Biomimetic Polyene Cyclizations.[1] Participation of the (Trimethylsilyl)acetylenic Group and the Total Synthesis of the *D*-Homosteroid System[2]

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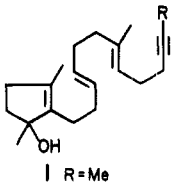
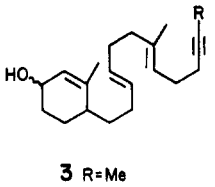
The aim of this study was to examine the (trimethylsilyl)acetylenic group as a terminator in biomimetic polyene cyclizations. Two cyclization substrates, **2** and **4**, containing this group were synthesized by the sequences outlined in Schemes I and II. Cyclization of trienynol **2** with trifluoroacetic acid in 1,2-dichloroethane containing ethylene carbonate afforded a 19% yield of presumed ketone **18**. Several difficulties such as the low yield in the cyclization step, the product purity, and the formation of side products in the synthetic scheme were encountered and led to the abandonment of this particular cyclization. Attention was then turned to trienynol **4** which was synthesized as depicted in Scheme II. Treatment of the substrate **4** with trifluoroacetic acid in 1,2-dichloroethane–ethylene carbonate for 3 h at −20 °C afforded a 55% yield of tetracyclic ketone **22**, the structure of which was confirmed by catalytic hydrogenation to afford a 96% yield of *dl*-5β-*D*-homoandrostan-7-one (**23**).

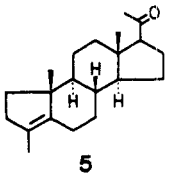
Biomimetic polyene cyclizations involving the methylacetylenic residue as the terminator have been described previously.[3,4] Thus, cyclization of trienynols **1** and **3** with



1 R = Me
2 R = $SiMe_3$



3 R = Me
4 R = $SiMe_3$



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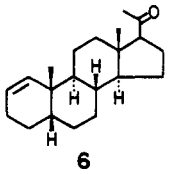

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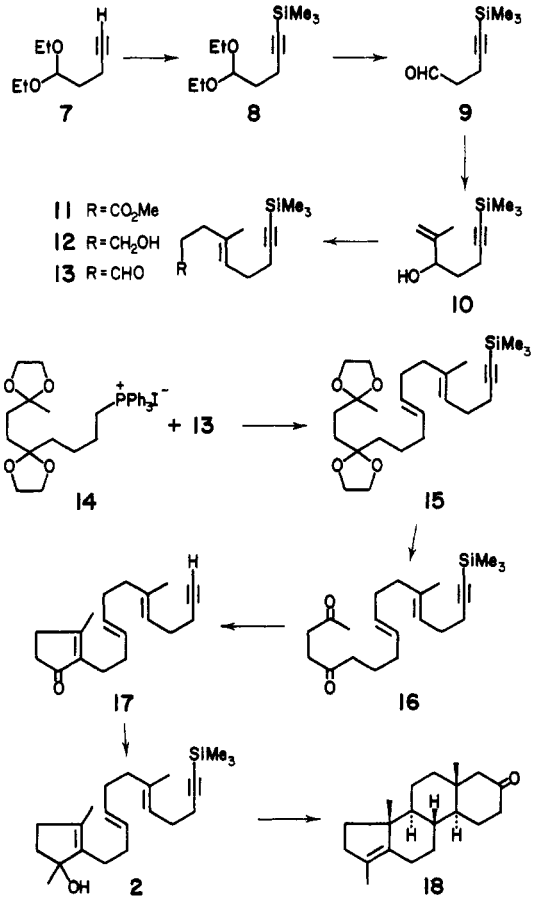
trifluoroacetic acid in 1,2-dichloroethane–ethylene carbonate and 1,1-difluoroethane–ethylene carbonate, respectively, led to the formation of **5** and **6**, respectively, which contain the five-membered D ring of steroids. The constitution of these products was established by further transformations of **5** and **6**, which led to syntheses of *dl*-progesterone.[3,4] With the aim of examining how various substituents influence the participation of the acetylenic bond as a terminating group, we chose to examine the allylic alcohols **2** and **4**, with the (trimethylsilyl)acetylenic residue appropriately positioned for terminating cyclizations. The present paper reports the synthesis and cyclization of these two substrates.

The synthesis of the allylic alcohol **2** was accomplished by a route (see Scheme I) which involved as the convergent step the Wittig–Schlosser condensation of the known[3] phosphonium salt **14** with the aldehyde **13**. The latter

Scheme I



substance was prepared by the sequence shown in Scheme I. Thus the known[5] diethoxypentyne **7** on treatment with *n*-butyllithium followed by trimethylchlorosilane gave a 68% yield of the silyl acetal **8** which was readily converted into the silyl aldehyde **9** in 88% yield by hydrolysis with dilute hydrochloric acid in THF. The aldehyde **9** was treated with isopropenylmagnesium bromide to afford the allylic alcohol **10** in 98% yield, which was converted into the ester **11** in 95% yield by the orthoacetate Claisen reaction.[6] The ester **11** was reduced with lithium aluminum

(1) (a) For a recent paper in the series on biomimetic polyene cyclizations, see: Garst, M. E.; Cheung, Y.-F.; Johnson, W. S. *J. Am. Chem. Soc.* **1979**, *101*, 4404-5. (b) For a recent review of biomimetic polyene cyclizations, see: Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51-98.

(2) For a preliminary account of this work, see: Johnson, W. S.; Yarnell, T. M.; Myers, R. F.; Morton, D. R. *Tetrahedron Lett.* **1978**, 2549-52.

(3) Gravestock, M. B.; Johnson, W. S.; McCarry, B. E.; Parry, R. J.; Ratcliffe, B. E. *J. Am. Chem. Soc.* **1978**, *100*, 4274-82.

(4) (a) Markezich, R. L.; Willy, W. E.; McCarry, B. E.; Johnson, W. S. *J. Am. Chem. Soc.* **1973**, *95*, 4414-6. (b) McCarry, B. E.; Markezich, R. L.; Johnson, W. S. *Ibid.* **1973**, *95*, 4416-7.

(5) Durand, M. H.; Piaux, L. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1959**, *248*, 2763-5.

