Rearrangement vs Homofragmentation: Chemical Consequences of Different σ-Relays on the Heterolysis of Sulfonate Esters Induced by Through-Bond Interactions

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An alcoholate function intramolecularly induces heterolysis of a sulfonate ester group in an apolar solvent via orbital interactions through three intervening C–C single bonds (TBI). It is shown that the reactivity of rigid *trans*-perhydronaphthalene-1,4-diol monosulfonate esters (**1–6**) upon treatment with sodium *tert*-amylate in refluxing benzene is only affected by the relative position of the hydroxyl function to the sulfonate ester group and not by the orientation of the hydroxyl group. The two chief pathways by which these compounds react are rearrangement (**1**, **3**, and **4**) and homofragmentation (**5** and **6**). Stereoelectronic effects play a dominant role here, except in compound **2** where steric factors primarily determine the reactivity and product outcome (ether formation). Homofragmentation is much faster than rearrangement and is only possible when a 1,3-bridged through-space interaction accompanies TBI. The extent of TBI as well as the product composition is strongly determined by the σ-relay of the three C–C bonds between the electron donor (alcoholate) and the electron acceptor (sulfonate ester bond). The results presented here are consistent with the trans rule and show the validity of similar proposals for biosynthetic processes.

Introduction

From our previous work on the total synthesis of sesquiterpenes with a cis-fused perhydroazulene skeleton,[1,2] it is known that stereochemically rigid *trans*-perhydronaphthalene-1,4-diol monosulfonate esters react smoothly upon treatment with sodium *tert*-amylate in refluxing *apolar* solvents like benzene or toluene. The formation of an alcoholate function intramolecularly induces heterolysis of the sulfonate ester group, probably via orbital interactions through the three intervening C–C bonds.[3] The resulting dipolar intermediates subsequently undergo rearrangement, β-elimination, or homofragmentation[4] dependent on the location and orientation (axial or equatorial) of the sulfonate ester.

From the studies on 1,4-diol monosulfonate esters in which the ring carbon atoms adjacent to the carbon atom bearing the sulfonate ester are unsubstituted,[3] it is concluded that a through-bond interaction (TBI) alone controls the reactivity of compounds with an axial sulfonate ester group, whereas the reactivity of the corresponding compounds in which the sulfonate ester group is equatorially oriented is determined by the sum of TBI and a 1,3-bridged through-space interaction. If 1,3-bridging occurs it can determine the product composition to a degree.

Experimental and theoretical studies[5,6] have demonstrated that the extent of TBI between an electron-rich function and an electron-poor bond also depends on the σ-relay (the geometry of the intervening σ-framework). No attempts have yet been made to relate the TBI to the geometry of the four-carbon chain between the electron-donating alcoholate function and the nucleofugal sulfonate ester in these compounds. Therefore, we decided to examine the mesylates **1–6** under the strongly basic conditions mentioned above. These compounds all have the same structural features around the mesylate group. Because we assume that the orientation of the alcohol function will probably have little influence on the reaction rate,[7] the actual geometry in the compounds **1–6** can be represented by the three partial structures **I–III** (Chart 1).

From the reactions of **1–6** with sodium *tert*-amylate in refluxing benzene we expect to gather more information about (i) to what extent transmission of TBI depends on the σ-relay, in particular in the situations **I–III** depicted in Chart 1, and (ii) the influence of the σ-relay on the product composition, or in other words, what are the chemical consequences if a certain σ-relay is operating.

Results and Discussion

The mesylates **1** and **2** were prepared from the known compounds **7**[1] and **8**,[3] respectively, via intermediates **9a** and **9b**, according to standard procedures (Scheme 1).

The readily available ketone **10**[8] was the starting material for the synthesis of the mesylates **3** and **4** (Scheme 2). Bromination of **10** with DBBA[9] yielded the bromide **11** which upon treatment with Li(*t*-BuO)$_3$AlH in THF at −78 °C afforded exclusively the 7β-alcohol **12**. An internal S_N2 reaction under the influence of *t*-BuOK in *t*-BuOH (**12** → **13**) went smoothly. Regioselective opening of the oxirane ring with LAH in refluxing THF and subsequent

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(1) Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; Brunekreef, G. A.; de Groot, A. *J. Org. Chem.* **1990**, *55*, 941.

(2) Jenniskens, L. H. D.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1991**, *56*, 6585.

(3) Orrū, R. V. A.; Wijnberg, J. B. P. A. Jenniskens, L. H. D.; de Groot, A. *J. Org. Chem.* **1993**, *58*, 1199.

(4) Fragmentation which generates a cyclopropane ring is termed homofragmentation. See: Flury, P.; Grob, C. A. *Helv. Chim. Acta* **1983**, *66*, 1971.

(5) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

(6) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395 and references cited therein.

(7) This assumption is based on the observation that 1,4-diol monosulfonate esters in which only the orientation of the alcohol function is different react with almost the same rate.[3]

(8) Kim, M.; Gross, R. S.; Sevestre, H.; Dunlap, N. K.; Watt, D. S. *J. Org. Chem.* **1988**, *53*, 93.

(9) Grundke, G.; Keese, W.; Rimpler, M. *Chem. Ber.* **1985**, *118*, 4288.

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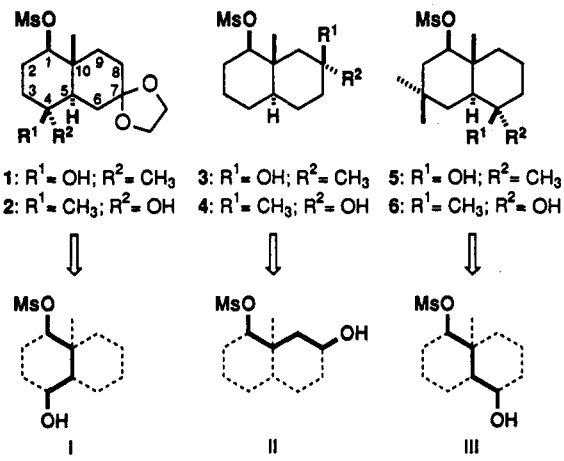
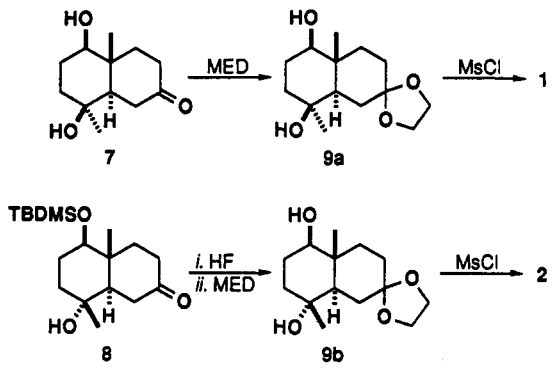
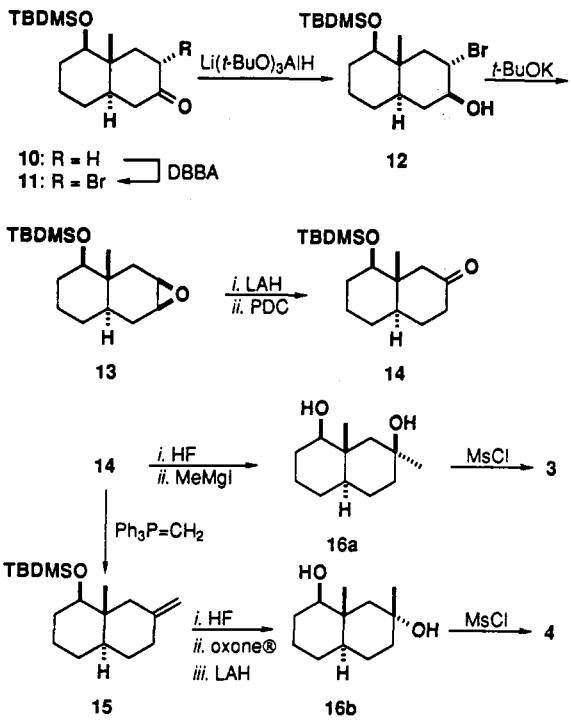
Chart 1



Scheme 1

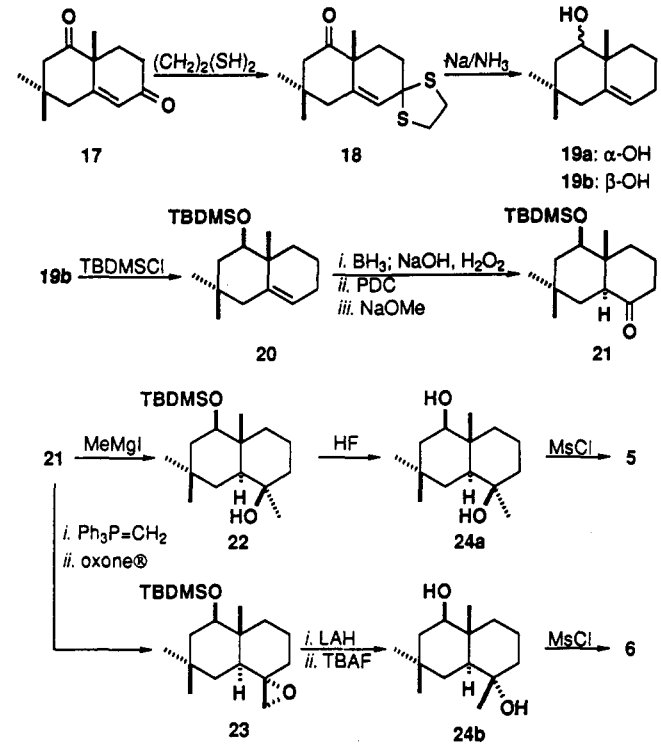


Scheme 2



oxidation with PDC converted **13** into the ketone **14**. The TBDMS ether bond of **14** was then cleaved with HF in aqueous acetonitrile, and the resulting hydroxy ketone was treated with an excess of MeMgI to afford the diol **16a**. For the preparation of diol **16b** ketone **14** was subjected to a Wittig reaction with $Ph_3P{=}CH_2$ in DMSO to yield the olefinic TBDMS ether **15**. Cleavage of the TBDMS ether bond of **15** followed by epoxidation with

Scheme 3



in situ generated dimethyldioxirane[10] and reduction with LAH led to the diol **16b** as the sole product. Treatment of the diols **16a** and **16b** with MsCl in pyridine provided the mesylates **3** and **4** in yields of 47 and 39%, respectively, overall from **10**.

