 1 H), 2.03–1.95 (m, 2 H), 1.95–1.78 (m, 2 H), 1.80 (ddd, J = 15, 6, 4 Hz, 1 H), 1.60 (ddd, J = 14, 14, 10 Hz, 1 H) 1.35 (br t, J = 10 Hz, 1 H), 1.35–1.25 (m, 1 H), 1.27 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 217.1, 129.5, 125.9, 96.3, 50.2, 48.0, 47.6, 42.3, 40.8, 38.0, 31.4, 27.6, 26.2, 26.0, 23.2, 21.9, 21.5; MS *m/z* (M^+) calcd 244.1827, obsd 244.1828. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.85; H, 9.80.

For **43**: colorless oil; IR (CCl_4, cm^{-1}) 3600, 1460, 1380, 1370, 1110, 1035; ^1H NMR (300 MHz, $CDCl_3$) δ 5.94 (d, J = 8 Hz, 1 H), 5.87 (d, J = 8 Hz, 1 H), 5.76 (br s, 1 H), 2.42 (br d, J = 10 Hz, 1 H), 2.20–1.95 (series of m, 3 H), 1.85–1.40 (series of m, 5 H), 1.33 (d, J = 12 Hz, 1 H), 1.24 (d, J = 12 Hz, 1 H), 1.20–1.00 (m, 1 H), 1.09 (s, 3 H), 0.98 (s, 3 H), 1.0–0.80 (m, 1 H), 0.85 (d, J = 7 Hz, 3 H), 0.69 (d, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.2, 137.33, 137.27, 126.1, 79.8, 50.8, 47.2, 42.3, 35.2, 33.4, 32.0, 31.0, 28.4, 25.2, 25.1, 22.1, 18.9, 15.2; MS *m/z* ($M^+ + 1$) calcd 261.2274, obsd 261.2218.

For **44**: colorless oil; IR (neat, cm^{-1}) 3580, 3500, 1470, 1370, 720; ^1H NMR (300 MHz, C_6D_6) δ 5.87 (d, J = 8.1 Hz, 1 H), 5.74 (d, J = 8.1 Hz, 1 H), 5.84 (m, 1 H), 2.94 (m, 1 H), 2.41 (dd, J = 6.8, 2.3 Hz, 1 H), 2.22 (m, 2 H), 1.80 (m, 3 H), 1.79 (d, J = 12.8 Hz, 1 H), 1.51 (br s, 1 H), 1.45 (dd, J = 3.1, 13.8 Hz, 1 H), 1.23 (s, 3 H), 1.22 (m, 1 H), 1.16 (m, 2 H), 1.03 (d, J = 7 Hz, 3 H), 0.96 (s, 3 H), 0.87 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 150.2, 139.9, 139.1, 127.7, 79.8, 57.2, 53.2, 42.3, 35.7, 35.5, 32.7, 30.33, 30.30, 25.13, 24.96, 22.9, 20.4, 16.1; MS *m/z* (M^+) calcd 260.2140, obsd 260.21234.

For **45** (as an inseparable mixture with the starting material): colorless oil; IR (neat, cm^{-1}) 3540, 1465, 1370, 700; ^1H NMR (300 MHz, C_6D_6) δ key signals 5.90 (d, J = 8.1 Hz, 1 H), 5.85 (d, J = 8.5 Hz, 1 H), 5.65 (d, J = 8.2 Hz, 1 H), 5.52 (d, J = 8.2 Hz, 1 H), 5.44 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 154.8, 139.4, 136.5, 125.4, 79.0, 58.0, 53.6, 44.7, 36.0, 35.1, 34.0, 31.9, 30.9, 30.3, 25.3, 22.6, 19.3, 16.0; MS *m/z* (M^+) calcd 260.2140, obsd 260.2123.

B. Bromide 12: 81% yield of a 21.5:2.2:3.9:1 mixture of **48**, **49**, and the two exo diastereomers.

For **48**: colorless crystals, mp 78–79 °C; IR (CCl_4, cm^{-1}) 3600, 1460, 1375, 1120, 1045, 710; ^1H NMR (300 MHz, C_6D_6) δ 5.95 (d, J = 2 Hz, 2 H), 5.75 (d, J = 3 Hz, 1 H), 2.88 (m, 1 H), 2.80 (m, 1 H), 2.03 (ddd, J = 10.5, 13.5, 3 Hz, 1 H), 1.55–1.52 (m, 4 H), 1.40 (dt, J = 1, 9 Hz, 1 H), 1.27 (d, J = 14 Hz, 1 H), 1.20 (tt, J = 12, 3 Hz, 2 H), 1.13–0.95 (series of m, 4 H), 1.12 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 156.2, 138.5, 138.1, 127.7, 78.9, 50.3, 48.6, 44.3, 42.4, 42.2, 35.2, 33.2, 31.6, 26.1, 25.3, 25.0, 19.5; MS *m/z* (M^+) calcd 244.1827, obsd 244.1825. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.42; H, 9.88.

