Chemical Consequences of Long-Range Orbital Interactions in Cholestane-3,7-diol Monosulfonate Esters. A Seven-Center Fragmentation

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The manifestation of through-five-bond interactions in the reactions of the rigid 1,5-diol monosulfonate esters (**1**−**3**), having an ideal all-trans geometry of the σ-relay, with sodium *tert*-amylate is investigated. It has been shown that the deprotonation of the alcohol group in **2** and **3**, which results in an increased electrofugal ability of this group, finds expression in a seven-center fragmentation. This fragmentation also illustrates that effective through-five-bond interactions exist between the alcoholate group and the carbocationic center which is generated during the heterolysis. The reaction outcome of mesylate **1** does not indicate effective through-bond interactions, and only elimination is observed. This difference can be attributed to the alkyl substituents on the γ- and α-positions to the mesylate group in **2** and **3**, respectively, which stimulate the seven-center fragmentation. Though a reasonable amount of fragmentation product is obtained from **3**, the through-five-bond interaction is not strong enough to dominate the reaction course completely and typical E1-like processes, i.e., elimination and rearrangement, are competitive. As expected, only a 1,2 Me-shift is observed in the reaction of the axial mesylate **4** where a gauche interaction is present in the geometry of the σ-relay. The presence of through-bond interactions in the reactions of **3** and **4** becomes apparent by comparison of the reactivity of **3** and **4** with their O-silylated analogs **5** and **6**.

Introduction

The best-known example of participation of the σ-framework in an intramolecular chemical reaction is the heterolytic Grob fragmentation,[1] which is almost certainly the result of orbital interactions through three σ-bonds.[2] The base-induced fragmentation of cyclic 1,3-diol monosulfonate esters, known as the Wharton reaction, is a typical example of the Grob fragmentation and finds widespread application in organic synthesis.[3]

The synthetic value of reactions in which orbital interactions through four σ-bonds are supposed to be operative is best illustrated with the intramolecular base-induced rearrangement and elimination reactions of trans-fused perhydronaphthalene-1,4-diol monosulfonate esters.[4,5] More detailed studies revealed that when these compounds possess an all-trans arrangement of the σ-bonds homofragmentation is the characteristic reaction pathway[6a−c] and that a more substituted σ-framework results in a higher reactivity of these compounds.[6d]

Reports on the chemical consequences of orbital interactions through more than four σ-bonds are scarce. Paddon-Row et al.[7] used the Birch reduction as a tool for exploring the chemical consequences of long-range orbital interactions through five and six σ-bonds and came to the conclusion that any chemical consequences arising from such interactions should be small. Grob et al.[8] examined the solvolysis of a number of 4-substituted (X) bicyclo[2.2.2.]octylsulfonate esters (X = COO^-, $CONH_2$, CH_2OH, and CH_2NH_2) to find out whether these saturated compounds are capable of undergoing seven-center fragmentation in which five σ-bonds are involved.[9] However, careful scrutiny of the reaction products revealed that only substitution and no seven-center fragmentation to 1,4-dimethylidenecyclohexane had occurred (Scheme 1). Grob concluded that for the weakly electron-donating substituents X mentioned above double hyperconjugation, as illustrated in structure **I**, does not progress to the point where fragmentation occurs and an energetically more favorable substitution reaction takes place.

More recently, Adcock et al.[10] reported the fragmentation to 1,4-dimethylidenecyclohexane in the reaction with the strongly electron-donating trimethylstannyl group as

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) Grob, C. A. *Angew. Chem.* **1969**, *81*, 543.
(2) Gleiter, R.; Stohrer, W.-D.; Hoffmann, R. *Helv. Chim. Acta* **1972**, *55*, 893.
(3) For an extensive review of the Wharton reaction, see: Caine, D. *Org. Prep. Proced. Int.* **1988**, *20*, 1.
(4) Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; Brunekreef, G. A.; de Groot, A. *J. Org. Chem.* **1990**, *55*, 941.
(5) Jenniskens, L. H. D.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1991**, *56*, 6585.
(6) (a) Orrū, R. V. A.; Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; de Groot, A. *J. Org. Chem.* **1993**, *58*, 1199. (b) Orrū, R. V. A.; Wijnberg, J. B. P. A.; Bouwman, C. T.; de Groot, A. *J. Org. Chem.* **1994**, *59*, 374. (c) Bastiaansen, P. M. F. M.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1995**, *60*, 4240. (d) Orrū, R. V. A.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1995**, *60*, 4233.
(7) Paddon-Row, M. N.; Hartcher, R. *J. Am. Chem. Soc.* **1980**, *102*, 671.
(8) Grob, C. A.; Rich, R. *Helv. Chim. Acta* **1979**, *62*, 2793 and references cited therein.
(9) Seven-center Beckmann-type fragmentations are known in the literature: (a) Eisele, W.; Grob, C. A.; Renk, E.; von Tschammer, H. *Helv. Chim. Acta* **1968**, *51*, 817. (b) Ibuka, T.; Mitsui, Y.; Hayashi, K.; Minakata, H.; Inubushi, Y. *Tetrahedron Lett.* **1981**, *22*, 4425. Also, seven-center fragmentations in which double bonds and/or highly strained ring systems are involved have been reported. For example, see: (c) Ho, T.-L. In *Heterolytic Fragmentation of Organic Molecules*; Wiley-Interscience: New York, 1993; Chapter 9 and references cited therein.
(10) Adcock, W.; Krstic, A. R.; Duggan, P. J.; Shiner, V. J., Jr.; Coope, J.; Ensinger, M. W. *J. Am. Chem. Soc.* **1990**, *112*, 3140.

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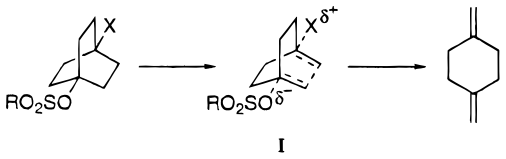
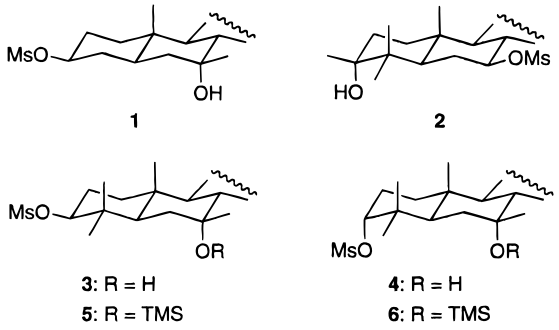
Scheme 1



I

Chart 1



1 **2**

3: R = H
5: R = TMS

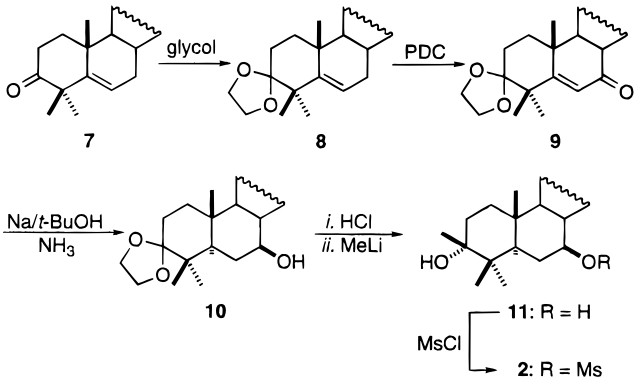
4: R = H
6: R = TMS

the substituent X. This and other related results[11] supported Grob's view that fragmentation can occur only when the group X is a sufficiently active electrofuge.[12]

In order to test this hypothesis, we started an investigation into the reaction behavior of *1,5-diol* monosulfonate esters under strongly basic nonsolvolytic conditions.[6] We hoped to demonstrate the seven-center fragmentation Grob had in mind because deprotonation of the hydroxyl group in these sulfonate esters would lead to a strongly increased electrofugal ability of the carbinol function.[13] Furthermore, it is known that structural features such as (1) an all-trans (zigzag) σ-relay,[14] (2) a tertiary alcohol function,[15] and (3) a higher degree of substitution of the σ-relay[16] all may favor fragmentation reactions. We therefore decided to investigate, as 1,5-diol monosulfonate esters, the easily accessible cholestane-3,7-diol monomesylates **1**−**4**[17] (Chart 1). In particular, the mesylates **2** and **3** possess all the favorable structural features for the occurrence of seven-center fragmentation.

There were two other reasons for selecting these particular cholestane derivatives for study. First, from the reactions of the mesylates **1**−**3**, having different alkyl substitution patterns, it was expected that further evidence for the accelerating effect of alkyl substituents in these processes would be obtained.[6d] Second, from the reaction of the axial mesylate **4**, we expected to get information on whether through-bond interactions (TBI) over five σ-bonds would still be significant for the product composition and reactivity of compounds having a nonzigzag σ-relay.

Scheme 2



7 **8** **9**

10

11: R = H
2: R = Ms

Additionally, the O-silylated mesylates **5** and **6** were subjected to the same strongly basic conditions as well to demonstrate again that the generation of an alcoholate function is crucial for the reactivity of these compounds.

Herein we report the results of our study.

Results and Discussion

The mesylate **1** was prepared from the known 3β-hydroxy-5α-cholestan-7-one[18] by mesylation and successive treatment with MeMgI at 0 °C.[19] The synthesis of mesylate **2** started with the readily available dimethylated ketone **7**.[20] Protection of the carbonyl group of **7** as its ethylene acetal **8** was followed by an allylic oxidation with PDC in refluxing pyridine[21] to give the enone **9** (Scheme 2). Treatment of **9** with Na in liquid NH_3 in the presence of *t*-BuOH (3 equiv) gave the 7β-hydroxy compound **10** as the sole product. Hydrolysis of the acetal function of **10** and subsequent treatment with MeLi afforded the diol **11**.[22] Finally, the secondary alcohol group of **11** was converted into a mesylate group to afford compound **2** in 34% overall yield from **7**.

