($CDCl_3$) δ 1.25 (s, 3 H), 1.5–2.0 (m, 4 H), 3.8 (m, 2 H), 4.85 (s, 1 H), 6.3–7.0 (br s, 1 H); mass spectrum, *m/e* 142 ($M^+ + 1$), 98, 83. Anal. Calcd for $C_7H_{11}NO_2$: C, 59.54; H, 7.86; N, 9.92. Found: C, 59.77; H, 7.80; N, 9.85. **Method 2.** Reaction of crude β-lactam **20b** (0.24 g) with $PhCH_2NH_2$ (0.12 g) in CH_2Cl_2 (10 mL) at −78 °C for 1 h and chromatography on silica gave **18c** (58 mg, 41%).

3-Benzyltetrahydropyran-2-one.[32] Ethyl 3-phenylpropanoate (11.4 mL) was added dropwise over 1 h to lithium diisopropylamine solution [from *n*-BuLi in hexane (3.0 M, 21.7 mL), *i*-Pr_2NH (9 mL), and THF (92 mL)] and HMPA (23 mL) at −78 °C. After a further 1 h, 1-iodo-3-[(trimethylsilyl)oxy]propane (13.7 g) was added rapidly. After 1 h at −78 °C the mixture was warmed up to room temperature over 30 min, recooled to −78 °C, and added to hydrochloric acid (10%, 100 mL). The mixture was extracted with Et_2O (500 mL), and the extract washed with saturated aqueous $Na_2S_2O_7$ and H_2O, dried ($MgSO_4$), and evaporated. The residue (17.1 g) and $TsOH·H_2O$ (0.12 g) in PhMe (800 mL) was refluxed for 2 h. Evaporation and chromatography of the residue on silica (eluant hexane:CH_2Cl_2:Et_2O 4:4:1) gave 3-benzyltetrahydropyran-2-one (8.3 g, 83%) as an oil: IR (film) 1730, 1245, 1150, 1070, 965, 740, 700 cm^{-1}; NMR ^1H ($CDCl_3$) δ 1.3–2.05 (m, 4 H), 2.5, 2.78 (m, 2 H), 3.23 (m, 1 H), 4.2 (t, 2 H, *J* = 6 Hz), 7.2 (s, 5 H); mass spectrum, *m/e* 190 (M^+·), 147, 118, 91. The product was used crude without further purification.

3-Benzyl-2-methoxytetrahydro-2*H*-pyran. Diisobutylaluminium hydride in PhMe (34% w/w, 27 mL) was added over 1 h to 3-benzyltetrahydropyran-2-one (8.3 g) in PhMe (100 mL) at −78 °C. After 1 h the hydrochloric acid (10%, 100 mL) and ice (100 g) were added. The mixture was extracted with Et_2O and the organic phase washed with saturated $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated. The resultant oil (6.5 g), MeOH (200 mL), and Amberlyst IR 120H resin (5 g) were stirred overnight at room temperature. Filtration, evaporation, reevaporation from toluene, and chromatography on silica gave 3-benzyl-2-methoxytetrahydro-2*H*-pyran (4.77 g, 53%) as an oil: IR (film) 1120, 1050, 960, 750, 700 cm^{-1}; NMR ^1H ($CDCl_3$) δ 1.3–1.7 (m, 4 H), 2.5 (m, 2 H), 3.28 (m, 1 H), 3.3 (s, 3 H), 3.5 (m, 2 H), 4.26 (d, 1 H, *J* = 3 Hz), 7.16 (s, 5 H); mass spectrum, *m/e* 206 (M^+·), 174, 118, 91. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.68; H, 8.80. Found: C, 75.90; 8.93.

5-Benzyl-3,4-dihydro-2*H*-pyran (19b). PhMe (300 mL), 3-benzyl-2-methoxytetrahydro-2*H*-pyran (4.77 g), and Amberlyst IR 120H (10 g) were refluxed for 4 h and distilled to small volume over a further 3 h. Filtration, evaporation, and chromatography on silica gave **19b** (1.6 g, 40%): mp 120–121 °C; IR ($CHCl_3$) 1665, 1130 cm^{-1}; NMR ^1H ($CDCl_3$) δ 1.76 (m, 4 H), 3.1 (s, 2 H), 3.8 (t, 2 H, *J* = 3 Hz), 6.23 (s, 1 H), 7.15 (s, 5 H); mass spectrum, *m/e* 174 (M^+·), 173, 131, 91, 83.

6-Benzyl-8-aza-2-oxabicyclo[4.2.0]-7-octanone (20e). Trifluoroacetyl isocyanate (0.16 g) and **19b** (0.18 g) in $CHCl_3$ (2 mL) were allowed to react for 3 weeks at room temperature. Evaporation gave crude **20d** (0.31 g) as a yellow oil: IR ($CDCl_3$) 1820, 1740, 1230, 1170 cm^{-1}; NMR ^1H ($CDCl_3$) δ 1.2–2.1 (m, 4 H), 2.78, 3.08 (ABq, 2 H, *J* = 14 Hz), 3.76 (t, 2 H, *J* = 6 Hz), 5.53 (s, 1 H), 7.23 (s, 5 H). Chromatography of the crude product on Florisil [eluant Et_2O (500 mL)] and rechromatography on silica (eluant hexane–CH_2Cl_2 gradient) gave the β-lactam **20e** (88 mg, 40%): mp 95–99 °C; IR ($CHCl_3$) 3410, 1765 cm^{-1}; NMR ^1H ($CDCl_3$) δ 1.3–2.2 (m, 4 H), 2.72, 3.05 (ABq, 2 H, *J* = 14 Hz), 3.76 (m, 2 H), 5.0 (s, 1 H), 6.5 (br s, 1 H), 7.3 (s, 5 H); mass spectrum, *m/e* 218 ($M^+ + 1$), 174, 129, 115, 91. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.85; H, 6.96; N, 6.45. Found: C, 71.52; H, 6.96; N, 6.47.

