(t), 25.38 (t), 25.14 (q), 22.62 (q), 20.02 (q), 13.05 (q), 8.92 (q), 8.35 (q) ppm; high-resolution mass spectrum calcd for $C_{14}H_{20}O$ 204.1514, found 204.1509.

10-Ethenylbicyclo[6.4.0]dodec-1-en-3-one (24). Compound **24** was obtained in 45% yield by using the general procedure: IR (film) 2940, 1660, 1615, 1260, 850 cm^{-1}; ^1H NMR ($CDCl_3$) 1.15–2.6 (16 H), 4.85 (m, 2 H), 5.75 (m, 1 H), 5.89 (s, 1 H) ppm; ^{13}C NMR ($CDCl_3$) 212.96 (s), 199.20 (s), 143.99 (d), 126.69 (d), 111.90 (t), 42.31 (d), 38.20 (d), 35.99 (t), 34.15 (t), 33.37 (t), 30.60 (t), 30.21 (t), 28.99 (t), 24.42 (t) ppm; high-resolution mass spectrum calcd for $C_{14}H_{20}O$ 204.1514, found 204.1515.

Acknowledgment. We thank Dr. Victor Wray, Gesellschaft für Biotechnologische Forschung, Braunschweig-Stöckheim, for carrying out the NOE difference spectra. This work was supported by the Deutsche Forschungsgemeinschaft (Heisenberg fellowship to D.S.), the Fonds der Chemischen Industrie, and the Alexander von Humboldt-Foundation (Humboldt fellowship to S.S.).

Registry No. **3a**, 5323-87-5; **3b**, 20643-20-3; **4a**, 110477-25-3; **4b**, 105222-80-8; **5a**, 115142-35-3; **6a**, 115142-36-4; **7a**, 115142-38-6; **8a**, 115142-39-7; **9**, 72535-08-1; **10b**, 115142-40-0; **11b**, 115142-41-1; **12**, 115142-42-2; **13**, 115142-43-3; **14a**, 115142-44-4; **14b**, 115142-45-5; **15a**, 115142-46-6; **16**, 115142-47-7; **17**, 115142-48-8; **18a**, 115142-49-9; **18b**, 115142-50-2; **19a**, 115142-51-3; **19b**, 115142-52-4; **20a**, 115223-79-5; **20b**, 115223-80-8; **21**, 105222-84-2; **22a**, 115142-53-5; **22b**, 115142-55-7; **23a**, 115142-54-6; **23b**, 105222-88-6; **24**, 115142-56-8; **25**, 115142-57-9; $Br(CH_2)_3C{\equiv}CCH_2SiMe_3$, 112129-48-3; $BrMg(CH_2)_3C{\equiv}CCHzSiMe_3$, 105222-94-4; $I(CH_2)_2CH{=}CHCH_2SiMe_3$, 105222-91-1; $I(CH_2)_2C{=}CCH_2SiMe_3$, 88996-00-3; $I(CH_2)_3CH{=}CHCH_2SiMe_3$, 115142-37-5; $I(CH_2)_3C{\equiv}CCH_2SiMe_3$, 88996-02-5; $BrMgCH{=}CH_2$, 1826-67-1; $BrMgCH{=}CHCH_3$, 14092-04-7; $CH_2{=}CHMgCl$, 3536-96-7; $EtAlCl_2$, 563-43-9; $TiCl_4$, 7550-45-0.

