of the $^2H/^1H$ ratios is by complete combustion of the organic matter to CO_2 and H_2O and reduction to H_2 in a uranium furnace and mass spectroscopic analysis of the isotropic ratio of the whole compound without any indication of isotopic ratios as a function of site within the molecule. Some effort has been made to be more selective in analysis of $^2H/^1H$ ratios. In particular, work has been done on the nonexchangable hydrogens of cellulose.[4,5] While these studies focused on one type of site by eliminating the hydroxyl hydrogens, the $^2H/^1H$ ratios were not site specific for the C–H hydrogens. Rauschenbach et al.[6] compared $^2H/^1H$ ratios for synthetic and fermented ethanols and also determined the isotopic ratio in the methyl group of the ethanol by oxidation to acetic acid and analysis of the corresponding acetate salt. Martin and Martin[7,8] recently have used ^2H NMR to show that the isotopic distribution of ^2H in ethyl and vinyl groups varies from molecule to molecule.

The full significance of observing site-specific isotopic effects upon the $^2H/^1H$ ratio is emphasized when it is realized that such information is not readily available from the traditional mass spectrometric methods of measuring isotope ratios. Although mass spectral methods are much more sensitive than NMR techniques and have a much larger dynamic range, such methods can only measure the average molecule $^2H/^1H$ isotope ratio because of the facile scrambling of the molecular hydrogens (both ^1H and ^2H) in the typical mass spectrometric ion. Futhermore, these hydrogen rearrangements can be isotopic selectivities as large as 10^5 in some instances.[9] Such large isotope effects would completely mask the significant but still smaller intramolecular ratios that we have been recently observing. Thus, high-field deuterium magnetic resonance, ^2H NMR, techniques provide a unique method for determining this potentially valuable information.

Site-specific isotopic ratios have the potential for more complete characterization of the rate-controlling processes in rather complex chemical and biosynthesis processes. Detailed information on mechanistic steps should be available from variations in the $^2H/^1H$ ratio as a function of molecular site. This technique, applicable at natural abundance, allows analysis without destruction of the sample and removes the possibility of artifical inhibition of a metabolic system by excess deuterium present in labeled compounds. Finally, as found in our two camphors, one may anticipate the opportunity of observing the chemical history of two identical molecules derived from different precursors from variations in the intramolecular $^2H/^1H$ ratios stampled into the molecule by alternative synthetic pathways. With improved sensitivity and spectral dispersion at very high fields, proton-decoupled ^2H NMR can now realize its full potential.[1] The significant isotope effects observed herein further enhance the importance of ^2H NMR techniques.

Experimental Section. The 76.77-MHz ^2H spectra were recorded on a Bruker WM500 spectrometer operating in Fourier transform mode. Methylcyclohexane and 1,1,3-trimethylcyclohexane were run as neat liquids, and *d*-camphor was prepared as a nearly saturated solution in chloroform. Each sample contained 10% tetramethylsilane as a chemical shift reference. Spectra requiring about 400 scans were acquired at 8-s intervals by utilizing a 90° pulse and a 2-s data aquisition of 2048 points. Broad-band decoupling at 5 W of power was used with the power reduced to 0.4 W during the interval between accumulations to allow the nuclear magnetization of the sample to recover under reduced dielectric heating. Free induction decays were filtered by using a Lorentzian to Gaussian line-shape transformation and zero filled to 8192 points before Fourier transformation. Assignment of resonance lines to specific molecular sites was accomplished from analysis of the corresponding 500-MHz proton spectra or from associating the protons with a specific carbon peak by using selective proton decoupling.