For the synthesis of the mesylates **3** and **4**, the double bond of **9** was reduced with Li in liquid NH_3 at reflux temperature (Scheme 3). The resulting ketone **12** was treated with an excess of MeMgI and then with HCl to afford predominantly the keto alcohol **13**. The stereochemistry of the hydroxyl group at C(7) in **13** was confirmed by X-ray crystallography.[23] After reduction of **13** with LAH and subsequent treatment with MsCl, the mesylate **3** was obtained in 66% overall yield from **9**. Reduction of **13** with L-Selectride (Aldrich) and mesylation of the resulting diol gave the mesylate **4** in 61% overall yield from **9**. Treatment of **3** and **4** with TMSCl

(11) (a) Adcock, W.; Coope, J.; Shiner, V. J., Jr.; Trout, N. A. *J. Org. Chem.* **1990**, *55*, 1411. (b) Lambert, J. B.; Salvador, L. A.; So, J.-H. *Organometallics* **1993**, *12*, 697.

(12) An electrofugal group can act as an electron donor in heterolytic fragmentation and splits off without the bonding electron pair: Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535.

(13) It has been demonstrated that an alcoholate group is a very active electrofuge in both the Wharton fragmentation[3] and the base-induced homofragmentation of 1,4-diol monosulfonate esters in apolar solvents like benzene or toluene.[6a−c]

(14) This structural feature guarantees that (a) the extent of orbital interactions through σ-bonds is maximized and (b) the five σ-bonds involved are properly aligned for fragmentation. See: (a) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395. (b) Reference 11b.

(15) In general, fragmentations that lead to ketones occur more readily than those producing aldehydes.[3]

(16) Fragmentation products containing more highly substituted olefins are more easily formed than those containing less highly substituted olefins. See ref 3 and ref 9c, p 7.

(17) The numbering system for the cholestane derivatives used in this study follows the original steroid numbering.

(18) Davies, A. R.; Summers, G. H. R. *J. Chem. Soc. C* **1967**, 1227.

(19) The stereochemistry of the hydroxyl group at C(7) could not be established by NMR measurements. Since in the Grignard reaction of **12** the favored attack of the reagent is from the β-side (see Scheme 3), a similar preferential approach is assumed to occur in the Grignard reaction leading to **1**.

(20) Woodward, R. B.; Patchett, A. A.; Barton, D. H. R.; Ives, D. A. J.; Kelly, R. B. *J. Chem. Soc.* **1957**, 1131.

(21) Parish, E. J.; Wei, T.-Y. *Synth. Commun.* **1987**, *17*, 1227.

(22) The stereochemistry of the hydroxyl group at C(3) could not be established by NMR measurements. Since the nucleophilic addition of MeLi to cholestan-2-one and 4a-methyl-*trans*-2-decalone at −78 °C proceeds preferentially from the equatorial β-side, the stereochemistry at C(3) was tentatively assigned as given in structure **11**. See: Macdonald, T. L.; Clark Still, W. *J. Am. Chem. Soc.* **1975**, *97*, 5280 and references cited therein. In this context, it is important to note that the reactivity of 1,4-diol monosulfonate esters upon treatment with sodium *tert*-amylate in refluxing benzene is not affected by the orientation of the hydroxyl group.[6b]

(23) Kooijman, H.; Spek, A. L. Manuscript in preparation.

Scheme 3

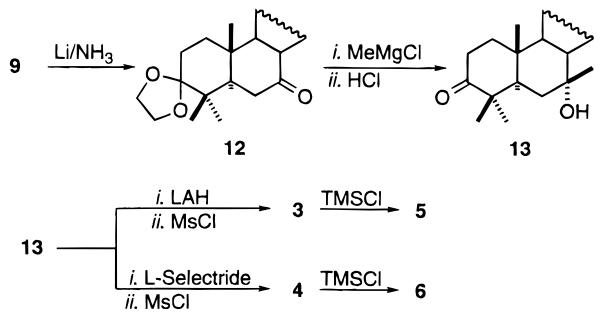
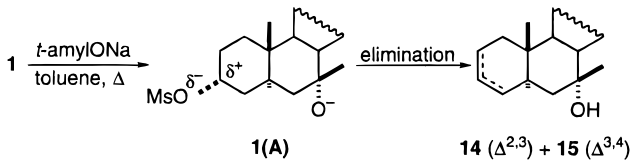


Table 1. Reactions of the Mesylates 1−6 with Sodium *tert*-Amylate[a]

entry	mesylate	products (%)[b]	recovery[c]
1	**1**	**14** (4)[d] + **15** (3)[d]	75
2	**2**	**16** (3) + **17** (6)[d] + **18** (32)[d]	51
3	**3**	**19** (20) + **20** (13) + **21** (22) + **22** (6)	17
4	**4**	**23** (6)[d] + **24** (48) + **25** (21)[d]	2
5	**5**	− (17)[e]	66
6	**6**	**26** (13)[d] + **27** (14)[d]	58

[a] All reactions were performed in refluxing toluene with ca. 5 equiv of sodium *tert*-amylate for 10 min. [b] Yield in parentheses. [c] Percentage of recovered starting material. [d] The yield of this product is based on NMR analysis. [e] Inseparable mixture of five probably olefinic compounds.

Scheme 4



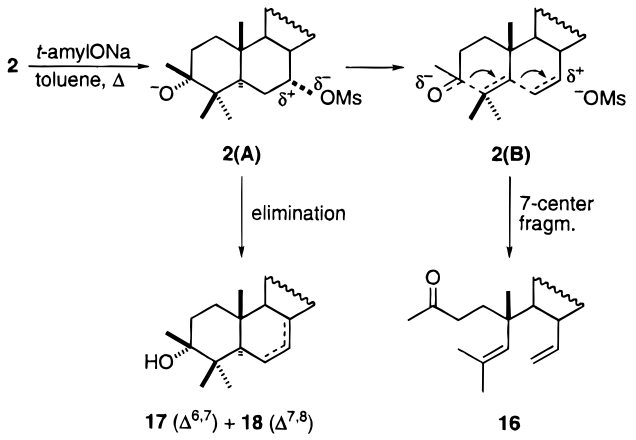
and HMDS afforded the corresponding O-silylated mesylates **5** and **6**, respectively, in high yields.

In order to obtain comparable data about the reactivity of the mesylates **1**−**6**, all reactions were run in refluxing toluene[24] with ca. 5 equiv of sodium *tert*-amylate for 10 min. Comparison of the quantities of recovered starting material gave a rough estimate of the relative reaction rates.[25] The results of these studies are collected in Table 1.

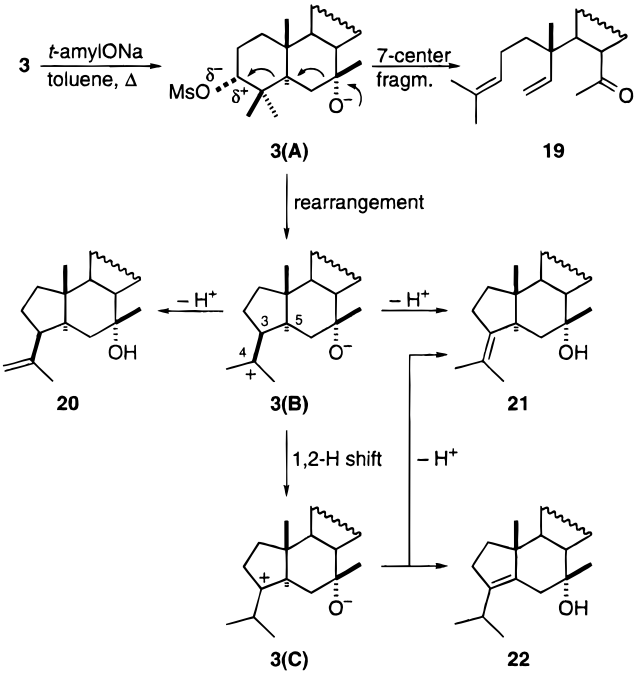
The reaction of the mesylate **1**[26] gave a small amount (7%) of an inseparable ca. 3:2 mixture of the olefins **14** and **15**, respectively, together with 75% of recovered starting material (entry 1, Scheme 4). In the ^{1}H NMR spectrum of the mixture, the olefinic signals of the major olefin **14** appear as a broad singlet ($W_{1/2} \approx 5$ Hz) at δ 5.59, while the corresponding signals of the minor olefin **15** resonate at δ 5.20 (br dd, $J = 2.2$, 10.0 Hz, 1 H) and 5.56 (m, 1 H). Similar differences in splitting pattern and chemical shift have been reported for the signals of the olefinic protons of 5α-cholest-2-ene and 5α-cholest-3-ene.[27]

The mesylate **2** reacted slightly faster than **1**, as follows from the lesser amount (51%) of recovered starting material, and afforded a small quantity (3%) of the fragmentation product **16**[28] together with an inseparable ca. 1:5 mixture (38%) of the olefins **17** and **18**, respectively (entry 2, Scheme 5). The NMR spectral data of **16** are fully consistent with the structure given in Scheme 5. Although the reaction pathway to **16** is only a minor side reaction, it is, to the best of our knowledge, the first example of a seven-center fragmentation over five single bonds in unstrained compounds.

Scheme 5



Scheme 6



The mesylate **3** reacted considerably faster than the mesylates **1** and **2** (17% of **3** was regained) (entry 3, Scheme 6). Four compounds were formed in this reaction: the seven-center fragmentation product **19** (20%)[28] and the olefins **20**, **21**, and **22** in 13, 22, and 6% yields, respectively. Also, in this case the NMR spectral data of the seven-center fragmentation product **19** are fully consistent with the assigned structure.

The mesylate **4** reacted the fastest of all the compounds studied. After the standard treatment, only a small amount of starting material (2%) could be regained (entry

(24) Toluene as solvent was preferred over benzene because it was expected that the reactivity of the mesylates studied would be moderate.