Enolization of 2-Decalones

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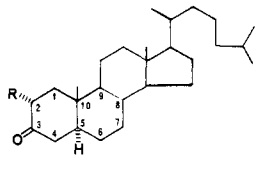
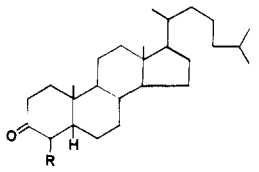
It is well-known that under thermodynamic conditions 5α-3-keto steroids such as 3-cholestanone enolize predominantly toward C-2, while the 5β-isomers enolize toward C-4. It has been tacitly assumed that 2-decalones, bicyclic analogues of the steroids, show similar selectivity. In a systematic investigation of the direction of enolization of 2-decalones, 11 bicyclic ketones plus two representative steroids have been converted to the corresponding trimethylsilyl enol ethers under thermodynamic conditions. The classical generalizations have been found to be valid for *trans*-2-decalones and steroidally locked *cis*-2-decalones with an angular methyl group. Nonsteroidally locked *cis*-2-decalones with an angular methyl enolize in a direction opposite to that predicted. Without an angular methyl, all three types of 2-decalones enolize in the predicted manner, but with attenuated regioselectivity. Molecular-mechanics calculations have been carried out for the olefins corresponding to decalone enols. With the exception of the nonsteroidal cis compounds with an angular methyl, the calculations agree well with the experimental data.

It has been known for many years that bromination, under acidic conditions of 5α-3-keto steroids such as 3-cholestanone (**1**) affords predominantly the 2-bromo 3-ketone **2**, while 5β-3-keto steroids (e.g., coprostanone, **3**) give 4-bromo 3-ketones **4**.[1] These observations have



1 R = H
2 R = Br



3 R = H
4 R = Br

usually been explained in terms of the relative stabilities of the enol precursors, intermediates in the bromination of ketones, and have been related to the stabilities of the corresponding olefins which have served as models for the enols.[1f,2]

On the basis of vector-analysis calculations[3] and subsequent semiquantitative empirical torsional analysis,[4] again using olefins as models, these observations have been extended to the bicyclic analogues of the steroids, the 2-decalones. More refined calculations for the cis olefins were carried out by using Hill calculations[5] and molecular mechanics.[6] These empirical or semiempirical analyses have consistently indicated that the decalones should enolize in the same regioselective sense as steroidal ketones which possess similar stereochemistry about the A–B ring fusion.

However, in contrast to the two steroid models **1** and **3**, the 2-decalones can be divided into six structural classes, two of which have trans ring fusions, and four cis. The *trans*-decalones are locked in a conformation similar to that of cholestanone (**1**) and may have or lack an angular substituent.[7] In contrast to the 5β-steroids **3**, which are

(1) (a) Djerassi, C.; Scholz, C. R. *J. Am. Chem. Soc.* **1948**, *70*, 417. (b) Corey, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 2301, 3297, 4382. (c) Fieser, L. F.; Dominguez, X. A. *J. Am. Chem. Soc.* **1953**, *75*, 1704. (d) Butenandt, A.; Wolf, A. *Chem. Ber.* **1935**, *68*, 2091. (e) Fieser, L. F.; Ettore, R. *J. Am. Chem. Soc.* **1953**, *75*, 3513. (f) Fieser, L. F.; Fieser, M. *Steroids*; Reinhold: New York, 1959; pp 37–41, 276–279 and references therein.

(2) (a) Villotti, R.; Ringold, H. J.; Djerassi, C. *J. Am. Chem. Soc.* **1960**, *82*, 5693 and earlier papers in this series. (b) Taylor presents an argument specific to 5β-steroids: Taylor, D. A. H. *Chem. Ind. (London)* **1954**, 250. (c) Dreiding, A. S. *Chem. Ind. (London)* **1954**, 1419.

(3) Corey, E. J.; Sneen, R. A. *J. Am. Chem. Soc.* **1955**, *77*, 2505.

(4) (a) Velluz, L.; Valls, J.; Nomine, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 181. (b) Bucourt, R.; Hainaut, D. *Bull. Soc. Chim. Fr.* **1965**, 1366.

(5) Liston, A. J. *J. Org. Chem.* **1966**, *31*, 2105.

(6) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J. *J. Am. Chem. Soc.* **1968**, *90*, 5773.