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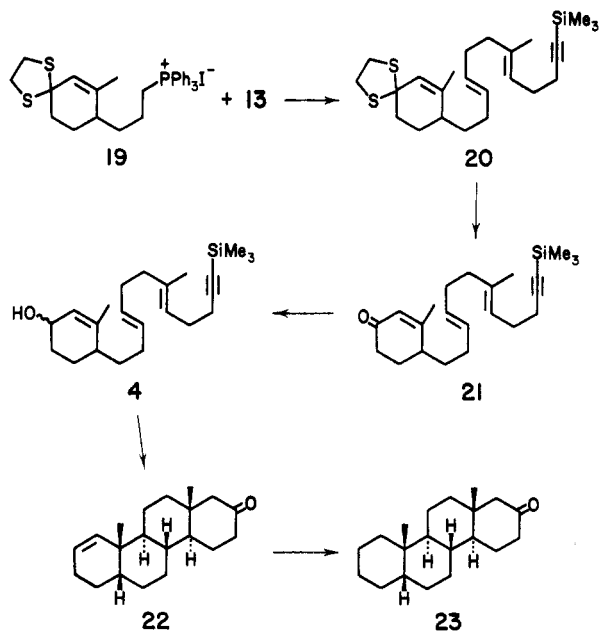
hydride in ether in quantitative yield to the corresponding alcohol **12** which was oxidized with Collins reagent[7] to the aldehyde **13** in 98% yield. Attempts to effect selective reduction of the ester **11** directly to the aldehyde with sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) afforded mixtures of **12** and **13** which proved to be difficult to separate.

The Wittig condensation of the aldehyde **13** with the phosphorane from the known[3] phosphonium salt **14** was performed according to the modification of Schlosser[8] for producing trans olefinic bonds. Thus a suspension of the phosphonium iodide **14** in THF was treated with 1 molar equiv of phenyllithium in THF to give a deep red solution of the ylide. Addition of the aldehyde **13** to the ylide solution at −78 °C followed by an additional 1.5 molar equiv of phenyllithium at −78 °C and sufficient ether to give a 1:1 ratio of THF to ether gave, after a final treatment with methanol at −30 °C, the condensation product **15** in 46% yield. Hydrolysis of the bis ketal **15** was effected in 90% yield with dilute methanolic hydrochloric acid to give the dione **16** which was converted into the cyclopentenone **17** with 5% aqueous potassium hydroxide in methanol. VPC examination of **17** showed a 9:1 mixture of the *trans,trans*-cyclopentenone **17** and presumably (in analogy to previous work[3]) the corresponding cis,trans isomer which was formed during the Wittig–Schlosser condensation. The alkaline conditions necessary for effecting the aldol cyclization of **16** also effected concomitant desilylation. Several of the aforementioned intermediates (**10**, **11**, **12**, **15**, and **16**) were also desilylated to afford the corresponding substance with hydrogen attached to the acetylenic bond, thus providing additional evidence as to the structures of the intermediary compounds.

The substrate **2**, contaminated with the corresponding trimethylsilyl ether, was obtained upon treatment of an ethereal solution of the ketone **17** with methyllithium followed by trimethylchlorosilane. Since this tertiary allylic alcohol was highly susceptible to dehydration, it was used directly in the cyclization step without purification.

Cyclization of the trienynol **2** was conducted at 0 °C for 3 h in 1,2-dichloroethane containing an excess of ethylene carbonate and trifluoroacetic acid.[3] The IR spectrum of the crude product showed absorption at 5.61 μm attributable to a trifluoroacetoxy group. This presumed enol trifluoroacetate[3] was treated with 5% aqueous potassium hydroxide in methanol to give material which appeared to be ketonic from the absorption at 5.85 μm in the IR spectrum. The ^{1}H NMR spectrum showed absorption for three protons as a singlet at δ 0.80 attributable to a C-18 methyl group, absorption for three protons as a singlet at δ 0.88 attributable to a C-19 methyl group, and absorption for three protons as a singlet at δ 1.62 attributable to a vinyl methyl group, indicating that this substance was indeed tetracyclic. No absorption was found at δ 2.13, indicating that this substance was not a methyl ketone like **5**. In analogy with the tetracyclic ketone **22** described below, which was formed in the cyclization of trienynol **4** and whose structure has been firmly established, this product is assigned the structure **18**. All attempts to effect purification of **18** by evaporative distillation, preparative TLC, column chromatography, or preparative VPC failed

Scheme II



to provide an analytically pure specimen. Moreover, the yield of crude **18** was only 19% from **17**, and efforts to improve the yield were abortive. In view of these difficulties and the premature loss of the trimethylsilyl residue (see above) further investigation of this particular cyclization was abandoned.

Another plan (see Scheme II) was envisaged in an effort to examine more thoroughly the effect of the (trimethylsilyl)acetylenic terminator in the cyclization of **4**. The synthesis of **4** involved as the convergent step the Wittig–Schlosser condensation of the aforementioned aldehyde **13** with the known[4] phosphonium salt **19** to give thioketal **20**. Thus the aldehyde **13** was allowed to interact with the phosphorane from **19** under the conditions described above for the condensation of **13** with **14**. The resulting thioketal **20** which was formed in quantitative yield was shown by VPC to consist of a 95:5 mixture presumably of the desired trans product **20** and the corresponding cis isomer of the newly formed olefinic bond, by analogy with previous work.[3] Hydrolysis of the thioketal residue in **20** was readily effected by using methyl iodide in aqueous acetonitrile[4,9] to give ketone **21** in 58% yield from aldehyde **13**. Reduction of the enone **21** with lithium aluminum hydride afforded the cyclization substrate **4** in 95% yield.

Cyclization of the trienynol **4** was carried out at −20 °C for 3 h in 1,2-dichloroethane containing an excess of ethylene carbonate and trifluoroacetic acid. After treatment with saturated aqueous sodium bicarbonate, preparative TLC afforded a solid product in 55% yield which on recrystallization twice from pentane–methanol afforded colorless needles, mp 107–110 °C. The constitution of this product was established as **22** by hydrogenation over 10% palladium-on-carbon in ethyl acetate to give, after recrystallization from methanol, a 96% yield of the racemic form of 5β-*D*-homoandrostan-17-one (**23**), mp 98–101 °C. The ^{1}H NMR and solution IR spectra were identical with the corresponding spectra of authentic (naturally derived) 5β-*D*-homoandrostan-17-one,[10] and the two samples gave

(6) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-t.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741–3.

(7) (a) Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363–6. (b) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000–4002.