For the synthesis of the mesylates **5** and **6** the known Robinson annulation product **17**[11] was converted into the cyclic thioacetal **18** by a known procedure[12] (Scheme 3). Upon treatment with sodium metal in liquid NH_3 at reflux temperature **18** was desulfurized, and at the same time its carbonyl function was reduced. In this way an easily separable 1:10 mixture of the alcohols **19a** and **19b**, respectively, was produced. Protection of the alcohol group as its TBDMS ether (**19b** → **20**) was successively followed by oxidative hydroboration (BH_3·THF, NaOH, H_2O_2), oxidation (PDC), and equilibration (NaOMe, MeOH) to give the trans-fused ketone **21**. This ketone could be used for the synthesis of both the mesylates **5** and **6**. Treatment of **21** with MeMgI in dry ether afforded the monoprotected diol **22**. Cleavage of the TBDMS ether bond (**22** → **24a**) and mesylation produced the mesylate **5** in an overall yield of 32% from **17**. A Wittig condensation of ketone **21** with $Ph_3P{=}CH_2$ in DMSO and subsequent epoxidation of the resulting exocyclic double bond with dimethyldioxirane afforded exclusively the epoxide **23**. After reduction of the oxirane ring with LAH in refluxing THF, removal of the TBDMS protecting group afforded the desired diol **24b**. Finally, treatment of **24b** with MsCl in pyridine provided the mesylate **6** in 44% overall yield from **17**.

In order to obtain comparable data about the reactivity of the mesylates **1**–**6**, all these compounds were subjected to the same reaction conditions. The reactions were run in benzene at reflux temperature with ca. 5 equiv of sodium *tert*-amylate during 10 min. By comparing the quantities

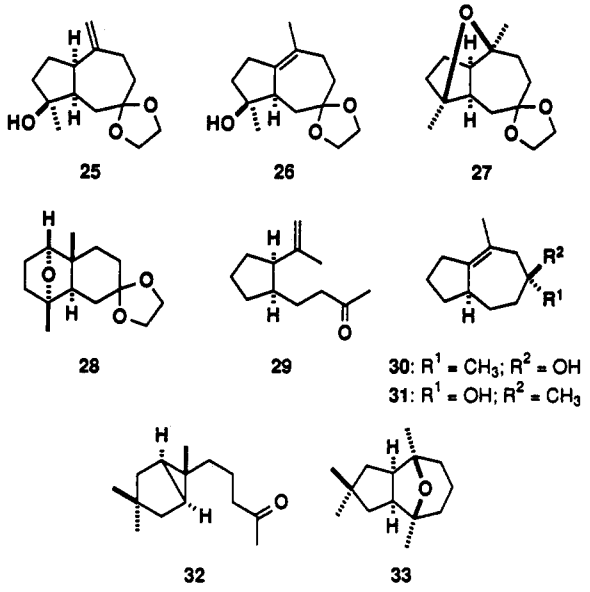
(10) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.
(11) Heathcock, C. H.; Gray, D. *Tetrahedron* **1971**, *27*, 1239.
(12) Ralls, J. W.; Riegel, B. *J. Am. Chem. Soc.* **1954**, *76*, 4479.

Table 1. Reactions of the Mesylates 1–6 with Sodium *tert*-Amylate[a]

entry	mesylate	products[b] (%)	recovery[c]
1	1	25 (76)[d]	21
2	2	28 (34)	66
3	3	29 (33)[e] + 30 (<10)	50
4	4	29 (32)[e] + 31 (8)	50
5	5	32 (76)[e]	
6	6	32 (72)[e]	

[a] All reactions were performed in refluxing benzene with ca. 5 equiv of sodium *tert*-amylate for 10 min. [b] Isolated yield in parentheses. [c] Percentage of recovered starting material. [d] The compounds 26 and 27 were also isolated in a combined yield of 2%. [e] Yield is somewhat diminished due to aldol condensations under the influence of sodium *tert*-amylate.

Chart 2



of recovered starting material a rough estimate of the relative reaction rates could be obtained. The results of these studies are collected in Table 1.

The mesylate **1** gave predominantly the rearranged product **25** (76%), together with small amounts of **26** and **27** (Table 1, entry 1).[1] The quantity of regained **1** in this reaction amounted to 21%.

After reaction of the mesylate **2**, in which C(4) has the opposite stereochemistry compared with **1**, a larger amount (66%) of starting material was regained (Table 1, entry 2). The sole product in this reaction was the cyclic ether **28** which was isolated in 34% yield. The presence of an ether bridge in **28** was concluded from its ^{1}H and ^{13}C NMR spectrum. In the ^{1}H NMR spectrum of **28** a one-proton signal appears at δ 4.09. The ^{13}C NMR spectrum of **28** shows a doublet and a singlet at δ 82.45 and 86.07, respectively.

Both the mesylates **3** and **4** gave the same quantity (50%) of recovered starting material (Table 1, entries 3 and 4). Also, the major product from these reactions was the same, i.e., the rearranged fragmentation product **29**. In both reactions the yield of **29** (33 and 32%, respectively) was somewhat diminished by aldol condensations.[13] An inseparable mixture (10%) of several minor products, with the rearranged olefin **30** as the main component, was formed during the reaction of **3**. As a minor product from the reaction of **4**, the rearranged olefin **31** was isolated in 8% yield.

(13) See ref 3 and references cited therein.

After the standard basic treatment of the mesylates **5** and **6**, no starting material could be detected (Table 1, entries 5 and 6). In both cases, only fragmentation was observed leading to the same product. The yield of this product, the cyclopropane derivative **32**, was 76% from **5** and 72% from **6**. Also in these reactions the product yields were diminished by aldol condensations. When the reaction time was shortened to 1 min, **32** was isolated in almost quantitative yield from both **5** and **6**. The proton-coupled ^{13}C NMR spectrum of **32** shows a two-carbon signal (doublet) with J = 165 Hz, which is consistent with the presence of a cyclopropane ring. Together with other NMR data, this confirms our structural assignment of **32**. In an additional experiment **5** was treated with lithium *tert*-amylate instead of sodium *tert*-amylate. After completion of this reaction (2 h), a considerable amount of the rearranged cyclic ether **33** was isolated next to **32**.

The results of these studies on **1**–**6** clearly show that a different location of the hydroxyl group strongly affects the course of the reactions of these compounds. The two chief pathways by which these compounds react are rearrangement (Table 1, entries 1, 3, and 4) and homofragmentation (Table 1, entries 5 and 6). Homofragmentation occurs in a very fast reaction; within 1 min the reactions with **5** and **6** are complete. The rearrangement reactions and the reaction in which the cyclic ether is formed (Table 1, entry 2) take much more time. Considerable amounts (21–66%) of starting material are recovered after a reaction time of 10 min. Completion of these reactions led to the same products and product ratios.

It is also demonstrated that two epimeric hydroxymesylates (e.g., **3** and **4** or **5** and **6**) react at approximately the same rate. These results confirm our assumption that the orientation of the hydroxyl group is not very important for the reactivity of these compounds. This is not so surprising if stereoelectronic effects, as is probably the case here, play a dominant role. An electron pair of an oxygen anion can always adopt the most favorable orientation required for reaction.[14] On the other hand, the difference in reaction rate between **3** and **5**, or between **4** and **6**, is spectacular. This proves that the reactivity of these compounds is closely connected with the *location* of the hydroxyl group.

The completely different product outcome (rearrangement versus cyclic ether formation) and the difference in reaction rate found for the epimers **1** and **2** must be attributed, in the first instance, to steric hindrance and not to stereoelectronic factors. From examination of molecular models, it appears that the diaxial steric interaction between the angular methyl group and the methyl group at C(4) in **2** forces the equatorial hydroxyl groups at C(4) and C(1) toward each other. Another consequence of this steric hindrance is that the C(5)–C(10) bond is no longer exactly antiperiplanar to the mesylate group and hence the tendency to rearrange will be diminished. As an overall result, ether formation is favored over rearrangement. Semiempirical MNDO calculations provide some support for the disruption of the antiperiplanarity as illustrated in the Newman projections along the C(1)–C(10) bond of **1** and **2** (Figure 1).[15] The

(14) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983.

(15) The Newman projections were drawn based on full geometry optimizations by means of the MNDO method. See: (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Reynolds, C. H. *J. Comput. Chem.* **1986**, *2*, 140.

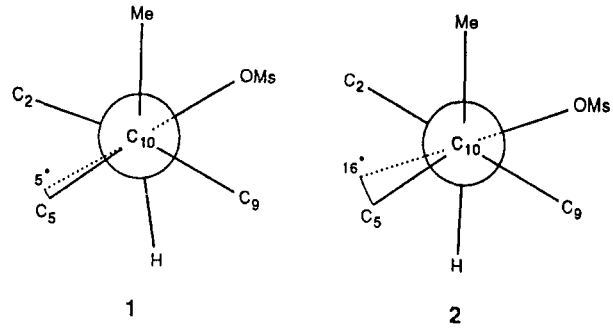
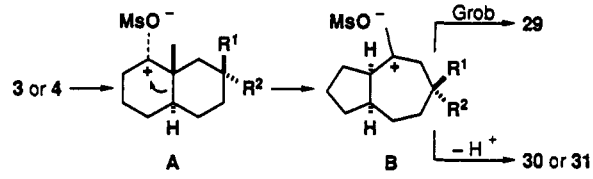


Figure 1.

