Substituent Effects on Through-Bond Orbital Interaction-Induced Heterolysis of Some Perhydronaphthalene-1,4-diol Monosulfonate Esters

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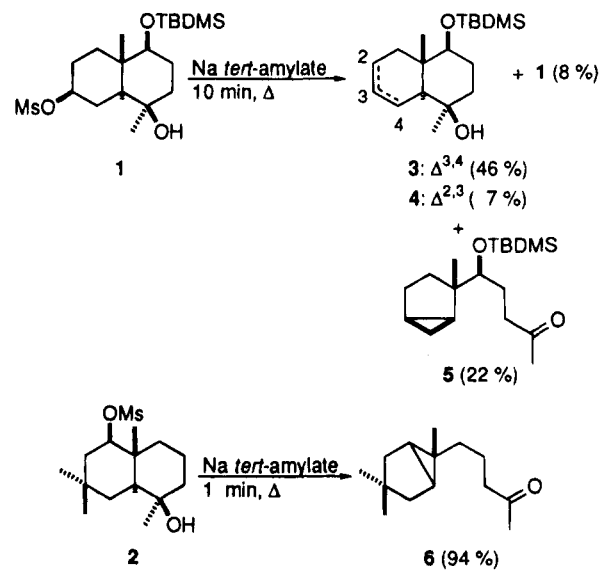
Substituent effects on the heterolysis of the perhydronaphthalene-1,4-diol monosulfonate esters **1**, **7**, and **8** induced by through-bond interactions (TBI) were studied. Evidence is found that, next to TBI, σ-participation is the most important stereoelectronic effect which determines the reactivity of these compounds under strongly basic conditions in refluxing benzene. Substituents at carbon atoms adjacent to the carbon atom bearing the sulfonate ester group increase the contribution of σ-participation which is expressed in a higher reactivity of these compounds. The product composition is primarily dependent on the degree of substitution at C(4). Homofragmentation and elimination are found when C(4) is unsubstituted as the reaction of mesylate **1** shows. Due to the repulsive 1,3-*peri* effect between the equatorial Me groups at C(4) and C(6) in the reaction of **7** and a combination of this 1,3-*peri* effect and the 4,4-dimethyl effect in that of **8**, the ideal W arrangement is distorted. Consequently, no homofragmentation is observed with these compounds, and other reaction pathways (elimination, 1,3-H and 1,2-Me shifts) are now favored.

Introduction

Through-bond orbital interactions (TBI) mediated via four σ-bonds are most likely responsible for the heterolysis of the sulfonate ester bond in reactions of cyclic 1,4-diol monosulfonate esters with a non-nucleophilic strong base in apolar solvents (benzene or toluene) at reflux temperature.[1] It has been demonstrated that the extent of TBI, but also the occurrence of through-space orbital interactions (TSI), critically depends on the geometry of the relaying σ-bonds between the electron donor (alcoholate anion) and the electron acceptor (sulfonate ester bond). A W arrangement of the σ-relay is the most favorable geometry for mediating TBI (trans rule) and, at the same time, a prerequisite for TSI to occur. Compounds possessing such a W arrangement exhibit homofragmentation as the characteristic reaction pathway. 1,4-Diol monosulfonate esters with a sickle-like arrangement react without participation of TSI, and consequently, no homofragmentation is observed in these cases. These findings are consistent with theoretical models concerning TBI and TSI.[2]

It is, however, questionable whether the geometry of the σ-relay is the only factor that will control the rate and product outcome of these reactions. From our previous work, it is already known that the orientation (axial or equatorial) of the hydroxyl group can determine the product composition to a high degree.[1c,d] In several situations, it was observed that the presence of an axial hydroxyl group results in a selective formation of olefinic products via intramolecular proton abstraction. If intramolecular deprotonation is unlikely on stereochemical grounds, other pathways (ether formation, homofragmentation) are preferred. Furthermore, comparison of the reactions of the mesylates **1** and **2**, both possessing a W arrangement of the σ-relay, shows that **1** reacts much slower and less selectively than **2** (Scheme 1).

Scheme 1



In compound **1**, the ring carbon atoms adjacent to the carbon atom bearing the sulfonate ester group are not substituted, whereas in **2**, one of these ring carbon atoms is fully substituted. The difference in reaction rate suggests that a higher degree of substitution of the σ-relay results in an increased reactivity of these compounds. Additional support for this supposition comes from the observation that 2-*exo*-1-methylnorbornyl tosylate solvolyzes 50 times faster than the corresponding compound without a C(1) Me group.[3] It is accepted that orbital interactions are involved in these solvolysis reactions.[4,5]

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

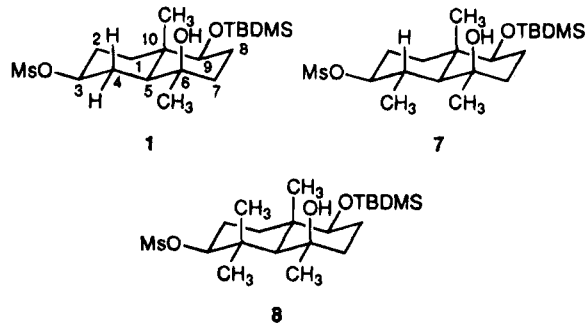
(1) (a) Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; Brunekreef, G. A.; de Groot, A. *J. Org. Chem.* **1990**, *55*, 941. (b) Jenniskens, L. H. D.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1991**, *56*, 6585. (c) Orrū, R. V. A.; Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; de Groot, A. *J. Org. Chem.* **1993**, *58*, 1199. (d) Orrū, R. V. A.; Wijnberg, J. B. P. A.; Bouwman, C. T.; de Groot, A. *J. Org. Chem.* **1994**, *59*, 374.

(2) For example, see: (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. (c) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395 and references cited therein.

(3) Hartman, G. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 6147.

0022-3263/95/1960-4233$09.00/0

Chart 1



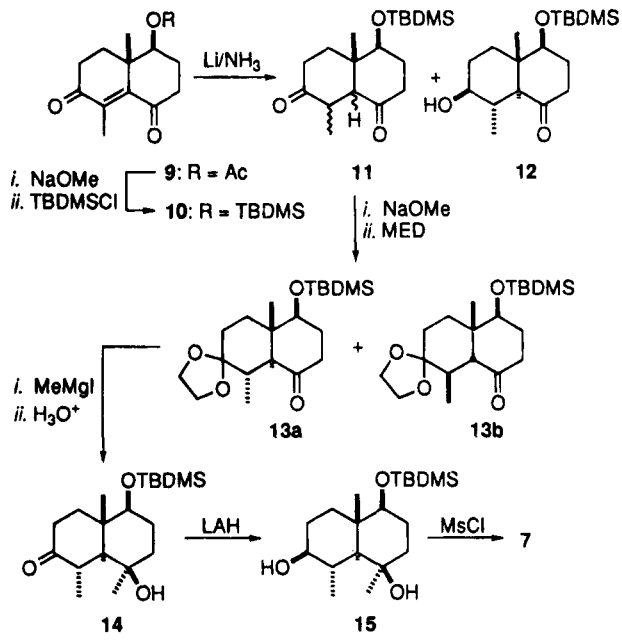
Similar accelerating effects of alkyl substituents may also occur in the TBI-induced heterolysis of 1,4-diol monosulfonate esters as the fast reaction of **2** suggests. To establish whether this is indeed the case, it was decided that the differently C(4)-substituted mesylates **1**, **7**, and **8**[6,7] (Chart 1) under the strongly basic conditions mentioned above would be examined. By comparing (i) their rates of reaction and (ii) their product composition, it was expected that more detailed information about these substituent effects on the TBI-induced heterolysis of sulfonate esters would be obtained.