Tricyclo[5.1.0.0^{2,8}]octa-3,5-diene (Octavalene)

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Received April 22, 1982

The unique properties of the $(CH)_8$ hydrocarbons[1] have attracted the attention of many organic chemists. As a member of this series the title compound (**8**) enjoys special interest. The butadiene bridge should substantially widen the dihedral angle of the bicyclo[1.1.0]butane system from the normal value of about 122°,[2] resulting in an increased strain energy. This, as well as the electronic interaction of the π system and the strained σ system, leads one to anticipate that **8** will exhibit unusual chemical and spectroscopic properties. Furthermore, the Woodward–Hoffmann rules allow a thermally induced [1,5] carbon shift. Repetition of this degenerate rearrangement would finally equilibrate all CH groups. Thus, **8** could be te bullvalene equivalent of the $(CH)_8$ family.

Interested in such prospects, several research groups have undertaken to synthesize **8**. When 8,8-dibromobicyclo[5.1.0]octa-2,4-diene was treated with methyllithium, the resulting carbene rearranged to a dihydropentalene[3,4] instead of inserting into the syn-6-CH bond as intended. Likewise, the tricarbonyl iron complex of the dibromide with methyllithium failed to give the desired insertion product.[5] In analogy to the preparation of benzvalene via cyclopentadienylcarbene[6] the intramolecular [2 + 1] or [6 + 1] cycloaddition of cycloheptatrienylcarbene to give **8** has been attempted. However, only cyclooctatetraene, heptafulvene, benzene, and acetylene could be identified as reaction products.[7] Also, the disrotatory opening of the cyclobutene portion in tetracyclo[4.2.0.0^{2,4}.0^{3,5}]oct-7-ene, which should produce **8**, could not be achieved without rearrangement of the bicyclo[1.1.0]butane system.[8] In addition, a straightforward route to prepare 4-bromooctavalene by cyclopropane ring enlargement of the dibromocarbene adduct of homobenzvalene and subsequent hydrogen bromide elimination failed because under all conditions tried a *trans*-bis(homobenzene) derivative was formed in the first step,[9,10] most probably in an acid-catalyzed process.[10] Here, we

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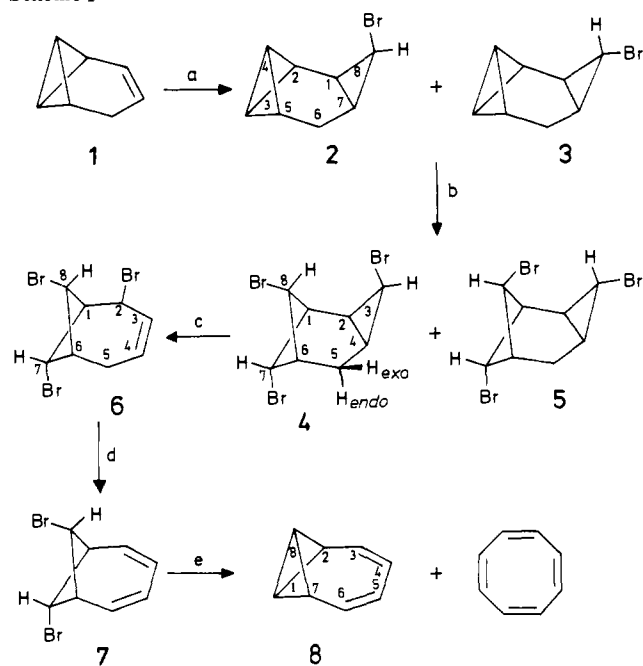(5) Epstein, S.; Thomson, P.; Yapp, C. J. *Science (Washington, D.C.)* **1977,** *198,* 1209–1215.
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Communications to the Editor

J. Am. Chem. Soc., Vol. 104, No. 16, 1982 4495

Scheme I

^{a} CH$_2$Br$_2$, NaN(SiMe$_3$)$_2$. ^{b} Pyridine hydrobomide perbromide in pyridine, −35 to 20 °C. ^{c} Acetonitrile, 100 °C, 7 h. ^{d} DBU in benzene, 30 °C, 40 h. ^{e} 0.95 equiv of *t*-BuLi, ether, −78 to 0 °C.

report the first synthesis of octavalene (**8**).