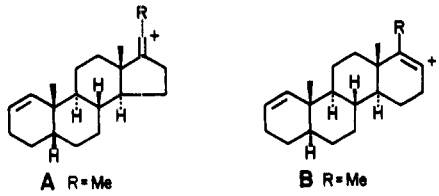
(8) Schlosser, M.; Christmann, K. F. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 126.

(9) While our work was in progress, M. Fetizon and M. Jurion [*J. Chem. Soc., Chem. Commun.* **1972**, 382–3] and W. H.-L. Chang [*Tetrahedron Lett.* **1972**, 1989–90] disclosed their independent discoveries of essentially the same procedure.

(10) Harding, K. E.; Leopold, E. J.; Hudrlik, A. M.; Johnson, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 2540–9.

identical responses in VPC coinjection experiments.

The formation of the five-membered D-ring ketone 6 from the cyclization of the trienynol 3 has been rationalized on the basis of a transition-state preference for formation of the linear vinyl cation A rather than the bent vinyl

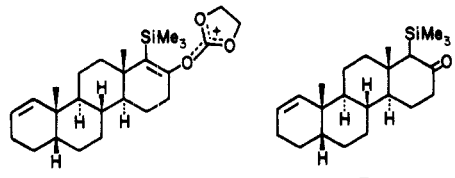


A R=Me
C R=SiMe$_3$

B R=Me
D R=SiMe$_3$

cation B and/or a steric destabilization of B relative to A due to larger nonbonded interactions between the methylene groups at C-7 and C-15 in the transition state leading to B rather than A.[3,11]

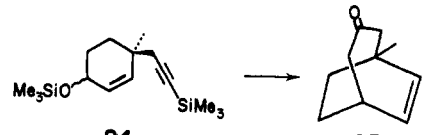
On the other hand, cyclization of trienynol 4, which contains the (trimethylsilyl)acetylenic terminator, affords the six-membered-ring ketone 22, presumably involving the bent vinyl cation D which reacts with ethylene carbonate to give E or with trifluoroacetic acid to give the



E

F

corresponding enol trifluoroacetate, either of which on treatment with bicarbonate is converted to the α-silyl ketone F, a type known to be cleaved[12] to the corresponding ketone with dilute base. There are at least two reasonable rationalizations which account for this observation. One is that the kinetically-favored vinyl cation C is initially formed and then rearranges to the more stable cation D. Such a rearrangement, namely, A → B, seems to occur when A is generated under certain conditions involving reaction of A with halide ion.[13] This apparent rearrangement may be due to a relief of torsional strain in the conversion of a 6/5 to a 6/6 trans-fused ring system.[14] An alternative possibility is that the six-membered D-ring bent vinyl cation D is formed directly in the cyclization, rather than via rearrangement. In this case, the intrinsic effects favoring the formation of the linear vinyl cation C might be overridden by other factors such as the tendency for a silicon atom to stabilize a carbonium ion β to it (and/or to destabilize a cation α to it)[15] and a possible steric preference for electrophilic attack at that acetylenic carbon which carries the bulkier substituent because of the probable angle of approach of reagents to the sp^1 bond.[11,16] Likewise, Heathcock[17] observed that the cyclization of silyl ether 24 with formic acid afforded ketone 25. This cyclization also appears to involve a preference for formation of a vinyl cationic intermediate with the positive charge β to the silicon atom.



24 25

Experimental Section[18]

General Considerations. The prefix *dl* has been omitted from the names of all racemic compounds described in this section. Microanalyses were performed by E. H. Meier and J. Consul, Department of Chemistry, Stanford University. Melting points were determined on a Kofler hot-stage microscope calibrated against totally immersed Anschutz thermometers. NMR spectra were recorded under the supervision of Dr. L. J. Durham on a Varian Associates T-60 spectrometer. Deuteriochloroform was used as the solvent unless indicated otherwise, and chemical shifts are reported as δ values in parts per million relative to tetramethylsilane. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Vapor-phase chromatographic (VPC) analyses were performed on a Hewlett-Packard HP 402 chromatograph using the following $^1/_8$-in. glass columns: 6 ft, 3% OV-17 and 6 ft, 3% XE-60 on Gas-Chrom Q. Helium was used as the carrier gas and disk-chart integrations are uncorrected for detector response. Analytical and preparative thin-layer chromatography (TLC) were performed by using silica gel HF_{254} (E. Merck AG) as the adsorbent at 0.25 and 0.75-mm thicknesses, respectively. "Evaporative distillation" refers to bulb-to-bulb short-path distillation in which the bulb was heated in a hot-air oven (Büchi Kugelrohrofen). The cited temperatures for these distillations refer to the maximum temperature attained by the oven during distillation and are thus not true boiling points.

4-Pentynal Diethyl Acetal (7). A published procedure[5] was modified. A solution of 7.58 g (45.7 mmol) of 3-chloropropanal diethyl acetal[19] in 10 mL of dry dimethyl sulfoxide was stirred while a solution of 5.52 g (60 mmol) of lithium acetylide–ethylenediamine complex in 25 mL of dry dimethyl sulfoxide was added slowly. The mixture was stirred at 15 °C for 3 h under nitrogen and then extracted with pentane[18] to give an oily residue. Distillation through a 20-cm Vigreux column afforded 6.88 g (91% yield) of acetylenic acetal 7 as a colorless liquid: bp 69–70 °C (17 mm) [lit.[5] bp 65–66 °C (15 mm)]; n^{25}_D 1.4215 (lit.[5] n^{20}_D 1.422); IR (film) 3.00 and 4.71 μm (C≡CH); ^{1}H NMR 1.18 (t, J = 7 Hz, 6, CH_3CH_2), 1.6–2.5 (m, 5, methylene protons, C≡CH), 3.4–3.9 (m, 4, CH_3CH_2), 4.60 (t, J = 5 Hz, 1, $(EtO)_2CH$).

5-(Trimethylsilyl)-4-pentynal Diethyl Acetal (8). A cold (−78 °C) solution of 6.88 g (44 mmol) of the aforementioned acetylenic acetal 7 in 100 mL of dry THF was stirred under nitrogen while 24 mL (48 mmol) of a 2.0 M solution of *n*-butyllithium in hexane was added. The solution was stirred at −78 °C for 1 h, after which time 6.6 mL (66 mmol) of trimethylchlorosilane was added all at once. The mixture was allowed to warm to room temperature, and stirring was continued for 18 h. The mixture was poured into 100 mL of saturated aqueous sodium

(11) Lansbury, P. T.; DuBois, G. E. *J. Chem. Soc., Chem. Commun.* **1971**, 1107–8. Lansbury, P. T.; Demmin, T. R.; DuBois, G. E.; Haddon, V. R. *J. Am. Chem. Soc.* **1975**, *97*, 394–403.