8-[(2,2,2-Trichloroethoxy)sulfonyl]-8-aza-6-methyl-2-oxabicyclo[4.2.0]-7-octanone (20a). Isocyanate **11a** (0.25) and **19a** (0.10 g) in $CHCl_3$ (4 mL) were allowed to stand at room temperature for 2 days. Evaporation gave crude **20a** (0.34 g) as an oil: IR ($CDCl_3$) 1800, 1400, 1130 cm^{-1}; NMR ^1H ($CDCl_3$) δ (inter alia) 1.4 (s, 3 H), 1.5–2.4 (m, 4 H), 3.9 (m, 2 H), 4.8 (s, 2 H), 5.42 (s, 1 H).

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Wharton Fragmentation of Monosulfonates of Methylhexahydroindandiols[1]

Drury Caine,*[2] Candice J. McCloskey, and Donald Van Derveer

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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(*Z*)-5-Methylcyclonon-5-en-1-one (**5**) was obtained by treatment of an 85:15 mixture of 4α- (**4a**) and 4β-(tosyloxy)-7aβ-hydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydroindan (**4e**) with potassium *tert*-butoxide in *tert*-butyl alcohol. The corresponding *E* isomer (**6**) was also produced in a small quantity in this experiment and in reasonable yield when 4β-(mesyloxy)-7aβ-hydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydroindan (**4b**) was reacted under similar conditions. However, the *E* enone was not isolated in pure form. The hexahydroindandiols which were used to prepare the monosulfonates were obtained by reduction of 3a,7a-epoxy-3a,4,5,6,7,7a-hexahydro-4-indanone (**7**) with lithium and liquid ammonia followed by addition of methyl iodide to give 7aβ-hydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydro-4-indanone (**8**) and then reduction of the carbonyl group in **8** with metal hydrides or lithium in liquid ammonia.

In connection with our investigation toward a total synthesis of the antileukemic diterpene jatrophatrione (**1**),[3] we became interested in the fragmentation reactions of 6/5 fused ring systems as a method of producing functionalized cyclononane derivatives. Recently, Patel and Dev[4] reported that the Wharton fragmentation procedure[5] can be used to convert the hydroxy tosylate **2** into (*Z*)-5-methylcyclonon-4-en-1-one (**3**). We now wish to describe our studies on the Wharton fragmentation of hydroxy sulfonates such as **4**, which are related to **2** but contain the leaving group in the six-membered ring, to yield (*Z*)-5-methylcyclonon-5-en-1-one (**5**) and its *E* isomer **6**.

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(2) Present address: Department of Chemistry, University of Alabama, University (Tuscaloosa), AL 35486.
(3) Torrance, S. J.; Wiedhopf, R. M.; Cole, J. R.; Arora, S. K.; Bates, R. B.; Beavers, W. A.; Cutler, R. S. *J. Org. Chem.* **1976**, *41*, 1855.
(4) Patel, H. A.; Dev, S. *Tetrahedron* **1981**, *37*, 1577.
(5) (a) Wharton, P. S. *J. Org. Chem.* **1961**, *26*, 4781. (b) For a review see: Reucroft, J.; Sammes, P. G. *Q. Rev., Chem. Soc.* **1971**, *25*, 166.

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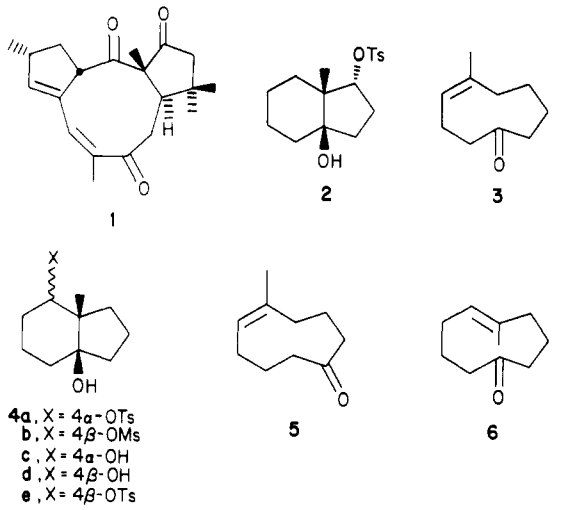
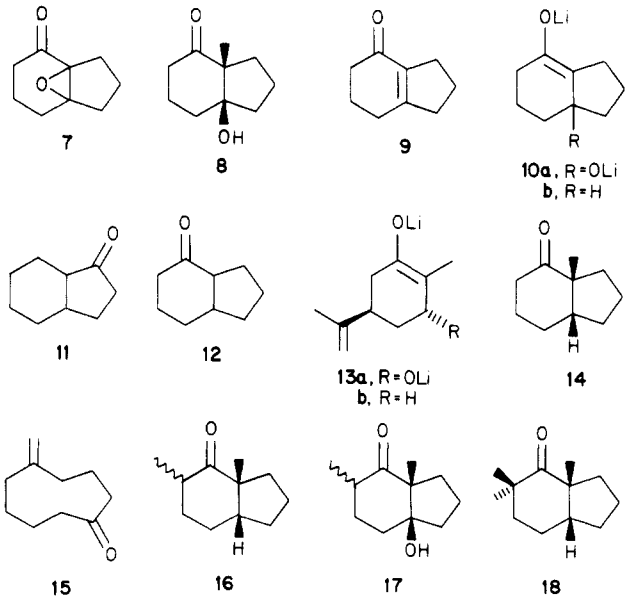


