

ate, and the reaction mixture was heated under reflux for 4 hr. Solvent removal and chromatographic separation gave 0.198 g (32%) of 2-methyl-3-phenylindole (8): mp 58° (lit.¹⁴ mp 59–60°); ¹H NMR δ_{Me₄Si} (CDCl₃) 2.28 (s, 3 H), 7.05–7.76 (m, 10 H); mass spectrum (70 eV) *m/e* 207 (M⁺).

Registry No.—1, 16483-98-0; 3, 3469-20-3; 5, 54879-94-6; 7a, 16205-14-4; 8, 4757-69-1; benzynes, 462-80-6.

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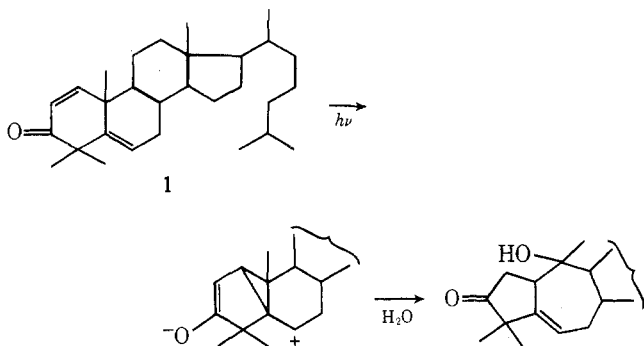
Photolysis of 4,4-Dimethylcholesta-1,5-dien-3-one

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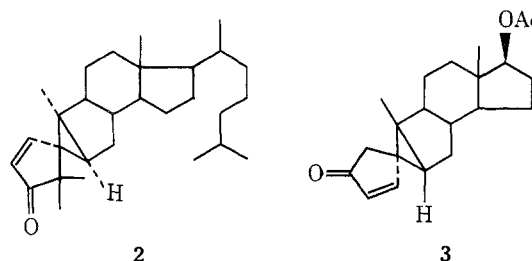
Received July 9, 1974

The photolysis of 4,4-dimethylcholesta-1,5-dien-3-one (1) has been examined in the hope that the AB portion of the steroid nucleus would rearrange to a hydroazulene system of the type found in the grayanotoxins.^{1–5} A plausible



mechanism can be written for this transformation and the change from a decalin system to a hydroazulene skeleton is frequently encountered in the photochemical reactions of dienones. Nonetheless this type of transformation was not encountered. Photolysis of 1 in either 95% ethanol or dioxane in the 250-nm region produced at least eight new compounds. However, photolysis at 300 nm in aqueous dioxane gave predominantly one new compound which is assigned structure 2.

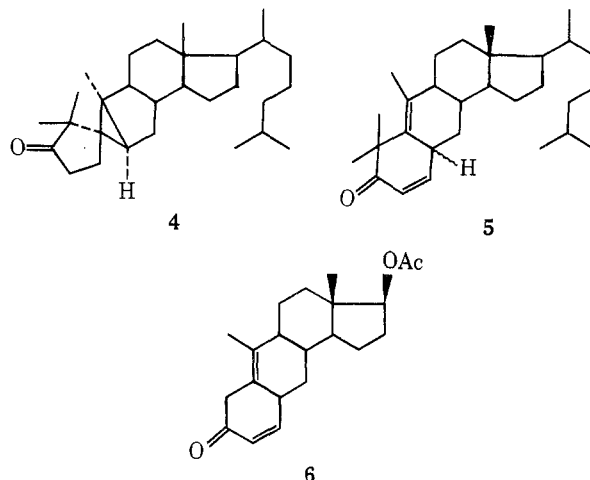
The formation of 2 is entirely expected from the elegant and extensive studies of Jeger, Schaffner, and their collaborators, who examined the photolysis of 3-oxo-17β-acetoxy-Δ^{1,5}-androstadiene which presents the same hexalone system only lacking the two methyl groups at C-4.⁷ The pho-



tolysis of 3-oxo-17β-acetoxy-Δ^{1,5}-androstadiene afforded the photoisomer 3 accompanied by three of its stereoisomers.

The structure of 2 follows from a comparison of its spectroscopic properties with those of 3. The ultraviolet spectrum of 2 showed λ_{max} 263 nm (ε 8800) whereas 3 exhibited λ_{max} 267 nm (ε 9750). The vinyl protons of 2 appeared as an AB quartet (δ 5.98 and 7.03, *J* = 6 Hz) similar to that found for 3 (δ 6.07 and 7.25, *J* = 6 Hz). The infrared spectrum of 2 had absorption maxima at 1707 and 1681 cm⁻¹ in good agreement with those found for 3.