(12) Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373–5. Brook, A. G.; Schwartz, N. V. *J. Org. Chem.* **1962**, *27*, 2311–5.

(13) Johnson, W. S.; Gravestock, M. B.; Parry, R. J.; Okorie, D. A. *J. Am. Chem. Soc.* **1972**, *94*, 8604–5. See also: Ward, C. E. Ph.D. Dissertation, Stanford University, 1977.

(14) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965; p 204.

(15) See, inter alia: Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153–207. Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.*, **1970**, *24*, 301–6; **1971**, *29*, 389–96. Eaborn, C.; Feichtmayr, F.; Horn, M.; Murrell, J. N. *Ibid.* **1974**, *77*, 39–43. Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715–25.

(16) (a) For a recent review of vinyl cations in these and other reactions, see: Stang, P. J. *Prog. Phys. Org. Chem.* **1973**, *10*, 205–325. (b) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–6.

(17) Kozar, L. G.; Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1977**, *42*, 1386–9.

(18) In cases where products were isolated by solvent extraction, the procedure generally followed was to extract the aqueous layer with several portions of the indicated solvent, and then the organic layers were combined and washed with water followed by saturated brine. The organic layer was dried over anhydrous sodium sulfate or magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure (water aspirator) by using a rotary evaporator. The use of the term "wash" indicates washing the combined organic layers with saturated aqueous sodium bicarbonate solution ("base wash"), with dilute aqueous hydrochloric acid ("acid wash"), or with the indicated solution prior to the aforementioned washing with water.

(19) Witzemann, E. J.; Evans, W. L.; Hass, H.; Schroeder, E. F. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 137.

chloride overlaid with 300 mL of ether. The organic layer was separated and dried over magnesium sulfate, and the solvent was removed (rotary evaporator) to afford an oily residue. Evaporative distillation at 58–60 °C (0.25 mm) afforded 6.18 g (68% yield) of acetylenic acetal **8** as a colorless liquid: n^{20}_D 1.4367; IR (film) 4.55 (C≡C), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$); 1.18 (t, J = 7 Hz, 6, CH_3CH_2), 1.6–2.5 (m, 4, methylene protons), 3.3–3.9 (m, 4, CH_3CH_2), 4.60 (t, J = 5 Hz, 1, $(EtO)_2CH$).

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.58. Found: C, 62.91; H, 10.48.

5-(Trimethylsilyl)-4-pentynal (9). A solution of 5.31 g (23.3 mmol) of the aforementioned acetal **8** in 100 mL of THF and 20 mL of 5% hydrochloric acid was stirred at room temperature under nitrogen for 3 h. Pentane extraction using a base wash[18] afforded a pale yellow oil which was purified by evaporative distillation at 125 °C (35 mm) to give 3.17 g (88% yield) of aldehyde **9** as a colorless oil, which showed one spot on TLC (R_f 0.2, 9:1 hexane–ether).

Chromatography on Florisil (9:1 hexane–ether) followed by evaporative distillation at 100 °C (30 mm) of a crude sample from a similar run afforded an analytical specimen of **9**: n^{20}_D 1.4531; IR (film) 4.55 (C≡C), 5.74 (C=O), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 2.5–2.7 (m, 4, methylene protons), 9.80 (br s, $W_{1/2}$ = 2 Hz, 1, CHO).

Anal. Calcd for $C_8H_{14}OSi$: C, 62.22; H, 9.14. Found: C, 62.44; H, 9.13.

2-Methyl-7-(trimethylsilyl)-1-hepten-6-yn-3-ol (10). A solution of 3.17 g (20.3 mmol) of the aforementioned aldehyde **9** in 15 mL of dry THF was added to a solution of isopropenylmagnesium bromide, prepared from 2.43 g (100 mmol) of magnesium turnings and 2.72 mL (3.70 g, 30 mmol) of 2-bromopropene in 60 mL of dry THF. The mixture was stirred for 3 h at room temperature, cooled to 0 °C, and then quenched by the addition of saturated aqueous ammonium chloride. Ether extraction using a base wash[18] gave a colorless oil which was purified by evaporative distillation at 70 °C (0.1 mm) to afford 3.90 g (98% yield) of alcohol **10**.

Chromatography on Florisil (9:1 hexane–ether) followed by evaporative distillation at 70 °C (0.1 mm) of a crude sample from a similar run afforded an analytical specimen: n^{20}_D 1.4664; IR (film) 2.90 (OH), 4.59 (C≡C), 6.06 and 11.1 ($R_2C=CH_2$), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.16 (s, 9, $SiMe_3$), 1.66 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl CH_3), 1.6–2.6 (m, 4, methylene protons), 4.22 (t, J = 6 Hz, 1, CHOH), 4.91 (m, 2, $C=CH_2$).

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.78; H, 10.26. Found: C, 67.26; H, 10.27.

A specimen of silyl alcohol **10** was desilylated by using a published procedure.[20] A solution of 409 mg (2.08 mmol) of crude silyl alcohol **10** in 10 mL of ethanol was stirred at room temperature while 20 mL (ca. 12 mmol) of a solution prepared from 9 g (0.053 mol) of silver nitrate, 20 mL of water, and 60 mL of ethanol was added. The mixture was stirred for ca. 30 min at room temperature, and then 10 mL (ca. 90 mmol) of a solution prepared from 12.5 g (0.19 mol) of potassium cyanide in 20 mL of water was added. The mixture was stirred at room temperature for 30 min and then extracted with pentane by using a base wash[18] to give 184 mg of pale yellow oil. An analytical specimen was prepared by chromatography on Florisil (9:1 hexane–ether) followed by evaporative distillation at 85 °C (15 mm) to give pure **2-methyl-1-hepten-6-yn-3-ol**: n^{20}_D 1.4656; IR (film) 2.7–3.1 (OH), 4.7 (C≡C), 6.06 and 11.1 μm ($R_2C=CH_2$); ^1H NMR 1.72 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl CH_3), 1.6–2.5 (m, 6, C≡CH, OH, methylene protons), 4.22 (t, J = 6 Hz, 1, CHOH), 4.94 (m, 2, $C=CH_2$).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.91; H, 9.77.