The synthesis of the sulfonates of the type 4 began with the reductive alkylation[6] of the 6/5 fused epoxy ketone **7**[7] with lithium in liquid ammonia followed by the addition of excess methyl iodide. According to GC analysis this reaction led to a complex mixture containing a major product and several minor products. The major product which made up 56% of the mixture was the hydroxy ketone 8 and its structure was established as described below. By comparison with authentic samples the mixture was also found to contain 2% of the starting epoxy ketone 7 and 4% of the methylhexahydroindanone **14**. The remaining reaction products were not isolated in pure form, but on the basis of GC–mass spectral analysis their structures were tentatively assigned as methylated derivatives of ketones 14 and 8, i.e., a ca. 1:1 mixture of dimethylhexahydroindanones **16** (24%), a ca. 1:1 mixture of dimethylhydroxyhexahydroindanones **17** (10%), and the trimethylhexahydroindanone **18** (4%).



Hydroxy ketone 8 was isolated by column chromatography of the reaction mixture on silica gel. It exhibited IR absorptions in CCl_4 at 3500 cm^{-1} for the hydroxyl group and at 1710 cm^{-1} for the carbonyl group. It showed a singlet at δ 1.18 ($CDCl_3$) in the ^1H NMR spectrum for the angular methyl group. In order to verify the stereochemical assignment of this compound, a single-crystal X-ray structure determination was performed on its 2,4-dinitrophenylhydrazone derivative. The molecular structure of this compound, as generated by ORTEP, is shown in Figure 1 with the 2,4-dinitrophenylhydrazone group deleted.

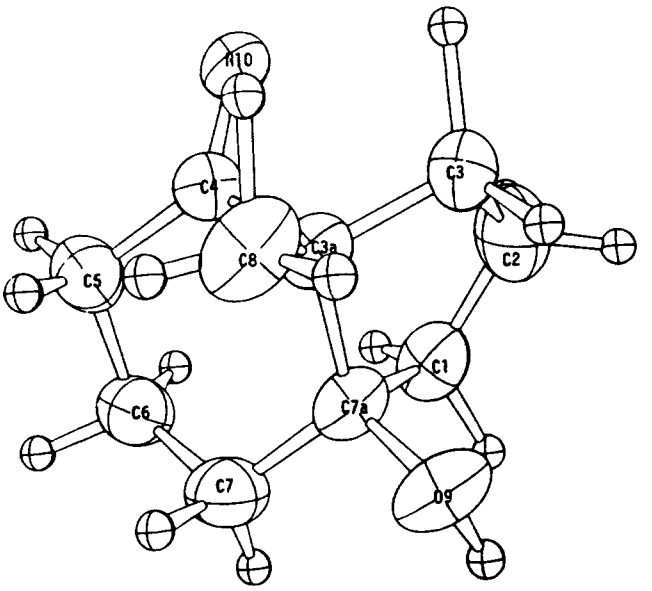


Figure 1.

The more substituted lithium enolate of the 6/5 fused hexahydroindanone **11** with the carbonyl group in the five-membered ring is known to undergo angular alkylation to give cis fused products with a high degree of stereoselectivity.[8] However, the angular alkylation of the related hexahydroindanone **12** with the carbonyl in the six-membered ring has apparently not been investigated. Also, it was not clear what influence, if any, the β-alkoxy group would have on the stereochemistry of alkylation of the enolate **10a**, the intermediate involved in the reduction–alkylation of **7**. Indeed, the β-alkoxy lithium enolate **13a**, which is formed by reductive cleavage of 2,3-epoxycarvone, has been shown[6d] to undergo axial alkylation with higher stereoselectivity than does the corresponding enolate **13b**, which has no β-substituent. This increase in stereoselectivity, which leads to the introduction of the new α-substituent trans to the β-substituent, has been ascribed[6d] to a steric effect of the alkoxy group. Apparently, in the alkylation of the enolate **10a** the tendency of bicyclic ketones to undergo angular alkylation to give cis fused products[8,9] strongly outweighs the steric effect of the β-alkoxy group which might have been expected to favor formation of the trans fused product.

In order to determine if the β-alkoxy group in **10a** actually influenced the stereoselectivity of the reaction in favor of the cis fused product 8, the related enolate **10b**, unsubstituted at the β carbon, was generated by reduction of the tetrahydroindanone **9**[7] with lithium in liquid ammonia and trapped with methyl iodide.[10] This led to a mixture of products which according to GC/MS analysis contained 87% of the cis fused hexahydroindanone **14**,[11]

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10% starting enone **9**, and 3% of a mixture of the 5α- and 5β-methyl derivatives of **14** (cf. **16**). Since the alkylation of both **10a** and **10b** gave only cis fused products, it does not appear that the β-alkoxy group has any significant influence on the stereochemical course of the alkylation reaction in these bicyclic systems.

