

= 5 Hz, CH<sub>3</sub>-21), 0.96 (s, CH<sub>3</sub>-4), 1.10 (s, CH<sub>3</sub>-4), 1.34 (s, CH-19), 6.06 (d, *J* = 6 Hz, CH-2), 7.72 (d, *J* = 6 Hz, CH-1); near ir (CCl<sub>4</sub>) 1.65  $\mu$ ; uv  $\lambda_{\max}$  (EtOH) 263 nm ( $\epsilon$  9400); mass spectrum *m/e* (rel intensity) 410 (40), 395 (26), 297 (70), 275 (100); CD (*c* 4.6  $\times$  10<sup>-4</sup>, cyclohexane)  $[\theta]_{370} +6800$ ,  $[\theta]_{352} +13500$ ,  $[\theta]_{338} +14100$ ,  $[\theta]_{325} +10300$ .

Anal. Calcd for C<sub>29</sub>H<sub>46</sub>O: C, 84.88; H, 11.22. Found: C, 84.80; H, 11.49.

**C. 6 $\beta$ ,10-Cyclo-(5*S*)-1(10 $\rightarrow$ 5)-abeo-4,4-dimethylcholest-1-en-3-one (2).** Elution with 2.5 l. of 30% benzene in hexane gave 370 mg (37%) of photoisomer 2; mp 72–72.5° from ethanol;  $[\alpha]_{D}^{25} -10.80^{\circ}$  (*c* 0.148); ir (CCl<sub>4</sub>) 1711 (C=O), 1681 (C=C), and 1591 cm<sup>-1</sup> (C=C); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.72 (s, CH<sub>3</sub>-18), 0.89 (d, *J* = 7 Hz, CH<sub>3</sub>-26, -27), 0.94 (d, *J* = 6 Hz, CH<sub>3</sub>-21), 1.06 (s, CH<sub>3</sub>-4), 1.17 (s, CH<sub>3</sub>-4), 1.37 (s, CH<sub>3</sub>-19), 5.98 (d, *J* = 6 Hz, CH-2), 7.03 (d, *J* = 6 Hz, CH-1); uv  $\lambda_{\max}$  (EtOH) 263 nm ( $\epsilon$  8800); mass spectrum *m/e* (rel intensity) 410 (25), 395 (15), 297 (70), and 275 (100); CD (*c* 4.7  $\times$  10<sup>-4</sup>, cyclohexane)  $[\theta]_{355} +520$ ,  $[\theta]_{342} +1040$ ,  $[\theta]_{322} +1080$ ,  $[\theta]_{310} +765$ .

Anal. Calcd for C<sub>29</sub>H<sub>46</sub>O: C, 84.88; H, 11.22. Found: C, 84.31; H, 11.25.

**Photolysis of Dienone 1 at 300 nm in Dioxane-Water.** Dienone 1 (1.08 g) was dissolved in 100 ml of pure dioxane and 5 ml of water. The solution was deoxygenated with nitrogen and photolyzed for 20 hr in a Pyrex tube using the 300-nm source. Isolation and separation as previously described afforded 700 mg of starting material, 200 mg of photoisomer 2 and a trace of unidentified material.

**Photolysis of Photoisomer 2.** A solution of 2 (41 mg, 0.10 mmol) in 1,4-dioxane (15.0 ml) and glacial acetic acid (0.90 ml) was placed in a 25  $\times$  200 mm Pyrex test tube and degassed by purging with nitrogen for 30 min. The solution was then irradiated at 3500 Å and 6°C under nitrogen. The progress of the reaction was followed by TLC. After 4 hr TLC showed that approximately half the starting material had been consumed. The mixture was evaporated under reduced pressure to approximately 20% of its original volume, taken up in 30 ml of toluene, and evaporated to a yellow gum. A <sup>1</sup>H NMR spectrum of this material showed only enone protons of 2 and 4.

This material was separated by preparative thin layer chromatography (silica gel GF, 50:50:4.5 benzene-heptane-2-propanol). Two bands were observed and photoisomer 4 (6 mg) was obtained from the more mobile band and identified by <sup>1</sup>H NMR and infrared spectroscopy. Photoisomer 2 (7 mg) was recovered from the less mobile band.