Methyl 4-Methyl-9-(trimethylsilyl)-*trans*-4-nonen-8-ynoate (11). An adaptation of a published procedure[6] was employed. A mixture of 3.92 g (20 mmol) of the aforementioned alcohol **10**, 8.0 g (66 mmol) of trimethyl orthoacetate, and 1 mL (1 g, 0.017 mol) of glacial acetic acid was heated at 110 °C under nitrogen for 12 h in a flask equipped with a condenser and a Dean–Stark trap. The mixture was cooled and then extracted with ether by using an acid wash followed by a base wash[18] to give a red oil which was purified by evaporative distillation at 70 °C (0.3 mm) to afford 4.78 g (95% yield) of ester **11** as a colorless liquid which was >95% pure by VPC (3% OV-17, 150 °C).

Chromatography on Florisil (9:1 hexane–ether) followed by evaporative distillation at 75 °C (0.2 mm) of a crude sample from a similar run afforded an analytical specimen: n^{20}_D 1.4660; IR (film) 4.59 (C≡C), 5.74 (C=O), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.16 (s, 9, $SiMe_3$), 1.66 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl CH_3), 2.15–2.50 (m, 8, methylene protons), 3.70 (s, 3, CO_2CH_3), 5.24 (m, 1, vinyl proton).

Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.62; H, 9.58. Found: C, 66.81; H, 9.64.

Desilylation as described above, except that a methanolic solution was used to prevent transesterification, followed by evaporative distillation at 60 °C (0.25 mm) gave an analytical sample of **methyl 4-methyl-*trans*-4-nonen-8-ynoate** as a colorless oil: n^{20}_D 1.4639; IR (film) 4.70 (C≡C), 5.73 μm (C=O); ^1H NMR 1.64 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl CH_3), 1.90 (t, J = 2 Hz, 1, C≡CH), 2.1–2.5 (m, 8, methylene protons), 3.68 (s, 3, CO_2CH_3), 5.24 (m, 1, vinyl proton).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.01; H, 8.94.

4-Methyl-9-(trimethylsilyl)-*trans*-4-nonen-8-ynol (12). A solution of 4.5 g (17.9 mmol) of the aforementioned silyl ester **11** in 10 mL of dry ether was added to a cold (0 °C) suspension of 761 mg (20 mmol) of lithium aluminum hydride in 100 mL of dry ether. The mixture was stirred under nitrogen at 0 °C for 1.5 h, and then 10 mL of a saturated aqueous ammonium chloride solution was added cautiously. Ether extraction[18] gave a cloudy oil which was purified by evaporative distillation at 120 °C (0.1 mm) to afford 4.0 g (100% yield) of silyl alcohol **12** as a colorless oil which showed one spot on TLC (R_f 0.4, 9:1 hexane–ether).

Chromatography on Florisil (17:3 hexane–ether) followed by evaporative distillation at 120 °C (0.1 mm) of a crude sample from a similar run afforded an analytical specimen: n^{20}_D 1.4766; IR (film) 2.95 (OH), 4.57 (C≡C), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.5–2.4 (m, 9, methylene protons, OH), 1.66 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl CH_3), 3.62 (t, J = 6 Hz, 2, CH_2OH), 5.24 (m, 1, vinyl proton).

Anal. Calcd for $C_{12}H_{24}OSi$: C, 69.57; H, 10.23. Found: C, 69.83; H, 10.84.

Desilylation as described above, followed by chromatography on Florisil (17:3 hexane–ether), and then evaporative distillation at 85 °C (0.1 mm) afforded an analytical specimen of **4-methyl-*trans*-4-nonen-8-ynol** as a colorless oil: n^{20}_D 1.4775; IR (film) 2.7–3.3 (OH), 4.71 μm (C≡C); ^1H NMR 1.5–2.4 (m, 10, methylene protons, OH and C≡CH), 1.66 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl methyl), 3.63 (t, J = 6 Hz, 2, CH_2OH), 5.28 (m, 1, vinyl proton).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.65; H, 10.59.

4-Methyl-9-(trimethylsilyl)-*trans*-4-nonen-8-ynal (13). Collins reagent[7] was prepared in situ[7b] by adding 2.2 g (21.6 mmol) of chromium trioxide to a solution of 3.37 mL (3.30 g, 42 mmol) of dry pyridine and 60 mL of dry methylene chloride. A solution of 800 mg (21.6 mmol) of the aforementioned silyl alcohol **12** in 5 mL of dry methylene chloride was added to the solution of Collins reagent, and the resulting mixture was stirred at room temperature for 20 min and then poured into 50 mL of saturated aqueous sodium bicarbonate overlaid with 200 mL of ether. Ether extraction using a base wash[18] gave a red oil which was purified by evaporative distillation at 80 °C (0.75 mm) to give 780 mg (98% yield) of silyl aldehyde **13** as a colorless oil which was not purified further: IR (film) 4.58 (C≡C), 5.76 (C=O), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.66 (br s, $W_{1/2}$ = 3 Hz, 3, vinyl CH_3), 2.1–2.6 (m, 8, methylene protons), 5.28 (m, 1, vinyl proton), 9.75 (br s, $W_{1/2}$ = 2 Hz, 1, CHO).

2,5-Bis(ethylenedioxy)-13-methyl-18-(trimethylsilyl)-*trans,trans*-9,13-octadecadien-17-yne (15). An adaptation of a published procedure[8] was employed. A dispersion of 2.34 g (3.7 mmol) of the known[3] phosphonium salt **14** in 15 mL of dry THF was stirred under argon while 1.5 mL (1.5 mmol) of a 1.0 M solution of phenyllithium in THF was added (enough was added so that a permanent yellow color was produced). The mixture was stirred for 15 min at room temperature, and then 3.4 mL (3.4

(20) Schmidt, H. M.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1138–42.