Ketones **14**, **16**, and **18**, which were produced along with hydroxy ketone **8** and contain no hydroxyl group at C-7, appear to be derived from reduction–methylation of tetrahydroindanone **9**. While this material was used to prepare epoxy ketone **7**, we ruled out the possibility that the latter was contaminated with a significant amount of the enone prior to the reduction–methylation reaction. Thus, enone **9** is apparently generated from **7** under the reaction conditions. Possibly, a proton is transferred from unreacted epoxy ketone **7** to the β-alkoxy group in the enolate **10a** and β-elimination of hydroxide ion occurs to give **9** which then undergoes reduction–methylation. Alternatively, **10a** may eliminate the elements of lithium oxide to give **9** in a manner analogous to the formation of substituted olefins from the reaction of simple epoxides with organolithium reagents discovered by Crandall and Lin.[12]

It was anticipated that metal hydride reduction of **8** would occur from the convex face of the molecule to give predominately the diol **4c** with an α-hydroxyl group at C-4. This proved to be the case, but reduction of **8** with lithium aluminum hydride in ether was not highly stereoselective and led to a 3:2 mixture of diol **4c** and its isomer **4d** with the 4-hydroxyl group β. Use of sodium borohydride in methanol, as the reducing agent, gave a 85:15 mixture of 4α,7aβ-diol **4c** and 4β,7aβ-diol **4d**.

Reduction of **8** with lithium in liquid ammonia gave a 3:2 mixture of **4d** and **4c**, respectively. The 4β-hydroxy compound should be more stable than its 4α-epimer. Thus, the lithium–ammonia reduction of **8**, which is presumably thermodynamically controlled,[10b] gave the expected result.

In order to obtain analytical samples of the isomeric diols the mixture produced from the lithium liquid ammonia reduction was subjected to column chromatography on silica gel. The 4α,7aβ-diol **4c** was obtained essentially pure. Its ^{1}H NMR spectrum ($CDCl_3$) showed a singlet at δ 1.10 for the angular methyl group and a doublet (J = 9.5 and 4.0 Hz) at δ 3.60 for the hydrogen atom at C-4. A sample of the 4β,7aβ-diol (**4d**) with a purity of ca. 90%, was also isolated. Its ^{1}H NMR spectrum ($CDCl_3$) showed a singlet at δ 0.97 for the angular methyl group and a multiplet at δ 3.37 for the hydrogen atom at C-4. The stereochemical assignments of diols **4c** and **4d** were based upon the results of the reductions of hydroxy ketone **8** under the various conditions described above and the conversion of each of these compounds into the expected cyclononenone upon derivatization and Wharton fragmentation.

The 85:15 mixture of **4c** and **4d**, obtained from the sodium borohydride reduction of **8**, was converted into a ca. 85:15 mixture of tosyloxy alcohols **4a** and **4e** upon treatment with excess tosyl chloride in dry pyridine at room temperature. This reaction required five days to reach completion. Attempted purification of this mixture by recrystallization or column chromatography led to extensive decomposition. Therefore, it was treated immediately with potassium *tert*-butoxide in *tert*-butyl alcohol to give a crude mixture which according to its ^{1}H NMR spectrum contained about 85% of (*Z*)-5-methylcyclononenone (**5**) and its *E* isomer **6** in about 78% yield. The mixture of cyclic enones was not separable by TLC with silica gel coated plates or by HPLC with a silica column. Column chromatography of the mixture on silica gel led to the isolation of a relatively pure sample of enone **5** in about 40% yield, but no pure *E* isomer **6** was obtained. The mixture of enones exhibited two peaks in a ca. 85:15 ratio on GLC (carbowax column). Upon collection of these peaks by preparative GLC the major component showed IR ($CHCl_3$) absorptions at 1700 cm^{-1} for the C=O stretch and at 825 cm^{-1} for the trisubstituted double bond and ^{1}H NMR absorptions at δ 1.67 (singlet) for the vinyl methyl group and δ 5.23 (triplet, J = 9 Hz) for the vinyl hydrogen at C-6. The cis relationship of the C-6 hydrogen atom and the methyl group on the double bond in **5** was confirmed by a nuclear Overhauser effect experiment.[13] Thus, irradiation of the methyl signal resulted in a >10% enhancement of the signal for the vinyl hydrogen. The minor GLC component was assumed to be the *E* enone **6**, but it did not show a signal for a vinyl methyl group in the ^{1}H NMR spectrum ($CDCl_3$). However, one proton absorptions at δ 4.68 (doublet, J = 0.3 Hz) and 4.92 (doublet, J = 0.3 Hz) characteristic of an exocyclic double bond were observed. Also, the IR spectrum ($CDCl_3$) showed an absorption at 890 cm^{-1} characteristic of the CH out-of-plane bending vibrations of a vinylidene group. On the basis of these and other spectral properties the exocyclic enone structure **15** was assigned to the collected material. Apparently, the *E* isomer **6** which according to ^{1}H NMR spectral analysis was present in the Wharton fragmentation mixture underwent isomerization on the hot (220 °C) metal surface of the injector port of the gas chromatograph. From examination of a model of the *E* enone **6** the molecule appears to be highly strained and the observed isomerization would lead to relief of this strain.