For the first exo isomer: oil; IR (neat, cm^{-1}) 3480, 1450, 1370, 1315, 1280, 1230, 1135, 1110, 1065, 1030; ^1H NMR (300 MHz, C_6D_6) δ 6.16 (d, J = 8 Hz, 1 H), 5.96 (d, J = 8 Hz, 1 H), 5.92 (d, J = 3 Hz, 1 H), 2.89 (d, J = 1.5 Hz, 1 H), 2.81 (d, J = 1 Hz, 1 H), 1.92 (d, J = 14.5 Hz, 2 H), 1.71–1.67 (m, 2 H), 1.65–1.0 (series of m, 9 H), 1.16 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 152.0, 140.2, 137.8, 130.8, 79.2, 51.1, 48.4, 45.1, 42.9, 42.8, 35.2, 34.7, 30.8, 26.1, 25.7, 25.0, 19.3; MS *m/z* (M^+) calcd 244.1827, obsd 244.1809.

For the second exo isomer: oil; IR (CCl_4, cm^{-1}) 3580, 1455, 1365, 1250, 1120, 1060, 990, 710; ^1H NMR (300 MHz, C_6D_6) δ 5.98 (d, J = 8 Hz, 1 H), 5.83 (d, J = 8 Hz, 1 H), 5.74 (d, J = 3 Hz, 1 H), 3.86 (m, 1 H), 1.86–1.61 (m, 4 H), 1.61–1.41 (m, 4 H), 1.40–0.50 (m, 12 H); ^{13}C NMR (75 MHz, C_6D_6) 153.3, 140.2, 137.3, 129.3, 79.0, 55.3, 49.0, 45.0, 44.0, 42.9, 35.5, 29.8, 26.1, 25.9 (2 C), 25.0, 20.9; MS *m/z* (M^+) calcd 244.1827, obsd 244.1815.

C. Bromide 10: 74% yield of a 29.5:8.2:1:1 mixture of **50**, **51**, and both exo diastereomers. Alcohols **50** and **51** could not be obtained pure.

For the **50/51** mixture: colorless oil; IR (neat, cm^{-1}) 3480, 1450, 1370; ^1H NMR (300 MHz, C_6D_6) key signals at δ 5.84 (m), 5.62 (br s), 5.46 (br s); ^{13}C NMR (75 MHz, C_6D_6) ppm 153.2, 150.3, 139.9, 138.8, 138.5, 137.5, 126.5, 123.7, 79.5 (2 C), 55.8, 53.6, 52.3, 52.2, 44.0, 43.3, 42.7, 42.6 (2 C), 40.1, 39.3, 35.5, 35.0, 34.8, 34.7, 34.6, 33.6, 32.3 (2 C), 30.6, 28.1, 27.1, 25.3, 25.2, 20.4, 19.4 (one C not observed); MS *m/z* ($M^+ - H_2O$) calcd 240.1878, obsd 240.1900. Anal. Calcd for $C_{18}H_{26}O$: C, 83.66; H, 10.15. Found: C, 83.34; H, 10.08.

For the exo diastereomers: ^{13}C NMR (75 MHz, C_6D_6) ppm key signals at 159.8, 155.5, 139.0, 138.2, 136.9, 134.5, 129.0, 123.8, 58.0, 53.2, 51.2, 46.4, 44.3, 41.7, 40.6, 36.0, 35.3, 34.5, 33.6, 32.3, 31.8, 28.4, 27.9, 27.1, 26.6, 25.3 (2 C), 19.6; MS *m/z* ($M^+ - H_2O$) calcd 240.1878, obsd 240.1910.

(3*R,3a*S**,5a*S**,9a*S**,9b*S**)-1,2,3,3a,5,5a,6,7,9a,9b-Decahydro-3-isopropyl-5a,8-dimethyl-4*H*-benz[*e*]inden-4-one (46):** procedure D; reflux 2 h; 70% yield, colorless hexagonal crystals, mp 74–75.5 °C; IR (KBr, cm^{-1}) 1705; ^1H NMR (500 MHz, C_6D_6) δ 5.16 (m, 1 H), 2.51 (m, 1 H), 2.47 (m, 2 H), 2.27 (m, 1 H), 2.08 (dd, J = 1.2, 12 Hz, 1 H), 1.99 (m, 1 H), 1.94 (d, J = 12 Hz, 1 H), 1.78 (m, 1 H), 1.64 (m, 1 H), 1.62 (m, 2 H), 1.58 (s, 3 H), 1.54 (dd, J = 7.4, 11 Hz, 1 H), 1.47 (m, 2 H), 1.30 (m, 1 H), 1.02 (d, J = 6.8 Hz, 3 H), 0.91 (d, J = 6.6 Hz, 3 H), 0.81 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 211.2, 132.3, 122.9, 55.6, 54.3, 52.9, 48.6, 42.4, 38.7, 32.5, 29.5, 29.2, 27.7, 27.2, 26.9, 23.6, 22.9, 22.7; MS m/z (M^+) calcd 260.2140, obsd 260.2153.