mmol) of a 1.0 M solution of phenyllithium in THF was slowly added. The resulting deep red solution of ylide was stirred at room temperature for 30 min and cooled to −78 °C, and then a solution of 758 mg (3.4 mmol) of the aforementioned crude aldehyde **13** in 3 mL of dry THF was added via syringe over a 15-min period. Stirring was performed for 20 min at −78 °C, and then an additional 5 mL of phenyllithium solution was added. The mixture was stirred at −78 °C for 45 min, and 27.9 mL of dry ether was added via syringe over a period of 1 h. The solution was slowly warmed to −30 °C and stirred for 20 min at this temperature, and then 2 mL of methanol was added slowly via syringe. The mixture was stirred at room temperature for 15 h and then concentrated under reduced pressure to give a red oil. The oil was dissolved in 10 mL of methylene chloride and then was added dropwise to 500 mL of hexane, with vigorous stirring, whereupon a white precipitate of triphenylphosphine oxide immediately formed. The solution was decanted, and the solvent was removed under reduced pressure to give 1.16 g of yellow oil. Chromatography on 40 g of Florisil (95:5 hexane–ether), followed by evaporative distillation at 200 °C (0.01 mm), afforded 737 mg (46% yield) of bis ketal **15** which showed one peak on VPC (3% XE-60, 210 °C): IR (film) 4.60 (C≡C), 8.00 and 11.85 ($SiCH_3$), 9.10 μm (COC); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.20 (s, 3, C-1 CH_3), 1.3–2.4 (m, 18, methylene protons), 1.68 (s, 3, vinyl CH_3), 3.92 (s, 8 ketal CH_2's), 5.0–5.4 (m, 3, vinyl protons).

Anal. Calcd for $C_{26}H_{44}O_4Si$: C, 69.64; H, 9.82. Found: C, 69.86; H, 9.81.

Desilylation of **15** is described below. A solution of 60 mg (0.13 mmol) of silyl bis ketal **15** in 12 mL of methanol and 3 mL of 5% aqueous potassium hydroxide was heated at 70 °C for 2 h. The mixture was cooled to room temperature and then extracted with ether[18] to give an oil which was purified by evaporative distillation at 165 °C (0.7 mm) to afford 50 mg (100% yield) of **2,5-bis(ethylenedioxy)-13-methyl-*trans,trans*-9,13-octadecadien-17-yne** as a colorless oil: IR (film) 4.75 (C≡C), 9.10 μm (COC); ^1H NMR 1.22 (s, 3, C-1, CH_3), 1.58 (s, 3, vinyl CH_3), 1.2–2.4 (m, 19, C≡CH, methylene protons), 3.82 (s, 8, ketal CH_2's), 5.0–5.5 (m, 3, vinyl protons).

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.41; H, 9.60. Found: C, 73.62; H, 9.77.

13-Methyl-18-(trimethylsilyl)-*trans,trans*-9,13-octadecadien-17-yne-2,5-dione (16). A mixture of 1.2 g (2.7 mmol) of the aforementioned bis ketal **15**, 25 mL of methanol, and 10 mL of 5% hydrochloric acid was stirred at room temperature for 24 h. Ether extraction[18] gave a yellow oil which was purified by evaporative distillation at 140 °C (0.1 mm) to afford 879 mg (90% yield) of dione **16** as a colorless oil which showed one peak on VPC (3% XE-60, 200 °C): IR (film) 4.60 (C≡C), 5.85 (C=O), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.60 (s, 3, vinyl CH_3), 1.7–2.5 (m, 18, methylene protons), 2.69 (s, 3, acetyl CH_3), 5.0–5.5 (m, 3, vinyl protons).

Anal. Calcd for $C_{22}H_{36}O_2Si$: C, 73.31; H, 10.00. Found: C, 73.05; H, 9.81.

Desilylation of **16** is described below. A solution of 0.7 g (4.12 mmol) of silver nitrate in 3 mL of methanol was added to a solution of 197 mg (0.55 mmol) of silyl dione **16** in 3 mL of methanol. The mixture was stirred at room temperature for 15 min, and then a solution of 0.9 g (13.8 mmol) of potassium cyanide in 1 mL of water was added. The mixture was then stirred until a clear solution was obtained. Ether extraction[18] gave a yellow oil which was purified by preparative TLC (R_f 0.69, 3:17 ethyl acetate–hexane) to afford 100 mg (64% yield) of **13-methyl-*trans,trans*-9,13-octadecadien-17-yne-2,5-dione** as a colorless oil. Evaporative distillation at 130 °C (0.02 mm) yielded an analytical specimen: IR (film) 4.70 (C≡C), 5.80 μm (C=O); ^1H NMR 1.60 (s, 3, vinyl CH_3), 1.7–2.5 (m, 19, methylene protons, C≡CH), 2.60 (s, 3, acetyl CH_3), 5.0–5.4 (m, 3, vinyl protons).

Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.17; H, 9.72. Found: C, 78.91; H, 9.55.

3-Methyl-2-(7-methyl-*trans,trans*-3,7-dodecadien-11-ynyl)-2-cyclopentenone (17). A solution of 0.1 g (0.28 mmol) of the aforementioned dione **16** in 10 mL of methanol and 4 mL of 5% aqueous potassium hydroxide was heated at reflux under nitrogen for 4 h. The mixture was cooled to room temperature and then extracted with ether[18] to give a yellow oil which was purified by evaporative distillation at 125 °C (0.25 mm) to afford 71 mg (95% yield) of cyclopentenone **17** as a colorless oil which showed two peaks in a ratio of 9:1 on VPC (3% XE-60, 160 °C), corresponding to the trans product **17** and presumably the cis disubstituted double bond isomer (C-3 of the side chain): IR (film) 4.70 (C≡C), 5.88 (C=O), ^1H NMR 1.60 (s, 3, vinyl CH_3), 1.80–2.55 (m, 17, methylene protons, C≡CH), 2.05 (s, 3, enone vinyl CH_3), 5.0–5.5 (m, 3, vinyl protons).

Anal. Calcd for $C_{19}H_{26}O$: C, 84.44; H, 9.63. Found: C, 84.25; H, 9.65.

1,3-Dimethyl-2-[7-methyl-12-(trimethylsilyl)-*trans,trans*-3,7-dodecadien-11-ynyl]-2-cyclopentenol (2). A cold (0 °C) solution of 55 mg (0.28 mmol) of the aforementioned cyclopentenone **17** in 2 mL of dry ether was stirred under nitrogen while 0.78 mL (0.56 mmol) of a 0.72 M solution of methyllithium in ether was added rapidly via syringe. The mixture was stirred at 0 °C for 30 min, 1 mL (856 mg, 0.8 mmol) of trimethylchlorosilane was added, and the mixture was stirred at 0 °C for an additional 30 min. Ether extraction[18] gave 86 mg of colorless oil which was shown by IR to be a mixture of the desired cyclopentenol **2** and its trimethylsilyl ether: IR (film) 2.95 (OH), 4.65 (C≡C), 8.00 and 11.90 ($SiCH_3$), 9.60 μm (COSi).