In an attempt to isolate the *E* enone **6**, the 4β,7aβ-diol **4d** was converted into the 4-mesyloxy derivative **4b** by reaction with mesyl chloride in dry pyridine for five days at room temperature. Diol **4d** was only partially converted to the corresponding tosyloxy derivative by reaction with tosyl chloride under the same conditions. Monomesylate **4b** was also highly unstable and was immediately reacted with potassium *tert*-butoxide in *tert*-butyl alcohol to give a 64% yield of a mixture of products which by integration of the ^{1}H NMR spectrum appeared to contain 63% of the (*E*)-5-methylcyclononenone (**6**), 17% of the diol **4d**, and 20% of the starting mesylate **4b**. However, attempted isolation of the pure *E* enone **6** by preparative TLC and column chromatography on silica gel were unsuccessful. The crude product mixture obtained from fragmentation of the mesylate **4b** showed ^{1}H NMR ($CDCl_3$) absorptions at δ 1.35 (s, 3 H, vinyl methyl) and 5.51 (m, 1 H, vinyl hydrogen), attributable to the *E* cyclononenone **6**. Examination of models indicates that in the most stable conformation of **6** the methyl group lies within the shielding cone of the carbonyl group. This presumably accounts for the relatively high field location of the vinyl methyl signal of **6**.

Experimental Section

General Procedures. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 299 spectrophotometer. Mass spectra were obtained with

(12) (a) Crandall, J. K.; Lin, L. H. C. *J. Am. Chem. Soc.* **1967**, *89*, 4527. (b) For another recent example of the loss of Li_2O from a β-lithio lithium alkoxide, see: Cohen, T.; Yu, L. C. *J. Org. Chem.* **1984**, *49*, 605.

(13) For a recent example of the use of this method to determine cycloalkene stereochemistry see: Clive, D. L. J.; Russell, C. G.; Suri, S. C. *J. Org. Chem.* **1982**, *47*, 1632.

a Varian MAT Model 112S spectrometer operating at 70 eV. Ionization was effected by electron impact. Reported masses are due to peaks of intensity greater than 20% of the base peak except where noted. Proton NMR spectra at 60 MHz were recorded on a Varian T-60A NMR spectrometer. Proton NMR spectra at 300 MHz and ^{13}C NMR spectra at 75 MHz were recorded on a Bruker Aspect 2000 NMR spectrometer. Spectra were recorded as solutions in $CDCl_3$ with tetramethylsilane as internal reference except where noted; signals are reported in ppm. The following abbreviations are used: s, singlet; d, doublet; t, triplet; b, broad.

GLC analyses and collections were carried out on an Aerograph Autoprep Model A-700 with either of the following: Column A, 20% SE-30 on Chromosorb W, 60–80 mesh, 10 ft × 0.25 in.; Column B, 30% Carbowax 20-M on Chromosorb W, 80–100 mesh, 10 ft × 0.25 in. The carrier gas was helium. Peak areas were determined by triangulation method. Analytical HPLC was performed on a laboratory Data Control instrument fitted with a RefractoMonitor III with a silica column (LDC no. 28701) at a pressure of 200 psi and a flow rate of 0.5 mL/min. Elemental analyses for all compounds except **4d** were performed by Atlantic Microlab, Inc., Atlanta, GA 30366. Analysis of the hygroscopic diol **4d** was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY 11377.

Tetrahydrofuran and diethyl ether were freshly distilled from benzophenone ketyl, kept over activated 4Å molecular sieves under a dry nitrogen atmosphere, and used immediately. Methanol was freshly distilled from magnesium methoxide. *tert*-Butyl alcohol was distilled from sodium and stored over 4Å molecular sieves under nitrogen. Pyridine was dried over NaOH for a few days before use. Methyl iodide was distilled from $CaCl_2$ and stored in the refrigerator over iron wire. Methylene chloride (Fisher certified), anhydrous ammonia (Matheson), and absolute alcohol were used as such. *p*-Toluenesulfonyl chloride was purified according to Perrin,[14] mp 67.5–68 °C (lit.[14] mp 69 °C). Methanesulfonyl chloride was distilled from P_2O_5 just before use. Lithium wire (Aldrich), sodium borohydride (Fisher), and potassium metal (Fisher) were used as obtained. All reactions were carried out under a dry nitrogen atmosphere in glassware that had been oven-dried, then flame-dried, and cooled under a stream of nitrogen.

3a,7a-Epoxy-3a,4,5,6,7,7a-hexahydro-4-indanone (7). To a solution of bicyclo[4.3.0]-1(6)-nonen-2-one[7] (25.0 g, 18.3 mmol) in methanol (130 mL) and 30% hydrogen peroxide (55 mL) at 5 °C was added dropwise with stirring aqueous 0.29 N potassium carbonate (55 mL) over a period of 45 min. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then poured into brine (400 mL) and extracted with diethyl ether. The organic layer was washed with brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure and distillation gave **7** (21.6 g, 78% yield) which was 97% pure by GC analysis (column A, 197 °C): bp 73–75 °C (1.5 mm) [lit.[7] bp 61–65 °C (0.6 mm)]; IR (CCl_4) 2960, 1705, 1440, 1370, 1270, 1250, 925, 865 cm^{-1}; 60 MHz ^1H NMR 1.13–2.73 (m, 12 H); 75 MHz ^{13}C NMR 18.4, 19.8, 24.4, 25.2, 31.0, 36.2, 68.6, 72.6, 206.5; mass spectrum, *m/e* (relative intensity) 152 (M^+, 3), 97 (100), 79 (21), 55 (26), 41 (31).

