= 5 Hz, CH₃-21), 0.96 (s, CH₃-4), 1.10 (s, CH₃-4), 1.34 (s, CH₋-19), 6.06 (d, J = 6 Hz, CH-2), 7.72 (d, J = 6 Hz, CH-1); near ir (CCl₄) 1.65 μ ; uv λ_{max} (EtOH) 263 nm (ϵ 9400); mass spectrum m/e (rel intensity) 410 (40), 395 (26), 297 (70), 275 (100); CD (c 4.6×10^{-4} , cyclohexane) $[\theta]_{370}$ +6800, $[\theta]_{352}$ +13500, $[\theta]_{338}$ +14100, $[\theta]_{325}$ +10300.

Anal. Calcd for C₂₉H₄₆O: C, 84.88; H, 11.22. Found: C, 84.80; H, 11.49.

С. 6β , 10-Cyclo-(5S)-1(10 \rightarrow 5)-abeo-4, 4-dimethylcholest-1en-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; $[\alpha]_{678}^{25}$ -10.80° (c 0.148); ir (CCl₄) 1711 (C=O), 1681 (C=C), and 1591 cm⁻¹ (C=C); ¹H NMR (CCl₄) δ 0.72 (s, CH₃-18), 0.89 (d, J = 7 Hz, CH_{3} -26, -27), 0.94 (d, J = 6 Hz, CH_{3} -21), 1.06 (s, CH_{3} -4), 1.17 (s, CH₃-4), 1.37 (s, CH₃-19), 5.98 (d, J = 6 Hz, CH-2), 7.03 (d, J = 6Hz, CH-1); uv λ_{max} (EtOH) 263 nm (ϵ 8800); mass spectrum m/e (rel intensity) 410 (25), 395 (15), 297 (70), and 275 (100); CD (c 4.7 × 10⁻⁴, cyclohexane) $[\theta]_{355}$ +520, $[\theta]_{342}$ +1040, $[\theta]_{322}$ +1080, $[\theta]_{310}$ +765.

Anal. Calcd for C29H46O: 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 25×200 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 ¹H 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 ¹H 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 α 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. Buildup 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 (CCl₄) 1750 (C==O) and 1637 cm⁻¹ (C==C); ¹H NMR (CCl₄) δ 0.76 (s, CH₃-18), 0.89 (d, J = 7 Hz, CH₃-26, -27), 0.95 (d, J = 6 Hz, CH₃-21), 1.07 (s, gem-CH₃-4), 1.52 (br s, CH₃-19), 2.04-3.00 (unstructured, miscellaneous peaks), 2.78 AX₂ pattern (d, J = 2 Hz, $-CH_2C=0$), 5.40 (t, J = 2 Hz, =CHCH₂C=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 C₂₉H₄₆O: 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_2O 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 ¹H NMR spectrum indicated the incorporation of deuterium at the α -methylene position: ¹H NMR (CCl₄) δ 0.76 (s, CH₃-18), 0.85, 0.91, 0.98 (m, CH₃-26, -27, -21), 1.06 (s, gem-CH₃-4), 1.50 (s, CH₃-19), 5.40 (s, CH-1).

4,4-Dimethyl-1(10 \rightarrow 5)-abeo-10(5 \rightarrow 6 α 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 (CCl₄) 1716 (C==O), 1591 cm⁻¹ (C==C); ¹H NMR (CCl₄) δ 0.72 (s, CH₃-18), 0.88 (d, J = 7 Hz, CH₃-26, -27), 0.93 (d, J = 6 Hz, CH₃-21), 0.99 (s, CH₃-4), 1.04 (s, CH₃-4), 1.67 (br s, CH₃-19), 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 CCl₄-Me₄Si gave $J_{1,2} = 6$ and $J_{2,5} =$ 2 Hz; uv showed only end absorption; mass spectrum m/e (rel intensity) 410 (20), 395 (18), 316 (13), 301 (100)

Anal. Calcd for C29H46O: 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_2O in three portions. The excess D_2O 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 (CCl₄) 1712 (C=O) and 1569 cm⁻¹ (C=C); ¹H NMR (CCl₄) δ 0.72 (s, CH₃-18), 0.84, 0.90 (complex m, CH₃-21, -26, -27), 0.98 (s, CH₃-4), 1.02 (s, CH₃-4), 1.67 (br s, CH₃-19), 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: ¹H NMR (CCl₄) & 0.76 (s, CH₃-18), 0.85, 0.91, 0.98 (complex m, CH₃-21, -26, -27), 1.50 (br s, CH₃-19), 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.

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 (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, To specify the internal standard tetramethylsilane. The following notations are employed in the presentation of ¹H NMR spectra: s = sin-glet, d = doublet, t = triplet, br s = broad singlet, complex m = complexmultiplet. A Perkin-Elmer Model 141 polarimeter having a sample cell path length of 1 dm was used in measuring the molecular rotations. Cir-cular dichroism spectra were taken on a Cary Model 6001 recording spectropolarimeter. Ultraviolet spectra were measured in 95% ethano 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 Chemanalytics, 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.