Analogous to the behavior of the dibromocarbene adduct of homobenzvalene, in the monobromocarbene adducts **2** and **3** the bicyclo[1.1.0]butane moiety does not survive the conditions necessary to effect the monobromocyclopropane ring opening. Therefore, we protected it by addition of bromine across the central bond. Subsequently, the butadiene bridge was constructed, and in the last step 1,3-elimination of the bromine atoms reestablished the bicyclo[1.1.0]butane central bond to complete the synthesis of **8**. The addition of halogens to the central bond of bicyclo-[1.1.0]butane[11] and some of its derivatives[12-15] and the formation of the bicyclo[1.1.0]butane system from 1,3-dihalocyclo-butanes[11-13,15,16] are known reactions. However, our example of this reaction sequence represents to our knowledge the first application of a protective group strategy in bicyclo[1.1.0]butane chemistry.

Scheme I details the preparation of **8**. Applying the method of Martel and Hiriart,[17] we added monobromocarbene to ho-mobenzvalene (**1**)[18] and obtained in 48% yield the stereoisomers **2** and **3**[19,20] as a 1:1 mixture. Bromination of the mixture afforded

the tribromides **4**[19,21] and **5**[19,22] in a ratio of 2:1, from which **4** was isolated in 54% yield as a crystalline solid after treatment with methanol. On the basis of the size of the coupling constants in bridged cyclobutanes[23] the stereochemistry of C-7 and C-8 in **4** and **5** follows unambiguously from the ^{1}H NMR spectra.

Although mechanistic investigations have not been carried out, the stereochemical outcome appears to support a radical pathway for the bromination of **2** and **3**. We assume that a bromine atom is added to C-3 from the sterically less hindered side with inversion, parallel with the reaction between thiophenol and bicyclo-[1.1.0]butane derivatives.[24] The resulting cyclobutyl radical may accept the second bromine atom in principle from both sides. Starting from **2**, however, the endo-bromine atom at the cyclo-propane ring interferes, thus allowing only the formation of **4**. The cyclobutyl radical originating from **3** experiences less steric hin-drance because the cyclopropane ring carries its bromine sub-stituent in the exo position. Then the second bromine enters to produce the cis-dibrominated cyclobutane derivative **5** in accord with the preferred stereochemical course in halogenations of bicyclo[1.1.0]butadiene derivatives.[11,13,15]

For well-known stereoelectronic reasons, **4** thermolyzed smoothly to the ring-enlarged tribromide **6**[19,25] (81% yield) at 100 °C in acetonitrile, while **5** decomposed above 150 °C to un-identified products. Elimination of hydrogen bromide from **6** with DBU gave in 74% yield **7**[19,26] and treatment of the latter with *tert*-butyllithium generated **8**[19,27] and cyclooctatetraene as a 4:1 mixture in 50% yield.

The NMR spectra of **8** reflect its C_{2v} symmetry. In CDCl$_3$ 1,8-H absorb as a triplet with $J_{1,2}$ = 3.0 Hz at δ 1.27, 2,7-H as multiplet at 2.97, and 3,6-H and 4,5-H give rise to multiplets at 5.72 and 6.13. The four carbon atom types resonate in C$_6$D$_6$ at δ −13.4 (C-1,8, J_{CH} = 207 Hz), 45.3 (C-2,7, J_{CH} = 147 Hz), 124.5 (C-4,5, J_{CH} = 155 Hz), and 137.6 (C-3,6, J_{CH} = 151 Hz). Compared to the bicyclo[1.1.0]butane bridgehead signal (δ −3[28]) the absorbance of C-1,8 is shifted upfield by 10.4 ppm despite the β substitution, which may indicate additional strain. That the signal of C-1,8 in **8** appears 61.7 ppm upfield from the cor-responding benzvalene resonance (δ 48.3[29]) is accommodated nicely by the proposed orbital interaction model,[29] since the π* orbitals of ethylene and 1,3-butadiene have different symmetry.

