by GLC and showed only a single vinyl methyl absorption at δ 1.57 in the 90-MHz ^{1}H NMR spectrum.

The ability to conduct the Cope rearrangement of acyclic 1,5-dienes in a catalytic fashion at room temperature should have significant implications in synthesis. We are continuing to explore the scope, mechanism, and synthetic applications of this mild carbon–carbon-bond-forming reaction.

Acknowledgments. This project was generously supported by grants from the National Science Foundation (CHE 76-06101A and CHE-7901833). The support of the Camille and Henry Dreyfus Foundation through a Teacher-Scholar Award to L.E.O. is also gratefully acknowledged. NMR and mass spectra were determined with spectrometers purchased with the assistance of departmental NSF instrumentation grants.

References and Notes

(1) Catalyzed Sigmatropic Rearrangements. 5. For part 4 see Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321.
(2) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.
(3) Methods typically exploit the acidity or basicity of a heteroatom substituent. Examples include the following. (a) Base catalyzed oxy-Cope rearrangement: Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *Ibid.* **1978**, *100*, 2242. (b) Acid catalyzed rearrangements of 1- or 3-acyl-1,5-dienes: Yates, P.; Eaton, P. *Tetrahedron Lett.* **1960**, *11*, 5. Cookson, R. C.; Hudec, J.; Williams, R. O. *Ibid.* **1960**, *22*, 29. Widner, U., Zsindely, J.; Hansen; H.-J., Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 75. Miller, B. *Acc. Chem. Res.* **1975**, *8*, 245.
(4) To our knowledge the only reports of catalyzed Cope rearrangements of 1,5-diene hydrocarbons are alumina catalysis of the Cope rearrangement of *meso*- and *dl*-3,4-diphenyl-1,5-hexadiene,[5] Ni(II) catalysis of the Cope rearrangement of *cis*-divinylcyclobutane,[6] and the Pd(II) and Pt(II) catalyzed rearrangements summarized in ref 7–10.
(5) Lutz, R. P.; Berg, H. A. J.; Wang, P. J. *J. Org. Chem.* **1976**, *41*, 2048.
(6) Heimbach, P.; Brenner, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 800.
(7) (a) Trebellas, J. C.; Olechowski, J. R.; Jonassen, H. B. *J. Organomet. Chem.* **1966**, *6*, 412. (b) Heimbach, P.; Molin, M. *Ibid.* **1973**, *49*, 477.
(8) The $PdCl_2$ promoted rearrangement of *trans,trans*-1,5-cyclononadienes has also been reported: Brown, E. D.; Sam, T. W.; Sutherland, J. K.; Torre, A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2326.
(9) Heimbach, P.; Molin, M. *J. Organomet. Chem.* **1973**, *49*, 483.
(10) Diene **1** was prepared from 1-phenyl-2-propanone by successive treatment with (a) KH and allyl bromide, and (b) methylenetriphenylphosphorane. Other dienes utilized in this study were prepared by related procedures.[11]
(11) New compounds were characterized by ^{1}H NMR, ^{13}C NMR (in most cases), IR, and low resolution mass spectra. All yields refer to isolated product of >96% purity as determined by GLC analysis.