7aβ-Hydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydro-4-indanone (8). To a solution of lithium (1.68 g, 0.34 mol) in dry liquid ammonia (45 mL) was added a solution of **7** (16.6 g, 10.9 mmol) in dry diethyl ether (100 mL) with stirring over a period of 30 min. The mixture was stirred for an additional 30 min and then dry ether (200 mL) was added followed by dropwise addition of methyl iodide (40 mL, 65 mmol) in dry ether (100 mL) over a period of 30 min. The ammonia was evaporated maintaining anhydrous condition, and then water (300 mL) was added. The water layer was saturated with sodium chloride and then extracted with ether. The organic layers were combined, washed with aqueous 0.1 M hydrochloric acid, saturated aqueous sodium bicarbonate, and brine, and then dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 12.8 g (70% yield) of a mixture which according to GC analysis (column A) contained 56% of a major product, hydroxy ketone **8**, and seven minor components. Two of the minor components which made up 2% and 4% of the mixture, respectively, were found by coinjection with authentic samples to be the starting epoxy ketone **7** and the methylhexahydroindanone **14**. The mixture was subjected to GC–mass spectral analysis and the structures of the five remaining components were tentatively assigned on the basis of their mass spectral data as a ca. 1:1 mixture of dimethylhexahydroindanones **16** (24%), a ca. 1:1 mixture of dimethylhydroxyhexahydroindanones **17** (10%), and trimethylhexahydroindanone **18** (4%). Column chromatography (silica gel, 100% methylene chloride to 10% ethyl acetate in methylene chloride) of the reaction mixture gave pure **8** (7.7 g, 42% yield) as pale yellow crystals: mp 100–102 °C; IR (CCl_4) 3610, 3500, 2940, 2870, 1710, 1460, 1440, 1370, 1340, 1310, 1090, 965 cm^{-1}; 300 MHz ^1H NMR 1.18 (s, 3 H), 1.44–2.00 (m, 10 H), 2.27–2.54 (m, 3 H); 75 MHz ^{13}C NMR 17.36, 17.95, 19.91, 31.37, 31.63, 35.61, 36.05, 59.46 (CCH_3), 93.0 (COH), 213.13; mass spectrum, *m/e* (relative intensity) 168 (M^+, 55), 150 (23), 110 (25), 108 (76), 107 (28), 98 (99), 97 (77), 95 (93), 93 (41), 84 (47), 83 (44), 81 (44), 79 (46), 71 (23), 70 (26), 69 (51), 67 (27), 55 (74), 43 (96), 42 (54), 41 (100), 39 (65). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.23; H, 9.58.

The mass spectra of the two components whose structures were tentatively assigned as the dimethylhexahydroindanones **16** showed *m/e* (relative intensity) 166 (M^+, 6), 125 (36), 111 (27), 108 (38), 95 (20), 81 (100), 67 (30), 55 (23), and 41 (22).

The mass spectra of the two components whose structures were tentatively assigned as the dimethylhydroxyhexahydroindanones **17** showed *m/e* (relative intensity) 182 (M^+, 31), 164 (20), 112 (23), 111 (20), 109 (69), 108 (86), 98 (54), 97 (100), 96 (31), 95 (24), 93 (48), 84 (43), 83 (41), 82 (27), 81 (67), 79 (26), 69 (56), 67 (35), 56 (25), 55 (49), 43 (60), 41 (70), and 39 (33).

The mass spectrum of the component whose structure was tentatively assigned as the trimethylhexahydroindanone **18** showed *m/e* (relative intensity) 180 (M^+, 13), 111 (42), 110 (66), 109 (27), 108 (35), 97 (59), 96 (38), 95 (42), 93 (21), 82 (25), 81 (100), 79 (29), 69 (22), 68 (36), 67 (63), 55 (44), 43 (20), 41 (50), and 39 (32).

***cis*-3a-Methyl-5,6,7,7a-tetrahydro-4(3a*H*)-indanone (14).** To a solution of lithium (0.27 g, 0.04 mol) in dry liquid ammonia (160 mL) was added dropwise a solution of enone **9** (2.2 g, 16.2 mmol) in dry diethyl ether (10 mL) over a period of 10 min. After stirring for 1 h the reaction mixture was diluted with dry ether (100 mL). After dropwise addition of a solution of methyl iodide (6 mL, 97 mmol) in ether (20 mL) over 20 min, the ammonia was allowed to evaporate under anhydrous conditions and the reaction mixture was hydrolyzed with water (50 mL). The layers were separated and the water layer was extracted with ether. The organic layers were combined, washed with 0.1 M hydrochloric acid, aqueous sodium bicarbonate, and brine. after drying over magnesium sulfate the solvent was removed under reduced pressure to give **14** as a pale yellow oil (2.2 g, 89% yield) which was 87% pure by GC analysis (column A, 155 °C). Enone **9** accounted for 10% of the crude product and 5-methyl-3aβ-methyl-5,6,7,7a-tetrahydro-4(3a*H*)-indanone (**16**) the remaining 3%. The 2,4-dinitrophenylhydrazone of **14** showed mp 130–132 °C (lit.[12] mp 132–132.5 °C). A pure sample of **14** was collected by GC (column A, 155 °C): IR (CCl_4) 2950, 2880, 1700, 1465, 1425, 1375, 1319, 1260, 1220, 1210, 1120, 1018, 670 cm^{-1} (lit.[12] 1702 cm^{-1}); 60 MHz ^1H NMR (C_6D_6) 1.02 (s, 3 H, CH_3), 1.1–2.53 (m, 13 H); 60 MHz ^1H NMR (CCl_4) 1.13 (s, 3 H, CH_3), 1.1–2.45 (m, 13 H) [the literature values[12] for the methyl group are 1.03 (C_6D_6) and 1.11 (CCl_4)]; mass spectrum, *m/e* (relative intensity) 152 (M^+, 12), 111 (91), 108 (41), 97 (40), 95 (31), 93 (32), 81 (100), 41 (36), 39 (33).