Results and Discussion

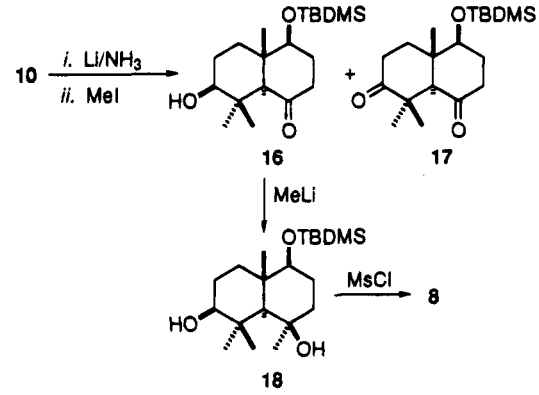
Mesylate **1** was prepared following a previously described procedure.[1b] The synthesis of both **7** and **8** started with the readily available unsaturated 1,4-dione **9**.[8] Saponification (NaOMe, MeOH) of **9** followed by treatment with TBDMSCl afforded the corresponding silyl ether **10** in 63% overall yield (Scheme 2). For the synthesis of mesylate **7**, the C(4)–C(5) double bond of **10** was reduced with Li in a 2:1 mixture of liquid NH_3 and THF to give an inseparable 3:5 mixture (69%) of two epimeric diones **11** and 3β-hydroxy ketone **12** (17%), respectively. Successive treatment of **11** with NaOMe and 2-butanone dioxolane (MED) produced a 7:2 mixture of the C(3)-monoacetalized diones **13a** and **13b**, respectively.[9] No bisacetal or C(6)-monoacetalized product was formed. After separation of this 7:2 mixture, pure **13a** was isolated in 65% overall yield from **11**. From ^{1}H–^{13}C-correlated 2D-NMR measurements, it was concluded that the doublet with J = 11.6 Hz at δ 2.32 in the ^{1}H NMR spectrum of **13a** must arise from H-5. Irradiation of this doublet gave a fairly strong NOE with H-9 at δ 3.72. These data of **13a** are consistent with an equatorial position of the Me group at C(4) and a trans ring junction. Further support for the *trans*-decalin skeleton of **13a** came from its ^{13}C NMR spectrum in which the angular Me signal appears at δ 11.29.[10]

Treatment of **13a** with MeMgI in ether followed by hydrolysis of the ethylene acetal function gave 6β-hydroxy ketone **14**. Reduction of **14** with LAH in THF afforded diol **15**[11] which was converted to mesylate **7**. The overall yield of **7** from **10** amounted to 30%.

Scheme 2



Scheme 3



A similar reaction sequence was followed for the synthesis of mesylate **8** (Scheme 3). Reductive alkylation[12] of **10** gave an easily separable mixture of 3β-hydroxy ketone **16** (47%) and the corresponding dione **17** (25%). The ^{1}H NMR spectrum of **16** shows a double doublet with J = 5.1 and 10.5 Hz at δ 3.07 which indicates the presence of an equatorial hydroxyl group at C(3). The ^{1}H–^{13}C-correlated 2D-NMR measurements demonstrated that the singlet at δ 1.97 in the ^{1}H NMR spectrum of **16** originates from H-5. The trans ring junction of **16** was ascertained by NOE difference experiments which showed strong NOEs between H-5 and both H-3 and H-9. Since alcohol **16** must be formed by reduction of the C(3) carbonyl function of **17**,[13] we assume that the ring junction of **17** is also trans.

Treatment of **16** with MeMgI in ether did not give any addition product; only starting material was recovered. Apparently, the sterically hindered carbonyl group of **16** is easily converted to its enolate, which, on hydrolysis, gives the original ketone. On the other hand, treatment

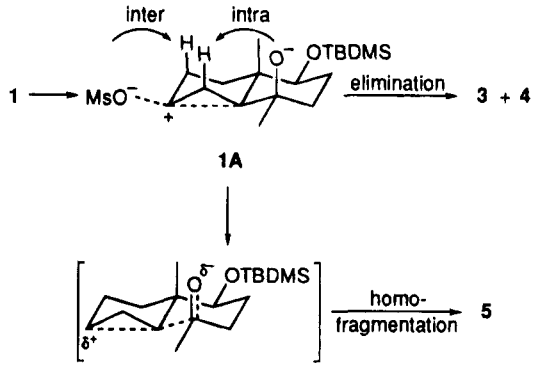
(4) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.
(5) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661.
(6) The numbering system given in structure **1** (Chart 1) will be followed throughout this paper.
(7) For practical reasons, this study is limited to compounds with an axial hydroxyl group at C(6). This is justifiable since the orientation of the alcohol group has little or no influence on the reaction rate. See refs 1c,d.
(8) Wijnberg, J. B. P. A.; Vader, J.; de Groot, Ae. *J. Org. Chem.* **1983**, *48*, 4380.
(9) Treatment of this 7:2 mixture with NaOMe in dry MeOH did not change the ratio.
(10) Browne, L. M.; Klinck, R. E.; Stothers, J. B. *Org. Magn. Reson.* **1979**, *12*, 561.
(11) Treatment of **12** with an excess of MeMgI also gave diol **15**.
(12) Stork, G.; Logusch, E. W. *J. Am. Chem. Soc.* **1980**, *102*, 1218, 1219.
(13) Caine, D. *Org. React.* **1976**, *23*, Chapter 1.

Table 1. Reactions of 1, 7, and 8 with Sodium *tert*-Amylate[a]

entry	mesylate	products (%)[b]	recovery[c]
1	1	**3** + **4** + **5** (20)[d]	80
2	**7**	**19** (34) + **20** (12) + **21** (32)	6
3	**8**	**22** (87)	11

[a] All reactions were performed in refluxing benzene with ca. 5 equiv of sodium *tert*-amylate for 2 min. [b] Isolated yield in parentheses. [c] Percentage of recovered starting material. [d] These products were isolated as a mixture in a ratio of 6.5:1:3, respectively.

Scheme 4



of **16** with MeLi in THF at −78 °C[14] proceeded smoothly and afforded diol **18**. Finally, treatment of **18** with MsCl in pyridine provided the mesylate **8** in 18% overall yield from **10**.