(3*R,3a*R**,5a*S**,9a*S**,9b*S**)-1,2,3,3a,5,5a,6,7,9a,9b-Decahydro-3-isopropyl-5a,8-dimethyl-4*H*-benz[*e*]inden-4-one (47).** Longer reaction times up to 2 d; 74% yield; colorless liquid; IR (neat, cm^{-1}) 1710; ^1H NMR (500 MHz, C_6D_6) δ 5.38 (s, 1 H), 2.35 (d, J = 2.5 Hz, 1 H), 2.31 (m, 1 H), 2.14 (dd, J = 9.4, 12.6 Hz, 1 H), 2.02 (m, 1 H), 1.98 (m, 1 H), 1.77 (m, 1 H), 1.66 (dd, J = 0.6, 12.5 Hz, 2 H), 1.61 (m, 1 H), 1.58 (d, J = 0.8 Hz, 3 H), 1.48 (m, 2 H), 1.36 (m, 3 H), 1.14 (ddd, J = 1.1, 6.2, 13.5 Hz, 1 H), 0.88 (d, J = 6.7 Hz, 3 H), 0.86 (s, 3 H), 0.84 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 208.04, 135.4, 119.5, 54.6, 47.9 (2 C), 43.3, 41.8, 39.2, 36.2, 32.7, 28.0, 27.5, 27.2, 27.0, 23.7, 21.4, 20.0; MS m/z (M^+) calcd 260.2140, obsd 260.2170. Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.89. Found: C, 83.09; H, 10.93.

The tosylhydrazone derivative **47b** was obtained as colorless crystals, mp 185–186 °C dec.

(4a*R,6a*R**,6b*R**,9a*R**,10a*R**,10b*R**)-3,4a,5,6a,6b,7,8,9,9a,-10,10a,10b-Dodecahydro-2,4a-dimethylpentaleno[2,1-*a*]naphthalen-6(4*H*)-one (52):** procedure D; reflux 2 h, 72% yield; colorless oil; ^1H NMR (300 MHz, C_6D_6) δ 5.38 (s, 1 H), 2.92 (m, 1 H), 2.22 (m, 2H), 1.90 (m, 3 H), 1.69–1.58 (m, 4 H), 1.58 (s, 3 H), 1.43–1.30 (m, 6H), 1.14 (m, 3 H), 0.83 (d, J = 4.1 Hz, 3 H); ^{13}C NMR (20 MHz, C_6D_6) ppm 216.4, 135.4, 119.4, 57.6, 47.4, 47.0, 43.0, 41.8, 40.6, 38.7, 36.3, 36.1, 33.5, 32.7, 28.0, 27.5, 25.6, 23.7; MS m/z (M^+) calcd 258.1983, obsd 258.2024.

(4a*R,6a*S**,6b*R**,9a*R**,10a*R**,10b*R**)-3,4a,5,6a,6b,7,8,9,9a,-10,10a,10b-Dodecahydro-2,4a-dimethylpentaleno[2,1-*a*]naphthalen-6(4*H*)-one (53):** Longer reaction times; 68% yield; ^1H NMR (300 MHz, C_6D_6) δ 5.15 (br s, 1 H), 2.57 (m, 2 H), 2.23 (d, J = 14 Hz, 1 H), 2.22 (m, 2 H), 2.00 (d, J = 14 Hz, 1 H), 1.82 (br s, 1 H), 1.70 (m, 5 H), 1.59 (s, 3 H), 1.57–1.29 (series of m, 4 H), 1.22–1.10 (series of m, 2 H), 0.85 (m, 1 H), 0.81 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 212.0, 133.4, 123.3, 54.5, 52.9, 48.1, 47.4, 44.6, 42.1, 36.3, 35.7, 35.6, 32.2, 29.1, 28.7, 27.6, 26.9, 23.8; MS m/z (M^+) calcd 258.1983, obsd 258.1993.

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Supplementary Material Available: Copies of ^1H NMR spectra of the compounds which lack combustion data (38 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.