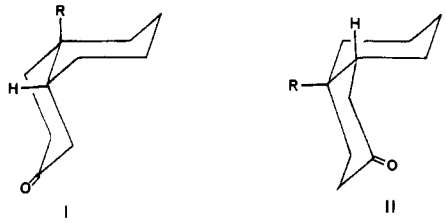
0022-3263/88/1953-3828$01.50/0

Table I. Composition of Trimethylsilyl Enol Ether Mixtures[a]

ketone (type)[b]	prod ratio (1,2:2,3)[c]	ΔG^d	ΔH^e
1 (TM)	10:90	1.30	1.65
3 (CMS)	93:7	−1.53	−1.02
5 (CMN)	23:77	0.71	−0.24
6 (TH)	27:73[f]	0.56	0.68
7 (TM)	7:93	1.53	1.65
8 (TM)	11:89	1.23	1.65
9 (TH)	21:79	0.78	0.68
10 (CMN)	15:85	1.02	−0.24
11 (CHN)	68:32[g]	−0.44	−0.66
12 (CMS)	89:11	−1.23	−1.02
13 (CHS)	63:37	−0.31	−0.11
14 (CMF)	46:54	0.09	
15 (CHF)	61:39[h]	−0.26	

[a] Enol ether mixtures were prepared as described in the Experimental Section by using TMSI/$(Me_3Si)_2NH/CH_2Cl_2$, 25 °C. [b] Type refers to ring fusion (C or T), presence or absence of an angular methyl (M or H), and for the cis isomers, the preferred conformation (S, steroidal; N, nonsteroidal; F, conformationally mobile). [c] Numbering is for decalones. Product ratios were determined by capillary GLC and were checked by ^{13}C NMR. All runs were carried out at least in duplicate with agreement to within ±4%. [d] Kilocalories per mole for equilibrium 1,2-isomer ⇌ 2,3-isomer at 25 °C. [e] Kilocalories per mole calculated by MM2. [f] House (ref 9a) reports 28:72 from equilibration of the enol acetates. [g] Reported for equilibration of the enol acetates, 59:41 (ref 9c). [h] Reported for equilibration of the enol acetates, 60:40 (ref 9a).

locked in conformation I, the bicyclic ketones have an alternative nonsteroidal conformation (II). The confor-



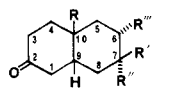
I II

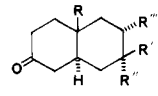
mational preference of any given substituted *cis*-2-decalone is biased by the nature and stereochemistry of the substituents. For both types of *cis*-decalone there is again the possibility of the presence or absence of an angular methyl group.

A number of examples of the direction of enolization of *trans*-2-decalones of both types have been described, and the results agree well with the generalizations that evolved from steroid chemistry. Those *trans*-2-decalones with an angular methyl group afford reaction products analogous to those from ketone **1**.[8] Without an angular methyl the effects are attenuated, but the general trend is the same.[9]

The *cis*-decalones without an angular substituent have been examined, and the results are somewhat ambiguous. Under apparently identical conditions, the same steroidally locked ketone has given in one case a mixture of enol acetates rich in the predicted isomer[9b] and in other experiments, by the same group, a mixture of enol acetates, which contained only 35% of the predicted isomer.[10] When an alternative method of enol acetylation was used, another steroidally locked *cis*-2-decalone gave results consistent with those in the steroid series.[9c,10] Two nonsteroidally locked *cis*-2-decalones also without an angular methyl group have been examined under two different procedures for forming enol acetates which gave from 50% to 100% of the expected isomers.[9c,10] The parent conformationally mobile unsubstituted *cis*-2-decalone gives a 60:40 ratio of enol acetates with the expected isomer predominating.[9a]

The situation with regard to *cis*-2-decalones with an angular methyl group is not well defined. No studies per se of this group of ketones have been reported, and only a few scattered well-characterized examples are available in the literature. Bromination of a steroidally locked ketone was found to proceed in a manner analogous to that of ketone **3**,[11] and the conformationally mobile parent member of the series gives a mixture of bromination products.[12] Apparently, the only nonsteroidally locked compound of this group to be examined is 7,7,10-trimethyl-2-decalone (**5**).[13] Two groups have described the bromination of **5** and found that the only isolable product is the 3β-bromo ketone.[14]





5 R, R′, R″ = Me, R‴ = H
10 R = Me, R′ = *i*-Pr, R″, R‴ = H
11 R, R‴ = H, R′, R″ = Me
12 R = Me, R′ = *i*-Pr, R″, R‴ = H
13 R, R′, R″ = H, R‴ = *i*-Pr
14 R = Me, R′, R″, R‴ = H
15 R, R′, R″, R‴ = H