(12) Representative spectral data follow. (a) **2**: IR (film) 3080, 3060, 3030, 2980, 2930, 1640, 1600, 1490, 1440, 990, 910 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.2 (m, C_6H_5), 6.28 (br s, $W_{h/2}$ = 5 Hz, PhC*H*=CMeR), 6.0–5.6 (m, C*H*=CH_2), 5.1–4.9 (m, CH=CH_2), 2.2–3.0 (m, CH_2C=), 1.85 (d, J = 1.3 Hz, =CCH_3); ^{13}C NMR ($CDCl_3$) δ 138.9 (*ipso*-Ph), 138.7 (C-5), 129.2 (*m*-Ph), 128.4 (*o*-Ph), 126.2 (*p*-Ph), 125.6 (C-1), 115.0 (C-6), 40.2 (C-3), 32.6 (C-4), 17.9 (CH_3); mass spectrum (rel intensity) (methane CI) *m/z* 173 (21), 131 (100), 91 (75). (b) **7**: IR (film) 3075, 2960, 1640, 990, 818 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.1–5.6 (m, C*H*=CH_2), 5.4–4.9 (m, =CH_2 and CH=C), 1.59 (d, J = 6.8 Hz, =CHCH_3), 0.96 (t, J = 7.6 Hz, CH_2CH_3); mass spectrum (rel intensity) (methane CI) *m/z* 125 (4), 109 (45), 95 (93), 83 (78), 55 (100).
(13) The unusually low stereoselectivity observed in the thermal rearrangement of **1** can be ascribed to destabilizing steric interactions[14] between the quasi-equatorial phenyl and the vinylic methyl in the "chair-transition state"[2] leading to the *E* isomer **2**.
(14) Cf. Johnson, F. *Chem. Rev.* **1968**, *68*, 375.
(15) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757. Couperus, P. A.; Clague, A. D. H.; van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426.
(16) Cf. Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic: New York, 1971; Vol. II, Chapter 3.
(17) A second-order rate constant (k_{cat} = 0.3 M^{-1} s^{-1}) for the catalyzed rearrangement in benzene can be estimated from the observed half-life of 220 s [$PdCl_2(PhCN)_2$, 0.010; **1**, 0.10 M]. The corresponding rate constant for the thermal isomerization of **1** (k = 3.4 × 10^{-11} s^{-1}) was estimated using 3-phenyl-1,5-hexadiene (**8**) as a model and the activation parameters of Dewar and Wade[18] for the Cope rearrangement of **8** in *o*-dichlorobenzene. The measured rate constant for thermal Cope rearrangement of **1** at 177 °C (k = 1.4 × 10^{-5} s^{-1}; benzene solvent) is slightly smaller than that calculated[18] for **8** at this temperature (k = 4.6 × 10^{-5} s^{-1}; *o*-dichlorobenzene solvent).
(18) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4417.
(19) A number of mercuric trifluoroacetate catalyzed [3,3]-sigmatropic rearrangements have been reported from our laboratory. Cf.: (a) Overman, L. E.; Campbell, C. B.; Knoll, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 4822. (b) Overman, L. E. *Ibid.* **1976**, *98*, 2901.
(20) No trace of **2** was detected by GLC, and >90% of **1** was recovered when **1** was treated with 0.1 equiv [0.4 equiv in the case of $Hg(OCOCF_3)_2$] of these catalysts for 24 h at room temperature in THF.
(21) Cf.: Hartley, F. R. *Chem. Rev.* **1973**, 163. Akermark, B.; Bäckvall, J.-E. *Tetrahedron Lett.* **1975**, 819. Pregaglia, G. F.; Conti, F.; Minasso, B. *J. Organomet. Chem.* **1973**, *47*, 165.
(22) The cyclization step of a "cyclization-induced rearrangement" mechanism[19a] for the Pd(II) catalyzed Cope rearrangements derives precedent from reported cyclizations of acyclic 1,5-dienes to give cyclohexane products under oxymetalation conditions. Cf.: Julia, M.; Fourneron, J.-D. *J. Chem. Res. (M)* **1978**, 5401 (S466). Renold, W.; Ohloff, G; Norin, T. *Helv. Chim. Acta* **1979**, *62*, 985.
(23) The same mixture of **6** and **7** was obtained when **7** was treated (28 h, THF, 25 °C) with 0.10 equiv of $PdCl_2(PhCN)_2$.
(24) Based on analogy with **2**. Unfortunately we did not obtain enough **7** for ^{13}C NMR analysis.