Scheme 4



(3): $R^1 = O^-$; $R^2 = CH_3$
(4): $R^1 = CH_3$; $R^2 = O^-$

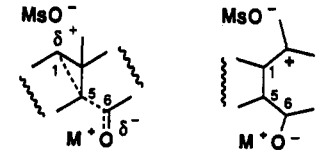
C(5)–C(10) bond in **1** deviates only 5° from the antiperiplanar orientation to the sulfonate ester bond. The C(5)–C(10) bond in **2**, on the other hand, diverges much more (16°).

Furthermore, it has been shown that in processes which involve initial ionization of a leaving group, the cationic center (or the developing cation) is stabilized by delocalization of a neighboring C–C bond.[16,17] The extent of this electronic delocalization depends on the alignment of the participating σ-bond with the leaving group.[18] The C(5)–C(10) bond in **2** is less favorably oriented for effective σ-participation in the ionization process than the one in **1**, and therefore **2** will react more slowly.

Rearrangement is the only reaction pathway observed for the mesylates **3** and **4** (entries 3 and 4). Just as the mesylate **1**[1] and probably also **2**, these compounds are supposed to react stepwise via dipolar intermediates. The initially formed dipolar intermediates **A(3)** and **A(4)** rapidly rearrange to the thermodynamically more stable intermediates **B(3)** and **B(4)** (Scheme 4). Both **B(3)** and **B(4)** give the cyclopentane derivative **29** as the major product via a fast Grob fragmentation. The formation of the minor products **30** and **31** from the intermediates **B** must be the result of a thermodynamically controlled proton loss. Olefin **31** can also be formed by an intramolecularly assisted proton abstraction.

As pointed out above, the (developing) cationic center generated at C(1) can be stabilized by delocalization of the C(5)–C(10) bond in these systems. It is suggested that electron-releasing substituents donate electrons to the participating σ-bond via TBI, thus enlarging the electron density of this bond and its ability to participate in the ionization process.[19] The slightly diminished reactivity of **3** and **4**, as compared with that of **1**, is easily understood

Chart 3



on this basis. In the mesylate **1** the hydroxyl group is separated by one C–C bond from the C(5)–C(10) bond, and in the mesylates **3** and **4** this number is two. The strongly electron-donating alkoxide group in **1** affects therefore the electron density of the C(5)–C(10) bond, and consequently, the reactivity, to a higher degree than it does in **3** and **4**.

A very fast homofragmentation is the only process observed for **5** and **6** upon treatment with sodium *tert*-amylate (Table 1, entries 5 and 6). No rearrangement or other products are formed. Both **5** and **6** react at the same rate, which proves again that the orientation of the hydroxyl group is not very important for the reactivity of these compounds. The selective formation of the cyclopropane derivative **32** can be explained if the assumption is made that through-space induction, which accompanies TBI,[20] involves bridging of the cationic center at C(1) by the back lobe of the C(5)–C(6)–O⁻ orbital. This homohyperconjugation effect,[21,22] as denoted by partial structure **C** in Chart 3, will ultimately lead to C(5)–C(1) bond formation with simultaneous breaking of the C(5)–C(6) bond.

The initially formed secondary carbocations in these processes can be expected to undergo rearrangement to more stable tertiary ions, with bridged ions being likely intermediates on the rearrangement path. The reactions of **5** with sodium and lithium *tert*-amylate support the existence of these bridged cationic intermediates. Being a bonding interaction, bridging is strengthened by electron donors and weakened by electron acceptors.[23] The strongly electron-donating alkoxide group with Na^+ as counterion pushes the back lobe of the C(5)–C(6)–O⁻ orbital toward the cationic center at C(1) to such an extent that **C** will be more stable than the rearranged tertiary cationic intermediate **D**. As a result, homofragmentation (formation of **32**) will be favored. On the other hand, replacement of Na^+ by Li^+ results in a decrease of the electron-donating ability of the alkoxide group.[24] This decrease of inductivity[25] leads to less bridging, and rearrangement (formation of **33**) can now compete favorably with homofragmentation. Cyclopropanoid bridged structures being comparable to **C** have been proposed as intermediates in cationic processes before.[26]

The extremely fast rate by which **5** and **6** react might be explained as the result of the sum of σ-participation, 1,3-bridging, and TBI. The contribution of σ-participation

(16) Jensen, F. R.; Smart, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 5686 and 5688.
(17) (a) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. (b) Hartmann, G. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 6147.
(18) Fischer, W.; Grob, C. A.; von Sprecher, G.; Waldner, A. *Tetrahedron Lett.* **1979**, *21*, 1905.
(19) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661.
(20) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.
(21) Adcock, W.; Kok, G. B. *J. Org. Chem.* **1987**, *52*, 356.
(22) Grob, C. A.; Gründel, M.; Sawlewicz, P. *Helv. Chim. Acta* **1988**, *71*, 1502.
(23) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.
(24) The Li^+–O⁻ bond has a more covalent character than the Na^+–O⁻ bond. See: Paquette, L. A.; Gilday, J. P. *J. Org. Chem.* **1988**, *53*, 4972. As a result, the electron-donating ability of the alkoxide function with Li^+ as the counterion will be diminished.
(25) This term was introduced by Grob[23] to designate the intensity with which the *I* effect is transmitted to the reaction center.
(26) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S.; Halley, K. A. *J. Org. Chem.* **1990**, *55*, 653.

in **5** and **6**, however, will be of the same magnitude as that in, for example, **3** and **4** because in all these compounds the C(5)–C(10) bond is antiperiplanar to the mesylate group. As a consequence, the large rate increase observed for **5** and **6** may not be ascribed to σ-participation. By comparing the reactivities of related mesylates relatively small rate enhancements are observed for reactions in which 1,3-bridging is operating.[3] These observations have led to the assumption that the contribution of 1,3-bridging on the reactivity of **5** and **6** is only modest. This should mean that TBI largely accounts for the large rate increase observed for **5** and **6**.

Since the extent of TBI depends on the geometry of the relaying σ-bonds, the observed differences in reaction rate of the compounds **1–6** can be principally attributed to the differently operating σ-relays **I–III**. Transmission of TBI is highly favored in **III** (W-like configuration), which finds expression in a very fast reaction of **5** and **6**. The deviation of the W arrangement in **I** and **II** makes the transmission of TBI more difficult, thereby reducing the reactivity of **1–4**. These results are consistent with the trans rule, which predicts that the extent of orbital interactions through σ-bonds is maximized for an all-trans arrangement of σ-bonds.[5]

Also, the product composition is strongly dependent on the geometry of the relaying σ-bonds. Rearrangement is found to occur preferentially with **I** and **II** as the operating σ-relays, whereas **III** shows homofragmentation as the main reaction path. This fragmentation process can only occur if the back lobe of the polarized C–C–O⁻ bond is in a proper position for dorsal C-participation in the ionization step (as is the case in the all-trans arrangement of σ-bonds). It is also noteworthy that processes similar to homofragmentation are thought to occur in the biosynthesis of certain compounds possessing a fused cyclopropane ring.[27–29]

Experimental Section[30]

Materials. The starting materials **7**,[2] **8**,[3] **10**,[6] and **17**[11] were prepared following previously described procedures. Compounds **25–27** have been fully characterized before.[1] A stock solution of sodium *tert*-amylate (3.2 M in toluene) was prepared by the procedure of Conia[31] and stored under an Ar atmosphere in a refrigerator.

(4′aα,5′α,8′α,8′aα)-Octahydro-4′a,8′-dimethylspiro[1,3-dioxolane-2,2′(1′*H*)-naphthalene]-5′,8′-diol (9a). To a solution of 1.31 g (6.16 mmol) of **7** in a mixture of 30 mL of CH_2Cl_2 and 30 mL of MED were added catalytic amounts of ethylene glycol and camphorsulfonic acid. The reaction mixture was stirred at rt for 24 h, after which time 1.5 mL of Et_3N was added. The reaction mixture was then diluted with 100 mL of CH_2Cl_2 and washed with 50 mL of brine. The organic layer was dried and evaporated to give the crude dioxolane **9a**. Recrystallization from MeOH and flash chromatography of the mother liquid (1:2 petroleum ether (bp 40–60 °C)/EtOAc) afforded 1.30 g (82%) of **9a**: mp 149–150 °C; ^{1}H NMR (200 MHz) δ 1.04 (s, 3 H), 1.12 (s, 3 H), 1.21–2.02 (m, 13 H), 3.26 (dd, *J* = 4.0, 11.4 Hz, 1 H), 3.89–3.98 (m, 4 H); ^{13}C NMR δ 11.47 (q), 26.62 (t), 29.55 (q), 30.34 (2t), 36.26 (t), 38.39 (s), 39.25 (t), 47.30 (d), 63.86 (t), 64.05 (t), 70.96 (s), 78.98 (d), 109.45 (s); MS *m/z* (relative intensity) 256 (M^+, 2), 238 (2), 206 (2), 198 (6), 167 (3), 139 (2), 99 (100); calcd for $C_{14}H_{24}O_4$ (M^+) *m/z* 256.1674, found *m/z* 256.1677. Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.59; H, 9.43. Found: C, 65.31; H, 9.44.