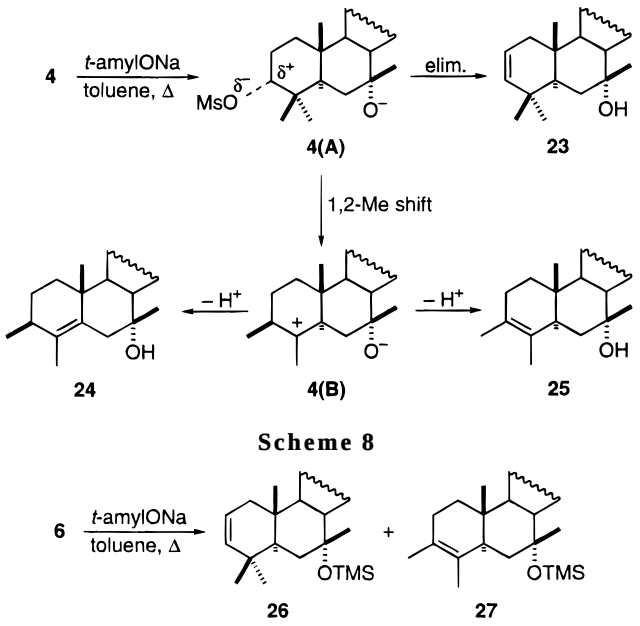
(25) The percentages of recovered starting material were somewhat lowered (up to 7%) by competing S−O bond scission.

(26) Treatment of (3β,5α,7α)-cholestane-3,7-diol 3-methanesulfonate with sodium *tert*-amylate in refluxing toluene afforded a complex mixture of products, probably as a result of alkoxide-induced intermolecular hydride shifts.[6c]

(27) Cragg, G. M. L.; Davey, C. W.; Hall, D. N.; Meakins, G. D.; Richards, E. E.; Whateley, T. L. *J. Chem. Soc. C* **1966**, 1266.

(28) It might be possible that the yield of this product was somewhat diminished due to aldol condensations under the influence of sodium *tert*-amylate.[6a]

Scheme 7



Scheme 8

4, Scheme 7). As products, the three olefins **23**, **24**, and **25** in a ratio of 1:8:3.5, respectively, were obtained. Column chromatography gave pure **24** (48%) and an inseparable mixture (27%) of **23** and **25**.

Compared with the mesylates **3** and **4**, the corresponding O-silylated mesylates **5** and **6** reacted more slowly (entries 5 and 6). The quantities of recovered starting material (66 and 58%, respectively) suggest that **6** reacts slightly faster than **5**. On the other hand, the product compositions are noticeably different. Whereas **5** produced a complex mixture (ca. 17%) of at least five olefinic compounds, **6** only gave two products: the $\Delta^{2,3}$ olefin **26** (13%) and the rearranged olefin **27** (14%) (Scheme 8).

The results collected in Table 1 clearly show that Me substitution at C(4) leads to an increase in reaction rate (entries 1−3). The occurrence of different product-forming pathways in the reactions of **1**−**3** can be connected with the presence (or absence) of Me substituents as well. Furthermore, it is evident that alkoxide formation is also important for the reactivity of these compounds as can be concluded from the differences in reaction rate between **3** and **5** and between **4** and **6** (entries 3−6). These observations have led to the assumption that the mesylates **1**−**4** react by a mechanism which is comparable with that proposed for the 1,4-diol monosulfonate esters.[6] This means that **1**−**4** will react via dipolar intermediates with intramolecular alkoxide-induced heterolysis of the mesylate bond as the rate-determining step. The dipolar intermediates in turn may undergo typical cationic reactions such as elimination, rearrangement, 1,2-Me shift, and/or fragmentation. The product compositions and reaction rates found for **1**−**4** are easily understood on this basis.

The equatorial mesylate **1**, which is supposed to react via the intermediate **1(A)**, undergoes a 1,2-elimination as the sole product-forming pathway (Scheme 4). The relatively slow formation of the olefins **14** and **15** suggests that intermediate **1(A)** is not very effectively stabilized by TBI.

The enhanced reactivity of mesylate **2**, compared with that of **1**, indicates that in intermediate **2(A)** the carbocationic center on C(7) is better stabilized than the one on C(3) in **1(A)** (Scheme 5). The higher degree of stabilization of **2(A)** can be attributed to enhanced σ-participation[6d,29] as result of the presence of the C(8)−C(14) bond next to the carbocationic center on C(7). It might be possible that the electron-donating Me substituents at C(4) also participate in the stabilization of **2(A)** by enlargement of the electron density of the σ-relay. Combined with the enhanced stability of the carbocation, this inductive donation will favor the reaction pathway leading to fragmentation via the double hyperconjugatively stabilized intermediate (or transition state) **2(B)**.[30] The formation of a small amount of fragmentation product **16** in the reaction of **2** can be attributed to this effect. Elimination leading to **17** and **18**, however, remains the main reaction pathway as the elimination: fragmentation ratio (ca. 13:1 in favor of elimination) indicates.

The difference in reaction rate found for the mesylates **2** and **3** can be explained similarly (Scheme 6). Stabilization by σ-participation will be more effective in **3(A)** than in **2(A)** because the C(4) atom adjacent to the carbocationic center in **3(A)** bears *two* alkyl substituents (Me groups), whereas in **2(A)** only *one* alkyl substituent, i.e., the C(8)−C(14) bond, is present next to the carbocationic center. In addition, cationic carbon atoms are better stabilized by alkyl substituents located at the α-position (as in **3(A)**) than by alkyl substituents at the γ-position (as in **2(A)**).[31] Consequently, TBI will be more effective in **3(A)** than in **2(A)**, which finds expression in the reactivity order **3** > **2** and the relatively high yield (20%) of the seven-center fragmentation product **19**.

The other compounds (**20**, **21**, and **22**) found in the reaction of **3** must be formed via rearrangement of the initially formed intermediate **3(A)** to the thermodynamically more stable intermediate **3(B)**. This tertiary carbocationic intermediate can undergo proton loss to give the olefins **20** and **21** but can also react further by way of a 1,2-H shift (C(3) → C(4)) to afford another tertiary intermediate (**3(C)**), which in turn can give additional **21** and the olefin **22**, the latter probably as the result of an intramolecularly assisted deprotonation.[32] The formation of **22** can only proceed stepwise, because a concerted mechanism starting from **3(B)** is not allowed for stereochemical reasons (both H-3 and H-5 have the α-orientation). It might be possible that **3(C)** is somewhat better stabilized than **3(B)**, because in **3(C)** the number of σ-bonds between the alcoholate function and the carbocationic center is reduced by one.[33]

The main reason for examining mesylate **4** was to find out to what extent an axially positioned leaving group influences the rate and course of these TBI-induced reactions. Seven-center fragmentation was not expected in this reaction because the required antiperiplanar relationship between the leaving group and the C(4)−C(5) bond is lacking.[11b] Instead, it was expected that a 1,2-Me shift would be the main reaction pathway since both the leaving mesylate group and the β-Me group at C(4) are axially positioned. The formation of the rear-

(29) (a) Jensen, F. R.; Smart, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 5686. (b) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715.

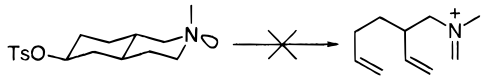
(30) Enhanced TBI should lead to increased fragmentation.[10]

(31) Bielmann, R.; Grob, C. A.; Küry, D.; Wei Yao, G. *Helv. Chim. Acta* **1985**, *68*, 2158.

(32) Since intramolecular alkoxide-assisted elimination is a highly favorable process,[6a] the formation of **21** from intermediate **3(C)** via an intermolecular proton abstraction will only be a minor reaction pathway.

(33) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575.

Scheme 9



ranged olefins **24** and **25** in which the intermediates **4(A)** and **4(B)** should be involved corresponds with this expectation (Scheme 7). Again, intramolecular deprotonation (48% of **24**) is preferred over intermolecular deprotonation (21% of **25**). An intermolecular antielimination explains the formation of olefin **23** from **4(A)**.

Finally, it is of interest to note that **4** reacts somewhat faster than **3**. According to the trans rule, one should expect the reverse order because of the all-trans arrangement of the σ-relay present in **3**.[14a] In order to explain this discrepancy, the results of the reactions of **3** and **4** are compared with those of the O-silylated mesylates **5** and **6**. These silyl ethers show a similar reactivity order as that found for **3** and **4**, i.e., compound **6** with an axial mesylate group reacts slightly faster than **5** in which an equatorial mesylate group is present. It is known that the tosylate esters of 4,4-dimethylcholestan-3α-ol and the 3β-epimer both react by an E1-like mechanism upon treatment with sodium *tert*-amylate in refluxing benzene.[34] Moreover, the 3α-epimer reacts two to three times faster than the 3β-epimer,[35] which can be attributed to relief of steric strain. A similar E1-like mechanism may also be operative in the closely related mesylates **5** and **6**, which are supposed to react *without* involvement of long-range orbital interactions.[6a] In contrast to **5** and **6**, the structurally related O-silylated trans-fused perhydronaphthalene-1,4-diol mesylates (equatorial and axial) lacking the Me groups at C(4) do not react at all under similar reaction conditions.[6a] Thus, the relatively high reactivity of **5** and **6** and their product composition can be associated with the steric and/or electronic effects of the Me groups at C(4). On the basis of these facts, it is assumed that the mesylates **3** and **4** also react via an E1-like mechanism but now *with* participation of TBI since both **3** and **4** react faster than their respective O-silylated analogs **5** and **6**. The influence of Me groups at C(4) will predominate over TBI in **3** and **4** because of the large distance between the alcoholate group and the mesylate ester.[33] On the other hand, it will be clear that the additional stabilization of the carbocationic intermediates by TBI is somewhat more pronounced in **3(A)** than in **4(A)** (trans rule), which finds expression in the formation of the seven-center fragmentation product **19** in the reaction of **3**.