Larry E. Overman,* Frederick M. Knoll
Department of Chemistry, University of California
Irvine, California 92717
Received August 27, 1979

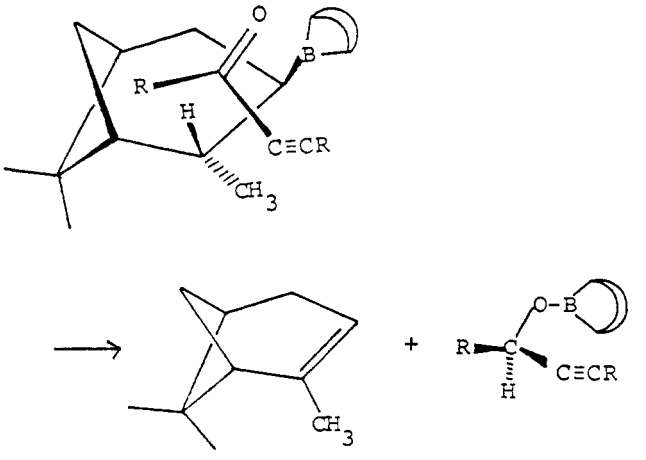
Reduction of α,β-Acetylenic Ketones with *B*-3-Pinanyl-9-borabicyclo[3.3.1]nonane. High Asymmetric Induction in Aliphatic Systems

Sir:

The introduction of asymmetry in a molecule by means of a chiral reagent is a potentially attractive strategy in natural product synthesis. One of the simplest and most useful transformations of this type is the reduction of a prochiral ketone to a carbinol. Several reagents will perform this reduction with high asymmetric induction in simple aryl substrates.[1,2] However, these reagents have been less successful with the aliphatic ketones of interest to most synthetic chemists. Herein we report that the chiral reducing agent prepared from (+)-α-pinene and 9-borabicyclo[3.3.1]nonane (9-BBN) will reduce α,β-acetylenic ketones under mild conditions to secondary propargylic alcohols of exceptionally high enantiomeric purity. Since the products from such reductions are useful intermediates in synthetic organic chemistry,[3] such a reagent may be of enormous practical value.

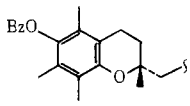
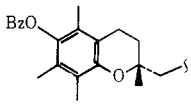
B-3-Pinanyl-9-BBN has been shown to be highly effective in the reduction of aldehydes to chiral 1-deuterio primary alcohols.[4] The alcohols from these reductions are consistently of the same configuration.[5] Similarly, all of the acetylenic ketones which we have examined are consistently reduced to the propargylic alcohols of the same absolute configuration. Alcohols of the opposite configuration may be obtained with the reagent prepared from (−)-α-pinene. These reactions are thought to proceed through the bimolecular exchange mechanism[6] depicted in Scheme I. The acetylene moiety seems to have the same steric influence as hydrogen in aldehyde reductions.[1a] This is to be contrasted to the $LiAlH_4$–Darvon alcohol or *N*-methylephedrine complexes which, it has been

Scheme I



0002-7863/80/1502-0867$01.00/0

Table I. Reductions of Alkynyl Ketones with *B*-(3)-α-Pinanyl-9-BBN

	ketone RCOC≡CR′ R	R′	% yield[a]	% ee[b]
1	C_6H_5	n-C_4H_9	72	89[c]
2	CH_3	C_6H_5	98	72 (78)
3	n-C_3H_7	n-C_6H_{13}	68	77[c]
4	n-C_5H_{11}	H	65	92[c]
5	$CH(CH_3)_2$	H	78	91 (99)
6		CH_3	77	85:15[d]
7		H	75	91:9[d]
8	CH_3	$CO_2C_2H_5$	59	71 (77)
9	n-C_5H_{11}	$CO_2C_2H_5$	72	85 (92)
10	C_6H_5	$CO_2C_2H_5$	64	92 (100)
11	$C(CH_3)_3$	CH_3	0	
12	CH_3	$C(CH_3)_3$	62	73[c]

[a] Isolated yield based on starting ketone. [b] Determine by analysis of the Eu(dcm)$_3$ shifted NMR spectrum. The numbers in parentheses are corrected for 92% ee α-pinene. [c] 100% optically pure (+)-α-pinene was used. [d] Diastereomeric ratio (*R,R* to *R,S*) determined by LC or NMR analysis of the mixture.

postulated, regard the acetylene function as an aromatic group.[7]