(4′aα,5′α,8′β,8′aβ)-Octahydro-4′a,8′-dimethylspiro[1,3-dioxolane-2,2′(1′*H*)-naphthalene]-5′,8′-diol (9b). To a solution of 1.68 g (5.15 mmol) of **8** in 100 mL of acetonitrile was added 3 mL of 40% aqueous HF. The mixture was stirred at rt for 2.5 h and then poured into 250 mL of saturated aqueous $NaHCO_3$. After extraction of the aqueous layer with four 50-mL portions of EtOAc, the combined organic layers were dried and evaporated to give 1.10 g (100%) of a dihydroxy ketone [^{1}H NMR (90 MHz) δ 0.89 (s, 3 H), 1.00 (s, 3 H), 1.21–2.59 (m, 13 H), 3.22 (m, 1 H)]. This crude product was treated with MED for 2.5 h as described above for the acetalization of **7**. Workup and flash chromatography (1:2 petroleum ether (bp 40–60 °C)/EtOAc) yielded 0.95 g (72%) of **9b**: ^{1}H NMR (200 MHz) δ 0.88 (s, 3 H), 1.06 (s, 3 H), 1.07–1.89 (m, 13 H), 3.32 (dd, *J* = 4.7, 10.7 Hz, 1 H), 3.83–3.98 (m, 4 H); ^{13}C NMR δ 11.94 (q), 21.88 (q), 28.47 (t), 30.10 (t), 30.46 (t), 37.57 (t), 38.49 (s), 49.95 (t), 49.73 (d), 63.97 (2t), 70.88 (s), 78.74 (d), 109.25 (s); MS *m/z* (relative intensity) 256 (M^+, 1.6), 238 (4), 206 (4), 198 (8), 167 (4), 139 (3), 99 (100); calcd for $C_{14}H_{24}O_4$ (M^+) *m/z* 256.1674, found *m/z* 256.1678.

(3α,4aβ,5β,8aα)-3-Bromo-5-[(*tert*-Butyldimethylsilyl)oxy]-octahydro-4a-methyl-2(1*H*)-naphthalenone (11). To a solution of 2.30 g (8.04 mmol) of DBBA in 95 mL of dry ether was added a solution of 5.10 g (17.0 mmol) of **10** in 40 mL of dry ether. The reaction mixture was allowed to stir at rt for 20 h. After filtration, the reaction mixture was washed with two 100-mL portions of water, dried, and evaporated. The residue was flash chromatographed (50:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 3.65 g (87%) of a white solid: mp 114–115 °C (from MeOH); ^{1}H NMR (90 MHz) δ −0.11 (s, 6 H), 0.70 (s, 9 H), 0.90 (s, 3 H), 1.12–1.79 (m, 9 H), 2.19 (d, *J* = 8.7 Hz, 1 H), 2.61 (dd, *J* = 7.2, 12.3 Hz, 1 H), 3.11 (m, 1 H), 4.54 (dd, *J* = 7.2, 13.8 Hz, 1 H); MS *m/z* (relative intensity) 376 (M^+, 0.2), 374 (M^+, 0.2), 319 (21), 317 (20), 253 (14), 240 (20), 239 (100), 163 (21), 121 (20), 75 (48), 73 (20); calcd for $C_{17}H_{31}Br^{79}O_2Si$ (M^+) *m/z* 374.1271, found *m/z* 374.1272. Anal. Calcd for $C_{17}H_{31}BrO_2Si$: C, 54.30; H, 8.32. Found: C, 54.70; H, 8.61.

(2α,3β,4aα,5α,8aβ)-3-Bromo-5-[(*tert*-Butyldimethylsilyl)-oxy]decahydro-4a-methyl-2-naphthalenol (12). To a stirred solution of 4.42 g (11.8 mmol) of **11** in 150 mL of dry THF was added 7.5 g (30 mmol) of Li(*t*-BuO)$_3$AlH at −78 °C. The reaction mixture was stirred at −78 °C for 3 h and then quenched by dropwise addition of 50 mL of saturated aqueous Na_2SO_4. The two-phase mixture was separated, and the aqueous layer was extracted with three 50-mL portions of EtOAc. The combined organic layers were washed with 50 mL of brine, dried, and evaporated. The resulting residue was flash chromatographed (30:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 4.42 g (99%) of **12** as white crystals: mp 82–85 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR (90 MHz) δ −0.18 (s, 6 H), 0.74 (s, 12 H), 0.90–1.80 (m, 10 H), 2.32 (dd, *J* = 12.5, 4.0 Hz, 1 H), 2.45 (br s, 1 H), 3.21 (dd, *J* = 5.0, 10.1 Hz, 1 H), 3.63 (m, 1 H), 4.18 (m, 1 H); MS *m/z* (relative intensity) 378 (M^+, 0.3), 376 (M^+, 0.3), 321 (6), 319 (6), 303 (9), 301 (9), 239 (6), 195 (4), 193 (4), 150 (34), 147 (100), 105 (34), 95 (11), 91 (12), 75 (31), 73 (17); calcd for $C_{17}H_{33}Br^{79}O_2Si$ (M^+) *m/z* 376.1434, found *m/z* 376.1431.

(2α,3β,4aα,5α,8aβ)-5-[(*tert*-Butyldimethylsilyl)oxy]octahydro-4a-methyl-1*H*,4*H*-naphthaleno[1,2-*b*]oxirane (13). To a stirred solution of 4.33 g (11.5 mmol) of **12** in 120 mL of dry *t*-BuOH was added 1.74 g (15.5 mmol) of *t*-BuOK. The reaction mixture was heated at reflux for 2 h, allowed to come to rt, and then poured into 150 mL of water. The aqueous solution was extracted with three 100-mL portions of petroleum ether (bp 40–60 °C). The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (30:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 2.91 g (85%) of **13**: ^{1}H NMR (90 MHz) δ −0.13 (s, 6 H), 0.79 (s, 12 H), 0.88–1.73 (m, 10 H), 2.20 (m, 1 H), 2.91–3.09 (m, 3 H); MS *m/z* (relative intensity) 296 (M^+, 1), 281 (1), 239 (46), 221 (67), 147 (67), 119 (20), 105 (47), 93 (15), 91 (29), 81 (15), 79 (20), 75 (100); calcd for $C_{17}H_{32}O_2Si$ (M^+) *m/z* 296.2171, found *m/z* 2 96.2169.

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(4aα,8β,8aβ)-8-[(*tert*-Butyldimethylsilyl)oxy]octahydro-8a-methyl-2(1*H*)-naphthalenone (14). To a solution of 2.73 g (9.22 mmol) of **13** in 150 mL of dry THF was added 0.85 g (22 mmol) of LAH at rt. The reaction mixture was refluxed for 90 min and then, after being cooled to 0 °C, quenched with 50 mL of saturated aqueous Na_2SO_4. The reaction mixture was extracted with three 100-mL portions of EtOAc. The organic layers were combined and dried. Evaporation yielded 2.66 g (97%) of a pale yellow oil [^{1}H NMR (90 MHz) δ 0.10 (s, 6 H), 0.79 (s, 9 H), 0.81–2.33 (m, 14 H), 0.92 (s, 3 H), 3.29 (m, 1 H), 4.07 (br s, 1 H)]. This oil was dissolved in 125 mL of CH_2Cl_2, and then 5.15 g (13.7 mmol) of PDC was added. The reaction mixture was allowed to stir at rt for 20 h and filtered through Celite, and the filter cake was washed with two 100-mL portions of CH_2Cl_2. The solvent was evaporated, and the resulting residue was flash chromatographed (20:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 2.39 g (88%) of **14** as a white solid: mp 117–119 °C (from diisopropyl ether); ^{1}H NMR (200 MHz) δ −0.02 (s, 3 H), 0.00 (s, 3 H), 0.71 (s, 3 H), 0.84 (s, 9 H), 1.15–2.09 (m, 11 H), 2.29 (m, 1 H), 2.47 (m, 1 H), 3.22 (dd, J = 4.7, 9.2 Hz, 1 H); ^{13}C NMR δ −5.07 (q), −4.26 (q), 10.37 (q), 17.77 (s), 23.68 (t), 25.60 (3q), 27.01 (t), 28.40 (t), 30.17 (t), 41.22 (t), 42.46 (d), 43.21 (s), 53.00 (t), 78.58 (d), 211.73 (s); MS m/z (relative intensity) 296 (M^+, 0.4), 281 (4), 239 (100), 181 (62), 157 (10), 147 (30), 115 (11), 107 (11), 75 (40), 73 (14); calcd for $C_{17}H_{32}O_2Si$ (M^+) m/z 296.2171, found m/z 296.2166. Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.88; H, 10.88. Found: C, 68.79; H, 10.99.

(1α,4aβ,8aα)-1-[(*tert*-Butyldimethylsilyl)oxy]decahydro-8a-methyl-7-methylenenaphthalene (15). To a stirred solution of 125 mL of 0.103 M (dimethylsulfinyl)sodium in dry DMSO was added 5.0 g (14 mmol) of Ph_3PCH_2Br in small portions at rt. The reaction mixture was stirred at 40 °C for 1 h, after which time a solution of 3.00 g (10.1 mmol) of **14** in 100 mL of dry DMSO was added dropwise. Stirring was continued at rt for 16 h. The reaction mixture was diluted with 200 mL of water and extracted with eight 35-mL portions of petroleum ether (bp 40–60 °C). The combined organic layers were washed with 100 mL of brine and dried. After evaporation, the remaining residue was flash chromatographed (petroleum ether (bp 40–60 °C)) to give 2.76 g (93%) of **15** as a colorless oil: ^{1}H NMR (90 MHz) δ 0.02 (s, 6 H), 0.72 (s, 3 H), 0.91 (s, 9 H), 1.02–2.49 (m, 13 H), 3.23 (dd, J = 5.5, 9.2 Hz, 1 H), 4.56 (br s, 1 H), 4.65 (br s, 1 H); MS m/z (relative intensity) 294 (M^+, 0.8), 279 (1), 237 (40), 219 (6), 161 (30), 119 (8), 105 (7), 91 (7), 75 (100), 41 (14); calcd for $C_{14}H_{25}OSi$ (M^+ − 57) m/z 237.1675, found m/z 237.1677.