The results of this study provide a good explanation for the nonoccurrence of fragmentation products in the solvolysis of the ϵ-amino tosylate studied by Grob et al. (Scheme 9).[8] In spite of the proper alignment of the σ-bonds, the absence of two alkyl substituents next to the carbon atom bearing the tosylate group and the presence of a weakly electron-donating alkylated amino group in this *trans*-perhydroisoquinoline system make seven-center fragmentation an unfavorable process, and only substitution will take place as Grob et al. found experimentally.

Concluding Remarks

These results clearly indicate that an alkoxide function can assist in the formation of a carbocationic center via TBI over *five* σ-bonds. However, the reaction course is not solely determined by these interactions and typical E1-like processes come into play, this in contrast to the previously studied 1,4-diol monosulfonate esters[6] where TBI over *four* σ-bonds is considered to be the main factor determining the reaction behavior of these compounds. Nevertheless, the involvement of through-five-bond interactions is reflected by the occurrence of seven-center fragmentation in the reactions of 1,5-diol monosulfonate esters in which the five σ-bonds are held in the all-trans geometry. The presence of alkyl substituents, especially on the α-position, which results in enhanced σ-participation is also a prerequisite for allowing seven-center fragmentation. The occurrence of seven-center fragmentation also supports Grob's view that the enhanced solvolysis rates of the 4-substituted bicyclo[2.2.2]octylsulfonate esters mentioned in the Introduction may be due to double hyperconjugation.[8,31] The synthetic value of this fragmentation reaction is limited because other more favorable reaction pathways, i.e., elimination and rearrangement, are preferred.

Though the occurrence of long-range orbital interactions through five σ-bonds still enhances the reaction rate of *1,5-diol* monosulfonate esters in comparison with systems that lack these interactions, a dramatic decrease in reaction rate is found with respect to the *1,4-diol* monosulfonate esters. In our opinion, the ability of an alcoholate function to induce intramolecularly the heterolysis of a remote sulfonate ester group has reached its limit with the 1,5-diol monosulfonate esters.

Experimental Section[36]

Materials. All reagents were purchased from Aldrich or Janssen and were used without further purification unless otherwise stated. A stock solution of sodium *tert*-amylate (3.2 M in toluene) was prepared by the procedure of Conia[37] and stored under an Ar atmosphere in a refrigerator. (3β,5α)-3-Hydroxycholestan-7-one[18] and 4,4-dimethylcholest-5-en-3-one (**7**)[20] were prepared following previously described procedures.

(3β,5α)-3-Hydroxycholestan-7-one Methanesulfonate. To a stirred solution of 2.80 g (6.95 mmol) of (3β,5α)-3-hydroxycholestan-7-one in 2.8 mL of dry pyridine was added 2.60 g (22.7 mmol) of MsCl. The reaction mixture was stirred at rt for 18 h and then poured into H_2O. The aqueous layer was extracted with $CHCl_3$ and washed successively with 5% HCl, water, 10% $KHCO_3$, and brine. After the product was dried and the solvent was evaporated, crystallization from $CHCl_3$/ether afforded 1.60 g (45%) of pure (3β,5α)-3-hydroxycholestan-7-one methanesulfonate: mp 167−168 °C; ^{1}H NMR δ 0.62 (s, 3 H), 0.75−2.43 (m, 29 H), 0.83 (d, J = 6.4 Hz, 6 H), 0.88 (d, J = 6.5 Hz, 3 H), 1.08 (s, 3 H), 2.98 (s, 3 H), 4.56 (m, 1 H); ^{13}C NMR δ 11.65 (q), 12.02 (q), 18.74 (q), 21.79 (t), 22.53 (q), 22.78 (q), 23.73 (t), 24.91 (t), 27.94 (d), 28.34 (2t), 34.84 (t), 35.60 (d), 35.65 (s), 35.72 (t), 36.08 (t), 38.58 (t), 38.72 (q), 39.41 (t), 42.44 (s), 45.59 (t), 46.37 (d), 48.79 (d), 49.86 (d), 54.70 (d), 54.95 (d), 80.61 (d), 211.04 (s); MS m/z (relative intensity) 480 (M^+, 22), 385 (10), 384 (21), 358 (30), 357 (100), 356 (17), 272 (11), 253 (9); HRMS calcd for $C_{28}H_{48}O_4S$ (M^+) 480.3273, found 480.3273. Anal. Calcd for $C_{28}H_{48}O_4S$: C, 69.95; H, 10.06. Found: C, 70.02; H, 10.21.

(3β,5α,7α)-7-Methylcholestane-3,7-diol 3-Methanesulfonate (1). To a stirred solution of 0.230 g (0.48 mmol) of

(34) Levisalles, J.; Pète, J.-P. *Bull. Soc. Chim. Fr.* **1967**, 3747.
(35) Arad, A.; Levisalles, J. *Bull. Soc. Chim. Fr.* **1972**, 1135.

(36) For a general description of the experimental procedures employed in this research, see ref 5. All NMR spectra were taken in $CDCl_3$ unless noted otherwise. Column chromatography was performed using Merck Silica Gel 60 (70-230 mesh). GC analysis was carried out with FID and a DB-5MS fused silica column, 15 m × 0.25 mm i.d., film thickness 0.10 μm, and H_2 as the carrier gas. For GC−MS analysis the same DB-5MS column was used.
(37) Conia, M. J.-M. *Bull. Soc. Chim. Fr.* **1950**, *17*, 537.

(3β,5α)-3-hydroxycholestan-7-one methanesulfonate in 50 mL of dry ether was added 0.48 mL (0.96 mmol) of MeMgI (2.0 M in ether) at once at 0 °C. The reaction mixture was stirred for 1 min and then carefully quenched with a small amount of saturated aqueous NH_4Cl. After the addition of 15 mL of H_2O, the two-phase mixture was separated, and the organic layer was washed with 10 mL of brine, dried, and evaporated. The remaining residue was flash chromatographed (3:1 petroleum ether (bp 40−60 °C)/EtOAc) to give 0.080 g of unreacted starting material and 0.101 g (42%) of **1**: ^{1}H NMR δ 0.66 (s, 3 H), 0.77 (s, 3 H), 0.80−2.05 (m, 30 H), 0.85 (d, J = 6.3 Hz, 6 H); 0.83 (d, J = 6.5 Hz, 3 H), 1.23 (s, 3 H); 2.97 (s, 3 H), 4.60 (m, 1 H); ^{13}C NMR δ 11.42 (q), 12.24 (q), 18.81 (q), 21.60 (t), 22.54 (q), 22.78 (q), 23.72 (t), 27.96 (d), 27.96 (t), 28.52 (t), 28.76 (t), 32.08 (q), 34.46 (t), 34.86 (s), 35.64 (d), 36.07 (t), 36.95 (t), 38.40 (d), 38.66 (q), 39.46 (t), 39.76 (t), 44.01 (s), 44.28 (d), 45.04 (t), 49.47 (d), 51.34 (d), 54.98 (d), 72.32 (s), 82.00 (d); MS m/z (relative intensity) 481 (M^+ − 15, 18), 385 (19), 383 (19), 367 (17), 332 (30), 256 (22), 97 (67), 83 (88), 69 (100), 55 (78); HRMS calcd for $C_{28}H_{49}O_4S$ (M^+ − 15) 481.3352, found 481.3353. Anal. Calcd for $C_{29}H_{52}O_4S$: C, 70.11; H, 10.55. Found: C, 70.30; H, 10.75.

4′,4′-Dimethylspiro[1,3-dioxolane-2,3′-cholest-5′-ene] (8). A solution of 8.00 g (19.4 mmol) of **7**, 0.347 g of camphorsulfonic acid, and 11 mL of ethylene glycol in 300 mL of toluene was refluxed in the flask equipped with a Dean−Stark column packed with 4 Å molecular sieves for 16 h, cooled, and poured into 100 mL of saturated aqueous $NaHCO_3$. The two-phase mixture was separated, and the aqueous layer was extracted with three 100 mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (25:1 petroleum ether (bp 40−60 °C)/EtOAc) to yield 8.14 g (92%) of **8**: ^{1}H NMR δ 0.66 (s, 3 H), 0.85 (d, J = 6.7 Hz, 6 H), 0.90−2.18 (m, 26 H), 0.91 (d, J = 6.5 Hz, 3 H), 1.03 (s, 3 H), 1.12 (s, 3 H), 1.22 (s, 3 H), 3.87−4.03 (m, 4 H), 5.52 (m, 1 H); ^{13}C NMR δ 11.83 (s), 18.66 (q), 20.53 (t), 21.66 (q), 22.36 (q), 22.53 (q), 22.79 (q), 23.79 (t), 24.16 (t), 26.81 (t), 27.98 (d), 28.25 (t), 29.81 (q), 30.87 (d), 32.31 (t), 35.24 (t), 35.76 (d), 36.16 (t), 36.24 (q), 39.49 (t), 39.71 (t), 42.19 (s), 44.79 (s), 50.55 (d), 55.95 (d), 57.17 (d), 64.84 (t), 65.20 (t), 113.19 (s), 119.90 (d), 149.64 (s); MS m/z (relative intensity) 456 (M^+, 3), 412 (2), 356 (1), 124 (2), 107 (1), 100 (5), 99 (100), 95 (1), 87 (1), 55 (2); HRMS calcd for $C_{31}H_{52}O_2$ (M^+) 456.3967, found 456.3967. Anal. Calcd for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 81.69; H, 11.71.