Reduction of α,β-acetylenic ketones is slow in comparison with aldehydes. Nevertheless complete reduction can be accomplished in reasonable time by using 2 equiv of the trialkylborane. Terminal acetylenic ketones and acetylenic keto esters were completely reduced after 8 h at room temperature. Internal acetylenic ketones required 1-4 days at room temperature or until no starting material was detectable by GLC or NMR. This kinetic differentiation may be due to a steric and/or electronic influence of the substituent on the acetylene. Recourse to heating as a means of accelerating the rate should be avoided. Enantiomeric purities were significantly lowered when the reaction mixtures were refluxed after 8 h at room temperature. The loss of selectivity may be attributed to a competitive dehydroboration-reduction mechanism.[6,8]

The reagent is widely applicable as seen by the variety of substrates in Table I. Chemical yields are generally good. The enantiomeric purities of the products range from 73 to 100%. The limiting factor in obtaining very high enantiomeric excesses is often the availability of α-pinene of high optical purity. Since methods exist for the preparation of optically pure α-pinene and for the isomerization of (−)-β-pinene to (−)-α-pinene, this problem is overcome.[9] The enantiomeric excess is somewhat sensitive to the size of the substituent on the ketone. Note, for example, the increasing enantioselectivity in the series of acetylenic keto esters in proceeding from the methyl ketone **8** to the phenyl ketone **10.** The bulky *tert*-butyl ketone **11** is the only substrate which did not reduce to the corresponding propargylic carbinol.[10] The reagent appears to be indifferent to the presence of other chiral centers in the molecule as the reduction of optically active **6** proceeds with essentially the same degree of asymmetric induction when executed with either (+)- or (−)-α-pinene.

The following is a typical experimental procedure. An oven-dried 50-mL round-bottom flask, equipped with a septum-capped side arm, magnetic stirring bar, reflux condenser, and stopcock adaptor connected to a mercury bubbler, was assembled while hot and flushed with a stream of nitrogen. Then 18.5 mL of a 0.54 M THF solution (10.0 mmol) of 9-BBN was added by syringe followed by 1.78 mL (11.0 mmol) of (+)-α-pinene ($[\alpha]^{25}_D$ +47.28°, 92% ee, distilled from $LiAlH_4$). The solution was stirred at reflux for 2.5 h. The solution was cooled to room temperature and 0.73 mL (5.0 mmol) of 4-phenyl-3-butyn-2-one (**2**) was injected into the flask. A yellow-orange color at this stage is characteristic in these reductions. Stirring at room temperature was continued for 48 h. Then 0.5 mL of acetaldehyde (excess) was added to the solution and stirring continued for 15 min. With the flask in a water bath, the solvent was removed by applying a water aspirator and stirring vigorously as a stream of nitrogen was passed over the solution. This operation was completed by stirring the residue at 40 °C under aspirator pressure for 10 min.[11] The flask was then filled with nitrogen and the liquid was dissolved in 12 mL of anhydrous diethyl ether. This solution was cooled in an ice bath and then treated with 0.66 mL (11 mmol) of ethanolamine. A white precipitate formed and the mixture was stirred for 15 min at 0 °C. The flask was then opened to air and the mixture filtered with suction. The solid was washed with 4 mL of cold ether. The combined filtrate was then washed with 20 mL of saturated aqueous sodium chloride, dried over magnesium sulfate, filtered, and concentrated to a clear oil. This was distilled from a Kugelrohr oven [pot temperature, 100 °C, (0.02 mmHg)] to provide 0.72 g (98%) of 4-phenyl-3-butyn-2-ol (α_D +51.8°). Examination of the NMR spectrum in the presence of tris(dicampholyl-d_2-methanato)europium(III), Eu(dcm)$_3$,[12] indicated an enantiomeric mixture of 86% *R*, 14% *S* (72% ee). In reductions of **8, 9,** and **10,** isolation of the γ-hydroxy-α,β-acetylenic esters was facilitated by elution of the crude products through a short silica gel column prior to distillation. Unless this precaution is taken, the pot contents rapidly decompose upon heating. The ketones used in these experiments were prepared in two steps from the appropriate aldehydes and alkynes or ethyl propiolate.[13]