(2α,4aβ,8α,8aα)-Decahydro-2,8a-dimethyl-2,8-naphthalenediol (16a). The TBDMS ether **14** (2.61 g, 8.81 mmol) was treated with HF as described for the desilylation of **8**. Workup afforded 1.59 g (99%) of a crude keto alcohol [^{1}H NMR (90 MHz) δ 0.75 (s, 3 H), 0.81–1.89 (m, 8 H), 1.90–2.59 (m, 6 H), 3.37 (m, 1 H)]. A solution of this crude product in 100 mL of dry ether was added dropwise to 10 mL of 2.6 M MeMgI in ether. The reaction mixture was stirred at rt for 30 min, after which time the excess MeMgI was destroyed cautiously with saturated aqueous NH_4Cl. After dilution with 100 mL of water, the two-phase mixture was separated and the aqueous layer was extracted with three 100-mL portions of EtOAc. The combined organic layers were washed with 100 mL of brine, dried, and evaporated. The remaining residue was crystallized from n-hexane to yield 1.31 g (76%) of **16a** as white crystals: mp 158–160 °C; ^{1}H NMR (200 MHz) δ 0.97–2.20 (m, 15 H), 1.02 (s, 3 H), 1.18 (s, 3 H), 3.14 (dd, J = 4.6, 10.6 Hz, 1 H); ^{13}C NMR δ 11.56 (q), 24.09 (t), 24.30 (t), 27.11 (t), 29.71 (t), 33.28 (q), 39.49 (s), 39.52 (t), 44.01 (d), 49.20 (t), 71.10 (s), 80.12 (d); MS m/z (relative intensity) 198 (M^+, 11), 183 (96), 180 (100), 162 (37), 147 (54), 122 (57), 107 (88), 95 (41), 85 (46), 81 (52); calcd for $C_{12}H_{22}O_2$ (M^+) m/z 198.1620, found m/z 198.1624. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.67; H, 11.18. Found: C, 72.40; H, 11.38.

(2α,4aα,8β,8aβ)-Decahydro-2,8a-dimethyl-2,8-naphthalenediol (16b). The silyl ether **15** (2.00 g, 6.80 mmol) was treated with HF for 2.5 h as described above. Workup yielded 1.19 g (97%) of an alcohol [^{1}H NMR (90 MHz) δ 0.81 (s, 3 H), 1.01–2.56 (m, 14 H), 3.39 (m, 1 H), 4.65 (br s, 1 H), 4.71 (br s, 1 H)]. To a solution of this crude product in 150 mL of CH_2Cl_2 were added 150 mL of acetone, 50 mL of water, 0.075 g of 18-crown-6, and 8.5 g of $NaHCO_3$. The mixture was stirred vigorously, and then 50 mL of 0.29 M Oxone (29 mmol of $KHSO_5$) in water was added dropwise at 0 °C. Stirring was continued for an additional 30 min, after which time 100 mL of 10% aqueous $Na_2S_2O_3$ and 150 mL of saturated aqueous $NaHCO_3$ were added. The two-phase mixture was separated, and the aqueous layer was extracted with seven 25-mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (10:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 0.90 g (67%) of a single epoxide [^{1}H NMR (200 MHz) δ 0.85 (s, 3 H), 1.01–1.85 (m, 14 H), 2.52–2.72 (m, 2 H), 3.28 (m, 1 H)]. To a solution of this epoxide in 300 mL of dry THF was added 0.75 g (19 mmol) of LAH at 0 °C. The reaction mixture was refluxed for 1 h and then, after cooling to 0 °C, carefully quenched with a small amount of saturated aqueous Na_2SO_4. The reaction mixture was dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting product was crystallized from n-hexane to afford 0.90 g (99%) of diol **16b** as white crystals: mp 141–143 °C; ^{1}H NMR (200 MHz) δ 0.74 (s, 3 H), 0.76–1.74 (m, 13 H), 1.34 (s, 3 H), 1.91–2.11 (m, 2 H), 3.18 (dd, J = 4.3, 10.6 Hz, 1 H); ^{13}C NMR δ 11.92 (q), 24.03 (t), 26.41 (t), 26.70 (t), 29.14 (q), 29.41 (t), 39.37 (s), 41.11 (t), 44.03 (d), 52.17 (t), 70.85 (s), 80.14 (d); MS m/z (relative intensity) 198 (M^+, 1.6), 183 (3), 180 (7), 147 (11), 124 (20), 107 (22), 81 (24), 67 (28), 55 (13), 43 (100); calcd for $C_{12}H_{20}O$ (M^+ − 18) m/z 180.1514, found m/z 180.1517. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.67; H, 11.18. Found: C, 72.45; 11.48.

(4′aα)-Tetrahydro-4′a,7′,7′-trimethylspiro[1,3-dithiolane-2,2′(3′*H*)-naphthalen]-5′(6′*H*)-one (18). To a stirred solution of 20.0 g (97.1 mmol) of **17** and 9.20 g of p-TsOH in 50 mL AcOH was added 10.5 mL (125 mmol) of 1,2-ethanedithiol. The mixture was stirred at rt for 18 h, poured into 100 mL of water, and then extracted with five 50-mL portions of CH_2Cl_2. The combined organic layers were washed with two 150-mL portions of 4 M aqueous NaOH and one 50-mL portion of water and then dried. Evaporation and crystallization from diisopropyl ether/EtOAc yielded 25.00 g (91%) of **18**: mp 150–153 °C; ^{1}H NMR (200 MHz) δ 0.72 (s, 3 H), 1.03 (s, 3 H), 1.23 (s, 3 H), 1.63–2.30 (m, 6 H), 2.45–2.60 (m, 2 H), 3.11–3.40 (m, 4 H), 5.59 (br s, 1 H); ^{13}C NMR δ 24.00 (q), 25.37 (q), 30.35 (t), 30.72 (q), 34.11 (s), 37.26 (t), 39.43 (t), 40.02 (t), 44.74 (t), 47.95 (s), 51.15 (t), 64.66 (s), 129.31 (d), 139.22 (s), 213.10 (s); MS m/z (relative intensity) 282 (M^+, 62), 267 (65), 264 (9), 254 (8), 239 (16), 221 (44), 189 (19), 118 (100), 105 (34), 91 (24), 83 (20), 41 (29); calcd for $C_{15}H_{22}OS_2$ (M^+) m/z 282.1112, found m/z 282.1112.

Dissolving Metal Reduction of 18. To dry, distilled NH_3 (250 mL) was added dropwise a solution of 25.6 g (90.0 mmol) of **18** in 100 mL of dry ether at −78 °C. To the vigorously stirred solution were added small pieces of sodium metal until the blue color persisted. The cooling bath was removed, and the blue solution was kept at reflux for 1 h. Saturated aqueous Na_2SO_4 (5 mL) was added cautiously to the reaction flask, and the ammonia was allowed to evaporate overnight. Water (300 mL) was added to the residue, and the aqueous phase was extracted with three 150-mL portions of EtOAc. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (20:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 1.39 g (8%) of α-hydroxy olefin **19a** and 14.02 g (80%) of its β-isomer **19b**.

(1α,8aβ)-1,2,3,4,6,7,8,8a-Octahydro-3,3,8a-trimethyl-1-naphthalenol (19a): ^{1}H NMR (200 MHz) δ 0.91 (s, 3 H), 0.97 (s, 3 H), 1.05 (s, 3 H), 1.23–2.24 (m, 11 H), 3.52 (m, 1 H), 5.51 (m, 1 H); ^{13}C NMR δ 19.36 (t), 25.02 (q), 25.44 (t), 28.16 (q), 31.65 (s), 32.11 (t), 33.11 (q), 39.06 (s), 41.62 (t), 45.04 (t), 76.91 (d), 124.67 (d), 138.04 (s); MS m/z (relative intensity) 194 (M^+, 23), 179 (14), 176 (65), 161 (57), 147 (48), 133 (45), 119 (24), 109 (92), 91 (64), 85 (72), 67 (71), 55 (45), 41 (100); calcd for $C_{13}H_{22}O$ (M^+) m/z 194.1670, found m/z 194.1669.

(1α,8aα)-1,2,3,4,6,7,8,8a-Octahydro-3,3,8a-trimethyl-1-naphthalenol (19b): ^{1}H NMR (200 MHz) δ 0.73–2.15 (m, 11 H), 0.80 (s, 3 H), 0.90 (s, 3 H), 0.93 (s, 3 H), 3.46 (dd, J = 8.1, 8.5 Hz, 1 H), 5.43 (m, 1 H); ^{13}C NMR δ 16.81 (q), 18.69 (t), 25.28 (q), 25.59 (t), 31.98 (q), 31.98 (s), 35.81 (t), 39.43 (s), 43.61 (t), 44.93 (t), 75.70 (d), 123.48 (d), 139.85 (s); MS m/z (relative intensity) 194 (M^+, 17), 179 (8), 176 (68), 161 (71), 147 (78), 133 (73), 120 (25), 109 (73), 91 (57), 85 (58), 67 (65), 41 (100); calcd for $C_{13}H_{22}O$ (M^+) m/z 194.1670, found m/z 194.1664.

(1α,8aα)-1-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,6,7,8,8a-octahydro-3,3,8a-trimethylnaphthalene (20). To a solution of 5.72 g (29.5 mmol) of **19b** in 200 mL of DMF were added 6.60 g (95.0 mmol) of imidazole and 7.01 g (46.6 mmol) of TBDMSCl. The reaction mixture was stirred at rt for 48 h and then poured into 250 mL of water. The two-phase mixture was separated, and the aqueous layer was extracted with 10 25-mL portions of CH_2Cl_2. The combined organic layers were washed with 100 mL of brine, dried, and evaporated. The resulting product was flash chromatographed (petroleum ether (bp 40–60 °C)) to give 8.12 g (89%) of **20** as a clear oil: ^{1}H NMR (200 MHz) δ 0.02 (s, 6 H), 0.81 (s, 3 H), 0.90 (s, 9 H), 0.93 (s, 3 H), 0.96 (s, 3 H), 1.20–1.81 (m, 7 H), 1.90–2.03 (m, 2 H), 2.13 (m, 1 H), 3.44 (dd, J = 4.8, 11.5 Hz, 1 H), 5.34 (m, 1 H); ^{13}C NMR δ −4.98 (q), −4.19 (q) 17.20 (q), 17.83 (s), 18.86 (t), 25.33 (q), 25.66 (3q), 25.66 (t), 31.69 (s), 32 .12 (q), 36.46 (t), 39.94 (s), 44.41 (t), 45.04 (t), 75.90 (d), 123.08 (d), 140.45 (s); MS m/z (relative intensity) 308 (M^+, 1.6), 293 (4), 251 (92), 199 (100), 177 (42), 176 (54), 151 (8), 133 (10), 75 (51); calcd for $C_{19}H_{36}OSi$ (M^+) m/z 308.2535, found m/z 308.2535.