**4,4-Dimethyl-1(10 $\rightarrow$ 5)-abeo-10(5 $\rightarrow$ 6 $\alpha$ H)-abeo-cholesta-1(5),9-dien-3-one (9).** Photoisomer 2 (100 mg) was taken up in 15 ml of glacial acetic acid and refluxed under nitrogen for 1.5 hr. Over this time, a new compound (9) was observed by TLC. Build-up of an impurity caused the solution to turn red and eventually dark. The acetic acid was removed with toluene on the rotatory evaporator and the 100 mg of gum was chromatographed on 3 g of silica gel. Elution with 300 ml of 10% benzene in hexane gave 94 mg (94%) of 9; mp 61.5–62.5° from ethanol; ir (CCl<sub>4</sub>) 1750 (C=O) and 1637 cm<sup>-1</sup> (C=C); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.76 (s, CH<sub>3</sub>-18), 0.89 (d, *J* = 7 Hz, CH<sub>3</sub>-26, -27), 0.95 (d, *J* = 6 Hz, CH<sub>3</sub>-21), 1.07 (s, *gem*-CH<sub>3</sub>-4), 1.52 (br s, CH<sub>3</sub>-19), 2.04–3.00 (unstructured, miscellaneous peaks), 2.78 AX<sub>2</sub> pattern (d, *J* = 2 Hz, -CH<sub>2</sub>C=O), 5.40 (t, *J* = 2 Hz, =CHCH<sub>2</sub>C=O); uv showed only end absorption; mass spectrum *m/e* (rel intensity) 410 (100), 395 (44), 382 (16), 367 (15), 353 (2), 340 (15), 325 (28), 297 (38).

Anal. Calcd for C<sub>29</sub>H<sub>46</sub>O: C, 84.88; H, 11.22. Found: C, 84.53; H, 11.39.

**Deuterium Exchange of Ketone 9.** A sample of 9 (100 mg) was taken up in dry THF (2 ml) and 0.3 ml of D<sub>2</sub>O was added. After the addition of two drops of acetyl chloride, the mixture was refluxed under nitrogen for 5.5 min. The solvent was removed on the rotatory evaporator, and the residue was taken up in 10 ml of ether and washed with deuterium oxide. The 100 mg of yellow gum resulting from evaporation of the ether was chromatographed on silica gel (2 g). Elution with 200 ml of hexane gave 80 mg of an oil whose <sup>1</sup>H NMR spectrum indicated the incorporation of deuterium at the  $\alpha$ -methylene position: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.76 (s, CH<sub>3</sub>-18), 0.85, 0.91, 0.98 (m, CH<sub>3</sub>-26, -27, -21), 1.06 (s, *gem*-CH<sub>3</sub>-4), 1.50 (s, CH<sub>3</sub>-19), 5.40 (s, CH-1).

**4,4-Dimethyl-1(10 $\rightarrow$ 5)-abeo-10(5 $\rightarrow$ 6 $\alpha$ H)-abeo-cholesta-1,9-dien-3-one (10).** To a solution of 9 (147 mg) in 3 ml of 95% ethanol under nitrogen was added 1.1 ml of 0.4 *N* aqueous sodium hydroxide. This mixture was stirred at reflux for 14 hr, cooled, poured into ether, washed with water until neutral, and dried over

magnesium sulfate. Removal of the solvent gave 125 mg of a red gum. Chromatography of 5 g of silica gel gave 100 mg of starting material and 23 mg of 10; mp 100–101.5°; ir (CCl<sub>4</sub>) 1716 (C=O), 1591 cm<sup>-1</sup> (C=C); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.72 (s, CH<sub>3</sub>-18), 0.88 (d, *J* = 7 Hz, CH<sub>3</sub>-26, -27), 0.93 (d, *J* = 6 Hz, CH<sub>3</sub>-21), 0.99 (s, CH<sub>3</sub>-4), 1.04 (s, CH<sub>3</sub>-4), 1.67 (br s, CH<sub>3</sub>-19), 1.72 (complex m, -CHC=), 2.69 (complex m, CH-5), 6.08 (dd, CH-2), 7.14 (dd, CH-1); decoupling experiments of the sample in CCl<sub>4</sub>-Me<sub>4</sub>Si gave *J*<sub>1,2</sub> = 6 and *J*<sub>2,5</sub> = 2 Hz; uv showed only end absorption; mass spectrum *m/e* (rel intensity) 410 (20), 395 (18), 316 (13), 301 (100).

Anal. Calcd for C<sub>29</sub>H<sub>46</sub>O: C, 84.88; H, 11.22. Found: C, 84.54; H, 11.45.