In conclusion, *B*-3-pinanyl-9-BBN is an attractive reagent for the preparation of chiral secondary propargylic carbinols of high enantiomeric purity. Reduction of certain acetylenic keto esters and terminal eynones proceeds with virtually quantitative asymmetric induction. This is a rare event in prochiral nonaromatic systems. *B*-3-Pinanyl-9-BBN compares favorably with the $LiAlH_4$–Darvon alcohol complex used by Brinkmeyer and Kapoor for the same purposes.[7] 9-BBN is a commercially available reagent.[14] Both enantiomers of α-pinene are also available in high optical purity. The reduction is easy to perform and large-scale reactions pose no problem. The pinene liberated in the reduction may be recycled without loss of optical purity. Finally, *B*-alkyl-9-BBN compounds are mild reagents which will tolerate the presence of other functional groups.[15]

The synthetic utility of propargylic alcohols has been amply demonstrated in the literature. For example the alcohol from the enantiomer of **6** has been used in the synthesis of α-tocopherol.[3a] Hydroxy alkynoates are especially useful precursors for the synthesis of naturally occurring optically active γ-lactones. We are currently engaged in such efforts.

Acknowledgment. We gratefully acknowledge the National Institutes of Health for their generous financial support. We also thank Noal Cohen and Hoffmann-La Roche for kindly supplying the α-tocopherol precursor **6**.

References and Notes

(1) Reviews on asymmetric synthesis: Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions", Reprint Edition; American Chemical Society: Washington, D.C., 1976. Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978,** 329. Kagan, H. B., Fiaud, J. C. *Top. Stereochem.* **1978,** *10,* 175.
(2) For example: Noyori, R.; Tomino, I., Tanimoto, Y. *J. Am. Chem. Soc.* **1979,** *101,* 3129. Mukaiyama, T.; Asami, M.; Hanna, J.; Kobayashi, S. *Chem. Lett.* **1977,** 783. Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973,** *38,* 1870. Asami, M.; Ohno, H.; Kobayashi, S.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1978,** *51,* 1869. Vigneron, J. P.; Jacquet, I. *Tetrahedron* **1976,** *32,* 939.
(3) (a) Chan, K.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1978,** *43,* 3435.

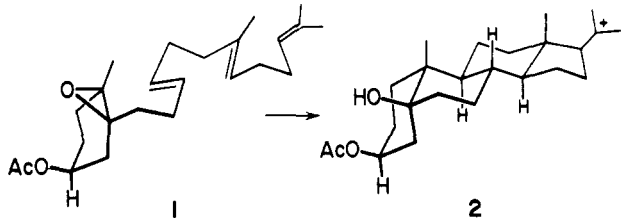
(b) Pirkle, W. H.; Boeder, C. W. *Ibid.* **1978,** *43,* 2091. (c) Herrmann, J. L.; Berger, M. H.; Schlessinger, R. H. *J. Am. Chem. Soc.,* **1979,** *101,* 1544. (d) Johnson, W. S.; Brinkmeyer, R. S.; Kapoor, V. M.; Yarnell, T. M. *Ibid.* **1977,** *99,* 8341. (e) Fried, J.; Lin, C.; Mehra, M.; Kao, W.; Dahren, P. *Ann. N.Y. Acad. Sci.* **1971,** *180,* 38.
(4) (a) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979,** *101,* 2352. (b) Midland, M. M.; Tramontano, A.; Zderic, S. A. *Ibid.* **1977,** *99,* 5211.
(5) The alcohol from reduction of 1-deuterio aldehydes with the reagent from (+)-α-pinene is of the *S* configuration.[4b]
(6) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Organomet. Chem.* **1977,** *134,* C17, **1978,** *156,* 203.
(7) Brinkmeyer, R. S.; Kapoor, V. M. *J. Am. Chem. Soc.* **1977,** *99,* 8339. Vigneron, J.-P.; Bloy, V. *Tetrahedron Lett.* **1979,** 2683.
(8) Midland, M. M.; Petre, J. E.; Zderic, S. A. *J. Organomet. Chem.,* in press.
(9) Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1976/1977,** *15,* 12. Cocker, W.; Shannon, P. V. R.; Staniland, P. A. *J. Chem. Soc. C* **1966,** 41. Brown, C. A. *Synthesis* **1978,** 754.
(10) A product was isolated from this reaction which appeared to be vinylic or allenic from spectral evidence.
(11) If the product is low boiling, the α-pinene may be removed at the stage by applying a 0.05-mm vacuum for 2 h while the flask is heated to 40 °C.[4]
(12) McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974,** *96,* 1038.
(13) The alcohols were prepared by addition of the lithio alkyne or lithio propiolate to the aldehydes at low temperature. They were purified and then oxidized to the ketones with Jones reagent. Midland, M. M.; Tramontano, A.; Cable, J. R. *J. Org. Chem.,* in press.
(14) Available from Aldrich Chemical Co.
(15) Midland, M. M.; Tramontano, A. *J. Org. Chem.* **1978,** *43,* 1470.
(16) Alfred P. Sloan Foundation Fellow, 1978–1980.
(17) National Science Foundation Undergraduate Research Participant, 1978.