(4aα,5α,8aβ)-5-[(*tert*-Butyldimethylsilyl)oxy]octahydro-4a,7,7-trimethyl-1(2*H*)-naphthalenone (21). To a stirred solution of 7.41 g (24.1 mmol) of **20** in 150 mL of dry THF, cooled to 0 °C, was added dropwise 35 mL (35 mmol) of BH_3·THF (1.0 M in THF). The reaction mixture was stirred at rt for 6 h and then heated at reflux for 1 h. The reaction mixture was cooled to 0 °C, and another 20 mL (20 mmol) of BH_3·THF (1.0 M in THF) was added dropwise. Stirring was continued at rt for an additional 30 min. The reaction mixture was cooled again to 0 °C, and 10 mL of water was added dropwise, immediately followed by addition of 45 mL of 4 M NaOH and 50 mL of 35% H_2O_2. The mixture was stirred at rt for 16 h and concentrated under reduced pressure. The remaining aqueous phase was extracted with six 100-mL portions of petroleum ether (bp 40–60 °C). The combined organic layers were dried and evaporated. The resulting clear oil was dissolved in 200 mL of CH_2Cl_2, and 10.0 g (25.1 mmol) of PDC was added. The reaction mixture was allowed to stir at rt for 20 h and filtered through Celite, and the filter cake was washed with two 100-mL portions of CH_2Cl_2. The solvent was evaporated under reduced pressure, and the resulting residue was dissolved in 200 mL of dry MeOH. After addition of 30 mL of 1 M NaOMe in dry MeOH, the solution was stirred for 1 h and then neutralized with 4 N HCl. MeOH was distilled off under reduced pressure, and the aqueous phase was extracted with seven 50-mL portions of EtOAc. The combined organic layers were dried and evaporated. Recrystallization from *n*-hexane gave 6.5 g (83%) of **21**: mp 80–81 °C; ^{1}H NMR (200 MHz) δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.67 (s, 3 H), 0.84 (s, 9 H), 0.87 (s, 3 H), 0.93 (s, 3 H), 1.15–1.50 (m, 5 H), 1.70–2.07 (m, 3 H), 2.20–2.38 (m, 3 H), 3.58 (dd, J = 5.6, 10.4 Hz, 1 H); ^{13}C NMR δ −5.01 (q), −4.22 (q), 10.48 (q), 17.77 (s), 22.39 (t), 25.57 (3q), 25.86 (q) 30.16 (s), 32.63 (t), 32.90 (q), 36.56 (t), 41.04 (t), 43.09 (t), 44.87 (s), 52.44 (d), 75.57 (d), 212.46 (s); MS m/z (relative intensity) 324 (M^+, 1.2), 267 (68), 225 (6), 175 (20), 133 (15), 119 (26), 105 (24), 75 (100), 41 (38); calcd for $C_{19}H_{36}O_2Si$ (M^+) m/z 324.2484, found m/z 324.2481. Anal. Calcd for $C_{19}H_{36}O_2Si$: C, 70.33; H, 11.18. Found: C, 70.54; H, 11.18.

(1α,4aα,5α,8aβ)-5-[(*tert*-Butyldimethylsilyl)oxy]decahydro-1,4a,7,7-tetramethyl-1-naphthalenol (22). The ketone **21** (3.11 g, 9.60 mmol) was treated with 2.6 M MeMgI in ether for 2 h as described for the synthesis of **16a**. After workup, the crude product was purified by flash chromatography (10:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 2.75 g (84%) of **22** as a clear oil: ^{1}H NMR (200 MHz) δ −0.01 (s, 6 H), 0.86 (s, 9 H), 0.91 (s, 3 H), 0.92 (s, 3 H), 0.94 (s, 3 H), 1.06–1.41 (m, 10 H), 1.11 (s, 3 H), 1.60–1.90 (m, 2 H), 3.25 (dd, J = 4.5, 11 Hz, 1 H); ^{13}C NMR δ −4.96 (q), −4.27 (q), 10.97 (q), 17.57 (t), 17.82 (s), 25.65 (3q), 26.69 (q), 30.40 (q), 30.41 (s), 33.24 (q), 33.24 (t), 37.56 (t), 39.55 (s), 40.95 (t), 43.33 (t), 46.18 (d), 71.77 (s), 77.01 (d); MS m/z (relative intensity) 340 (M^+, 0.5), 283 (1), 265 (100), 247 (2), 189 (10), 169 (20), 107 (10), 95 (13), 75 (72), 55 (14), 43 (37); calcd for $C_{20}H_{40}O_2Si$ (M^+) m/z 340.2797, found m/z 340.2797.

(1α,4aβ,5β,8aα)-5-[(*tert*-Butyldimethylsilyl)oxy]octahydro-4a,7,7-trimethylspiro[naphthalene-1(2*H*),2′-oxirane] (23). The procedure described for the synthesis of **15** was employed by using 75 mL of 0.33 M (dimethylsulfinyl)sodium in dry DMSO, 10.8 g (30 mmol) of Ph_3PCH_3Br, and 2.50 g (7.71 mmol) of **21** in 50 mL of dry ether.[32] When the dropwise addition of the etheral solution was complete, ether was distilled off at 50 °C. After the solution was stirred at rt for an additional 1 h, the usual workup afforded 2.26 g of a clear oil [^{1}H NMR (200 MHz) δ 0.02 (s, 6 H), 0.62 (s, 3 H), 0.86 (s, 9 H), 0.93 (s, 3 H), 0.94 (s, 3 H), 1.01–1.98 (m, 10 H), 2.28 (m, 1 H), 3.47 (dd, J = 5.0, 11.1 Hz, 1 H), 4.42 (br s, 1 H), 4.70 (br s, 1 H)]. This crude product was treated with Oxone for 21 h as described for the synthesis of **16b**. Workup and flash chromatography (25:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 2.276 g (87%) of **23** as a clear oil: ^{1}H NMR (200 MHz) δ 0.00 (s, 6 H), 0.75 (s, 3 H), 0.83–1.94 (m, 11 H), 0.84 (s, 9 H), 0.88 (s, 3 H), 0.90 (s, 3 H), 2.48 (d, J = 4.7 Hz, 1 H), 2.69 (br d, J = 4.7 Hz, 1 H), 3.41 (dd, J = 5.4, 10.5 Hz, 1 H); ^{13}C NMR δ −4.96 (q), −4.24 (q), 10.16 (q), 17.82 (s), 20.72 (t), 25.63 (3q), 25.84 (q), 30.48 (s), 31.82 (t), 33.19 (q), 35.30 (t), 37.30 (t), 41.69 (s), 41.69 (d), 43.61 (t), 50.60 (t), 58.76 (s), 76.37 (d); MS m/z (relative intensity) 338 (M^+, 0.1), 323 (3), 281 (100), 263 (4), 251 (4), 199 (11), 189 (17), 132 (17), 76 (56); calcd for $C_{20}H_{38}O_2Si$ (M^+) m/z 338.2641, found m/z 338.2641.

(1α,4aα,5α,8aβ)-Decahydro-1,4a,7,7-tetramethyl-1,5-naphthalenediol (24a). To a solution of 2.50 g (7.35 mmol) of **22** in 75 mL of acetonitrile were added five drops of 40% aqueous HF. The reaction mixture was stirred at rt for 2 h. Then two drops of 40% aqueous HF were added every 2 h over a period of 8 h. After this time, the reaction mixture was poured into 150 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with five 25-mL portions of CH_2Cl_2, after which the combined organic layers were dried and evaporated. The crude product was flash chromatographed (5:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 1.27 g (76%) of **24a**: mp 133–135 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR (200 MHz) δ 0.93 (s, 3 H), 0.95 (s, 3 H), 0.97 (s, 3 H), 0.98–1.92 (m, 13 H), 1.13 (s, 3 H), 3.29 (dd, J = 6.7, 9.7 Hz, 1 H); ^{13}C NMR δ 10.65 (q), 17.40 (t), 26.70 (q), 30.65 (q), 30.65 (s), 33.13 (q), 33.30 (t), 36.94 (t), 39.15 (s), 40.88 (t), 42.76 (t), 45.96 (d), 71.62 (s), 76.77 (d); MS m/z (relative intensity) 226 (M^+, 1.3), 211 (8), 193 (6), 190 (12), 175 (10), 150 (30), 135 (20), 95 (21), 71 (28), 43 (100); calcd for $C_{14}H_{26}O_2$ (M^+) m/z 226.1933, found m/z 226.1935. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.32; H, 11.72.