4′,4′-Dimethylspiro[1,3-dioxolane-2,3′-cholest-5′-en-7′-one] (9). To a stirred solution of 8.14 g (17.9 mmol) of **8** and 1.00 g of 3 Å molecular sieves in 400 mL of dry pyridine was added 80.0 g of PDC. The reaction mixture was heated at reflux for 2 h, cooled, and then poured into 750 mL of brine. The aqueous layer was extracted with six 250 mL portions of CH_2Cl_2, and the combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (25:1 petroleum ether (bp 40−60 °C)/EtOAc) to yield 7.29 g (87%) of **9**: ^{1}H NMR δ 0.67 (s, 3 H), 0.84 (d, J = 6.7 Hz, 6 H), 0.90 (d, J = 6.5 Hz, 3 H), 0.90−2.40 (m, 24 H), 1.06 (s, 3 H), 1.31 (s, 3 H), 1.32 (s, 3 H), 3.87−4.03 (m, 4 H), 5.88 (s, 1 H); ^{13}C NMR δ 11.90 (q), 18.80 (q), 20.13 (q), 20.81 (t), 21.50 (q), 22.51 (q), 22.79 (q), 23.81 (t), 26.39 (t), 26.56 (t), 27.96 (d), 28.32 (q), 28.54 (t), 34.18 (t), 35.76 (d), 36.13 (t), 37.94 (s), 38.82 (t), 39.43 (t), 43.34 (s), 45.21 (d), 45.86 (s), 50.70 (d), 51.56 (d), 54.77 (d), 65.00 (t), 65.30 (t), 112.20 (s), 124.88 (d), 175.78 (s), 202.79 (s); MS m/z (relative intensity) 470 (M^+, 2), 455 (1), 149 (1), 100 (4), 99 (100), 69 (2), 57 (1), 55 (3), 43 (1); HRMS calcd for $C_{31}H_{50}O_3$ (M^+) 470.3760, found 470.3757. Anal. Calcd for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71. Found: C, 79.29; H, 10.90.

(5′α,7′β)-4′,4′-Dimethylspiro[1,3-dioxolane-2,3′-cholestan-7′-ol] (10). To a stirred solution of 1.60 g (69.6 mmol) of Na in 200 mL of refluxing liquid NH_3 was added dropwise a solution of 2.18 g (4.64 mmol) of **9** and 1.03 g (13.9 mmol) of *t*-BuOH in 50 mL of THF. After the addition was complete, the reaction mixture was stirred at reflux temperature for 1 h, and then 10.0 g of solid NH_4Cl was added. NH_3 was allowed to evaporate overnight, and 100 mL of H_2O was cautiously added to the residue. The aqueous phase was extracted with five 100 mL portions of ether. The combined organic layers were dried and evaporated, and the resulting product was flash chromatographed (10:1 petroleum ether (bp 40−60 °C)/EtOAc) to give 1.75 g (80%) of **10**: ^{1}H NMR δ 0.60−2.03 (m, 28 H), 0.63 (s, 3 H), 0.80 (s, 3 H), 0.81 (s, 3 H), 0.84 (s, 3 H), 0.87 (d, J = 7.1 Hz, 3 H), 0.91 (d, J = 6.7 Hz, 6 H), 3.32 (m, $W_{1/2}$ = 15 Hz, 1 H), 3.80−4.02 (m, 4 H); ^{13}C NMR δ 12.05 (q), 14.29 (q), 18.74 (q), 19.90 (q), 20.77 (t), 22.49 (q), 22.76 (2q), 23.81 (t), 26.90 (t), 27.02 (t), 27.93 (d), 28.68 (t), 31.39 (t), 35.62 (d), 35.64 (s), 35.72 (t), 36.15 (t), 39.45 (t), 39.81 (t), 41.88 (s), 43.02 (d), 43.14 (s), 49.68 (d), 53.84 (d), 55.14 (d), 55.76 (d), 64.72 (t), 64.83 (t), 76.14 (d), 113.08 (s); MS m/z (relative intensity) 474 (M^+, 2), 431 (2), 109 (1), 100 (9), 99 (100), 95 (2), 81 (2), 69 (2), 55 (2), 43 (1); HRMS calcd for $C_{31}H_{54}O_3$ (M^+) 474.4073, found 474.4070. Anal. Calcd for $C_{31}H_{54}O_3$: C, 78.42; H, 11.47. Found: C, 78.60; H, 11.68.

(3α,5α,7β)-3,4,4-Trimethylcholestane-3,7-diol (11). To a stirred solution of 0.867 g (1.84 mmol) of **10** in 200 mL of acetone was added 4 mL of 4 N HCl. The reaction mixture was stirred at rt for 3 h and then neutralized with 10 mL of saturated aqueous $NaHCO_3$. After concentration under reduced pressure, the remaining aqueous solution was extracted with 50 mL of CH_2Cl_2. The organic layer was washed with 15 mL of brine, dried, and evaporated. The so-obtained crude (5α,7β)-7-hydroxy-4,4-dimethylcholestan-3-one (0.777 g, 99%) was dissolved in 30 mL of THF and cooled to −78 °C. After addition of 5.7 mL of 1.6 M MeLi, the reaction mixture was stirred at −78 °C for 10 min and allowed to warm to rt over a 2 h period. The excess of MeLi was then cautiously destroyed with a small amount of saturated aqueous NH_4Cl. After dilution with 25 mL of ether, the organic layer was washed with 10 mL of brine, dried, and evaporated. The remaining residue[38] was flash chromatographed (5:1 petroleum ether (bp 40−60 °C)/EtOAc) to give 0.469 g (57%) of pure **11**: ^{1}H NMR δ 0.64 (s, 3 H), 0.65 (m, 1 H), 0.72−1.92 (m, 27 H), 0.83 (s, 3 H), 0.84 (d, J = 6.1 Hz, 6 H), 0.88 (s, 3 H), 0.89 (s, 3 H), 0.89 (d, J = 6.3 Hz, 3 H), 1.17 (s, 3 H), 1.98 (m, 1 H), 3.34 (ddd, J = 5.4, 10.4, 10.4 Hz, 1 H); ^{13}C NMR δ 12.06 (q), 14.67 (q), 18.75 (q), 18.82 (q), 20.74 (t), 22.50 (q), 22.75 (q), 23.07 (q), 23.83 (t), 24.36 (q), 26.88 (t), 27.95 (d), 28.69 (t), 31.84 (t), 34.20 (t), 35.63 (d), 36.15 (t), 36.30 (s), 36.45 (t), 39.44 (t), 39.79 (t), 40.71 (s), 43.02 (d), 43.44 (s), 49.63 (d), 54.52 (d), 55.20 (d), 55.76 (d), 75.05 (s), 76.33 (d); MS m/z (relative intensity) 446 (M^+, 2), 428 (5), 375 (18), 374 (28), 358 (38), 357 (100), 149 (19), 123 (13), 122 (10), 95 (12); HRMS calcd for $C_{30}H_{54}O_2$ (M^+) 446.4138, found 446.4127. Anal. Calcd for $C_{30}H_{54}O_2$: C, 80.65; H, 12.18. Found: C, 80.65; H, 11.93.

(3α,5α,7β)-3,4,4-Trimethylcholestane-3,7-diol 7-Methanesulfonate (2). To a solution of 0.439 g (0.98 mmol) of **11** in 20 mL of dry pyridine was added 0.200 g (1.75 mmol) of MsCl. The reaction mixture was stirred at rt overnight and then concentrated under reduced pressure. The resulting residue was taken up in 50 mL of EtOAc and washed successively with two 15 mL portions of saturated aqueous $NaHCO_3$ and one 15 mL portion of brine. The organic layer was dried and evaporated, and the remaining residue was flash chromatographed (5:1 petroleum ether (bp 40−60 °C)/EtOAc) to give 0.487 g (94%) of **2**: ^{1}H NMR δ 0.63 (s, 3 H), 0.64−1.94 (m, 26 H), 0.82 (s, 3 H), 0.85 (s, 3 H), 0.86 (d, J = 7.7 Hz, 6 H), 0.87 (d, J = 7.7 Hz, 3 H), 0.90 (s, 3 H), 1.23 (s, 3 H), 1.98 (m, 1 H), 2.20 (m, 1 H), 2.99 (s, 3 H), 4.47 (ddd, J = 5.5, 10.6, 10.6 Hz, 1 H); ^{13}C NMR δ 11.98 (q), 14.54 (q), 18.75 (q), 18.89 (q), 20.80 (t), 22.53 (q), 22.78 (q), 23.08 (q), 23.72 (t), 24.26 (q), 25.97 (t), 27.94 (d), 28.50 (t), 29.87 (t), 33.97 (t), 35.52 (d), 35.91 (t), 36.04 (t), 36.18 (s), 39.34 (t), 39.40 (t), 40.00 (q), 40.30 (d), 40.77 (s), 43.43 (s), 49.37 (d), 54.58 (d), 54.77 (d), 55.07 (d), 74.86 (s), 86.54 (d); MS m/z (relative intensity) 428 (M^+ − 96, 47), 411 (30), 410 (71), 395 (27), 358 (54), 357 (100), 274 (22), 149 (26), 135 (21), 95 (25); HRMS calcd for $C_{30}H_{52}O$ (M^+ − 96) 428.4018, found 428.4019. Anal. Calcd for $C_{31}H_{56}O_4S$: C, 70.94; H, 10.76. Found: C, 70.88; H, 11.18.

(5′α)-4′,4′-Dimethylspiro[1,3-dioxolane-2,3′-cholestan-

(38) The NMR spectrum of this crude product revealed the presence of unreacted (5α,7β)-7-hydroxy-4,4-dimethylcholestan-3-one (~30%) and, probably, the C(3) epimer of **11** (~10%).

7′-one] (12). A solution of 2.58 g (5.48 mmol) of **9** and 0.425 g (5.74 mmol) of *t*-BuOH in 50 mL of THF was added dropwise to a stirred solution of 0.515 g (74.6 mmol) of Li in 200 mL of liquid NH_3 at reflux temperature. After the addition was complete, stirring was continued for 10 min, and 10.0 g of solid NH_4Cl was added. Workup as described for the synthesis of **10** was followed by flash chromatography (10:1 petroleum ether (bp 40−60 °C)/EtOAc) to yield 2.33 g (90%) of **12**: ^{1}H NMR δ 0.61 (s, 3 H), 0.78 (s, 3 H), 0.80−2.44 (m, 27 H), 0.83 (d, J = 6.5 Hz, 6 H), 0.87 (d, J = 7.7 Hz, 3 H), 0.96 (s, 3 H), 1.12 (s, 3 H), 3.80−3.98 (m, 4 H); ^{13}C NMR δ 11.99 (q), 13.66 (q), 18.75 (q), 19.53 (q), 21.12 (t), 22.51 (q), 22.57 (q), 22.75 (q), 23.72 (t), 25.09 (t), 27.04 (t), 27.94 (d), 28.39 (t), 34.89 (t), 35.61 (d), 36.10 (t), 36.73 (s), 38.57 (t), 39.43 (t), 39.82 (t), 42.36 (s), 42.60 (s), 48.90 (d), 49.56 (d), 53.89 (d), 54.88 (d), 55.66 (d), 64.92 (2t), 112.66 (s), 212.71 (s); MS m/z (relative intensity) 472 (M^+, 1), 457 (1), 169 (1), 131 (1), 121 (1), 119 (2), 107 (1), 100 (10), 99 (100), 69 (3); HRMS calcd for $C_{31}H_{52}O_3$ (M^+) 472.3916, found 472.3915. Anal. Calcd for $C_{31}H_{52}O_3$: C, 78.76; H, 11.09. Found: C, 78.96; H, 11.32.