4α,7aβ-Dihydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydroindan (4c). Sodium borohydride (0.23 g, 6 mmol) was added in small portions to a solution of **8** (1.0 g, 6 mmol) in dry methanol (50 mL). The reaction mixture was stirred overnight at room temperature. Workup was accomplished by addition of 1 M hydrochloric acid (5 mL) followed by removal of most of the solvent under reduced pressure. The residue was taken up in ether and the organic layer was washed with water, aqueous sodium bicarbonate, and brine. After drying over magnesium sulfate, the solvent was removed under reduced pressure to give a crude product (0.61 g, 60% yield) which was 84% pure by GC analysis (column A, 190 °C) and consisted of an 85:15 mixture of the

(14) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1966; p 268.

α-hydroxy diol **4c** and the β-hydroxy diol **4d**, respectively. The minor components were not characterized. Reduction of **8** with lithium aluminum hydride in ether gave a 3:2 mixture of diols **4c** and **4d**. A purified sample of **4c**, obtained by column chromatography on silica gel (30–60% ethyl acetate/hexane), showed the following physical properties: mp 79–81 °C; IR ($CHCl_3$) 3607, 3420, 2960, 2940, 2875, 1460, 1375, 1175, 1025, 1007, 986, 905 cm^{-1}; 300 MHz ^1H NMR 1.1 (s, 3 H), 1.35–1.95 (m, 14 H), 3.60 (dd, 1 H, J = 9.5, 4.0 Hz); GC–mass spectrum, m/e (relative intensity) 153 (M − 15, 5), 152 (36), 137 (42), 134 (68), 119 (35), 110 (27), 108 (43), 98 (32), 97 (40), 96 (38), 94 (46), 84 (25), 82 (23), 81 (47), 79 (32), 71 (23), 67 (30), 55 (48), 43 (100), 42 (31), 41 (76), 39 (42). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.46; H, 10.66.

(*Z*)-5-Methylcyclonon-5-en-1-one (5). To a solution of the 85:15 mixture of diols **4c** and **4d** (0.5 g, 3 mmol) in dry pyridine (10 mL) was added *p*-toluenesulfonyl chloride (0.61 g, 3.2 mmol). The reaction mixture was stirred at room temperature for 5 days until tosylation was complete. Workup was accomplished by hydrolysis with brine (10 mL) followed by extraction with ether. The ether layer was washed with water and brine and then dried. Removal of solvent under reduced pressure, with the unstable tosylate being kept cold and in the dark, gave a yellow oil (0.76 g, 78% yield) which consisted of 85% α-tosylate **4a** and 15% β-tosylate **4b** by integration of the NMR spectrum. 4α-Tosylate **4a** of the mixture showed the following: 300 MHz ^1H NMR 0.81 (s, 3 H), 1.1–2.0 (m, 13 H), 2.34 (s, 3 H), 4.49 (dd, 1 H, 9.5, 4 Hz), 7.47 (dd, 7.0 Hz). The mixture of unstable tosylates was used immediately in the next step.

To a solution of the 85:15 mixture of **4a** and **4e** (0.5 g, 1.5 mmol) in dry *tert*-butyl alcohol (15 mL) at 40 °C was added rapidly with stirring 1 N potassium *tert*-butoxide in *tert*-butyl alcohol (4.6 mL, 3 equiv). The reaction mixture was stirred for 1 h at 40 °C, and then water was added until a clear red solution obtained. The water layer was extracted with 2:1 pentane:ether and the organic layer was washed with water, 0.1 M aqueous sodium hydroxide, aqueous sodium bicarbonate, and brine. After drying, the solvent was removed under reduced pressure to give a pale yellow oil (0.19 g, 85% yield) which showed a major peak (85%) by GC analysis (column B, 160 °C) corresponding to **5** and a minor peak (15%) corresponding to exocyclic enone **15**. Column chromatography (silica gel, 20% ether in hexane) gave 90 mg of pure *Z* isomer **5** (40% yield). Separation of mixtures of *Z* and *E* cyclononenones by either preparative TLC or HPLC (silica gel, 30% ether–hexane) could not be effected. Pure samples of **5** and the *exo*-methylene isomer **15** were collected by GLC for spectral analysis. (*Z*)-5-Methylcyclonon-5-en-1-one (**5**) showed the following: IR ($CHCl_3$) 2930, 2860, 1700, 1445, 1375, 1350, 1165, 1125, 1100, 880, 825 cm^{-1}; 300 MHz ^1H NMR 1.67 (s, 3 H), 1.86–2.50 (m, 10 H), 5.23 (t, 1 H, J = 9 Hz); 25 MHz ^{13}C NMR 23.5, 23.6, 25.2, 25.7, 28.9, 41.6, 125.7, 136.3, 217.1; mass spectrum, m/e (relative intensity) 152 (M^+, 10), 137 (23), 134 (33), 119 (22), 95 (25), 94 (100), 84 (37), 83 (30), 81 (22), 79 (52), 71 (54), 69 (20), 67 (30), 58 (23), 55 (28), 43 (79), 41 (30). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.99; H, 10.59. Exact mass calcd 152.1197, found 152.1219.

A sample was prepared for a nuclear Overhauser effect experiment by degassing a solution of GC-collected **5** in chloroform-*d* in an NMR tube followed by sealing under nitrogen. Irradiation of the methyl group signal at δ 1.67 resulted in a >10% enhancement of the vinyl hydrogen signal at δ 5.23.