6 R, R′, R″, R‴ = H
7 R = Me, R′, R″, R‴ = H
8 R = Me, R′ = *i*-Pr, R″, R‴ = H
9 R, R′, R″ = H, R‴ = *i*-Pr

In order to provide a definitive answer to this classical but unresolved problem in conformational analysis, we have undertaken a systematic study of the direction of enolization, under thermodynamic conditions, of a series of 2-decalones. These ketones include at least one member of each of the six groups mentioned above, plus steroidal ketones **1** and **3**.

The *trans*-decalones included the parent ketone **6**, 10-methyl-2-decalone (**7**), and two compounds (**8**[15] and **9**[16]) with substituents in ring B. Nonsteroidally locked *cis*-2-decalones included **5**,[14] 7α-isopropyl-10β-methyl-2-decalone (**10**),[17] and one ketone lacking an angular methyl (**11**).[18] Two steroidally locked *cis*-ketones, **12** and **13**,[16] with and without an angular methyl group, respectively, were investigated, as were the two parent, conformationally mobile *cis*-decalones **14** and **15**. With the exception of ketone **12**, all of the decalones are known compounds and were pre-

(7) The most common angular substituent in both natural products and synthetic intermediates is a methyl group and was the only group considered in this study.
(8) (a) Riniker, B.; Kalvoda, J.; Arigoni, D.; Furst, A.; Jeger, O.; Gold, A. M.; Woodward, R. B. *J. Am. Chem. Soc.* **1954**, *76*, 313. (b) Trost, B. M.; Salzmann, T. N. *J. Am. Chem. Soc.* **1973**, *95*, 6840 and many other references.
(9) (a) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 1341. (b) Favre, H.; Huet, F.; Varfalvy, L. *Can. J. Chem.* **1971**, *49*, 1776. (c) Favre, H.; Liston, A. J. *Can. J. Chem.* **1964**, *42*, 268.
(10) Favre, H.; Liston, A. J. *Can. J. Chem.* **1969**, *47*, 3233.
(11) Harayama, T.; Cho, H.; Inubishi, Y. *Tetrahedron Lett.* **1975**, 2693.
(12) (a) Elliott, D. R.; Robinson, M. J. T.; Riddell, F. G. *Tetrahedron Lett.* **1965**, 1693. (b) Yanagita and Tahara report a single bromo ketone from this reaction; however, the structure is uncertain: Yanagita, M.; Tahara, A. *J. Org. Chem.* **1953**, *18*, 792.
(13) The numbering system is that commonly used for the decalones and is indicated in **5**. The conventional numbering system for the steroids is depicted in **1**.
(14) (a) Halsall, T. G.; Thomas, D. B. *J. Chem. Soc.* **1956**, 2431. (b) Ellis, J. E.; Dutcher, J. S.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 2670. Halsall's group carried out a careful study of the bromination and noted that a nonsteroidal *cis*-2-decalone might well enolize differently than a 5β-steroid (see ref 2c).
(15) Fringuelli, F.; Tatichi, A. *J. Chem. Soc.* **1971**, 1809.
(16) Bozzato, G.; Pesaro, M.; Schudel, P.; Hag-Inderbitzin, M.; Erickson, R. E. (Givaudan L. et Cie S.A.) Switz. 554934; *Chem. Abstr.* **1975**, *82*, 98214*p*; Switz. 554145; *Chem. Abstr.* **1975**, *83*, 27717*q*; Switz. 542803; *Chem. Abstr.* **1974**, *80*, 956145; Ger. Offen. 2,107,413; *Chem. Abstr.* **1971**, *75*, 151432*s*.
(17) Djerassi, C.; Burakevich, J.; Chamberlin, J. W.; Elad, D.; Toda, T.; Stork, G. *J. Am. Chem. Soc.* **1964**, *86*, 465.
(18) Bruderlein, H.; Dufort, N.; Favre, A.; Liston, A. J. *Can. J. Chem.* **1963**, *41*, 2908.

pared by the published procedures or obvious alternative routes.[19]

Although a variety of procedures are available for preparing derivatives of the thermodynamic (equilibrium) mixture of enols from cyclic ketones, a most convenient method appeared to be that described by Miller and McKean,[20] which forms a thermodynamic mixture of trimethylsilyl enol ethers by using iodotrimethylsilane and hexamethyldisilazane at ambient temperature. Decalones **5** through **15**, plus steroidal ketones **1** and **3**, were subjected to these conditions, and the results are summarized in Table I.