Cyclization of Trienynol 2 with Trifluoroacetic Acid and Ethylene Carbonate in 1,2-Dichloroethane. 3-Methyl-*A*-nor-*D*-homo-3-androsten-17-one (18). A mixture of 86 mg of the aforementioned crude trienynol **2**, 4 mL of 1,2-dichloroethane, and 0.1 g of ethylene carbonate (crystallized from the melt) was stirred under nitrogen at 0 °C while 0.15 mL (231 mg, 2.0 mmol) of trifluoroacetic acid was added slowly. The resulting mixture was stirred at 0 °C for 3 h and then extracted with ether with a base wash[18] to give a red oil: IR (film) 2.95 (OH), 5.61 (trifluoroacetate C=O), 5.85 μm (C=O). A mixture of the aforementioned red oil, 10 mL of methanol, and 3 mL of 5% aqueous potassium hydroxide was stirred at room temperature under nitrogen for 15 h and extracted with ether with an acid wash followed by a base wash[18] to give 62 mg of dark red oil. Preparative TLC (R_f 0.5, 1:1 hexane–ether) gave 15 mg (19% yield from **17**) of a colorless oil, presumably ketone **18**, which was evaporatively distilled at 200 °C (0.007 mm) to afford a specimen of **18** which showed one peak with a small shoulder on VPC (3% XE-60, 180 °C). Efforts to effect further purification of this sample by preparative VPC (3% XE-60, 3% OV-17) were unsuccessful: IR (film) 5.85 μm (C=O); ^1H NMR 0.80 (s, 3, C-18 CH_3), 0.88 (s, 3, C-19 CH_3), 1.62 (s, 3, vinyl CH_3).

Anal. Calcd for $C_{20}H_{30}O$: C, 83.92; H, 10.94. Found: C, 83.12; H, 10.11.

3-Methyl-4-(7-methyl-12-(trimethylsilyl)-*trans,trans*-3,7-dodecadien-11-ynyl)-2-cyclohexenone Ethylene Thioketal (20). An adaptation of a published procedure[8] was employed. A dispersion of 1.73 g (2.8 mmol) of the known[4] phosphonium salt **19** in 10 mL of dry THF was stirred under argon while 1.62 mL (0.97 mmol) of a 0.6 M solution of phenyllithium in THF was added (enough was added so that a permanent yellow color was produced). The mixture was stirred for 20 min at room temperature, and then 4.33 mL (2.6 mmol) of a 0.6 M solution of phenyllithium in THF was slowly added. The resulting deep red solution of ylide was stirred at room temperature for 30 min, cooled to −78 °C and stirred for 30 min. A solution of 564 mg (2.54 mmol) of the aforementioned aldehyde **13** in 3 mL of dry THF was then added via syringe over a 20-min period. This mixture was stirred for 20 min at −78 °C, and then an additional 5.0 mL (3.8 mmol) of phenyllithium solution was added dropwise followed by 24 mL of dry ether over a period of 45 min. The solution was stirred for 30 min at −78 °C, slowly warmed to −30 °C, and stirred at this temperature for 20 min. A 2-mL portion of methanol was added slowly via syringe, and the mixture was stirred at room temperature for 17 h and then concentrated under reduced pressure to give a red oil. The oil was dissolved in 10 mL of methylene chloride and then was added dropwise to 500 mL of hexane, with vigorous stirring, whereupon a white precipitate of triphenylphosphine oxide immediately formed. The solution was decanted, and the solvent was removed under reduced pressure to give 1.18 g (100% yield) of crude thioketal **20** as a yellow oil which showed two peaks in a ratio of 95:5 on VPC (3% OV-17, 200 °C), corresponding to the trans product **20** and presumably the cis disubstituted double bond isomer. The crude thioketal **20** was not purified further.

An analytical specimen of thioketal **20** was prepared from the corresponding ketone **21** in the following manner. A solution of 0.1 g (0.28 mmol) of ketone **21** in 2 mL of methylene chloride was stirred under nitrogen while 0.13 mL (1.46 g, 1.6 mmol) of 1,2-ethanedithiol and 0.01 mL (11.5 mg, 0.08 mmol) of boron trifluoride etherate were added. The mixture was stirred for 16 h at room temperature and then extracted with chloroform by using a wash with 5% aqueous potassium hydroxide[18] to give an oil which was purified by evaporative distillation to afford 120 mg (99% yield) of thioketal **20** as a colorless oil: IR (film) 4.65 (C≡C), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.69 (s, 6, vinyl CH_3's), 1.8–2.4 (m, 17, methylene and methine protons), 3.35 (s, 4, $-SCH_2CH_2S-$), 5.00–5.55 (m, 3, side-chain C-3, C-4, and C-8 vinyl protons), 5.60 (s, 1, C-2 vinyl proton).

Anal. Calcd for $C_{25}H_{40}S_2Si$: C, 69.40; H, 9.32; Si, 14.84. Found: C, 69.15; H, 9.21; Si, 14.9.

3-Methyl-4-(7-methyl-12-(trimethylsilyl)-*trans,trans*-3,7-dodecadien-11-ynyl)-2-cyclohexenone (21). A solution of 1.18 g (2.53 mmol) of the aforementioned crude thioketal **20**, 35.4 mL of acetonitrile, 9.4 mL of water, and 4.0 mL (9.12 g, 64 mmol) of methyl iodide was stirred under nitrogen at 40 °C for 19 h. Ether extraction using a wash with dilute aqueous sodium thiosulfate followed by 5% aqueous potassium hydroxide[18] gave a pale yellow oil which was purified by chromatography on 65 g of Florisil (95:5 hexane–ether) followed by evaporative distillation at 155 °C (0.007 mm) to afford 522 mg (58% yield from aldehyde **13**) of cyclohexenone **21** as a colorless oil: IR (film) 4.65 (C≡C), 6.00 (C=O), 6.15 (C=C), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.60 (s, 3, side-chain vinyl CH_3), 1.8–2.5 (m, 17, methylene and methine protons), 1.96 (br s, 3, enone vinyl CH_3), 5.0–5.3 (m, 3, side-chain vinyl protons), 5.82 (br s, 1, enone vinyl proton).