At 80 °C the ^{1}H NMR spectrum of **8** is still unchanged, thus providing evidence that the automerization discussed above does not take place rapidly. At that temperature **8** rearranged slowly to cyclooctatetraene. We cannot exclude the possibility that this reaction was catalyzed by traces of acid.

Application of the above reaction sequence to the dibromo-carbene adduct of homobenzvalene produces 4-bromooctavalene as a pure crystalline solid with mp 30–32 °C, which has been fully

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(18) Christl, M.; Freitag, G.; Brüntrup, G. *Chem. Ber.* **1978**, *111*, 2320–2333. The synthesis has been improved. Now we obtain **1** in three steps from benzvalene with an overall yield of 42%.

(19) Satisfactory elemental analyses were obtained for all new compounds except **8**, which has not been obtained completely pure yet.

(20) Bp 30 °C (0.1 torr); ^{1}H NMR of the mixture (CDCl$_3$, 400 MHz) δ 0.89 (1 H, q, *J* = 8.8 Hz), 0.99–1.06 (2 H, m), 1.32 (1 H, dt, *J* = 10.8, 3.0 Hz), 1.40–1.54 (4 H, m), 1.56–1.68 (2 H, m), 1.79 (1 H, ddd, *J* = 13.7, 9.0, 2.4 Hz), 1.90 (1 H, dt, *J* = 10.8, 3.0 Hz), 2.22–2.29 (2 H, m), 2.59 (1 H, quint, *J* = 3.3 Hz), 2.82 (1 H, dd, *J* = 3.3, 2.5 Hz), 2.82 (1 H, quint, *J* = 3.3 Hz), 3.16 (1 H, t, *J* 7.4 Hz); ^{13}C NMR (CDCl$_3$) δ 1.9 (d), 5.9 (d), 7.0 (d), 10.1 (d), 10.3 (d), 11.2 (d), 17.58 (t), 17.63 (d), 18.3 (t), 19.1 (d), 27.1 (d), 35.3 (d), 36.9 (d), 37.2 (d), 38.2 (d), 41.7 (d).

(21) Mp 86–87 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.48 (4-H, ≈qd, $J_{2,4}$ = $J_{4,5-endo}$ = 9.0 Hz, $J_{3,4}$ = 7.8 Hz, $J_{4,5-exo}$ = 1.5 Hz), 1.62 (2-H, ddd, $J_{1,2}$ = 6.0 Hz, $J_{2,3}$ = 7.8 Hz), 2.19 (5-H$_{exo}$, dt, $J_{5-endo,5-exo}$ = 15.0 Hz, $J_{5-exo,6}$ = 1.5 Hz), 2.50 (5-H$_{endo}$, ddd, $J_{5-endo,6}$ = 4.5 Hz), 2.70 (6-H, ≈qd, $J_{1,6}$ = $J_{6,7}$ = 5.1 Hz), 3.20 (1-H, ≈q, $J_{1,7}$ = 5.1 Hz), 3.52 (3-H, t), 5.34 (7-H, t), 5.45 (8-H, s). This orientation of C-7 and C-8 has not been proved but seems plausible on the basis of the assumed mechanism.

(22) Mp 89–90 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.50 (4-H, m), 1.72 (2-H, dddd, $J_{1,2}$ = 4.8 Hz, $J_{2,3}$ = 3.0 Hz, $J_{2,4}$ = 9.9 Hz, $J_{2,8}$ = 1.0 Hz), 2.26–2.37 (5-H$_{endo}$, 5-H$_{exo}$, m), 2.69 (6-H, m), 3.19 (1-H, dq, $J_{1,7}$ = 4.8 Hz, $J_{1,8}$ = 6.0 Hz), 4.18 (7-H, t, $J_{6,7}$ = 4.8 Hz), 4.20 (8-H, tt, $J_{6,8}$ = 6.0 Hz, $J_{5-endo,8}$ = 1.0 Hz), 4.84 (3-H, t, $J_{3,4}$ = 3.0 Hz).