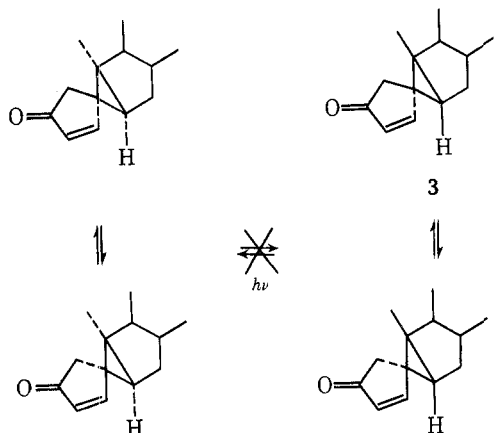
Photolysis of dienone 1 at 350 nm in dioxane-acetic acid gave 2 along with two new photoisomers, 4 and 5. Photoisomer 4 is clearly a stereoisomer of 2. Moreover, photolysis of 2 leads to the formation of 4. The third photoisomer is assigned structure 5 based on its spectroscopic properties which are very similar to those found for compound 6 obtained from the photolysis of 3-oxo-17β-acetoxy-Δ^{1,5}-androstadiene.



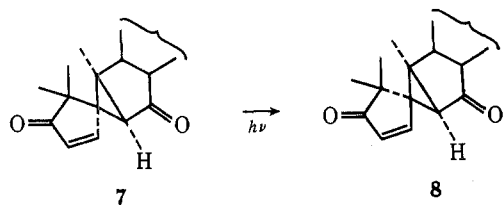
The infrared spectrum of 5 showed carbonyl absorption at 1667 cm⁻¹ and double bond absorption at 1640 cm⁻¹. The ¹H NMR spectrum showed an AB quartet (δ 5.79 and 6.45, *J* = 10 Hz) whereas the ultraviolet spectrum showed a maximum at 227 nm. These spectroscopic characteristics are in good agreement with those found for 6.

The remaining structural problem is the stereochemistry of the spiro photoisomers. It was shown previously in the studies of 3 and its stereoisomers that the four stereoisomers formed two pairs. Members of one pair reached a photostationary state but did not give rise to either member of the other pair. Extensive degradations and circular dichroism measurements indicated that members of a pair were related to one another by change in the stereochemistry of the spiro carbon.

Moreover, members of a pair showed enantiomeric circular dichroism curves. However, in the case at hand, both of the stereoisomers we obtain had positive circular dichroism curves. Although we did not establish that the spiro photoisomers 2 and 4 achieve a photostationary state, it was established that photolysis of 2 gives rise to 4 and following



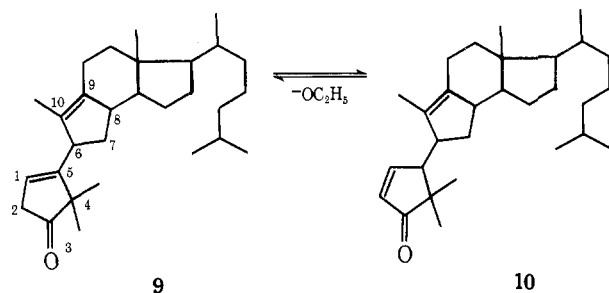
the progress of the photolysis of dienone 1, photoisomer 4 appeared only after substantial quantities of 2 had been produced. The situation may be similar to that observed in the photolysis of the closely related dienone, 3,7-dioxo-4,4-dimethyl-17 β -acetoxy- $\Delta^{1,5}$ -androstadiene. In that case, photolysis produced the two photoisomers shown below and it was established that photoisomer 7 was the precursor to 8 and that the isomerization of 7 to 8 is irreversible.⁸



In any event, the cyclopropane ring juncture was not changed in any of the previous photochemical studies. Hence, we make the assumption that the spiro photoisomers in the present study have the same stereochemistry at the cyclopropane ring juncture. The ¹H NMR spectra and the circular dichroism measurements are consistent with the stereochemistry indicated for photoisomer 4. Thus 4 showed an intense positive Cotton effect and the vinyl proton at C-1 were found at δ 7.72 which compares favorably with the properties of the relevant photoisomer from the photolysis of 3-oxo-17 β -acetoxy- $\Delta^{1,5}$ -androstadiene (an intense positive Cotton effect; δ 7.92 for the C-1 proton). The stereochemistry of 2 is thus as shown in structural formula 2, differing from 4 only in the configuration of the spiro carbon. Moreover, subsequent chemical transformations indicate that 2 and 4 have the same configuration at C-6, which is consistent with the stereochemical proposals. Both spiro photoisomers were subjected to the action of hot acetic acid. A single compound was produced in high yield in both instances. The chemical transformations and spectroscopic properties of this material indicate structure 9.

The infrared spectrum of 9 showed carbonyl absorption at 1750 cm^{-1} ascribed to a cyclopentanone moiety along with absorption at 1637 cm^{-1} indicating a carbon-carbon double bond. The ultraviolet spectrum did not show absorption characteristic of conjugated double bonds. The ¹H NMR spectrum showed a two-proton doublet ($J = 2$ Hz) at δ 2.78 ascribed to the C-2 protons coupled to the vinyl proton at C-1 which appears as a triplet at δ 5.40. Treatment of 9 with deuterium oxide and acid in tetrahydrofuran resulted in the incorporation of two deuteriums and the ¹H NMR spectrum showed the expected changes, namely, the loss of the signal at δ 2.78 and the collapse of the triplet at δ 5.40 to a singlet.