Steroidal ketones **1** and **3** gave results in accord with those observed on bromination.[1,2] As expected, the *trans*-2-decalones with an angular methyl group (**7** and **8**) afforded a preponderance of the 2,3-enol ether.[8] A *cis*-decalone with an angular methyl, locked in the steroidal conformation (**12**), as expected, gave a product distribution similar to that of coprostanone.[11]

However, the two cis ketones with an angular methyl and nonsteroidal conformation (**5** and **10**) gave predominantly the 2,3-isomer. The structure of the major isomer obtained from ketone **5** was confirmed by ozonization to an aldehyde acid, the NMR spectrum of which was in accord with the assigned structure. Although these results are expected on the basis of the bromination of **5**,[14] they are contrary to the predictions based on the conformational analysis of the corresponding octalins.[4] The results for the conformationally mobile decalone **14** are intermediate between those for the steroidal and nonsteroidal conformers. The Miller–McKean procedure for generating silyl enol ethers under thermodynamic conditions[20] appeared to be reliable, and the observation that conformationally mobile decalone **14** gave a product ratio intermediate between those of the two types of conformationally locked ketones tended to confirm this. However, in order to ensure that the results obtained for nonsteroidal decalones **5** and **10** did in fact represent equilibrium conditions, **5** was converted to a silyl enol ether mixture by using standard conditions of strong base and thermodynamic enolate conditions (LDA/THF). Under these conditions, the 1,2/2,3-enol ether ratio was 41:59 (vs 23:77 with TMSI).[21]

Analysis of the conformations of the *trans*-octalins lacking an angular methyl, as well as equilibration data by others,[4,9] indicates that the energy difference between the 1,2- and 2,3-isomers should be rather small. The experimental results for ketones **6** and **9** (Table I) agree well with both the reported data and the conformational arguments.

For the *cis*-decalones without an angular methyl, locked in either a steroidal (**13**) or nonsteroidal conformation (**11**), the 1,2-isomer was the major product (approximately 2:1). These data are in reasonable agreement with those reported previously.[9,10] The conformationally mobile unsubstituted *cis*-decalone (**15**) predictably gave similar results, which were within experimental error of those reported.[9a]

Molecular-mechanics calculations using the MM2 program were carried out for the olefins (octalins) corresponding to the regioisomeric enols derived from all six types of substrate decalones.[22,23] The MM2 program provides strain energies (ΔH), while the equilibration data in Table I provide free energies (ΔG); however, entropy differences between double-bond isomers should be quite small. A direct comparison between the calculated and experimental relative energies of the various double-bond isomers would thus appear to be at least semiquantitatively valid.

For the *trans*-octalins, the 2,3-olefins are calculated to be more stable by 1.65 kcal/mol with an angular methyl and by 0.68 kcal/mol in the absence of this substituent. The experimentally determined free energies are 1.37 and 0.68 kcal/mol, respectively.[24] For the cis-steroidal ketones, the 1,2-olefins are calculated to be more stable than the 2,3-isomers by 1.02 and 0.11 kcal/mol for the compounds with and without angular methyl, respectively. The values found experimentally are 1.65 and 0.31 kcal/mol. For the cis nonsteroidally locked compounds without an angular methyl, the calculated and experimental values are 0.66 and 0.45 kcal/mol, respectively.