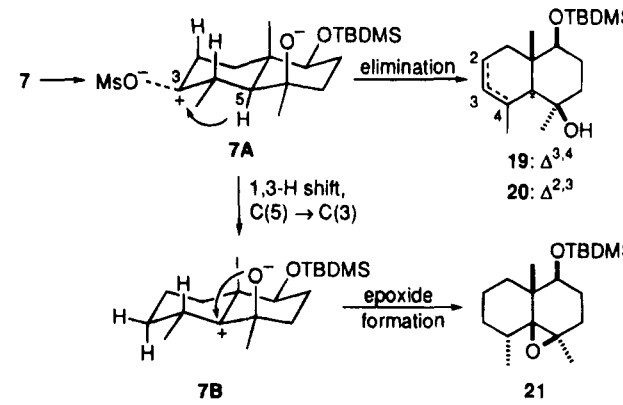
In order to obtain comparable data about the reactivity of the mesylates **1**, **7**, and **8**, all three compounds were subjected to the same reaction conditions. The reactions were run in refluxing benzene with ca. 5 equiv of sodium *tert*-amylate during 2 min. Comparison of the quantities of recovered starting material gave a rough estimate of the relative reaction rates. The results of these studies are collected in Table 1.

The 2 min reaction of mesylate **1** gave a mixture of the known olefins **3** and **4** and the homofragmentation product **5** in ca. 20% total yield (entry 1, Scheme 4).[1c] The quantity of recovered **1** amounted to 80%. After completion of the reaction (15 min), a 6.5:1 mixture of **3** and **4** and pure **5**[15] could be isolated in 55 and 24% yield, respectively.

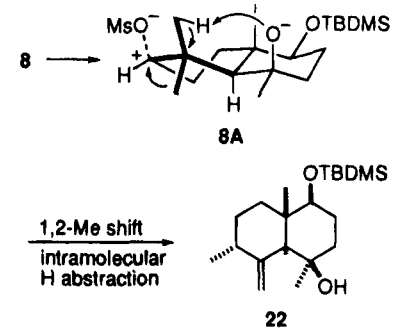
Both **7** and **8** react much faster than **1** as follows from the quantities of recovered starting material (6 and 11%, respectively) after a reaction time of 2 min. The mesylate **7** gave a rather complex product mixture from which the olefins **19** (34%) and **20** (12%) and epoxide **21** (32%) could be isolated (entry 2, Scheme 5). The structure of the epoxide **21** follows from the NMR data. The two singlets at δ 63.07 and 65.56 in the ^{13}C NMR spectrum of **21** are the main characteristics for the presence of the epoxide ring.

The reaction of dimethylated mesylate **8** proceeded with high selectivity to give the rearranged olefin **22** (87%) as the sole product (entry 3, Scheme 6). The axial orientation of the Me group at C(3) follows from the rather small multiplet ($W_{1/2} \approx 12$ Hz) for the allylic H-3 at δ 2.50. No diaxial coupling constant could be observed. Irradiation of the broad singlet for H-5 at δ 1.95 which

Scheme 5



Scheme 6



gave a NOE with the C(3) Me group confirms the axial orientation of the C(3) Me group. Together with other NMR data, these observations establish the identity of **22**.

The results collected in Table 1 show that Me substituents at C(4) lead to an increase in reaction rate. The occurrence of different reaction pathways can also be connected with the presence (or absence) of these substituents. Mesylate **1** shows elimination and homofragmention as the only processes. The two chief pathways by which the monomethylated mesylate **7** reacts are elimination and epoxide formation. A 1,2-Me shift (C(4) → C(3)) accompanied by selective proton abstraction is the exclusive process observed for dimethylated mesylate **8**.

Since it is believed that this type of reaction proceeds via dipolar intermediates,[1] semiempirical MNDO geometry optimizations[16] on the initially formed dipolar intermediates **1A**, **7A**, and **8A** may help to explain these differences in reaction rate and product formation. From these calculations, it appears that the dihedral angle for H(α)−C(5)−C(4)−H(β) in **1A** amounts to 180° which indicates an ideal W arrangement of the σ-relay. In **7A**, this angle is −170° which corresponds with a deviation of +10° from the ideal W arrangement. The calculations on **8A** show a dihedral angle of +140° for H(α)−C(5)−C(4)−Me(β) from which a deviation of −40° follows. The Newman projections **I**, **II**, and **III** along the C(5)−C(4) bond of the intermediates **1A**, **7A**, and **8A**, respectively, represent these situations more clearly (Figure 1).[17]

When the extent of TBI and, consequently, the reaction rate would be determined only by the σ-relay, one might

(14) Under these conditions, enolization is much less important: Buhler, J. D. *J. Org. Chem.* **1973**, *38*, 904.

(15) The yield of **5** is somewhat diminished due to aldol condensations under the influence of sodium *tert*-amylate. See ref 1c.

(16) (a) The QCPE No. 455 program was used. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (c) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(17) The Newman projections **I**−**III** were drawn on the basis of full geometry optimizations by means of the MNDO method. See ref 16a.

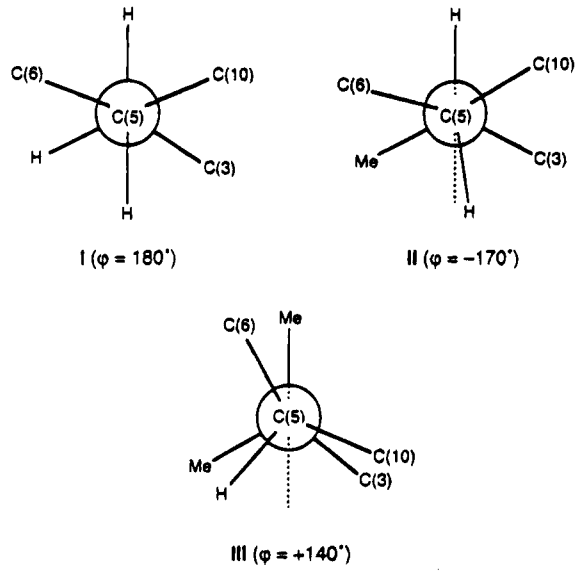


Figure 1. Dihedral angles φ between the axial substituents at C(4) (H or Me) and H-5 from the Newman projections **I**, **II**, and **III** along the C(5)−C(4) bond for the intermediates **1A**, **7A**, and **8A** respectively.

expect a faster reaction for **1** than for **7** (slightly) and **8** (considerably), due to the deviations of +10 and −40° found for **7A** and **8A**, respectively. The considerable rate increase observed for both **7** and **8** must therefore be ascribed to σ-participation[18,19] which is apparently much more effective in **7A** and **8A** than in **1A**.