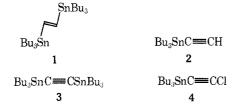
Preparation of trans-1,2-Bis(tri-n-butylstannyl)ethylene

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Recently we have described the use of trans-1,2-bis(trin-butylstannyl)ethylene (1) as a reagent for the synthesis of acetylenes including some types which are not otherwise accessible.¹ A number of other applications of this valuable reagent are presently being investigated in these laboratories, especially in connection with total synthesis of natural products. Because of the potentially broad range of utility of 1 a convenient, large-scale preparation was desirable. Although 1 is prepared by simply heating a neat mixture of 1 equiv of tri-n-butyltin hydride with 1 equiv of tri-n-butylethynylstannane (2),¹⁻³ the preparation of 2 in quantity by current procedures is complicated and cumbersome.



Reaction of tri-n-butyltin halides with ethynylmagnesium halides⁴ or with sodium acetylide in ether⁵ results in only a very low yield of 2, the major side product being bis-(tri-n-butylstannyl)acetylene (3).⁶ A modification of the latter process has been described⁷ in which 1 equiv of trin-butyltin chloride in ether is added to a solution of sodium acetylide prepared in liquid ammonia. Although this procedure results in a higher yield of 2, the reaction in our hands was found to be very capricious and usually resulted in large amounts of the side product 3.

A new method has been developed for the synthesis of 1 which possesses the advantages of (1) high yield, (2) applicability on a large scale, (3) avoidance of low temperatures or the use of liquid ammonia, and (4) elimination of further reaction of 2 and specifically the by-product 3. Tri-n-butyltin chloride was added to the readily prepared anion, lithium chloroacetylide,⁸ and the product, tri-n-butylchloroethynylstannane (4), was isolated in 83% yield by distillation. Treatment of 4 with 2 equiv of tri-n-butyltin hydride afforded tri-n-butyltin chloride (99%) and trans-1,2-bis-(tri-n-butylstannyl)ethylene (1, 86%) by direct distillation of the reaction mixture. The readily separated tri-n-butyltin chloride was very pure and could be recycled for the preparation of more 1.

Experimental Section

trans-1,2-Bis(tri-n-butylstannyl)ethylene (1). To a cooled (0°) solution of 50.0 ml (82.4 mmol) of 1.65 M methyllithium in ether under an argon atmosphere was added dropwise a solution of 3.2 ml (42 mmol) of trans-1,2-dichloroethylene in 15 ml of ether during 1 hr (gas evolution). The mixture was warmed to room temperature, stirred for 90 min, then recooled (0°), and 11.1 ml (41.2 mmol) of tri-n-butyltin chloride was added. After stirring for 1 hr at room temperature, 1 ml of methyl iodide was added and stirring was continued for 30 min. The mixture was filtered (quickly in the air) through a pad of Celite and concentrated in vacuo. Distillation at bp 100-105° (0.01 mm) afforded 12.0 g (83%) of pure chloroacetylene 4, ir (neat) 4.72 μ . This material could be used in the next step; redistillation did not change the spectra.

A neat mixture of 17.8 g (50.9 mmol) of tri-n-butylchloroethynylstannane, 29.7 g (102 mmol) of tri-n-butyltin hydride, and 0.18 g of azobisisobutyronitrile were heated at 90° for 4 hr. Distillation afforded 16.4 g (99%) of tri-n-butyltin chloride, bp 102-105° (0.1 mm), and 26.4 g (86%) of *trans*-bis(tri-*n*-butylstannyl)ethylene (1)¹: bp 175–195° (0.07 mm); ir (neat, partial) 6.83 and 10.4 μ ; NMR (CCl₄) δ 0.50–1.90 (br m, 54 H) and 6.85 (s, 2 H, $J_{117Sn-H} =$ 106, $J_{119Sn-H} = 110$ Hz). The NMR, ir, and near ir spectra of 1 were identical with those of material prepared as previously de-scribed.^{1,9}

Registry No.-1, 14275-61-7; trans-1,2-dichloroethylene, 156-60-5; tri-n-butyltin chloride, 1461-22-9.

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The Structure of Hallol¹

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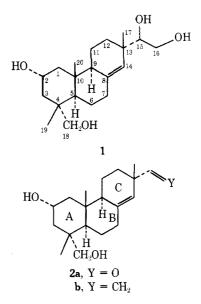
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A study of the heartwood constituents of the New Zealand podocarp Podocarpus hallii Kirk has revealed the presence of the terpenic substances sugiol, podocarpic acid, totarol, its 19-hydroxy and 19-oxo derivatives,² sellowin A,³ and a compound (B, mp 204°) of unknown constitution.² The following discussion shows the latter, herewith named hallol, to be 8(14)-sandaracopimaren- 2α , 15ξ , 16, 18-tetrol (1).



Both elemental and mass spectral analyses indicate the compound to possess a C₂₀H₃₄O₄ molecular framework, while the mass spectrum of a sample exposed to deuterium oxide reveals the incorporation of four deuteriums and hence the presence of a hydrogen on each of the oxygens. The ¹H NMR spectrum of a deuteriomethanol solution contains three methyl singlets at 0.82, 0.87, and 0.97 ppm, a six-hydrogen multiplet at 2.9-4.0 ppm corresponding to two oxymethylenes and two oxymethines, and an olefinic hydrogen multiplet at 5.32 ppm. These facts are accommo-