M. Mark Midland,*[16] Deborah C. McDowell
Robert L. Hatch,[17] Alfonso Tramontano
Department of Chemistry, University of California
Riverside, California 92521
Received July 30, 1979

Stereoselective Generation of a Nonaromatic, 3,5-Dioxygenated Steroidal System through Tricyclization of a Polyene Oxide

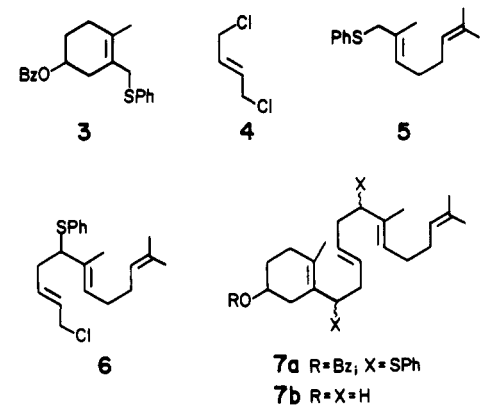
Sir:

Although the biogenetic-type, total synthesis of various naturally occurring polycyclic terpenoids from squalene oxide variants has been achieved,[1] the fabrication of traditional steroids by polycyclization of polyene oxides so far has not been realized.[2] As a preliminary assay, we have now synthesized and studied the behavior of the monocyclic epoxide (±)-**1**,[3] finding that—despite the considerable dissimilarity from squalene oxide and the attendant need to bypass numerous steps parallel to those in the biosynthetic pathway—it undergoes an uncommon tricyclization, giving the A/B cis 3,5-dioxygenated steroidal cation (±)-**2**, the precise result predicted by stereoelectronic theories of epoxide ring opening and polyene cyclization.[4,5]



1 **2**

Epoxide **1** can be readily assembled from building blocks **3**,[6] **4**, and **5**.[7,8] After generation of the anion by treatment of sulfide **5** with BuLi (THF, −78°), alkylation[9] with dichloride **4** (−78 °C room temperature) gave (59%) *trans,trans*-trienyl halide **6**,[10] an oil purified by medium pressure liquid chromatography (MPLC): NMR (100 MHz, $CDCl_3$) δ 1.55 (3 H, br s) and 1.64 (6 H, br s) ($C{=}CCH_3$), 1.87 (4 H, m) and 2.43 (2 H, m) ($C{=}CCH_2$–), 3.60 (1 H, t, J = 8 Hz) (CHS), 4.00