The extent of σ-participation depends in the first place on the alignment of the neighboring C(4)−C(5) bond with the leaving group.[20] According to the MNDO calculations, this bond is antiperiplanar to the developing carbocationic 2p orbital at C(3) in **1A** as well as in **7A**, and this should mean a similar degree of stabilization by σ-participation in both intermediates. However, the presence of the C(4) Me group in **7A** strengthens the stabilization by σ-participation,[19] and consequently, **7** will react faster than **1** (entries 1 and 2).

In line with this reasoning, the presence of two Me groups at C(4) in mesylate **8** should lead to a higher reactivity of **8** in comparison with that of **7**. However, the overall stabilizing effect of two Me groups is less than expected as follows from the approximately equal amounts of recovered starting material (entries 2 and 3). Because the antiperiplanar relationship between the C(4)−C(5) bond and the 2p orbital of the developing carbocationic center at C(3) in **8A** is distorted (vide infra), delocalization of the C(4)−C(5) bond will contribute less to the stabilization of this intermediate.[21] As a consequence, the overall stabilizing effect of the two C(4) Me substituents will be reduced. In mesylate **2**, one of the carbon atoms adjacent to the carbon atom bearing the sulfonate ester group is also disubstituted, but the W arrangement of the σ-relay is not distorted. This means that both stereoelectronic effects (TBI and σ-participation) can operate efficiently, finding expression in a fast reaction with, in this specific case, homofragmentation as the exclusive pathway.[1d]

The MNDO calculations are also useful for explaining the differences in reaction outcome. From the dihedral angle of 180°, the occurrence of homofragmentation in the reaction of **1** is easily understood (Scheme 4). In the reaction of **7**, the deviation of +10° found for **7A** seems rather small to explain the absence of homofragmentation products.[22] It is therefore believed that a bridged intermediate like **1A**, which can give rise to homofragmentation, is sterically disfavored in the reaction of **7** because of the 1,3-*peri* effect[23] between the equatorial Me groups at C(4) and C(6). Apparently, in this situation, the direct 1,3-H shift (C(5) → C(3)) leading to the tertiary carbocationic intermediate **7B** is preferred over homofragmentation.[24,25] Successive (or simultaneous) ring closure explains the formation of epoxide **21** (Scheme 5). Consecutive 1,2-H shifts (C(4) → C(3) and C(5) → C(4)) are rejected as an explanation for the formation of **21**, owing to the stereospecificity of these shifts.

Due to flattening of ring B,[26] the alignment of the C(6) alkoxide group and β-H-4 in intermediate **7A** is less favorable for intramolecular elimination in comparison with the situation in intermediate **1A**. The interatomic distance between the oxyanion at C(6) and β-H-4 in **1A** is about 2.7 Å, which falls within the critical distance (2.9 Å) for an easy intramolecular proton abstraction,[27] whereas this distance in **7A** amounts to more than 3 Å. Consequently, more intermolecular elimination will occur in the reaction of **7** as is confirmed by the 3:1 ratio found for **19** and **20**, respectively.

From the MNDO calculations on intermediate **8A**, it follows that the conformation of ring A is more (twist)-boatlike. Co-operation of the 1,3-*peri* effect and the 4,4-dimethyl effect[28] in **8A** is considered to be responsible for this deformation through which both the mesylate group at C(3) and the α-Me at C(4) adopt a pseudoaxial orientation. In other words, the mesylate group and the α-Me at C(4) tend to an antiperiplanar relationship, and this allows for an easy 1,2-Me shift. The exclusive formation of the exocyclic double bond in **21** can be explained by a simultaneous intramolecular proton abstraction (Scheme 6).

Summarizing these and previous results from our laboratory, we may state that TBI and σ-participation are the most important stereoelectronic effects which principally determine the reactivity of perhydronaphthalene-1,4-diol monosulfonate esters upon treatment with sodium *tert*-amylate in refluxing benzene.[29] Substituents

(18) Jensen, F. R.; Smart, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 5686.
(19) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715.
(20) Fischer, W.; Grob, C. A.; von Sprecher, G.; Waldner, A. *Tetrahedron Lett.* **1979**, 1905.
(21) It might be possible that the pseudoaxial relationship between the 2p orbital of the developing carbocationic center at C(3) and the α-Me at C(4) in **8A** partly compensates for this loss in σ-participation.
(22) Separation of the product mixture from the reaction of **7** by column chromatography gave an unseparable mixture (15%) of at least four products. Although the identity of these compounds could not be established, the ^{13}C NMR spectrum of this mixture revealed that no homofragmentation (or aldol condensation) products were formed.
(23) Shibata, T.; Ohkura, T.; Shimizu, N.; Inayama, S. *Heterocycles* **1986**, *24*, 893.
(24) 1,3-H shifts are frequently observed in carbocationic processes: (a) Grob, C. A.; Waldner, A.; Zutter, U. *Helv. Chim. Acta* **1984**, *67*, 717. (b) Fuso, F.; Grob, C. A.; Sawlewicz, P.; Yao, G. W. *Helv. Chim. Acta* **1986**, *69*, 2098.
(25) A similar 1,3-H shift as a result of less effective bridging has been noticed after treatment of the C(6) stereoisomer of **1** with lithium *tert*-amylate. See ref 1c.
(26) The flattening of ring B bearing the alkoxide group must be the result of the 1,3-*peri* effect which forces the C(6) Me group in a more downward position.
(27) Menger, F. M.; Chow, J. F.; Kaiserman, H.; Vasquez, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4996.
(28) It is known from CD measurements that ring A of 4,4-dimethyl-3-keto steroids adopts a (twist)boat conformation: Tsuda, Y.; Kiuchi, F. *Chem. Pharm. Bull.* **1984**, *32*, 4806 and references cited therein.

at carbon atoms adjacent to the carbon atom bearing the sulfonate ester group will increase the contribution of σ-participation which finds expression in a higher reactivity of these compounds. If 1,3-bridging (TSI) occurs, the influence of TSI on the reactivity is modest which is consistent with theoretical considerations[19] and our previous findings.[1d] In cases where the ideal W arrangement is not distorted by alkyl substituents, the co-operation of TBI and σ-participation results in a fast reaction as is previously found for mesylate **2**.