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(25) Mp 57–58 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.37, 2.65 (5-H$_{endo}$ and 5-H$_{exo}$, ≈dtt each, $J_{5-endo,5-exo}$ = 20.1 Hz, $J_{4,5}$ = $J_{5,6}$ = 4.2, 3.6 Hz, $J_{2,5}$ = $J_{3,5}$ = 2.0 Hz), 3.10 (6-H, ≈dq; $J_{1,6}$ = 4.5 Hz, $J_{6,7}$ = 7.8 Hz), 3.44 (1-H, m), 4.43 (8-H, s), 4.83 (2-H, m), 5.25 (7-H, t, $J_{1,7}$ = 7.8 Hz), 5.57 (4-H, dm, $J_{3,4}$ = 12.3 Hz) 5.83 (3-H, dm). The stereochemistry at C-2 is not known.

(26) Mp 61–62 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.43 (1,6-H, m), 4.36 (8-H, s), 5.31 (7-H, t, $J_{1,7}$ = 7.1 Hz), 5.76, 6.09 (2,5-H, 3,4-H, m each).

(27) The boiling point is similar to that of COT, because the mixture of **8** and COT evaporates at 20 °C (0.1 torr) and condenses in a trap kept at −78 °C.

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characterized by analytical and spectral data.

Total Synthesis of (+)-Phyllanthocin

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The crude ethanol extract obtained from the root of *Phyllanthus acuminatus* Vahl[1,2] was found to inhibit growth in the P388 leukemia system in mice. Kupchan and co-workers traced the interesting pharmacological properties to a bisabolane sesquiterpene glycoside, (+)-phyllanthoside (**1**).[1] Although the structure

2 R=CH₃
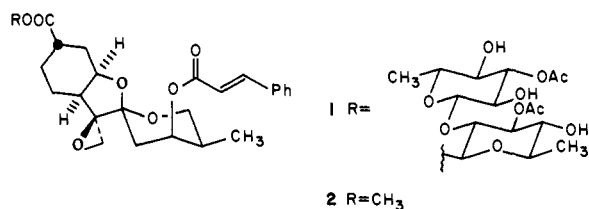
of the corresponding aglycone, (+)-phyllanthocin (**2**), was elucidated by single-crystal X-ray diffraction, the exact nature of the sugar moiety in **1** and the absolute configurations of **1** and **2** remained unknown. Recently Pettit and co-workers determined the structure of phyllanthose, the novel disaccharide portion of **1**, as well as the structures of several closely related tumor inhibitory sesquiterpene glycosides.[3] Studies pertaining to phyllanthoside's pronounced activity against the NCI murine B16 melanoma have reached the level of advanced preclinical trials.[4] We report herein the first synthesis and the absolute configuration of (+)-phyllanthocin (**2**).
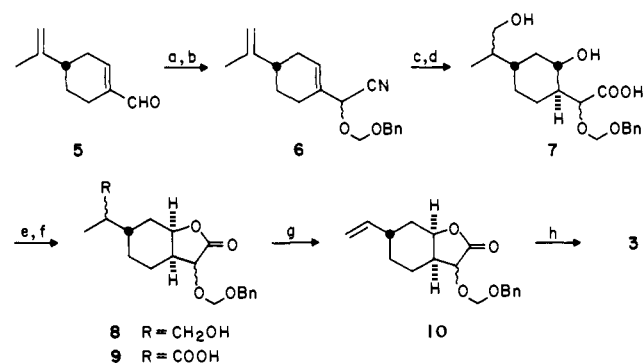
The spiroketal moiety of **2** readily lent itself to the retrosynthetic dissection illustrated in eq 1. Although the convergency of such
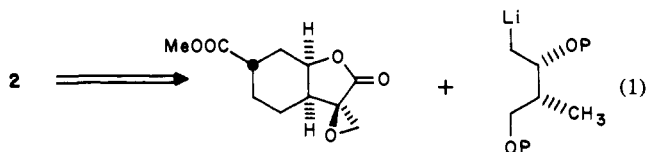

an approach seemed attractive, several problems pertaining to stereocontrol remained. Notably, since the absolute configuration of **2** was unknown, entry into either enantiomeric series was essential. We settled on **3** and **4** as our two pivotal intermediates.