(1α,4aβ,5β,8aα)-Decahydro-1,4a,7,7-tetramethyl-1,5-naphthalenediol (24b). The epoxide **23** (2.01 g, 5.95 mmol) was treated with LAH for 2 h as described for the reduction of **13**. The excess LAH was destroyed by careful addition of a small amount of saturated aqueous Na_2SO_4 to the cooled reaction mixture. After drying and evaporation, flash chromatography (15:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 1.90 g of a clear oil. This oil was taken up in 150 mL of DMSO, and 7.5 mL of TBAF (1.1 M in THF) was added. The reaction mixture was stirred at 100 °C for 90 min and then poured into 100 mL of water. The aqueous mixture was extracted with eight 25-mL portions of EtOAc. The combined organic layers were dried and evaporated. Flash chromatography (10:1–5:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 1.09 (82%) of **24b** as a white solid: mp 161–162 °C (from petroleum ether (bp 40–60 °C)/EtOAc); ^{1}H NMR (200 MHz) δ 0.78 (s, 3 H), 0.95 (s, 3 H), 0.96 (s, 3 H), 1.01–1.81 (m, 13 H), 1.11 (s, 3 H), 3.34 (m, 1 H); ^{13}C NMR δ 10.56 (q), 19.59 (t), 22.89 (q), 26.38 (q), 30.62 (s), 33.20 (q), 33.21 (t), 36.65 (t), 40.06 (s), 42.86 (t), 42.94 (t), 48.76 (d), 71.63 (s) , 77.17 (d); MS m/z (relative intensity) 226 (M^+, 3), 208 (8), 193 (22), 190 (17), 175 (14), 150 (100), 135 (35), 95 (28), 70 (50), 43 (47); calcd for $C_{14}H_{26}O_2$ (M^+) m/z 226.1933, found m/z 226.1933. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.52; H, 11.97.

General Procedure for the Preparation of Mesylates 1–6. Method A. To a solution (0.1–0.15 M) of the corresponding diols **9a** and **9b** in dry pyridine was added MsCl (ca. 1.5 equiv). The reaction was stirred at rt and followed by TLC.[33] At completion, the mixture was concentrated at reduced pressure. The remaining residue was submitted directly to flash chromatography (1:1 petroleum ether (bp 40–60 °C)/EtOAc). By using this procedure the mesylates **1** and **2** were prepared.

(32) Compound **21** is insoluble in DMSO.

(33) If the reaction appears to be proceeding too slowly (>20 h), heating at 40 °C may be helpful.

(4'aα,5'α,8'α,8'aα)-Octahydro-4'a,8'-dimethylspiro[1,3-dioxolane-2,2'(1'H)-naphthalene]-5',8'-diol 5'-(methanesulfonate) (1): yield 96%; mp 155 °C (from diisopropyl ether) dec; ^{1}H NMR (200 MHz) δ 1.13 (s, 3 H), 1.14 (s, 3 H), 1.33–2.01 (m, 11 H), 2.17 (m, 1 H), 2.99 (s, 3 H), 3.85–4.00 (m, 4 H), 4.35 (dd, J = 4.3, 11.9 Hz, 1 H); ^{13}C NMR δ 12.14 (q), 24.69 (t), 29.35 (q), 30.04 (t), 30.30 (t), 36.25 (t), 38.04 (s), 38.44 (q), 38.90 (t), 47.66 (d), 63.85 (t), 64.14 (t), 70.35 (s), 89.77 (d), 108.95 (s); MS m/z (relative intensity) 319 (M^+ – 15, 1.5), 316 (2), 238 (44), 221 (17), 209 (21), 181 (15), 167 (25), 99 (100), 86 (70), 71 (48); calcd for $C_{14}H_{23}O_6S$ (M^+ – 15) m/z 319.1215, found m/z 319.1218. Anal. Calcd for $C_{15}H_{26}O_6S$: C, 53.87; H, 7.84. Found: C, 53.96; H, 7.78.

(4'aα,5'α,8'β,8'aβ)-Octahydro-4'a,8'-dimethylspiro[1,3-dioxolane-2,2'(1'H)-naphthalene]-5',8'-diol 5'-(methanesulfonate) (2): yield 77%; mp 144–145 °C (from diisopropyl ether); ^{1}H NMR (200 MHz) δ 0.97 (s, 3 H), 1.09 (s, 3 H), 1.38–2.10 (m, 12 H), 2.97 (s, 3 H), 3.83–4.08 (m, 4 H), 4.35 (dd, J = 4.7, 11.2 Hz, 1 H); ^{13}C NMR δ 12.63 (q), 21.99 (q), 26.50 (t), 30.04 (t), 30.26 (t), 37.58 (t), 38.29 (s), 38.37 (q), 40.44 (t), 50.05 (d), 63.95 (t), 64.13 (t), 70.21 (s), 89.04 (d), 108.64 (s); MS m/z (relative intensity) 334 (M^+, < 0.1), 319 (2), 316 (1), 238 (44), 221 (20), 209 (25), 181 (11), 167 (23), 99 (100), 86 (40); calcd for $C_{15}H_{26}O_6S$ (M^+) m/z 334.1450, found m/z 334.1452. Anal. Calcd for $C_{15}H_{26}O_6S$: C, 53.87; H, 7.84. Found: C, 53.71; H, 7.87.

Method B. The corresponding diols **16a**, **16b**, **24a**, and **24b** were treated with MsCl as above, except that, after concentration, the residues were taken up in EtOAc and washed successively with two portions of 10% aqueous H_2SO_4, two portions of saturated aqueous $NaHCO_3$, and one portion of brine. After drying and evaporation, further purification may be accomplished by flash chromatography or by recrystallization. By using this procedure the mesylates **3–6** were prepared.

(2α,4aβ,8α,8aα)-Decahydro-2,8a-dimethyl-2,8-naphthalenediol 8-(methanesulfonate) (3): yield 97%; mp 105–107 °C (from diisopropyl ether); ^{1}H NMR (200 MHz) δ 0.98–2.00 (m, 14 H), 1.10 (s, 3 H), 1.19 (s, 3 H), 2.97 (s, 3 H), 4.27 (dd, J = 5.5, 10.6 Hz, 1 H); ^{13}C NMR δ 11.81 (q), 23.80 (t), 24.15 (t), 26.53 (t), 27.58 (t), 33.27 (q), 38.71 (q), 39.32 (s), 39.32 (t), 44.38 (d), 48.72 (t), 70.21 (s), 90.74 (d); MS m/z (relative intensity) 261 (M^+ – 15, 13), 180 (52), 165 (100), 147 (35), 123 (87), 110 (57), 96 (33), 81 (30), 71 (24), 43 (52); calcd for $C_{12}H_{21}O_4S$ (M^+ – 15) m/z 261.1161, found m/z 261.1171. Anal. Calcd for $C_{13}H_{24}O_4S$: C, 56.49; H, 8.75. Found: C, 56.56; H, 8.91.

(2α,4aα,8β,8aβ)-Decahydro-2,8a-dimethyl-2,8-naphthalenediol 8-(methanesulfonate) (4): yield 98%; mp 90–92 °C (from pentane/diisopropyl ether); ^{1}H NMR (200 MHz) δ 0.86 (s, 3 H), 0.93–1.50 (m, 9 H), 1.29 (s, 3 H), 1.65–1.98 (m, 5 H), 2.98 (s, 3 H), 4.29 (dd, J = 5.1, 11.0 Hz, 1 H); ^{13}C NMR δ 12.61 (q), 23.73 (t), 26.19 (2t), 27.66 (t), 29.09 (q), 38.54 (q), 39.01 (s), 40.88 (t), 44.40 (d), 52.05 (t), 70.39 (s), 91.00 (d); MS m/z (relative intensity) 261 (M^+ – 15, 5), 180 (61), 165 (57), 147 (50), 123 (100), 110 (71), 96 (39), 81 (43), 43 (57); calcd for $C_{12}H_{21}O_4S$ (M^+ – 15) m/z 261.1161, found m/z 261.1163. Anal. Calcd for $C_{13}H_{24}O_4S$: C, 56.49; H, 8.75. Found: C, 56.42; H, 8.82.

(1α,4aα,5α,8aβ)-Decahydro-1,4a,7,7-tetramethyl-1,5-naphthalenediol 5-(methanesulfonate) (5): yield 92%; mp 108–110 °C (from diisopropyl ether); ^{1}H NMR (200 MHz) δ 0.97 (s, 3 H), 1.00 (s, 3 H), 1.04 (s, 3 H), 1.08–1.90 (m, 12 H), 1.14 (s, 3 H), 2.96 (s, 3 H), 4.38 (dd, J = 6.2, 10.7 Hz, 1 H); ^{13}C NMR δ 11.66 (q), 17.14 (t), 26.33 (q), 30.63 (q), 31.12 (s), 32.81 (q), 33.04 (t), 37.11 (t), 38.58 (q), 38.88 (s), 40.74 (2t), 46.05 (d), 71.45 (s), 88.46 (d); MS m/z (relative intensity) 289 (M^+ – 15, 7), 208 (14), 190 (21), 175 (27), 150 (100), 135 (33), 96 (39), 82 (27), 43 (45); calcd for $C_{14}H_{25}O_4S$ (M^+ – 15) m/z 289.1473, found m/z 289.1474. Anal. Calcd for $C_{15}H_{28}O_4S$: C, 59.17; H, 9.27. Found: C, 59.04; H, 9.31.

(1α,4aβ,5β,8aα)-Decahydro-1,4a,7,7-tetramethyl-1,5-naphthalenediol 5-(methanesulfonate) (6): yield 94%; mp 102 °C (from pentane); ^{1}H NMR (200 MHz) δ 0.86 (s, 3 H), 1.00 (s, 6 H), 1.03–1.84 (m, 12 H), 1.12 (s, 3 H), 2.96 (s, 3 H), 4.42 (dd, J = 7.1, 9.7 Hz, 1 H); ^{13}C NMR δ 11.55 (q), 19.30 (t), 22.85 (q), 25.92 (q), 31.23 (s), 32.86 (q), 32.86 (t), 36.75 (t), 38.61 (q), 39.67 (s), 40.96 (t), 42.61 (t), 48.73 (d), 71.35 (s), 88.66 (d); MS m/z (relative intensity) 289 (M^+ – 15, 7), 208 (18), 190 (38), 175 (34), 150 (100), 135 (38), 124 (40), 96 (50), 82 (34), 43 (22); calcd for $C_{14}H_{25}O_4S$ (M^+ – 15) m/z 289.1473, found m/z 289.1473. Anal. Calcd for $C_{15}H_{28}O_4S$: C, 59.17; H, 9.27. Found: C, 58.90; H, 9.28.