Experimental Section[30]

Materials. All reagents were purchased from Aldrich or Janssen and were used without further purification unless otherwise noted. 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. Mesylate **1**[1b] and 1,4-dione **9**[8] were prepared following previously described procedures. The compounds **3**, **4**, and **5** have been characterized before.[1c]

(4α,4aα)-4-[(*tert*-Butyldimethylsilyl)oxy]-3,4,4a,5-tetrahydro-4a,8-dimethylnaphthalene-1(2*H*),7(6*H*)-dione (10). To a stirred solution of 12.46 g (19.82 mmol) of 1,4-dione **9** in 200 mL of dry MeOH was added 30 mL of 1 M NaOMe in dry MeOH at 0 °C. The solution was stirred at rt for 1 h and then neutralized with 4 N HCl. The organic solvent was distilled off under reduced pressure, and the remaining aqueous phase was extracted with seven 50 mL portions of EtOAc. The combined organic layers were dried and evaporated. Flash chromatography (1:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 8.02 g of crude alcohol [^{1}H NMR δ 1.05 (s, 3 H), 1.69 (s, 3 H), 1.85–2.16 (m, 4 H), 2.33–2.57 (m, 4 H), 2.88 (d, J = 5.0 Hz, 1 H), 3.85 (dd, J = 4.7, 8.9 Hz, 1 H)]. To a solution of this alcohol 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 40 °C for 5 d and then poured into 250 mL of H_2O. 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. Flash chromatography (10:1 petroleum ether (bp 40–60 °C)/EtOAc) yielded 10.20 g (63%) of **10** as a white solid: mp 63–65 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 0.06 (s, 6 H), 0.88 (s, 9 H), 1.08 (s, 3 H), 1.75 (s, 3 H), 1.77–2.09 (m, 4 H), 2.33–2.55 (m, 4 H), 3.81 (dd, J = 5.8, 9.8 Hz, 1 H); ^{13}C NMR δ −5.08 (q), −4.25 (q), 12.35 (q), 15.26 (q), 17.75 (s), 25.49 (3q), 29.13 (t), 33.17 (t), 33.74 (t), 39.87 (t), 43.94 (s), 76.26 (d), 133.13 (s), 153.38 (s), 199.28 (s), 204.13 (s); MS m/z (relative intensity) 322 (M^+, 1), 307 (3), 265 (81), 247 (18), 173 (17), 143 (29), 75 (100), 41 (23); HRMS calcd for $C_{14}H_{21}O_3Si$ (M^+ − 57) 265.1260, found 265.1259. Anal. Calcd for $C_{18}H_{30}O_3Si$: C, 67.03; H, 9.38. Found: C, 67.11; H, 9.70.

Li/NH$_3$ Reduction of 10. To vigorously stirred dry liquid NH_3 (30 mL) were added small pieces of Li (0.20 g) at −78 °C. A solution of 0.50 g (1.55 mmol) of **10** in 15 mL of dry THF was added dropwise at −78 °C, and the reaction mixture was allowed to stir at reflux temperature for 30 min. After quick evaporation of NH_3 under reduced pressure, the remaining THF solution was stirred at 0 °C for 30 min. Then 0.50 g of NH_4Cl was added at once to the vigorously stirred reaction mixture. After stirring for an additional 15 min, the mixture was poured into 50 mL of ice–water and extracted with three 75 mL portions of EtOAc. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (15:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 0.088 g (17%) of **(4α,4aα,7α,8β,8aβ)-4-[(*tert*-butyldimethylsilyl)oxy]octahydro-7-hydroxy-4,8-dimethyl-1(2*H*)-naphthalenone (12):** ^{1}H NMR δ 0.04 (s, 6 H), 0.86 (s, 12 H), 1.05 (d, J = 7.1 Hz, 3 H), 1.15 (m, 1 H), 1.51–1.89 (m, 5 H), 1.98–2.09 (m, 2 H), 2.20–2.47 (m, 3 H), 3.49–3.64 (m, 2 H); ^{13}C NMR δ −4.98 (q), −4.25 (q), 9.44 (q), 14.77 (q), 17.77 (s), 25.06 (t), 25.55 (3q), 29.70 (t), 33.28 (d), 36.50 (t), 38.68 (t), 44.37 (s), 56.54 (d), 73.13 (d), 78.16 (d), 209.19 (s); MS m/z (relative intensity) 311 (M^+ − 15, 1), 269 (100), 252 (25), 177 (18), 159 (23), 135 (46), 75 (37); HRMS calcd for $C_{17}H_{31}O_3Si$ (M^+ − 15) 311.2042, found 311.2041. The reaction also yielded 0.347 g (69%) of **11** as a 3:5 mixture of two epimers.[32] A sample of 0.90 g (2.78 mmol) of **11** was treated with NaOMe as described above for **9**. After workup, the crude product was dissolved in a mixture of 10 mL of CH_2Cl_2 and 10 mL of MED. To this solution 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 mixture was diluted with 100 mL of CH_2Cl_2 and washed with 50 mL of brine. After the mixture was dried and evaporated, flash chromatography (15:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded, in order of elution, 0.663 g (65%) of pure **13a**, 0.091 g (9%) of a 4:1 mixture of **13a** and **13b**, respectively, and 0.200 g (19%) of pure **13b**. The spectroscopic data of **13a** and **13b** are shown below.

(4′α,4′aα,8′β,8′aβ)-4′-[(*tert*-Butyldimethylsilyl)oxy]octahydro-4′a,8′-dimethylspiro[1,3-dioxolane-2,7′(6′*H*)-naphthalen]-1′(2′*H*)-one (13a): ^{1}H NMR δ 0.03 (s, 6 H), 0.74 (s, 3 H), 0.79 (d, J = 7.7 Hz, 3 H), 0.82 (s, 9 H), 1.29–2.25 (m, 9 H), 2.32 (d, J = 11.6 Hz, 1 H), 3.72 (dd, J = 5.2, 10.8 Hz, 1 H), 3.82–3.91 (m, 4 H); ^{13}C NMR δ −4.78 (q), −4.08 (q), 11.01 (q), 11.29 (q), 17.94 (q), 25.76 (3q), 30.29 (t), 31.90 (t), 34.31 (d), 35.01 (t), 40.27 (t), 43.85 (s), 58.28 (d), 64.97 (t), 65.12 (t), 77.57 (d), 110.55 (s), 209.97 (s); MS m/z (relative intensity) 368 (M^+, 0.9), 311 (24), 249 (4), 193 (11), 175 (8), 99 (100), 75 (30), 41 (11); HRMS calcd for $C_{20}H_{36}O_4Si$ (M^+) 368.2383, found 368.2383.

(4′α,4′aα,8′α,8′aα)-4′-[(*tert*-Butyldimethylsilyl)oxy]octahydro-4′a,8′-dimethylspiro[1,3-dioxolane-2,7′(6′*H*)-naphthalen]-1′(2′*H*)-one (13b): ^{1}H NMR δ −0.01 (s, 6 H), 0.68 (d, J = 5.7 Hz, 3 H), 0.81 (s, 3 H), 0.84 (s, 9 H), 0.96–2.49 (m, 10 H), 3.79–3.91 (m, 4 H), 4.36 (dd, J = 5.4, 11.1 Hz, 1 H); ^{13}C NMR δ −4.91 (q), −4.22 (q), 11.07 (q), 18.01 (s), 20.98 (q), 25.74 (3q), 30.51 (t), 30.68 (t), 32.35 (t), 36.30 (t), 37.85 (d), 41.23 (s), 63.39 (d), 65.08 (t), 65.38 (t), 66.66 (d), 109.09 (s), 212.17 (s); MS m/z (relative intensity) 368 (M^+, <0.1), 311 (45), 249 (11), 223 (10), 183 (13), 99 (100), 75 (40), 41 (14); HRMS calcd for $C_{20}H_{36}O_4Si$ (M^+) 368.2383, found 368.2385.