(5α,7α)-7-hydroxy-4,4,7-trimethylcholestan-3-one (13). To a stirred solution of 2.31 g (4.89 mmol) of **12** in 50 mL of dry ether was added 7.0 mL (18.2 mmol) of MeMgI (2.6 M in ether) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at rt for an additional 1 h. The excess of MeMgI was then 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 crude product was treated with HCl in acetone as described for the synthesis of **11**. After workup, the crude product was purified by flash chromatography (10:1 petroleum ether (bp 40−60 °C)/ EtOAc) to give 1.75 g (81%) of **13**: ^{1}H NMR δ 0.67 (s, 3 H), 0.84 (d, J = 6.5 Hz, 6 H), 0.91 (d, J = 6.6 Hz, 3 H), 0.95−2.05 (m, 26 H), 1.00 (s, 3 H), 1.02 (s, 3 H), 1.05 (s, 3 H), 1.30 (s, 3 H), 2.31 (m, 1 H), 2.62 (m, 1 H); ^{13}C NMR δ 12.25 (q), 13.16 (q), 18.86 (q), 21.34 (t), 21.72 (q), 22.57 (q), 22.81 (q), 23.70 (t), 25.32 (q), 29.97 (t), 28.01 (d), 28.57 (t), 32.44 (q), 34.75 (t), 35.68 (d), 36.12 (t), 36.26 (s), 38.46 (t), 39.50 (t), 39.58 (t), 39.70 (t), 43.98 (s), 44.00 (d), 47.04 (s), 48.63 (d), 51.11 (d), 51.36 (d), 55.03 (d), 72.46 (s), 216.99 (s); MS m/z (relative intensity) 444 (M^+, 56), 430 (29), 429 (100), 426 (45), 411 (21), 341 (48), 340 (21), 125 (28), 43 (20); HRMS calcd for $C_{30}H_{52}O_2$ (M^+) 444.3967, found 444.3967. Anal. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 80.88; H, 12.06.

(3β,5α,7α)-4,4,7-Trimethylcholestane-3,7-diol 3-Methanesulfonate (3). To a stirred solution of 0.645 g (1.45 mmol) of **13** in 50 mL of dry THF was added 0.080 g (2.11 mmol) of LAH at −78 °C. The reaction mixture was stirred at −78 °C for 2 h and at rt for an additional 30 min. The reaction mixture was then carefully quenched with a small amount of saturated aqueous Na_2SO_4. After addition of 50 mL of CH_2Cl_2, the organic layer was dried and evaporated. The remaining residue was flash chromatographed (5:1 petroleum ether (bp 40−60 °C)/EtOAc) to give 0.643 g (99%) of a diol (^{1}H NMR δ 0.63 (s, 3 H), 0.73−2.00 (m, 29 H), 0.76 (s, 3 H), 0.80 (s, 3 H), 0.84 (d, J = 6.5 Hz, 6 H), 0.89 (d, J = 6.5 Hz, 3 H), 0.94 (s, 3 H), 1.26 (s, 3 H), 3.22 (m, 1 H)). This diol (0.528 g, 1.18 mmol) was treated with MsCl as described for the synthesis of **2**. After workup, the crude product was purified by flash chromatography (5:1 petroleum ether (bp 40−60 °C)/EtOAc) to yield 0.566 g (91%) of **3**: ^{1}H NMR (C_6D_6) δ 0.70 (s, 3 H), 0.71 (s, 3 H), 0.76−2.10 (m, 28 H), 0.84 (s, 3 H), 0.95 (d, J = 6.8 Hz, 6 H), 1.03 (s, 3 H), 1.08 (d, J = 6.4 Hz, 3 H), 1.23 (s, 3 H), 2.38 (s, 3 H), 4.36 (dd, J = 4.5, 11.9 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 12.11 (q), 13.16 (q), 16.09 (q), 18.93 (q), 21.02 (t), 22.48 (q), 22.75 (q), 24.05 (t), 25.63 (t), 27.72 (q), 28.00 (t), 28.11 (d), 28.69 (t), 32.21 (q), 35.86 (d), 36.33 (t), 37.12 (s), 37.12 (t), 37.85 (s), 37.94 (q), 38.83 (t), 39.62 (t), 39.90 (t), 43.76 (d), 43.97 (s), 47.64 (d), 51.01 (d), 51.27 (d), 55.26 (d), 71.67 (s), 89.21 (d); MS m/z (relative intensity) 524 (M^+, 1), 509 (30), 428 (26), 413 (20), 411 (37), 410 (100), 395 (51), 367 (16), 121 (23), 95 (20); HRMS calcd for $C_{31}H_{56}O_4S$ (M^+) 524.3899, found 524.3899. Anal. Calcd for $C_{31}H_{56}O_4S$: C, 70.94; H, 10.76. Found: C, 70.98; H, 10.98.

(3α,5α,7α)-4,4,7-Trimethylcholestane-3,7-diol 3-Methanesulfonate (4). To a solution of 0.608 g (1.37 mmol) of **13** in 25 mL of dry THF was added dropwise 4.1 mL (4.1 mmol) of L-Selectride (1 M in THF) at −78 °C. The solution was stirred at −78 °C for 2 h and allowed to come to rt overnight. The reaction mixture was cooled again to 0 °C and cautiously quenched with 3 mL of EtOH followed by the addition of 3 mL of 4 M NaOH and 3 mL of 35% H_2O_2, and stirring was continued at rt for 6 h. The reaction mixture was then concentrated under reduced pressure, taken up in 50 mL of H_2O, and extracted with four 25 mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated. The remaining residue was treated with MsCl as described for the synthesis of **2**. After workup, the crude product was purified by flash chromatography (5:1 petroleum ether (bp 40−60 °C)/ EtOAc) to yield 0.605 g (84%) of **4**: ^{1}H NMR (C_6D_6) δ 0.70 (s, 6 H), 0.71 (s, 3 H), 0.85−2.06 (m, 28 H), 0.99 (d, J = 6.8 Hz, 6 H), 1.01 (s, 3 H), 1.06 (d, J = 6.6 Hz, 3 H), 1.23 (s, 3 H), 2.36 (s, 3 H), 4.50 (br s, $W_{1/2}$ = 6.3 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 12.12 (q), 13.14 (q), 18.90 (q), 20.86 (t), 21.41 (q), 22.45 (q), 22.69 (q), 24.06 (t), 24.26 (t), 27.99 (t), 28.05 (q), 28.08 (d), 28.61 (t), 32.19 (t), 32.30 (q), 35.81 (d), 36.03 (t), 36.30 (s), 36.62 (s), 37.88 (q), 38.72 (t), 39.61 (t), 39.68 (t), 42.64 (d), 43.71 (s), 44.19 (d), 51.13 (d), 51.25 (d), 55.25 (d), 71.54 (s), 87.09 (d); MS m/z (relative intensity) 524 (M^+, 0.3), 509 (1), 428 (7), 413 (11), 411 (28), 410 (100), 395 (45), 121 (10), 109 (9), 95 (11); HRMS calcd for $C_{31}H_{56}O_4S$ (M^+) 524.3899, found 524.3897. Anal. Calcd for $C_{31}H_{56}O_4S$: C, 70.94; H, 10.76. Found: C, 71.14; H, 11.05.

(3β,5α,7α)-4,4,7-Trimethyl-7-[(trimethylsilyl)oxy]-cholestan-3-ol 3-Methanesulfonate (5). To a stirred solution of 0.217 g (0.41 mmol) of mesylate **3** in 10 mL of dry pyridine were added 0.330 g (2.0 mmol) of hexamethyldisilazane (HMDS) and 0.650 g (6.0 mmol) of TMSCl. The reaction mixture was stirred at 50 °C for 20 h and then neutralized with 10 mL of saturated aqueous $NaHCO_3$. The reaction mixture was concentrated under reduced pressure, and the concentrate was taken up in 50 mL of EtOAc. The organic layer was washed with 25 mL of brine, dried, and evaporated. The remaining residue was flash chromatographed (10:1 petroleum ether (bp 40−60 °C)/EtOAc) to give 0.233 g (95%) of **5**: ^{1}H NMR δ 0.09 (s, 9 H), 0.60 (s, 3 H), 0.75−2.03 (m, 27 H), 0.83 (s, 6 H), 0.85 (d, J = 6.5 Hz, 6 H), 0.89 (d, J = 6.5 Hz, 3 H), 0.97 (s, 3 H), 1.30 (s, 3 H), 3.00 (s, 3 H), 4.35 (dd, J = 5.1, 11.0 Hz, 1 H); ^{13}C NMR δ 2.68 (3q), 12.26 (q), 13.54 (q), 16.32 (q), 18.90 (q), 20.84 (t), 22.51 (q), 22.80 (q), 23.97 (t), 25.67 (t), 27.74 (t), 27.94 (d), 28.38 (q), 28.50 (t), 31.71 (q), 35.73 (d), 36.06 (s), 36.15 (t), 37.37 (t), 38.06 (s), 38.79 (q), 39.18 (t), 39.47 (t), 39.50 (t), 43.55 (s), 45.68 (d), 47.74 (d), 50.37 (d), 50.98 (d), 55.02 (d), 75.85 (s), 90.78 (d); MS m/z (relative intensity) 596 (M^+, 9), 500 (35), 485 (13), 419 (32), 418 (100), 410 (69), 395 (17), 210 (12), 143 (34), 73 (18); HRMS calcd for $C_{34}H_{64}O_4SSi$ (M^+) 596.4295, found 596.4298. Anal. Calcd for $C_{34}H_{64}O_4SSi$: C, 68.41; H, 10.81. Found: C, 68.14; H, 10.92.