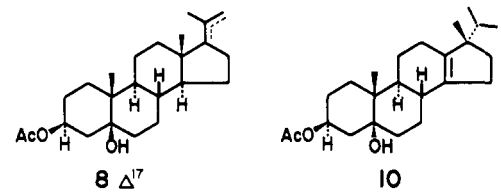


3 **4** **5**

6 **7a** R=Bz; X=SPh
7b R=X=H

(2 H, m) (CH_2Cl), 5.01 (2 H, m) and 5.68 (2 H, m) (C=CH), 7.28 (5 H, m) (C_6H_5–). Trienyl halide **6** was used in turn to alkylate (THF, −78 °C–10°) the BuLi-produced anion of sulfide **3**, thereby generating *trans,trans*-tetraenyl polyether **7a**[10] (59%; 67%, based on consumed **3**): NMR (60 MHz, $CDCl_3$) δ 1.25 (3 H, br s), 1.54 (3 H, br s), and 1.62 (6 H, br s) ($C{=}CCH_3$), 3.51 (2 H, m), 4.16 (1 H, t, J = 8 Hz) (CHS–, CHO–), 4.58 (2 H, s) (CH_2O–), 5.00 (2 H, m) and 5.39 (2 H, m) (C=CH), 6.99–7.51 (15 H, m) (C_6H_5–). Complete benzylic-allylic reduction of **7a** was effected by Li–$EtNH_2$ at −78 °C, thereby providing (76%) tetraenyl alcohol **7b**:[10,11] NMR (60 MHz, $CDCl_3$) δ 1.59 (9 H, br s) and 1.66 (3 H, br s) ($C{=}CCH_3$), 3.87 (1 H, m) (CHO(H)), 4.91–5.53 (4 H, m) (C=CH). Regio- and stereoselective epoxidation of the cyclohexenol moiety in **7b** was achieved through the $Mo(CO)_6$-catalyzed action of t-$C_4H_9O_2H$ (toluene, room temperature),[12] followed by acetylation (Ac_2O–pyridine), giving (67% from **7b**) epoxy acetate **1**:[10,11] NMR (100 MHz, $CDCl_3$) δ 1.29 (3 H, s) ($-OCCH_3$), 1.59 (6 H, br s) and 1.68 (3 H, br s) ($C{=}CCH_3$), 2.01 (3 H, s) ($-OCOCH_3$), 4.62 (1 H, m) (CHOCO–), 5.10 (2 H, m) and 5.39 (2 H, m) (C=CH).

Cyclization of epoxide **1** can be effected, for example, by treatment with 6 equiv of BF_3·Et_2O in CH_2Cl_2 for 2 h at −75 °C, followed by 1 h at −10 to −20 °C. The sole steroidal product (25%) was isolated by preparative TLC ($CH_3CO_2C_2H_5$–C_6H_{14} on silica gel), followed by preparative GC (OV-210 on Chromosorb WAW, 250 °C). Of the three tetracycles which might reasonably derive from cation **2**, viz., **8**–**10**, the **1**-derived substance was identified as (±)-**10** in that



8 Δ^{17}
9 Δ^{20}
10

it was indistinguishable, on the basis of TLC, GC, MS, and IR and NMR spectral comparison, from an authentic sample of **10**, secured by BF_3·Et_2O-induced rearrangement (CH_2Cl_2, −20 to −10 °C) of **8** or **9** from natural sources:[13] NMR (100 MHz, $CDCl_3$) δ 0.74 (3 H, d, J = 7 Hz) and 0.84 (3 H, d, J = 7 Hz) ($CH(CH_3)_2$, 0.94 (3 H, s) and 0.96 (3 H, s) ($-CH_3$), 2.08 (3 H, s) (CH_3CO_2–), 5.23 (1H, m) (CHO–); high resolution MS M^+ ($C_{24}H_{38}O_3$), $M^+ - C_3H_7$, $M^+ - (C_3H_7, H_2O)$, $M^+ - (C_3H_7, H_2O, C_2H_4O_2)$. This structural assignment was corroborated by cocrystallization to a constant radioactivity level per unit mass of a radioactive sample of the Δ^4-3β-ol[14] corresponding to (±)-**10**, admixed with authentic, nonradioactive material, mp 117–119 °C.[15] The constitution of cation **2** follows from the structure and stereochemistry of **10**.

0002-7863/80/1502-0869$01.00/0