(1α,4aβ,5β,8β,8aα)-5-[(*tert*-Butyldimethylsilyl)oxy]octahydro-8-hydroxy-1,4a,8-trimethyl-2(3*H*)-naphthalenone (14). A solution of **13a** (0.60 g, 1.63 mmol) in 25 mL of dry ether was added dropwise to 3 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 cautiously destroyed with saturated aqueous NH_4Cl. After dilution with 100 mL of H_2O, 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 taken up in 25 mL of acetone, and 1.5 mL of 4 N HCl was added. The reaction mixture was stirred at rt for 3 h and then neutralized with 15% aqueous NaOH. After dilution with 100 mL of H_2O, the reaction mixture was extracted with three 50 mL portions of EtOAc. The combined organic layers were washed with 50 mL of brine, dried, and evaporated. Flash chromatography (10:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.385 g (70%) of **14**: ^{1}H NMR δ 0.01 (s, 3 H), 0.03 (s, 3 H), 0.86 (s, 9 H), 0.93 (s, 3 H), 1.21 (s, 3 H), 1.27 (d, J = 9.0 Hz, 3 H), 1.33–2.09 (m, 8 H), 2.32–2.59 (m, 3 H), 3.24 (dd, J = 3.8, 11.1 Hz, 1 H); ^{13}C NMR δ −5.08 (q), −4.13 (q), 13.32 (q), 17.81 (s), 21.74 (q), 25.59 (3q), 26.96 (t), 30.24 (q), 33.22 (t), 34.58 (t), 39.57 (t), 39.90 (s), 42.70 (d), 56.31 (d), 71.43 (s), 78.47 (d), 216.98 (s); MS m/z (relative intensity) 283 (M^+ − 57, 47), 265 (15), 191 (100), 174

(29) The reactivity of norbornane-1,4-diol monosulfonate esters is determined by the same stereoelectronic effects: Bastiaansen, P. M. F. M.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1995**, *60*, in press.

(30) For a general description of the experimental procedures employed in this research, see ref 1b. ^{1}H–^{13}C-correlated 2D-NMR measurements were performed at 200 MHz, using delay times in the pulse sequence of 3.3 and 2.2 ms.

(31) Conia, M. J.-M. *Bull. Soc. Chim.* **1950**, *17*, 537.

(32) A larger scale reduction of **10** gave **11** and **12** in 35 and 22% yield, respectively.

(21), 149 (79), 133 (78), 76 (89); HRMS calcd for $C_{15}H_{27}O_3Si$ ($M^+ - 57$) 283.1729, found 283.1732.

(1α,4α,4aα,7α,8β,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-decahydro-1,4a,8-trimethyl-1,7-naphthalenediol (15). To a solution of ketone **14** (0.28 g, 0.81 mmol) in 40 mL of dry THF was added 0.70 g (18 mmol) of LAH. The reaction mixture was allowed to stir at rt for 10 min and then quenched by the careful addition of a small amount of saturated aqueous Na_2SO_4. The reaction mixture was dried and evaporated. The remaining residue was purified by crystallization from 5:1 diisopropyl ether/EtOAc to give 0.255 g (92%) of **15**: mp 84–85 °C; ^1H NMR δ −0.09 (s, 3 H), −0.08 (s, 3 H), 0.75 (s, 9 H), 0.83–1.62 (m, 8 H), 1.02 (s, 3 H), 1.11 (d, J = 6.8 Hz, 3 H), 1.25 (s, 3 H), 1.64–1.85 (m, 4 H), 2.92–3.07 (m, 2 H); ^{13}C NMR δ −5.25 (q), −4.34 (q), 12.63 (q), 17.20 (q), 17.68 (s), 25.47 (3q), 26.72 (t), 30.37 (t), 34.14 (q), 36.67 (t), 37.00 (d), 40.32 (s), 41.96 (t), 54.22 (d), 72.38 (s), 76.20 (d), 79.48 (d); MS m/z (relative intensity) 285 ($M^+ - 57$, 2), 267 (20), 175 (100), 133 (26), 120 (23), 96 (20), 73 (30); HRMS calcd for $C_{15}H_{29}O_3Si$ ($M^+ - 57$) 285.1886, found 285.1888. Anal. Calcd for $C_{19}H_{38}O_3Si$: C, 66.61; H, 11.18. Found: C, 66.38; H, 11.37.

Reductive Alkylation of 10. The procedure described above for the Li/NH_3 reduction was employed by using 0.90 g of Li, 100 mL of freshly distilled NH_3, and a solution of 2.49 g (7.74 mmol) of dione **10** in 50 mL of dry THF. After quick evaporation of NH_3, 0.50 mL (8.02 mmol) of MeI in 10 mL of dry THF was added dropwise at 0 °C. The mixture was allowed to stir at this temperature for 10 min, poured into 500 mL of ice-water, and then extracted with six 200 mL portions of EtOAc. The combined organic layers were washed with 100 mL of brine, dried, and evaporated. The remaining residue was flash chromatographed (15:1 petroleum ether (bp 40–60 °C)/EtOAc) to yield 0.649 g (25%) of **(4α,4aα,8aβ)-4-[(*tert*-butyldimethylsilyl)oxy]hexahydro-4a,8,8-trimethyl-1(2*H*),7(6*H*)-naphthalenedione (17):** mp 67–69 °C (from petroleum ether (bp 40–60 °C)); ^1H NMR δ 0.04 (s, 3 H), 0.06 (s, 3 H), 0.85 (s, 9 H), 1.08 (s, 3 H), 1.12 (s, 3 H), 1.48 (m, 1 H), 1.44 (s, 3 H), 1.75–2.35 (m, 7 H), 2.77 (m, 1 H), 3.64 (dd, J = 5.5, 10.3 Hz, 1 H); ^{13}C NMR δ −5.04 (q), −4.241 (q), 13.53 (q), 17.74 (s), 21.61 (q), 23.73 (q), 25.52 (3q), 30.74 (t), 33.68 (t), 37.74 (t), 40.61 (t), 43.23 (s), 46.45 (s), 61.45 (d), 78.29 (d), 208.32 (s), 214.06 (s); MS m/z (relative intensity) 338 (M^+, 0.2), 323 (2), 281 (60), 183 (26), 171 (29), 147 (35), 75 (100), 41 (41); HRMS calcd for $C_{19}H_{34}O_3Si$ (M^+) 338.2277, found 338.2277. Anal. Calcd for $C_{19}H_{34}O_3Si$: C, 67.41; H, 10.12. Found: C, 67.88; H, 10.58. Further elution afforded 1.25 g (47%) of **(4α,4aα,7α,8aβ)-4-[(*tert*-butyldimethylsilyl)oxy]octahydro-7-hydroxy-4a,8,8-trimethyl-1(2*H*)-naphthalenone (16):** mp 134–135 °C (from diisopropyl ether); ^1H NMR δ 0.03 (s, 6 H), 0.85 (s, 12 H), 1.04 (s, 3 H), 1.15 (s, 3 H), 1.41–2.00 (m, 8 H), 2.10–2.39 (m, 2 H), 3.07 (dd, J = 5.1, 10.5 Hz, 1 H), 3.58 (dd, J = 5.2, 10.6 Hz, 1 H); ^{13}C NMR δ −4.97 (q), −4.22 (q), 13.66 (q), 14.73 (q), 17.77 (s), 25.55 (3q), 26.47 (t), 27.23 (q), 30.96 (t), 36.62 (t), 37.12 (s), 40.78 (t), 43.54 (s), 61.27 (d), 78.57 (d), 78.88 (d), 109.20 (s); MS m/z (relative intensity) 325 (M^+ − 15, 2.8), 297 (17), 283 (100), 164 (11), 149 (20), 73 (41), 41 (29); HRMS calcd for $C_{18}H_{33}O_3Si$ ($M^+ - 15$) 325.2199, found 325.2200. Anal. Calcd for $C_{19}H_{36}O_3Si$: C, 67.01; H, 10.65. Found: C, 66.72; H, 10.82.