Reactions of Mesylates 1–6 with Sodium *tert*-Amylate. General Procedure. All reactions were carried out on 0.50–1.00 mmol of mesylate at a concentration of ca. 0.1 M in dry benzene. These solutions were degassed and refluxed under an Ar atmosphere. Ca. 5 equiv of sodium *tert*-amylate (3.2 M in toluene) was added at once, via syringe, to the refluxing solution of the mesylate. Unless otherwise indicated, the reaction mixture was heated at reflux temperature for 10 min, quenched with precooled saturated aqueous NH_4Cl, and then quickly cooled to 0 °C. The mixture was vigorously stirred for 20 min, followed by extraction with ten 15-mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated to afford the crude reaction product. Product ratios, yields, and pure compounds were obtained by chromatographical techniques.

a. The general procedure was employed by using 0.167 g (0.50 mmol) of **1**. Workup and flash chromatography (15:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 0.091 g (76%) of **25** and 0.036 g (21%) of unreacted **5**. Small amounts (combined yield 2%) of **26** and **27** were also obtained.

b. The general procedure was employed by using 0.167 g (0.50 mmol) of **2**. Workup and flash chromatography (10:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.041 g (34%) of **(4'aα,5'β,8'β,8'aβ)-octahydro-5',8'-epoxy-4'a,8'-dimethylspiro[1,3-dioxolane-2,2'(1'H)-naphthalene] (28)**: ^{1}H NMR (200 MHz) δ 0.88 (m, 1 H) 0.92 (s, 3 H), 1.11–1.77 (m, 8 H), 1.30 (s, 3 H), 1.78–2.04 (m, 2 H), 3.90 (br s, 4 H), 4.09 (d, J = 4.0 Hz, 1 H); ^{13}C NMR δ 16.84 (q), 19.90 (q), 28.89 (t), 30.44 (t), 31.06 (t), 33.54 (t), 35.19 (t), 40.99 (s), 56.14 (d), 63.58 (t), 64.26 (t), 82.45 (d), 86.07 (s), 110.22 (s); MS m/z (relative intensity) 238 (M^+, 8), 195 (4), 176 (4), 99 (100), 86 (62); calcd for $C_{14}H_{22}O_3$ (M^+) m/z 238.1569, found m/z 238.1571. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.26; H, 9.28. Further elution afforded 0.110 g (66%) of unreacted **2**.

c. The general procedure was employed by using 0.138 g (0.50 mmol) of **3**. Workup and flash chromatography (10:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.045 g of a mixture of at least three compounds and 0.069 g (50%) of unreacted **3**. Careful column chromatography of the mixture (0.045 g) on silica gel (70–230 mesh) (1:0 to 50:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded, in order of elution, 0.008 g of a "dimeric" oil[34] [MS calcd for $C_{24}H_{38}O$ (M^+) m/z 342.3035, found m/z 342.3061], 0.030 g (33%) of **29** as a clear oil, and 0.009 g (10%) of an inseparable mixture of several compounds with probably **30** as the main component. The spectroscopic data of **29** and **30** are shown below.

4-[(1'α,2'α)-2'-(1-methylethenyl)cyclopent-1'-yl]butan-2-one (29): ^{1}H NMR (200 MHz) δ 1.01–1.91 (m, 9 H), 1.71 (br s, 3 H), 2.09 (s, 3 H), 2.31–2.46 (m, 3 H), 4.65 (br s, 1 H), 4.78 (br s, 1 H); ^{13}C NMR δ 22.32 (t), 23.17 (q), 23.48 (t), 27.15 (t), 29.64 (q), 29.86 (t), 40.39 (d), 42.40 (t), 50.40 (d), 110.34 (t), 145.84 (s), 209.18 (s); MS m/z (relative intensity) 180 (M^+, 8), 165 (2), 162 (3), 148 (10), 137 (17), 122 (100), 108 (25), 96 (24), 83 (24), 69 (29); calcd for $C_{12}H_{20}O$ (M^+) m/z 180.1514, found m/z 180.1514.

(6α,8aβ)-1,2,3,5,6,7,8,8a-Octahydro-4,6-dimethyl-6-azulenol (30): ^{1}H NMR (main peaks, 200 MHz) δ 1.21 (s, 3 H) 1.54 (br s, 3 H); MS m/z (relative intensity) 180 (M^+, 16), 162 (6), 122 (100).

d. The general procedure was employed by using 0.276 g (1.00 mmol) of **4**. Workup and flash chromatography (5:1 petroleum ether (bp 40–60 °C)/EtOAc) gave, in order of elution, 0.014 g of the above-mentioned "dimeric" oil, 0.057 g (32%) of **29**, and 0.014 g (8%) of **(6α,8aα)-1,2,3,5,6,7,8,8a-octahydro-4,6-dimethyl-6-azulenol (31)**: mp 126–127 °C (from diisopropyl ether); ^{1}H NMR (200 MHz) δ 1.16 (s, 3 H), 1.16–2.47 (m, 13 H), 1.62 (br s, 3H), 2.57 (br d, J = 13.4 Hz, 1 H); ^{13}C NMR δ 23.25 (q), 24.64 (q), 25.05 (t), 30.91 (t), 31.78 (t), 35.61 (t), 42.72 (d), 45.76 (t), 49.28 (t), 70.71 (s), 123.14 (s), 142.79 (s); MS m/z (relative intensity) 180 (M^+, 11), 162 (71), 147 (64), 135 (79), 123 (100), 110 (70), 94 (15), 80 (17), 68 (14); calcd for $C_{12}H_{20}O$ (M^+) m/z 180.1514, found m/z 180.1512. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.92; H, 11.20. Further elution provided 0.138 g (50%) of unreacted **4**.

(34) Although the structure of this compound could not be elucidated, its formation is probably the result of an aldol condensation reaction of **29** under the influence of the strong base used in this reaction. Also see ref 3 and references cited therein.

e. The general procedure was employed by using 0.152 g (0.50 mmol) of **5**. Workup and flash chromatography (50:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.020 g of a "dimeric" oil[35] [MS calcd for $C_{28}H_{46}O$ (M^+) m/z 398.3396, found m/z 398.3486] and 0.080 g (76%) of **5-[(1′α,2′α,6′α)-1′,4′,4′-trimethylbicyclo[3.1.0]-hexan-1′-yl]pentan-2-one (32)**: ^1H NMR (200 MHz) δ 0.86 (s, 3 H), 0.89 (s, 3 H), 0.97 (s, 3 H), 0.98–1.70 (m, 10 H), 2.09 (s, 3 H), 2.34 (t, J = 7.4 Hz, 2 H); ^{13}C NMR δ 11.22 (q), 20.80 (t), 26.31 (q), 26.65 (s), 29.52 (q), 30.36 (2d, J = 165 Hz), 30.62 (q), 39.00 (2t), 40.73 (t), 43.56 (t), 50.14 (s), 208.75 (s); MS m/z (relative intensity) 208 (M^+, 0.6), 193 (5), 190 (6), 175 (12), 150 (49), 135 (60), 107 (19), 95 (37), 81 (45), 43 (100); calcd for $C_{14}H_{24}O$ (M^+) m/z 208.1827, found m/z 208.1829.

f. The same as above, except that the reaction mixture was heated at reflux for 1 min. After workup and flash chromatography, **32** was isolated in 94% yield.

g. The general procedure was employed by using 0.152 g (0.50 mmol) of **6**. Workup and flash chromatography (100:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.027 g of the above-mentioned "dimeric" oil and 0.075 g (72%) of **32**.

h. The same as above, except that the reaction mixture was heated at reflux for 1 min. After workup and flash chromatography, **32** was obtained in 96% yield.

Reaction of Mesylate 5 with Lithium *tert*-Amylate. The general procedure was employed by using 0.152 g (0.50 mmol) of **5**, except that 1.4 mL of lithium *tert*-amylate[36] (1.8 M in toluene) was used instead of sodium *tert*-amylate and that the reaction was run until completion (2 h). Workup and flash chromatography (100:1 petroleum ether (bp 40–60 °C)/EtOAc) gave, in order of elution, 0.032 g of the above-mentioned "dimeric" oil, 0.030 g (28%) of **33**, and 0.035 g (34%) of **32**. The spectroscopic data of **33** are shown below.

(3aα,4β,8β,8aα)-Decahydro-2,2,4,8-tetramethyl-4,8-epoxyazulene (33): ^1H NMR (200 MHz) δ 0.89 (s, 3 H), 1.04 (s, 3 H), 1.11 (s, 6 H), 1.14–1.81 (m, 10 H), 2.39–2.56 (m, 2 H); ^{13}C NMR δ 17.50 (t), 22.77 (2q), 25.43 (q), 28.33 (q), 36.90 (2t), 40.56 (s), 42.22 (2t), 50.95 (2d), 79.83 (2s); MS m/z (relative intensity) 208 (M^+, 25), 190 (42), 175 (40), 147 (31), 123 (54), 109 (78), 91 (52), 85 (78), 41 (100); calcd for $C_{14}H_{24}O$ (M^+) m/z 208.1827, found m/z 208.1826.

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Abbreviations: DBBA, dibromobarbituric acid; MED, 2-butanone dioxolane; MNDO, modified neglect of diatomic overlap; Oxone, a mixture of $KHSO_5$, $KHSO_4$, and K_2SO_4 in the ratio of 2:1:1, respectively; TBAF, tetrabutylammonium fluoride.

Supplementary Material Available: ^1H NMR spectra for compounds **9b, 12, 13, 15, 18, 19a, 19b, 20, 22, 23, 29, 32,** and **33** (13 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.

(35) This "dimeric" oil is probably formed from **32**. See ref 31 for further remarks.

(36) Lithium *tert*-amylate was prepared by the procedure described in ref 3.