We prepared lactone **3** starting with (*S*)-(-)-perilla aldehyde (**5**) in eight steps as illustrated in Scheme I. Several features warrant comment. The thexylborane-mediated hydroboration-

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(2) The plant collection providing the original sample of phyllanthoside was incorrectly believed to be *P. brasiliensis.* Subsequently, this was shown to be an error (ref 3).

(3) Pettit, G. R.; Cragg, G. M.; Gust, D.; Brown, P. *Can. J. Chem.* **1982,** *60,* 544.

(4) We thank Dr. Matthew Suffness of the National Cancer Institute for this information. Phyllanthocin (**2**) has been shown to exhibit no antitumor activity (ref 1, 3).

(5) Either antipode of perilla aldehyde can be purchased from Research Organics Inc., Belleville, NJ.

Scheme I

a, KCN/HOAc/diethyl ether/25 °C (95% yield); b, PhCH₂OCH₂Cl/C₅H₅N/60 °C (51% yield); c, thexylborane/ THF/−40 °C H₂O/NaOAc (83% yield); d, KOH/ethanol/100 °C (95% yield); e, EtOOCN=NCOOEt/PPh₃/THF/−20 °C; f, Jones' reagent/acetone 0 °C (81% yield from **7**); g, Ph(OAc)₄/Cu(OAc)₂/ C₅H₅N/benzene/80 °C (82% yield); h, LDA/THF/−78 °C PhCH₂OCH₂Cl/THF/HMPA/−60 °C (71% yield)
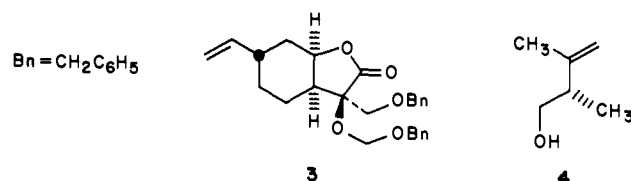
oxidation of **6** was modeled after the totally stereoselective hydroboration of limonene by Brown.[6] Analogous to this is the stereocontrol derived from cyclic borane **11**. Phosphonium salt
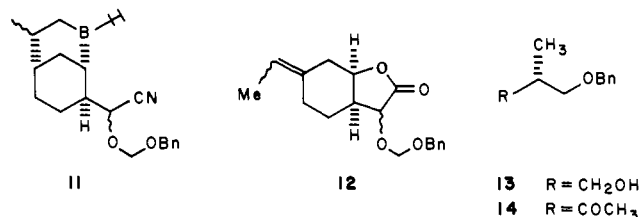
induced lactonization proceeded with the anticipated[7] complete inversion of configuration at the alcohol center as shown by comparison of **8** with a sample of the corresponding trans-fused lactone prepared by acid-catalyzed closure. Oxidative decarboxylation of **9** by the method of Kochi[8] produced **10** as a readily separable mixture of epimers *free of regioisomeric impurities corresponding to* **12**. Although a preference for the formation of the desired terminal alkene was expected,[9] this exclusive Hofmann orientation was not. Highly stereoselective (≥95%) benzyloxymethylation[10] of the lithium enolate derived from **10** afforded **3** as a white, crystalline solid (mp 50–51 °C). High stereoselectivities in the alkylations of similar systems have been observed.[11]

Throughout the sequence depicted in Scheme I there are a variety of intermediates that contain one or two random asymmetric centers. Although the eventual destruction of these centers made them inconsequential to the final outcome, they made product analyses in the developmental stages problematic. However, through exhaustive searches for isomeric products and

(6) Brown, H. C.; Pfaffenberger, C. D. *J. Am. Chem. Soc.* **1967,** *89,* 5475. For excellent leading references to cyclic hydroborations see: Still, W. C.; Darst, K. P. *J. Am. Chem. Soc.* **1980,** *102,* 7385.

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