(1α,4α,4aα,7α,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-decahydro-1,4a,8,8-tetramethyl-1,7-naphthalenediol (18). To a stirred solution of 10 mL (16 mmol) of MeLi (1.6 M in ether), cooled to −78 °C, was added dropwise a solution of 0.35 g (1.03 mmol) of **16** in 25 mL of dry THF over a period of 15 min. When the addition was complete, the reaction mixture was allowed to stir at −78 °C for 1.5 h. The excess MeLi was then quenched by careful addition of saturated aqueous NH_4Cl. After addition of 50 mL of H_2O, the two-phase mixture was separated and the aqueous layer was extracted with three 25 mL portions of EtOAc. The combined organic layers were washed with 50 mL of brine, dried, and evaporated. The crude product was purified by crystallization from diisopropyl ether to give 0.275 g (75%) of **18** as white crystals: mp 140–141 °C; ^1H NMR δ 0.00 (s, 3 H), 0.02 (s, 3 H), 0.86 (s, 9 H), 1.19 (s, 3 H), 1.21 (s, 3 H), 1.23 (s, 3 H), 1.36–1.87 (m, 11 H), 1.41 (s, 3 H), 3.00–3.16 (m, 2 H); ^{13}C NMR δ −5.01 (q), −4.11 (q), 15.29 (q), 16.61 (q), 17.83 (s), 25.65 (3q), 27.19 (t), 27.47 (t), 31.35 (q), 34.62 (q), 38.25 (t), 41.01 (s), 41.40 (s), 43.39 (t), 56.89 (d), 75.08 (s), 79.08 (d), 80.68 (d); MS m/z (relative intensity) 299 ($M^+ - 57$, 2), 189 (100), 159 (12), 133 (50), 73 (32), 41 (27); HRMS calcd for $C_{16}H_{31}O_3Si$ ($M^+ - 57$) 299.2037, found 299.2037. Anal. Calcd for $C_{20}H_{40}O_3Si$: C, 67.36; H, 11.31. Found: C, 67.88; H, 11.36.

General Procedure for the Preparation of Mesylates 7 and 8. To a solution (0.1–0.15 M) of the diol **15** or **18** in dry pyridine was added MsCl (ca. 1.5 equiv). The reaction mixture was stirred at rt and the reaction progress was monitored by TLC. At completion, the residue was 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 the mixture was dried and evaporated, further purification was accomplished by flash chromatography or by crystallization.

(1α,4α,4aα,7α,8β,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-decahydro-1,4a,8-trimethyl-1,7-naphthalenediol 7-methanesulfonate (7): yield 100%; mp 115–116 °C (from petroleum ether (bp 40–60 °C)); ^1H NMR δ −0.01 (s, 3 H), 0.01 (s, 3 H), 0.85 (s, 9 H), 0.90–1.94 (m, 8 H), 1.07 (s, 3 H), 1.22 (d, J = 6.4 Hz, 3 H), 1.30 (s, 3 H), 2.08–2.24 (m, 3 H), 3.00 (s, 3 H), 3.09 (dd, J = 3.8, 11.1 Hz, 1 H), 4.29 (m, $W_{1/2} \approx 21$ Hz, 1 H); ^{13}C NMR δ −5.09 (q), −4.17 (q), 12.66 (q), 17.47 (q), 17.79 (s), 25.60 (3q), 26.63 (t), 28.60 (t), 34.47 (q), 34.90 (d), 36.34 (t), 38.77 (q), 40.30 (s), 42.60 (t), 54.27 (d), 72.43 (s), 79.14 (d), 87.89 (d); MS m/z (relative intensity) 307 ($M^+ - 113$, <0.1), 292 (0.2), 268 (14), 250 (11), 200 (13), 176 (100), 159 (20), 135 (28), 120 (64), 96 (50), 75 (55); HRMS calcd for $C_{19}H_{35}OSi$ ($M^+ - 113$) 307.2457, found 307.2454. Anal. Calcd for $C_{20}H_{40}O_5SSi$: C, 57.10; H, 9.58. Found: C, 56.79; H, 9.70.

(1α,4α,4aα,7α,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-decahydro-1,4a,8,8-tetramethyl-1,7-naphthalenediol 7-methanesulfonate (8): yield 82%; ^1H NMR (C_6D_6) δ 0.11 (s, 6 H), 0.74–1.43 (m, 6 H), 1.02 (s, 9 H), 1.17 (s, 3 H), 1.26 (s, 3 H), 1.32 (s, 3 H), 1.38 (s, 3 H), 1.82–2.10 (m, 4 H), 2.39 (s, 3 H), 2.88 (dd, J = 3.6, 11.2 Hz, 1 H), 4.30 (dd, J = 5.1, 11.7 Hz, 1 H); ^{13}C NMR δ −4.97 (q), −4.19 (q), 15.00 (q), 17.69 (q), 17.79 (s), 24.96 (t), 25.64 (3q), 27.53 (t), 30.78 (q), 34.62 (q), 37.50 (t), 38.25 (q), 40.50 (s), 41.14 (s), 43.48 (t), 56.31 (d), 74.16 (s), 80.44 (d), 89.20 (d); MS m/z (relative intensity) 362 ($M^+ - 72$, 3.3), 281 (6), 265 (7), 190 (77), 153 (57), 147 (30), 121 (23), 75 (100); HRMS calcd for $C_{17}H_{33}O_5SSi$ ($M^+ - 72$) 362.1583, found 362.1577.