Given the assumptions inherent in comparing strain energies calculated by MM2 and experimentally determined free energies, the agreement between the calculated and experimental energies is quite acceptable for the five of the six types of decalones cited above. However, for nonsteroidally locked *cis*-decalones with an angular methyl, MM2 favors the 1,2-octalin by 0.24 kcal/mol while the experimental data indicate that the 2,3-enol is favored by 0.86 kcal/mol.[25] This difference (1.1 kcal/mol) is considerably greater than that noted for any of the other classes of decalones, and we have, at this point, no explanation for the failure of the MM2 calculations to agree adequately with the experimental data in this instance.[26]

The results of this study indicate that the conventional observation that *cis*- and *trans*-2-decalones enolize in the same regiochemical sense as 5α- and 5β-3-keto steroids, respectively, is valid, but with definite restrictions. That is, *trans*-2-decalones and *cis*-2-decalones that are locked in a steroidal conformation and that have an angular methyl do behave similarly to the steroids. However, nonsteroidally locked *cis*-2-decalones with an angular methyl give predominantly the "wrong" 2,3-enol. Without an angular substituent, the *trans*-decalones afford enol mixtures containing predominantly the 2,3-isomer, but the relative amount is somewhat less than when an angular methyl is present. Those *cis*-2-decalones without an angular methyl give approximately a 2:1 ratio of 1,2- to 2,3-

(19) The details of the synthesis of the decalones are available in the Ph.D. dissertation of Balke, W. H., Clemson University, Dec 1987. The syntheses of ketones **12**, which is previously unreported, and **9** and **13**, both described only in the patent literature, are described in the Experimental Section.

(20) Miller, R. D.; McKean, D. R. *Synthesis* **1979**, 730.

(21) House and Trost (ref 9a) found similar differences in comparing equilibrium mixtures of enol acetates and enolates derived from decalones **6** and **15**.

(22) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) QCPE 395.

(23) For several molecules, the MM2 calculations were carried out for enols and/or methyl and *tert*-butyl enol ethers. There were no significant differences in calculated energies. However, for these structures assumptions had to be made concerning structural parameters used in the MM2 program. Prof. D. Liotta (Emory University) has calculated the relative stabilities of the trimethylsilyl enol ethers for the nonsteroidal conformer of 10-methyl-*cis*-2-decalone and finds that the 1,2-isomer is favored by 0.11 kcal/mol. (Private communication to J.W.H.)

(24) Values of ΔG were calculated at 25 °C by using as K the average of the experimental results in Table I for each type of decalone. The steroid data are included with those for the bicyclic ketones of the same type.

(25) A number of alternative ring-A conformations for the 2,3-octalin were examined to insure that the calculated energy did not represent a false minimum.

(26) The obvious suggestion that the experimental results do not represent equilibrium appears most unlikely: Both decalones (**5** and **10**) examined gave predominantly the 2,3-enol ether, and conformationally mobile decalone **14** gave results intermediate between the steroidal and nonsteroidal examples. Also, formation of the enolate of **5** under thermodynamic conditions gave the 2,3-enol ether as the major product. Finally, these data agree with the bromination experiments described by others (ref 14).

enol, whether in a steroidal or nonsteroidal conformation.

The explanation offered for the relative stabilities of the isomeric octalins (and by extension the direction of enolization of 2-decalones) has been based on interactions between an angular substituent and axial hydrogens in the trans isomers and between an axial methylene and axial hydrogens in *cis*-octalins.[3,4] However, examination of the detailed steric energy output (compression, bending, van der Waals, and torsional strain) from MM2 indicates that these interactions are relatively unimportant and that the energy differences between isomeric pairs of octalins are due to various combinations of torsional effects, nonbonded interactions, and angle strain which are rather evenly distributed throughout a given molecule. If these data represent a correct assessment of the conformational factors responsible for the observed regiochemistry of enolization of the decalones, it becomes apparent that simple conformational arguments do not provide an adequate explanation of the experimental results.