(3α,5α,7α)-4,4,7-Trimethyl-7-[(trimethylsilyl)oxy]-cholestan-3-ol 3-Methanesulfonate (6). The mesylate **4** (0.300 g, 0.57 mmol) was treated with HMDS and TMSCl for 24 h as described above for the synthesis of **5**. Workup and flash chromatography (10:1 petroleum ether (bp 40−60 °C)/ EtOAc) yielded 0.307 g (90%) of **6**: ^{1}H NMR δ 0.09 (s, 9 H), 0.61 (s, 3 H), 0.80−2.00 (m, 27 H), 0.82 (s, 3 H), 0.84 (d, J = 6.8 Hz, 6 H), 0.88 (d, J = 6.5 Hz, 3 H), 0.89 (s, 3 H), 0.96 (s, 3 H), 1.29 (s, 3 H), 2.99 (s, 3 H), 4.52 (br s, $W_{1/2}$ = 4.0 Hz, 1 H); ^{13}C NMR δ 2.61 (3q), 12.26 (q), 13.54 (q), 18.90 (q), 20.61 (t), 21.79 (q), 22.53 (q), 22.81 (q), 24.00 (t), 24.39 (t), 27.79 (t), 27.94 (d), 28.54 (q), 28.54 (t), 31.84 (q), 32.15 (t), 35.78 (d), 36.06 (s), 36.16 (t), 36.91 (s), 38.63 (q), 38.88 (t), 39.47 (2t), 42.06 (d), 43.49 (s), 45.89 (d), 50.37 (d), 51.16 (d), 55.08 (d), 75.84 (s), 88.17 (d); MS m/z (relative intensity) 596 (M^+, 5), 500 (11), 485 (10), 419 (33), 418 (100), 410 (64), 395 (28), 210 (8), 143 (17), 73 (10); HRMS calcd for $C_{34}H_{64}O_4SSi$ (M^+) 596.4295, found 596.4297. Anal. Calcd for $C_{34}H_{64}O_4SSi$: C, 68.41; H, 10.81. Found: C, 68.38; H, 11.00.

Reactions of Mesylates 1−6 with Sodium *tert*-Amylate. General Procedure. All reactions were carried out at a concentration of ca. 0.1 M mesylate in dry toluene. The

solutions were degassed and refluxed under an Ar atmosphere. Approximately 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 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 five portions of EtOAc. The combined organic layers were dried and evaporated under reduced pressure to afford the crude reaction products. Unless noted otherwise, product ratios, yields, and pure compounds were obtained by chromatographical techniques.

a. The general procedure was employed by using 0.093 g (0.19 mmol) of **1**. Workup and flash chromatography (100:1 to 2:1 petroleum ether (bp 40−60 °C)/EtOAc) afforded 0.005 g (7%) of an inseparable 3:2 mixture[39] of **14** and **15**, respectively, and 0.070 g (75%) of unreacted **1**.

(5α,7α)-7-Methylcholest-2-en-7-ol (14): ^{1}H NMR (main peak) δ 5.59 (br s, $W_{1/2} \approx 5$ Hz, 2 H); HRMS (3:2 mixture) calcd for $C_{28}H_{48}O$ (M^+) 400.3705, found 400.3703.

(5α,7α)-7-Methylcholest-3-en-7-ol (15): ^{1}H NMR (main peaks) δ 5.20 (br dd, J = 2.2, 10.0 Hz, 1 H), 5.56 (m, 1 H).

b. The general procedure was employed by using 0.336 g (0.64 mmol) of **2**. Workup and flash chromatography (50:1 to 2:1 petroleum ether (bp 40−60 °C)/EtOAc) afforded 0.008 g (3%) of **16**, 0.104 g (38%) of an inseparable 1:5 mixture[39] of **17** and **18**, respectively, and 0.172 g (51%) of unreacted **2**. The spectroscopic data of **16**, **17**, and **18** are shown below.

16: ^{1}H NMR δ 0.67 (s, 3 H), 0.85 (d, J = 6.7 Hz, 6 H), 0.84−2.08 (m, 21 H), 0.88 (d, J = 6.7 Hz, 3 H), 1.00 (s, 3 H), 1.56 (d, J = 1.1 Hz, 3 H), 1.60 (d, J = 1.2 Hz, 3 H), 2.11 (s, 3 H), 2.15−2.50 (m, 3 H), 4.66 (dd, J = 2.3, 9.9 Hz, 1 H), 4.69 (dd, J = 2.3, 16.9 Hz, 1 H), 4.79 (br s, 1 H), 5.36 (dt, J = 9.9, 16.9 Hz, 1 H); ^{13}C NMR δ 11.96 (q), 18.57 (q), 19.26 (q), 21.81 (q), 22.54 (t), 22.71 (q), 22.80 (q), 23.78 (t), 26.08 (t), 27.63 (t), 27.98 (q), 27.98 (d), 30.05 (q), 33.60 (t), 35.84 (d), 36.00 (t), 39.46 (t), 39.72 (t), 39.99 (t), 41.19 (s), 41.96 (s), 45.97 (d), 52.28 (d), 54.13 (d), 56.54 (d), 110.04 (t), 128.96 (s), 135.47 (d), 144.48 (d), 210.24 (s); MS m/z (relative intensity) 428 (M^+, 6), 357 (35), 354 (7), 301 (7), 179 (9), 153 (100), 149 (25), 135 (85), 95 (43), 43 (37); HRMS calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4014.

(3α,5α)-3,4,4-Trimethylcholest-6-en-3-ol (17): ^{1}H NMR (main peaks) δ 0.66 (s, 3 H), 1.19 (s, 3 H), 5.56 (br s, 2 H); ^{13}C NMR (main peaks) δ 12.11 (q), 14.17 (q), 34.25 (t), 34.25 (t), 34.68 (t), 37.00 (d), 53.00 (d), 54.49 (d), 126.88 (d), 130.40 (d); MS m/z (relative intensity) 410 ($M^+ - 18$, 2), 297 (1), 147 (5), 136 (8), 122 (20), 121 (18), 105 (18), 69 (20), 55 (46), 43 (100); HRMS (1:5 mixture) calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4017.

(3α,5α)-3,4,4-Trimethylcholest-7-en-3-ol (18): ^{1}H NMR (main peaks) δ 0.50 (s, 3 H), 0.83 (d, J = 6.7 Hz, 6 H), 0.84 (s, 3 H), 0.85 (s, 3 H), 0.98 (s, 3 H), 0.90 (d, J = 6.3 Hz, 3 H), 1.18 (s, 3 H), 5.20 (m, 1 H); ^{13}C NMR (main peaks) δ 11.77 (q), 15.05 (q), 18.82 (q), 20.96 (t), 23.52 (t), 23.90 (t), 24.41 (q), 27.96 (d), 36.10 (t), 36.18 (d), 48.39 (d), 52.46 (d), 54.86 (d), 56.05 (d), 75.20 (s), 118.18 (d), 138.79 (s); MS m/z (relative intensity) 428 (M^+, 0.4), 161 (4), 149 (4), 119 (9), 95 (13), 71 (38), 69 (16), 57 (31), 55 (26), 43 (100).

c. The general procedure was employed by using 0.252 g (0.48 mmol) of **3**. Workup and flash chromatography (100:1 to 2:1 petroleum ether (bp 40−60 °C)/EtOAc) afforded 0.040 g (20%) of **19**, 0.026 g (13%) of **20**, 0.045 g (22%) of **21**, 0.012 g (6%) of **22**, and 0.043 g (17%) of unreacted **3**. The spectroscopic data of **19**−**22** are shown below.

19: ^{1}H NMR δ 0.63 (s, 3 H), 0.84 (d, J = 6.6 Hz, 6 H), 0.80−2.16 (m, 23 H), 0.89 (d, J = 6.5 Hz, 3 H), 0.96 (s, 3 H), 1.54 (br s, 3 H), 1.64 (br s, 3 H), 2.04 (s, 3 H), 2.44 (m, 1 H), 4.86 (br d, J = 10.7 Hz, 1 H), 4.89 (dd, J = 1.5, 17.6 Hz, 1 H); 5.01 (br t, J = 7.0 Hz, 1 H), 5.61 (dd, J = 10.7, 17.6 Hz, 1 H); ^{13}C NMR δ 11.34 (q), 16.60 (q), 17.55 (q), 18.59 (q), 21.52 (t), 22.49 (q), 22.66 (t), 22.74 (q), 23.73 (t), 25.04 (t), 25.63 (q), 27.94 (t), 27.94 (d), 34.61 (q), 35.76 (d), 36.01 (t), 38.97 (t), 39.42 (t), 40.63 (t), 42.14 (s), 43.07 (s), 45.32 (d), 51.42 (d), 53.61 (d), 54.95 (d), 112.09 (t), 124.84 (d), 131.08 (s), 147.66 (d), 213.82 (s); MS m/z (relative intensity) 428 (M^+, 11), 411 (31), 410 (100), 396 (17), 395 (51), 137 (46), 121 (14), 109 (11), 95 (19), 43 (13); HRMS calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4014.