Treatment of 9 with 0.1 N sodium hydroxide in aqueous ethanol gave a mixture of materials from which 9 was isolated (68%) and an isomerization product (16%) which is



assigned structure 10. The infrared spectrum of 10 shows absorptions at 1716 and 1591 cm^{-1} ascribed to the cyclopentenone moiety whereas the ultraviolet spectrum showed a maximum at 213 nm (ϵ 12700). The ultraviolet absorption maximum is at somewhat shorter wavelength with a greater extinction coefficient than the corresponding values for cyclopentenone. However, the shape of the curve, the position of the maximum, and the extinction coefficient are very well approximated by adding the ultraviolet absorption spectra for cyclopentenone and 1,2-dimethylcyclohexene. The ¹H NMR spectrum of 10 revealed two complex one-proton multiplets at δ 6.08 and 7.14 ascribed to the vinyl protons at C-2 and C-1, respectively. Decoupling experiments yielded the coupling constants between the protons at C-1, -2, and -5 (see Experimental Section). The base peak of the mass spectrum appears at m/e 310, suggesting that the most prominent fragmentation is the loss of the entire A ring by cleavage of the doubly allylic single bond joining the A ring to the remainder of the molecule.

That the conversion of 9 to 10 is a simple base-catalyzed double bond isomerization is indicated by an experiment in which pure 10 gave rise to 9 under the equilibrating conditions. Equilibration of 9 in deuterated solvent afforded doubly deuterated 10 in 15% yield. The ¹H NMR spectrum of this material showed a singlet at δ 6.08 and 2.69, ascribed to the protons at C-2 and C-5, respectively, were missing. The same experiment afforded doubly deuterated 9 which exhibited the same ¹H NMR spectrum as the material produced by acid-catalyzed exchange.

These data would seem to secure the structures of the photochemical products and the material produced by acid-catalyzed rearrangement of the spiro photoisomers except for some stereochemical questions.

Experimental Section⁹

Photolysis of 4,4-Dimethylcholesta-1,5-dien-3-one in Acetic Acid-Dioxane. A sample of 4,4-dimethylcholesta-1,5-dien-3-one⁶ (1.6 g) was dissolved in 120 ml of dioxane-containing 6% acetic acid. The solution was placed in a 30 \times 404 mm Pyrex tube and nitrogen was bubbled through for 30 min. The solution was photolyzed at 6° for 30 min. Removal of the solvent gave a light yellow gum.

A. 4,4-Dimethyl-1(10 \rightarrow 6 ξ)-abeo-cholesta-1,5(10)-dien-3-one (5). The crude photolysis product obtained above was chromatographed on silica gel (50 g). Elution with 2 l. of 20% benzene in hexane gave a mixture (600 mg) of starting dienone and 5. Further elution afforded 200 mg (ca. 20% based on unrecovered starting material) of 5: mp 83–85.5° from ethanol; ir (CCl₄) 1667 (C=O), 1640 (C=C), and 1570 cm^{-1} (C=C); ¹H NMR (CCl₄) δ 0.74 (s, CH₃-18), 0.85, 0.91, 0.95 (m, CH₃-21, -26, and -27), 1.30 (s, CH₃-4), 1.44 (s, CH₃-4), 1.19 (br s, CH₃-19), 3.29 (complex m, CH-6), 5.79 (d, $J = 10$ Hz, CH-2), 6.45 (d, $J = 10$ Hz, CH-1); uv λ_{max} (EtOH) 227 nm (ϵ 9200); and the mass spectrum had a molecular ion (m/e) peak of 410 (calcd mol wt 410.17).

Anal. Calcd for C₂₉H₄₆O: C, 84.88; H, 11.22. Found: C, 84.98; H, 11.42.

B. 6 β ,10-Cyclo-(5R)-1(10 \rightarrow 5)-abeo-4,4-dimethylcholesta-1-en-3-one (4). Further elution with 2.5 l. of 25% benzene in hexanes gave 360 mg (36%) of photoisomer 4: mp 107–108° from ethanol; ir (CCl₄) 1712 (C=O), 1670 (C=C), and 1575 cm^{-1} (C=C); ¹H NMR (CCl₄) δ 0.73 (s, CH₃-18), 0.88 (d, $J = 7$ Hz, CH₃-26, -27), 0.94 (d, J

= 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 \times 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.

C. 6 β ,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 (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, CH₃-26, -27), 0.94 (d, *J* = 6 Hz, CH₃-21), 1.06 (s, CH₃-4), 1.17 (s, CH₃-4), 1.37 (s, CH₃-19), 5.98 (d, *J* = 6 Hz, CH-2), 7.03 (d, *J* = 6 Hz, 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 \times 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 \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 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. 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 (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, -CH₂C=O), 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 D₂O 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 D₂O in three portions. The excess D₂O 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) δ 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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- 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, δ values, relative to the internal standard tetramethylsilane. The following notations are employed in the presentation of ¹H 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