**Deuteration of 10.** Sodium deuterioxide was prepared by treating 150 mg of freshly cut sodium with 8 ml of ethanol-*O-d* containing 1 ml of deuterium oxide. To this solution was added 100 mg of 9 in 1 ml of ethanol-*O-d*. The solution under nitrogen was refluxed for 3 hr, taken up in 8 ml of ether, and washed to neutrality with 3 ml of D<sub>2</sub>O in three portions. The excess D<sub>2</sub>O was removed on the rotatory evaporator using dioxane and the resulting yellow oil chromatographed on 6 g of silica gel. Elution with 200 ml of 30% benzene-hexane gave 15 mg of 10, isolated as an oil; ir (CCl<sub>4</sub>) 1712 (C=O) and 1569 cm<sup>-1</sup> (C=C); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.72 (s, CH<sub>3</sub>-18), 0.84, 0.90 (complex m, CH<sub>3</sub>-21, -26, -27), 0.98 (s, CH<sub>3</sub>-4), 1.02 (s, CH<sub>3</sub>-4), 1.67 (br s, CH<sub>3</sub>-19), 7.13 (s, CH-1); mass spectrum *m/e* (rel intensity) 412 (16), 411 (8), 410 (6), 397 (8), 318 (5), 310 (100). Recovered 9 showed incorporation of two deuterium atoms: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.76 (s, CH<sub>3</sub>-18), 0.85, 0.91, 0.98 (complex m, CH<sub>3</sub>-21, -26, -27), 1.50 (br s, CH<sub>3</sub>-19), 5.40 (s, CH-1).

**Registry No.**—1, 6384-44-7; 2, 56761-43-4; 4, 56782-71-9; 5, 56761-44-5; 9, 56761-45-6; 9 dideuterio, 56782-72-0; 10, 56761-46-7; 10 dideuterio, 56761-47-8.

## References and Notes

- (1) S. Gasa, N. Hamanaka, T. Okuno, J. Omi, M. Watanabe, and T. Matsumoto, *Tetrahedron*, **28**, 4905 (1972).
- (2) H. Hikino, N. Shoji, S. Koriyama, T. Ohta, Y. Hikino, and T. Takemoto, *Chem. Pharm. Bull.*, **18**, 2357 (1970).
- (3) H. Hikino, M. Ogura, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.*, **18**, 1071 (1970).
- (4) P. Naranayan, M. Rohrl, K. Zechmeister, and W. Hoppe, *Tetrahedron Lett.*, 3943 (1970).
- (5) Z. Kumazawa and R. Iriye, *Tetrahedron Lett.*, 927 (1970).
- (6) V. Petrow, I. Stuart-Webb, B. Sturgeon, W. Adams, and D. Patel, *J. Chem. Soc.*, 4490 (1957).
- (7) B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **48**, 1680 (1965).
- (8) S. Domb and K. Schaffner, *Helv. Chim. Acta*, **53**, 1765 (1970).
- (9) Melting points (measured in open capillaries) are corrected. Infrared spectra were recorded with Beckman IR-7 and IR-5 spectrophotometers. Proton magnetic resonance spectra were measured with a Varian HA-100 spectrophotometer. Chemical shifts are reported in parts per million,  $\delta$  values, relative to the internal standard tetramethylsilane. The following notations are employed in the presentation of <sup>1</sup>H NMR spectra: s = singlet, d = doublet, t = triplet, br s = broad singlet, complex m = complex multiplet. A Perkin-Elmer Model 141 polarimeter having a sample cell path length of 1 dm was used in measuring the molecular rotations. Circular dichroism spectra were taken on a Cary Model 6001 recording spectropolarimeter. Ultraviolet spectra were measured in 95% ethanol solution on a Cary Model 15 recording spectrometer. A Consolidated Electrodynamics Corp. Model 21-110 mass spectrometer at 70 eV was used to obtain mass spectra. Carbon and hydrogen microanalyses were completed by Chemanalytix, Inc., Tempe, Ariz., and by the University of Oregon. Anhydrous magnesium sulfate was utilized in drying samples. Column chromatography employed J. T. Baker silica gel powder, 60–200 mesh. TLC spots on 5  $\times$  20 cm Baker-flex qualitative plates were visualized with uv light and by spraying the dried plates with 3% ceric sulfate in 10% sulfuric acid and subsequent heating. All ultraviolet irradiations were carried out in a Rayonet photochemical reactor from the Southern New England Ultraviolet Co.

## Preparation of

### *trans*-1,2-Bis(tri-*n*-butylstannyl)ethylene

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Recently we have described the use of *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene (1) as a reagent for the synthesis