20: ^{1}H NMR δ 0.68 (s, 3 H), 0.72 (s, 3 H), 0.85 (d, J = 6.6 Hz, 6 H), 0.82−2.03 (m, 28 H), 0.91 (d, J = 6.5 Hz, 3 H), 1.27 (s, 3 H), 1.75 (s, 3 H), 2.71 (m, 1 H), 4.82 (d, J = 7.7 Hz, 2 H); ^{13}C NMR δ 12.37 (q), 13.47 (q), 18.90 (q), 22.52 (q), 22.75 (q), 23.76 (2t), 25.24 (q), 27.75 (t), 27.76 (t), 27.96 (d), 28.45 (t), 32.30 (q), 35.64 (d), 36.12 (t), 39.48 (t), 39.82 (s), 39.82 (2t), 41.31 (t), 44.50 (d), 44.50 (s), 46.04 (d), 47.46 (d), 51.28 (d), 51.50 (d), 55.10 (d), 73.71 (s), 110.62 (t), 148.13 (s); MS m/z (relative intensity) 428 (M^+, 73), 413 (25), 411 (29), 410 (100), 395 (54), 161 (25), 121 (38), 109 (32), 95 (35), 43 (38); HRMS calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4013.

21: ^{1}H NMR δ 0.60 (s, 3 H), 0.68 (s, 3 H), 0.80−2.33 (m, 28 H), 0.85 (d, J = 6.9 Hz, 6 H), 0.91 (d, J = 6.4 Hz, 3 H), 1.28 (s, 3 H), 1.58 (br s, 3 H), 1.69 (br s, 3 H); ^{13}C NMR δ 12.35 (q), 13.30 (q), 18.90 (q), 19.84 (q), 22.53 (q), 22.76 (q), 22.91 (q), 23.68 (t), 23.75 (t), 27.74 (t), 27.97 (d), 28.48 (t), 29.22 (t), 32.30 (q), 35.65 (d), 36.12 (t), 37.43 (t), 39.49 (t), 39.86 (t), 43.36 (t), 44.05 (d), 44.27 (s), 44.41 (s), 49.41 (d), 49.79 (d), 51.19 (d), 55.13 (d), 73.33 (s), 121.47 (s), 135.42 (s); MS m/z (relative intensity) 428 (M^+, 8), 411 (29), 410 (100), 395 (40), 367 (32), 163 (17), 137 (19), 109 (18), 95 (22), 43 (22); HRMS calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4016.

22: ^{1}H NMR δ 0.68 (s, 3 H), 0.80−2.33 (m, 27 H), 0.85 (d, J = 6.3 Hz, 6 H), 0.89 (s, 3 H), 0.91 (d, J = 6.7 Hz, 3 H), 0.93 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 1.29 (s, 3 H), 2.65 (qq, J = 6.8, 6.8 Hz, 1 H); ^{13}C NMR δ 12.38 (q), 18.10 (q), 18.99 (q), 21.26 (q), 22.21 (q), 22.56 (q), 22.79 (q), 23.34 (t), 23.83 (t), 26.23 (d), 27.82 (t), 28.01 (d), 28.37 (t), 28.57 (t), 30.48 (q), 35.62 (d), 36.17 (t), 37.72 (t), 39.54 (t), 39.82 (t), 40.37 (t), 44.42 (s), 45.63 (d), 49.57 (s), 50.77 (d), 51.39 (d), 55.06 (d), 73.06 (s), 136.14 (s), 140.88 (s); MS m/z (relative intensity) 428 (M^+, 11), 411 (35), 410 (96), 395 (78), 367 (48), 189 (22), 161 (25), 137 (100), 121 (20), 43 (31); HRMS calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4017.

d. The general procedure was employed by using 0.213 g (0.41 mmol) of **4**. Workup and flash chromatography (250:1 to 2:1 petroleum ether (bp 40−60 °C)/EtOAc) afforded 0.084 g (48%) of **24**, 0.048 g (27%) of an inseparable 1:3.5 mixture[39] of **23** and **25**, respectively, and 0.005 g (2%) of unreacted **4**. The spectroscopic data of **23**,[40] **24**, and **25**[40] are shown below.

(5α,7α)-4,4,7-Trimethylcholest-2-en-7-ol (23): ^{1}H NMR (main peaks) δ 0.66 (s, 3 H), 0.84 (d, J = 6.5 Hz, 6 H), 1.29 (s, 3 H), 5.33−5.52 (m, 2 H); ^{13}C NMR (main peaks) δ 12.14 (q), 12.91 (q), 31.46 (q), 39.73 (t), 42.55 (t), 44.04 (d), 45.01 (d), 50.04 (d), 51.41 (d), 121.64 (d), 137.64 (d); MS m/z (relative intensity) 410 ($M^+ - 18$, 5), 395 (5), 161 (15), 147 (14), 137 (63), 121 (74), 119 (43), 109 (50), 107 (61), 69 (100); HRMS (1:3.5 mixture) calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4020.

(3*β*,7α)-3,4,7-Trimethylcholest-4-en-7-ol (24): ^{1}H NMR (C_6D_6) δ 0.70 (s, 3 H), 0.80−2.15 (m, 28 H), 0.92 (d, J = 6.1 Hz, 6 H), 0.95 (s, 3 H), 0.95 (d, J = 6.4 Hz, 3 H), 1.00 (d, J = 6.3 Hz, 3 H), 1.32 (s, 3 H), 1.63 (s, 3 H); ^{13}C NMR (C_6D_6) δ 12.35 (q), 16.63 (q), 18.93 (q), 19.91 (2q), 22.29 (t), 22.48 (q), 22.75 (q), 24.08 (t), 27.82 (t), 28.11 (d), 28.79 (2t), 30.61 (q), 35.87 (2d), 36.33 (t), 36.50 (t), 37.71 (s), 39.62 (t), 40.16 (t), 42.90 (t), 43.90 (s), 45.24 (d), 50.48 (d), 51.79 (d), 55.31 (d), 73.18 (s), 131.69 (s), 134.10 (s); MS m/z (relative intensity) 428 (M^+, 11), 411 (33), 410 (100), 396 (22), 395 (59), 187 (13), 163 (14), 137 (47), 95 (28); HRMS calcd for $C_{30}H_{52}O$ (M^+) 428.4018, found 428.4018.

(5α,7α)-3,4,7-Trimethylcholest-3-en-7-ol (25): ^{1}H NMR (main peaks) δ 0.67 (s, 3 H), 0.84 (d, J = 6.5 Hz, 6 H), 1.27 (s, 3 H), 1.53 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR (main peaks) δ 11.90 (q), 12.35 (q), 15.45 (q), 18.84 (q), 19.38 (d), 21.54 (t), 22.54 (q), 22.78 (q), 27.98 (d), 29.58 (t), 32.25 (q), 35.72 (d), 36.10 (t), 43.10 (d), 43.76 (d), 49.29 (d), 51.74 (d), 55.07 (d), 72.58 (s), 125.11 (s), 126.08 (s); MS m/z (relative intensity) 410 ($M^+ - 18$, 2), 395 (2), 135 (7), 121 (10), 119 (6), 109 (14), 107 (10), 95 (21), 57 (31), 43 (100).

(39) This ratio was determined by ^{1}H NMR analysis.

(40) The mass spectral data of this compound were obtained by GC−MS analysis.

e. The general procedure was employed by using 0.168 g (0.28 mmol) of **5**. Workup and flash chromatography (100:1 to 50:1 petroleum ether (bp 40−60 °C)/EtOAc) gave 0.024 g (17%) of a complex mixture of at least five apolar compounds and 0.111 g (66%) of unreacted **5**.

f. The general procedure was employed by using 0.191 g (0.32 mmol) of **6**. Workup and flash chromatography (100:1 to 2:1 petroleum ether (bp 40−60 °C)/EtOAc) afforded 0.044 g (27%) of an inseparable ca. 1:1 mixture[39] of **26** and **27** and 0.111 g (58%) of unreacted **6**. The spectroscopic data of **26** and **27** are shown below.[41]

(5α,7α)-4,4,7-Trimethyl-7-[(trimethylsilyl)oxy]cholest-2-ene (26): ^{1}H NMR (main peaks) δ 0.10 (s, 9 H), 0.65 (s, 3 H), 0.86 (d, J = 6.3 Hz, 6 H), 0.94 (s, 3 H), 1.32 (s, 3 H), 5.35−5.55 (m, 2 H); ^{13}C NMR (main peaks) δ 2.65 (3q), 18.91 (q), 20.96 (t), 24.00 (t), 28.60 (t), 32.07 (q), 40.19 (t), 40.98 (t), 44.58 (d), 46.01 (d), 49.12 (d), 51.29 (d), 75.70 (s), 121.93 (d), 137.79 (d); MS m/z (relative intensity) 418 (M^+ − 82, 5), 210 (4), 175 (6), 143 (9), 95 (18), 81 (17), 75 (31), 73 (60), 57 (32), 43 (100); HRMS (1:1 mixture) calcd for $C_{33}H_{60}OSi$ (M^+) 500.4414, found 500.4416.

(41) Careful column chromatography afforded a small sample of a ca. 1:2 mixture of **26** and **27**, respectively. With this mixture the structures of **26** and **27** could be established by spectroscopic analysis (^{1}H and ^{13}C NMR and GC−MS).

(5α,7α)-3,4,7-Trimethyl-7-[(trimethylsilyl)oxy]cholest-3-ene (27): ^{1}H NMR (main peaks) δ 0.10 (s, 9 H), 0.63 (s, 3 H), 0.83 (d, J = 6.5 Hz, 6 H), 1.26 (s, 3 H), 1.54 (br s, 3 H), 1.60 (br s, 3 H); ^{13}C NMR (main peaks) δ 2.65 (3q), 19.35 (q), 21.48 (t), 27.70 (t), 29.74 (t), 31.80 (q), 45.62 (d), 48.50 (d), 51.72 (d), 75.91 (s), 124.82 (s), 126.63 (s); MS m/z (relative intensity) 410 (M^+ − 90, 22), 396 (30), 201 (21), 179 (16), 161 (17), 109 (51), 75 (69), 73 (79), 57 (100), 43 (75).

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Supporting Information Available: ^{1}H NMR spectra for compounds **16**, **19**−**22**, and **24** (6 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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