Experimental Section

Infrared spectra are reported in reciprocal centimeters (cm^{-1}) measured as neat films between NaCl plates or as KBr pellets by using a Perkin-Elmer Model 1310 or Nicolet 5DX spectrometer. All ^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q (90 MHz) or an IBM Instruments NR200-AF (200 MHz) Fourier transform NMR spectrometer by using either $CDCl_3$ or C_6D_6 as solvent. Chemical shifts are reported in parts per million relative to tetramethylsilane (δ). The center signal of $CDCl_3$ (δ 77.0) or the center signal of C_6D_6 (δ 128.5) was used as the internal standard for ^{13}C spectra. ^{13}C chemical shifts are reported in parts per million relative to TMS (δ). GC–MS analyses were performed on a Hewlett-Packard 5985 gas chromatograph/mass spectrometer at 70 eV. Columns employed were 1.0 m × 2.0 mm 2% OV-101 on 100–200-mesh Chromosorb WHP and 2.0 m × 2.0 mm 10% Carbowax 20M on 80–100-mesh Chromosorb WHP. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 3B dual FID chromatograph with a Sigma 15 data station. Columns used included a 6 ft × 0.125 in. 10% Carbowax 20M on 80–100-mesh Chromosorb WHP, a 6 ft × 0.125 in. SE-30 on 80–100-mesh Chromosorb W, and a 30 m × 0.53 mm × 1.0 μm film thickness Supelcowax 10 WCOT fused silica capillary column. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Triethylamine, hexamethyldisilazane, dimethylformamide (DMF), and 1,4-dioxane were freshly distilled from CaH_2. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Distilled CH_2Cl_2 was stored over molecular sieves. Distilled benzene and commercial anhydrous ether were stored over sodium wire. Butyllithium was standardized against 1,3-diphenylacetone *p*-tosylhydrazone.[27]

Substrate Ketones. Ten of the 11 2-decalones (**5–11, 13–15**) and steroidal ketones **1** and **3** are known compounds which with the exception of **9** and **13** have been adequately described in earlier publications (see text for references).

6α-Isopropyl-*trans*-2-decalone (9). Reduction of 0.100 g (0.521 mmol) of 6α-isopropyl-$\Delta^{1,9}$-2-octalone using Li/NH_3 under the usual conditions followed by chromatography on silica gel gave 0.092 g (91%) of ketone **9**. Capillary GLC indicated that the material was homogeneous: IR 2957, 2924, 2871, 1713 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.90–1.00 (m, 16 H), 0.87 (d, J = 6.59 Hz, 6 H); GC–MS, m/z (relative intensity) 195 (12) 194 (M^+, 50) 81 (67), 41 (100). This ketone was described previously in the patent literature.[16]

10β-Methyl-7β-isopropyl-*cis*-2-decalone (12). To a solution of 1.50 g (7.27 mmol) of 7β-isopropyl-10β-$\Delta^{1,9}$-2-octalone in 40 mL of 95% EtOH were added 0.15 g of 10% palladium on carbon and 3.0 mL of 10% aqueous KOH. The reaction mixture was hydrogenated at 20 psi for 12 h. Filtration of the solution followed by removal of the solvent gave 1.42 g of a colorless liquid, which was a mixture of saturated ketone and alcohol. The crude material was subjected to Jones oxidation under the usual conditions to give 1.38 g of yellowish liquid, which was purified by bulb-to-bulb distillation to give 1.16 g (77%) of colorless liquid. Although GLC indicated that this material was homogeneous, the retention time was the same as that of the known trans isomer. The 200-MHz NMR spectrum of this compound indicated that it was a mixture containing approximately 20% of the trans isomer. Purification was attempted by conversion to the semicarbazone followed by recrystallization to a charp melting point and hydrolysis to the ketone: bp 125–130 °C (0.25 mm); IR 2955, 2933, 2867, 1718 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.65–1.15 (m, 15 H), 1.01, trans isomer and 1.04, cis isomer (s, total of 3 H), 0.88 (d, J = 6.6 Hz, 6 H); GC–MS, m/z (relative intensity) 208 (M^+, 28), 28), 147 (100), 95 (72), 81 (96), 67 (75). Semicarbazone, mp 185–187 °C. Anal. Calcd for $C_{15}H_{27}ON_3$: C, 67.88; H, 10.25; N, 15.83. Found: C, 67.81; H, 10.31; N, 15.77.