Anal. Calcd for $C_{23}H_{36}OSi$: C, 77.51; H, 10.17; Si, 7.91. Found: C, 77.25; H, 10.17; Si, 7.9.

3-Methyl-4-(7-methyl-12-(trimethylsilyl)-*trans,trans*-3,7-dodecadien-11-ynyl)-2-cyclohexenol (4). A cold (−20 °C) suspension of 50 mg (1.25 mmol) of lithium aluminum hydride in 10 mL of dry ether was stirred while a solution of 389 mg (1.07 mmol) of the aforementioned cyclohexenone **21** in 5 mL of dry ether was added. The mixture was stirred at −20 °C for 1 h and then quenched by the addition of 4 mL of saturated aqueous ammonium chloride. Ether extraction[18] gave a colorless oil which was purified by evaporative distillation at 140 °C (0.007 mm) to afford 365 mg (95% yield) of cyclohexenol **4** as a colorless oil: IR (film) 2.95 (OH), 4.60 (C≡C), 6.00 (C=C), 8.00 and 11.85 μm ($SiCH_3$); ^1H NMR 0.15 (s, 9, $SiMe_3$), 1.60 (s, 3, side-chain vinyl CH_3), 1.65 (s, 3, ring vinyl CH_3), 1.8–2.4 (m, 17, methylene and methine protons), 4.0–4.2 (m, br s, 1, CHOH), 5.0–5.6 (m, 4, vinyl protons).

Anal. Calcd for $C_{23}H_{38}OSi$: C, 77.10; H, 10.39; Si, 7.61. Found: C, 76.85; H, 10.29; Si, 7.9.

Cyclization of Trienynol 4 with Trifluoroacetic Acid and Ethylene Carbonate in 1,2-Dichloroethane. Δ^1-5β-*D*-Homoandrosten-17-one (22). A solution of 220 mg (0.61 mmol) of the aforementioned trienynol **4** and 1.0 g of ethylene carbonate (crystallized from the melt) in 15 mL of 1,2-dichloroethane was stirred under nitrogen at −20 °C while 0.5 mL (770 mg, 6.8 mmol) of trifluoroacetic acid was added in a dropwise manner. The resulting mixture was stirred at −20 °C for 3 h and then quenched by the careful addition of 10 mL of saturated aqueous sodium bicarbonate. The mixture was allowed to warm to room temperature and then was extracted with ether with a base wash[18] to give a turbid oil which was purified by preparative TLC (R_f 0.4, 3:1 hexane–ethyl acetate) to afford 96 mg (55% yield) of ketone **22** as a white solid.

Two recrystallizations from 9:1 pentane–methanol afforded an analytical specimen of **22** as white needles: mp 107–110 °C; IR (CCl_4) 5.85 (C=O), 14.00 μm (cis RCH=CHR); ^1H NMR 0.79 (s, 3, C-18 CH_3), 0.99 (s, 3, C-19 CH_3), 1.00–1.75 (m, 8, methylene and methine protons), 1.8–2.5 (m, 4, CH_2COCH_2), 5.60 (s, 2, C-1 and C-2 vinyl protons); ^1H NMR (C_6D_6) 0.60 (s, 3, C-18 CH_3), 0.91 (s, 3, C-19 CH_3), 1.0–2.5 (m, 18, methylene and methine protons), 5.61 (s, 2, C-1 and C-2 vinyl protons).

Anal. Calcd for $C_{20}H_{30}O$: C, 83.85; H, 10.55. Found: C, 83.84; H, 10.56.

5β-*D*-Homoandrostan-17-one (23). A 90-mg sample (0.32 mmol) of the aforementioned ketone, mp 106–108 °C, in 13 mL of ethyl acetate was hydrogenated at room temperature and atmospheric pressure for 15 h over 5 mg of 10% palladium-on-carbon. The catalyst was removed by filtration, and then the solvent was removed at reduced pressure to give a colorless oil which crystallized on standing. Recrystallization from methanol afforded 87 mg (96% yield) of 5β-D-homoandrostan-17-one (**23**) as a white solid, mp 98–101 °C, which showed one peak on VPC (3% OV-17, 200 °C). The ^1H NMR and solution IR spectra were identical with the corresponding spectra of authentic (naturally derived) 5β-*D*-homoandrostan-17-one,[10] and the two samples gave identical responses in VPC coinjection experiments: IR (CCl_4) 5.85 μm (C=O); ^1H NMR 0.79 (s, 3, C-18 CH_3), 0.92 (s, 3, C-19 CH_3), 1.0–2.0 (m, methylene protons), 2.0–2.5 (m, 4, CH_2COCH_2); ^1H NMR (C_6D_6) 0.69 (s, 3, C-18 CH_3), 0.85 (s, 3, C-19 CH_3), 1.0–2.0 (m, 22, methylene and methine protons), 2.0–2.5 (m, 4, CH_2COCH_2).

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Registry No. 2, 72867-76-6; **4**, 68654-91-1; **7**, 68654-84-2; **8**, 68707-00-6; **9**, 68654-85-3; **10**, 72867-77-7; **11**, 72867-78-8; **12**, 72867-79-9; **13**, 72867-80-2; **14**, 33548-59-3; **15**, 72867-81-3; **16**, 72867-82-4; **17**, isomer 1, 72867-83-5; **17**, isomer 2, 72867-84-6; **18**, 72881-34-6; **19**, 42723-36-4; **20**, isomer 1, 72867-85-7; **20**, isomer 2, 72867-86-8; **21**, 72867-87-9; **22**, 52289-41-5; **23**, 52289-74-4; 3-chloropropanal diethyl acetal, 35573-93-4; 2-bromopropene, 557-93-7; 2-methyl-1-hepten-6-yn-3-ol, 72867-88-0; methyl 4-methyl-*trans*-4-nonen-8-ynoate, 72867-89-1; 4-methyl-*trans*-4-nonen-8-ynol, 72867-90-4; 2,5-bis(ethylenedioxy)-13-methyl-*trans,trans*-9,13-octadecadien-17-yne, 72867-91-5; 13-methyl-*trans,trans*-9,13-octadecadien-17-yne-2,5-dione, 72867-92-6.