Reactions of Mesylates 1, 7, and 8 with Sodium *tert*-Amylate. General Procedure. All reactions were carried out on 0.20–0.50 mmol of mesylate at a concentration of ca. 0.1 M in dry benzene. The solution was degassed and refluxed under an Ar atmosphere. Circa 5 equiv of sodium *tert*-amylate (3.2 M in toluene) was added at once, via syringe, to the refluxing solution of the mesylate. The reaction mixture was heated at reflux temperature for 2 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 10 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 0.100 g (0.25 mmol) of **1**. Workup and flash chromatography (1:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 0.015 g (20%) of a 6.5:1:3 mixture of **3**, **4**, and **5**, respectively, and 0.080 g (80%) of unreacted **1**. Completion of the reaction (15 min) gave 55% of a 6.5:1 mixture of **3** and **4**, respectively, and 24% of **5**.

b. The general procedure was employed by using 0.214 g (0.51 mmol) of **7**. Workup and flash chromatography (5:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 0.154 g of a complex product mixture and 0.012 g (6%) of unreacted **7**. Repeated column chromatography (250:1 petroleum ether (bp 40–60 °C)/EtOAc) on the mixture (0.154 g) gave, in order of elution, 0.053 g (32%) of **21**, 0.025 g (ca. 15%) of an unidentified mixture of, according to GC, at least four products, 0.056 g (34%) of **19**, and 0.020 g (12%) of **20**. The spectroscopic data of **19–21** are shown below.

(1α,4α,4aα,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,-4a,5,6,8a-octahydro-1,4a,8-trimethyl-1-naphthalenol (19): ^{1}H NMR δ 0.03 (m, 6 H), 0.81−1.35 (m, 3 H), 0.88 (s, 9 H), 1.00 (s, 3 H), 1.40−1.76 (m, 4 H), 1.41 (s, 3 H), 1.81−2.16 (m, 3 H), 1.99 (s, 3 H), 3.23 (dd, J = 4.1, 11.4 Hz, 1 H), 5.43 (br s, 1 H); ^{13}C NMR δ −5.06 (q), −4.12 (q), 11.80 (q), 17.85 (s), 22.81 (t), 25.65 (3q), 25.27 (q), 26.82 (t), 33.19 (q), 35.10 (t), 39.59 (s), 41.87 (t), 52.92 (d), 71.92 (s), 78.49 (d), 126.25 (d), 132.98 (s); MS m/z (relative intensity) 324 (M^+, <0.1), 309 (4), 176 (0.5), 267 (17), 252 (62), 215 (15), 175 (100), 150 (24), 120 (31), 75 (35); HRMS calcd for $C_{15}H_{27}O_2Si$ (M^+ − 57) 267.1780, found 267.1785.

(1α,4α,4aα,8β,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,4a,5,8,8a-octahydro-1,4a,8-trimethyl-1-naphthalenol (20): ^{1}H NMR δ 0.02 (s, 3 H), 0.03 (s, 3 H), 0.87 (s, 9 H), 0.95−1.30 (m, 2 H), 1.02 (s, 3 H), 1.20 (d, J = 6.6 Hz, 3 H), 1.28 (s, 3 H), 1.41−2.11 (m, 6 H), 2.39 (m, 1 H), 3.23 (dd, J = 4.1, 11.3 Hz, 1 H), 5.39−5.59 (m, 2 H); ^{13}C NMR δ −5.06 (q), −4.12 (q), 13.55 (q), 17.83 (s), 23.96 (q), 25.63 (3q), 27.07 (t), 29.28 (d), 33.30 (q), 35.10 (t), 39.93 (t), 39.93 (s), 40.63 (t), 53.79 (d), 71.28 (s), 79.22 (d), 122.73 (d), 134.70 (d); MS m/z (relative intensity) 309 (M^+ − 15, <0.1), 267 (29), 252 (12), 175 (100), 160 (21), 119 (45), 75 (35); HRMS calcd for $C_{15}H_{27}O_2Si$ (M^+ − 57) 267.1780, found 267.1780.

(1α,4α,4aα,8β,8aα)-4-[(*tert*-Butyldimethylsilyl)oxy]octahydro-1,4a,8-trimethyl-2(3*H*)-naphthaleno[1,2-*b*]oxirane (21): ^{1}H NMR (C_6D_6) δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.86 (d, J = 7.1 Hz, 3 H), 0.99−1.96 (m, 11 H), 1.02 (s, 9 H), 1.18 (s, 3 H), 1.34 (s, 3 H), 3.23 (dd, J = 3.1, 11.27 Hz, 1 H); ^{13}C NMR (C_6D_6) δ −5.23 (q), −4.27 (q), 14.93 (q), 17.80 (s), 19.71 (2q), 25.58 (3q), 25.58 (t), 27.00 (t), 27.00 (d), 31.22 (t), 33.27 (t), 33.73 (t), 39.29 (s), 63.07 (s), 65.56 (s), 77.31 (d); MS m/z (relative intensity) 324 (M^+, <0.1), 309 (1), 267 (100), 175 (48), 166 (42), 143 (26), 120 (28), 77 (44); HRMS calcd for $C_{15}H_{27}O_2Si$ (M^+ − 57) 267.1780, found 267.1783.

c. The general procedure was employed by using 0.100 g (0.23 mmol) of **8**. Workup and flash chromatography (100:1 petroleum ether (bp 40−60 °C)/EtOAc) gave 0.011 g (11%) of unreacted **3** and 0.068 g (87%) of **(1α,4α,4aα,7β,8aβ)-4-[(*tert*-butyldimethylsilyl)oxy]octahydro-1,4a,7-trimethyl-8-methylene-(7*H*)-1-naphthalenol (22):** ^{1}H NMR δ 0.03 (s, 3 H), 0.04 (s, 3 H), 0.87 (s, 9 H), 0.92−1.91 (m, 9 H), 0.96 (s, 3 H), 1.05 (d, J = 7.2 Hz, 3 H), 1.27 (s, 3 H), 1.95 (br s, 1 H), 2.50 (m, $W_{1/2} \approx$ 12 Hz, 1 H), 3.33 (dd, J = 4.1, 11.5 Hz, 1 H), 5.08 (br s, 1 H), 5.16 (br s, 1 H); ^{13}C NMR δ −5.03 (q), −4.08 (q), 12.92 (q), 17.83 (s), 18.50 (q), 25.63 (3q), 26.54 (t), 28.90 (t), 29.08 (q), 35.27 (t), 40.89 (t), 40.89 (d), 42.69 (s), 50.12 (d), 71.43 (s), 80.04 (d), 110.24 (t), 149.46 (s); MS m/z (relative intensity) 338 (M^+, <0.1), 323 (0.3), 281 (11), 189 (100), 147 (14), 120 (15), 76 (31); HRMS calcd for $C_{16}H_{29}O_2Si$ (M^+ − 57) 281.1937, found 281.1937.

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Supplementary Material Available: ^{1}H NMR spectra for compounds **8**, **12**, **13a,b**, **14**, and **19**−**22** (9 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.

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