5-Methylindenecyclononanone **15** showed the following: IR ($CHCl_3$) 2910, 2850, 1715, 1680, 1435, 1345, 1310, 1280, 1085, 960, 890 cm^{-1}; 300 MHz ^1H NMR 1.32–2.37 (m, 14 H), 4.68 (d, 1 H, J = 0.3 Hz), 4.92 (d, 1 H, J = 0.3 Hz); mass spectrum, m/e (relative intensity) 152 (M^+, 0.1), 134 (56), 119 (86), 109 (23), 106 (34), 105 (56), 95 (35), 91 (67), 84 (28), 81 (26), 79 (100), 77 (22), 67 (36), 55 (30), 53 (24), 43 (20), 41 (48), 39 (50). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.97; H, 10.62.

4β,7aβ-Dihydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydroindan (4d). Lithium (0.12 g, 4 mol) was added slowly in small pieces to a stirred solution of **8** (0.74 g, 4.4 mmol) in ammonia (35 mL) and ethanol (1 mL) until the blue color persisted. The reaction mixture was stirred for 1.5 h and then the ammonia was evaporated under anhydrous conditions. Saturated aqueous ammonium chloride (10 mL) was added, the layers were separated, and the water layer was extracted with ether. The organic layers were combined and washed with water, 0.1 M hydrochloric acid, aqueous sodium bicarbonate, and brine. After the solution was dried, the solvent was removed under reduced pressure to give a colorless oil (0.51 g, 68% yield) which was shown by analysis (column A, 180 °C) to consist of a 3:2 mixture of diols **4d** and **4c**, respectively. Column chromatography on silica gel (30%–60% ethyl acetate in hexane) gave slightly impure diol **4d** (ca. 100 mg) which was recrystallized from ether–hexane to give the pure material: mp 101–103 °C; IR ($CDCl_3$) 3680, 3605, 3640, 3350, 2970, 2945, 2880, 1600, 1450, 1375, 1260, 1047, 1030, 1012, 990, 920, 880, 755 cm^{-1}; 60 MHz ^1H NMR 0.97 (s, 3 H), 1.1–2.0 (m, 14 H), 3.37 (m, 1 H); mass spectrum, m/e (relative intensity) 155 (M − 15, 0.6), 152 (17), 137 (61), 134 (81), 124 (22), 119 (60), 111 (25), 110 (36), 109 (64), 108 (24), 105 (25), 99 (26), 98 (47), 97 (54), 96 (58), 95 (59), 94 (60), 93 (36), 84 (34), 83 (44), 82 (36), 81 (77), 79 (53), 71 (40), 70 (24), 69 (38), 68 (32), 67 (52), 57 (36), 55 (76), 53 (27), 44 (22), 43 (100), 41 (90), 39 (48). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.59; H, 10.77.

(*E*)-5-Methylcyclonon-5-en-1-one (6). To a solution of **4d** (1.9 g, 11 mmol) in dry pyridine (35 mL) was added freshly distilled methanesulfonyl chloride (1.6 g, 14 mmol). The reaction mixture was stirred for 5 days at room temperature to complete mesylation. Workup gave a yellow oil (1.5 g, 54% yield) which consisted of the 4β-mesylate **4b** and a small amount of diol **4d** and showed the following spectral characteristics: 60 MHz ^1H NMR 1.07 (s, 3 H), 1.1–2.4 (m, 13 H), 2.97 (s, 3 H), 4.32 (m, 1 H). The unstable mesylate was used immediately in the next step.

A solution of the crude **4b** (1.5 g, 6 mmol) in dry *tert*-butyl alcohol (25 mL) was heated to 40 °C. A solution of 1 N potassium *tert*-butoxide in *tert*-butyl alcohol (24 mL, 4 equiv) was quickly added and the mixture was stirred for 1 h at 40 °C. Workup gave a yellow oil (0.6 g, 64% yield) which consisted of 63% cyclononenone **6**, 16% β-diol **4d**, and 21% 4β-mesylate **4b** by NMR analysis. Distillation of the crude oil under reduced pressure (bp 35–36 °C (0.23 mm)) gave a pale yellow oil which was largely enone **6** but still contained diol **4d** and mesylate **4b**. This oil showed the following spectral data attributable to enone **6**: 300 MHz ^1H NMR 1.35 (s, 3 H), 1.4–2.6 (m, 12 H), 5.51 (m, 1 H); mass spectrum, m/e (relative intensity) 152 (M^+, 21), 137 (33), 134 (66), 119 (47), 111 (27), 109 (42), 106 (21), 105 (28), 97 (27), 96 (43), 95 (45), 94 (51), 93 (36), 91 (33), 84 (31), 82 (31), 81 (89), 79 (100), 68 (45), 67 (78), 55 (68), 53 (32), 43 (30), 41 (69), 39 (49); IR ($CHCl_3$) 2930, 2860, 1683, 1445, 1380, 1340, 1155 cm^{-1}; exact mass calcd 152.1197, found 152.1209.

Attempts to obtain the cyclononenone **6** in purer form were unsuccessful. Preparative TLC (Merck silica gel, 250μ) led to decomposition of the compound as did column chromatography on alumina (20% ether in hexane).

Supplementary Material Available: A description of the data collection and solution of the structure of the 2,4-dinitrophenylhydrazone of 7aβ-hydroxy-3aβ-methyl-3a,4,5,6,7,7a-hexahydroindan-4-one (**8**), tables of the positional and anisotropic temperature parameters of the non-hydrogen atoms, positional and isotropic temperature parameters of the hydrogen atoms, and tables of bond distances and angles (8 pages). Ordering information is given on any current masthead page.