6α-Isopropyl-*cis*-2-decalone (13). To a solution of 4.59 g (23.9 mmol) of 6α-isopropyl-$\Delta^{1,9}$-2-octalone in 200 mL of 95% ethanol were added 0.46 g of 10% palladium on charcoal and 4.6 mL of concentrated HCl. The reaction mixture was hydrogenated at 30 psi for 8 h. The solution was filtered through Celite, and the solvent was removed to give 4.66 g of yellow oil. This material was a mixture of ketone and alcohol, and it was subjected to Jones oxidation under the usual conditions to give 4.46 g of oil, which was purified by bulb-to-bulb distillation, bp 105–110 °C (0.25 mm), to give 4.41 g (95%) of colorless liquid. Analysis by capillary GLC indicated that this material was contaminated with 7% of the trans ketone described above: IR 2957, 2924, 2871, 1713 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.80–1.00 (m, 16 H), 0.91 (d, J = 6.35 Hz, 6 H); GC–MS, m/z (relative intensity) 195 (13), 194 (M^+, 49), 81 (68), 67 (76), 41 (100.0). This ketone was described previously in the patent literature.[16]

General Procedure for Preparation of the Trimethylsilyl Enol Ethers. The basic procedure was that of Miller and McKean,[20] slightly modified to ensure complete equilibration of products. The ketone to be reacted (1.03 mmol) was dissolved in 20.0 mL of dry CH_2Cl_2 and placed in an oven-dried 50-mL two-necked flask fitted with a magnetic stirrer. An atmosphere of dry nitrogen was established, and the mixture was cooled to −30 °C. By means of a microsyringe, 0.280 mL (1.24 mmol) of freshly distilled hexamethyldisilazane and 0.161 mL (1.13 mmol) of commercial iodotrimethylsilane (TMSI) were added to the cooled reaction mixture. The temperature was maintained at −30 °C for 30 min and was then allowed to warm slowly to room temperature. The reaction mixture was stirred at room temperature for 24–36 h, the resulting slurry was transferred to test tubes and centrifuged, and the supernatant liquid was washed with two 10-mL portions of saturated aqueous $NaHCO_3$ in a prechilled separatory funnel. The CH_2Cl_2 solution was dried over Na_2SO_4. A 1-mL aliquot of this solution was used for capillary GLC and GC–MS analyses. Filtration of the solution followed by removal of the solvent in vacuo gave the crude trimethylsilyl enol ether mixture. This mixture was analyzed by capillary GLC, GC–MS, and ^1H and ^{13}C NMR. All runs were carried out at least in duplicate, and in those cases in which the *cis*-decalone was contaminated with the trans isomer, direct comparison with the trimethylsilyl enol ether mixture obtained from the *trans*-decalone was carried out. The results are summarized in Table I.

Trimethylsilyl Enol Ether Mixture from 7,7,10-Trimethyl-*cis*-2-decalone (5) via Enolates. To a solution of 0.200 g (1.03 mmol) of ketone **5** in 15 mL of THF, containing one crystal of 2,2′-bipyridyl, was added 0.130 mL (0.93 mmol) of diisopropylamine. To the stirred mixture was added slowly 0.850 mL (0.93 mmol) of 1.10 M *n*-butyllithium, and the reaction mixture was stirred at 25 °C for 18 h and then quenched with a solution of 0.191 mL (1.37 mmol) of Me_3SiCl in 2 mL of THF. After being stirred for 1 h at 25 °C, the solution was diluted with 50 mL of dry pentane, washed with cold saturated $NaHCO_3$, and dried over Na_2SO_4. Capillary GLC analysis indicated a 59:41 ratio of 2,3- to 1,2-silyl enol ethers in addition to recovered ketone **5**: GC–MS, m/z (relative intensity) (2,3-isomer) 266 (M^+, 11), 142 (60), 127 (100), 75 (63), (1,2-isomer) 266 (M^+, 32), 142 (68), 127 (96), 73 (100); ^{13}C NMR δ (2,3-isomer) 101.6, 148.6, (1,2-isomer) 109.4, 149.4.

(27) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.