sesquiterpenoids is given in Figure 1. In this scheme, solvolysis of 6 with participation of the homoallylic double bond would give rise to 5.[8] Protonation of the tetrasubstituted double bond of the bicyclo[3.1.0]hex-2-ene ring system of 5 or solvolysis of 6 without double bond participation could lead to cation A, which upon rearrangement to cation B provides an immediate precursor for 2 and 4. (Another likely deprotonation product from B, 7, has not yet been observed.) On this basis, bicyclolaurencenol is simply the cyclopropylcarbinyl cousin of the homoallylic halide, α-snyderol, and its rearranged dehydrohalogenation products.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer, ultraviolet spectra on a Beckman DB-G spectrophotometer, and optical rotations on a Perkin-Elmer Model 141 polarimeter. Mass spectra were obtained on an Associated Electronic Industries MS-902 mass spectrometer operated at 70 eV. ^{1}H NMR spectra were obtained on a Varian EM-390 spectrometer; chemical shifts are reported in parts per million (δ units) downfield from tetramethylsilane as an internal standard. Only well-resolved resonances are described.

Isolation of Sesquiterpene Alcohols 2, 3, 4, and 5. Specimens of *Laurencia intricata* were collected at depths of 1–3 feet in Castle Harbour, Bermuda in October 1979, and preserved in acetone prior to analysis. The acetone extracts were decanted and concentrated under reduced pressure. The residual aqueous phase was extracted with CH_2Cl_2 to yield a dark green syrup (4.5 g), which was chromatographed on Florisil. Fourteen fractions were collected from the Florisil column (136 g) by elution with mixtures of hexane, ethyl acetate, and methanol of gradually increasing polarity. ^{1}H NMR analysis of fractions 1–3 indicated the presence of a series of sesquiterpenes containing vinyl groups. Further chromatography of fractions 1–3 on silica gel (135 g of Biosil A, 200–400 mesh), eluting with hexane–ether (9:1) gave a mixture of sesquiterpenes. The mixture was separated on silica gel (44 g Woelm, 32–63 μm) impregnated with 10% $AgNO_3$; elution with hexane–ether mixtures yielded the four sesquiterpene alcohols 5, 2, 3, and 4. Final purification of each component was accomplished by gel filtration through Sephadex LH-20 (2 × 100 cm) with CH_2Cl_2–MeOH (1:1). Alcohol 2 was obtained as a colorless oil [15 mg, $[\alpha]^{25}_D$ + 29.0° (*c* 0.84, $CHCl_3$)], 3 as a colorless oil [18 mg, $[\alpha]^{25}_D$ −12.1° (*c* 0.48, $CHCl_3$)], dactylenol, 4, as a colorless oil (62 mg).

Bicyclolaurencenol (5). Bicyclolaurencenol (30 mg) was obtained as a colorless oil: $[\alpha]^{25}_D$ −16.1° (*c* 0.67, $CHCl_3$); IR (CCl_4) ν_{max} 3580, 3045, 1640, 990, 915 cm^{-1}; UV (cyclohexane) λ_{max} 227 nm (ε 3400); ^{1}H NMR ($CDCl_3$) δ 5.96 (1 H, dd, *J* = 17.25, 10.5 Hz), 5.27 (1 H, dd, *J* = 17.25, 1.5 Hz), 5.07 (1 H, dd, *J* = 10.5, 1.5 Hz), 1.66 (3 H, s), 1.27 (3 H, s), 1.04 (3 H, s), 0.99 (3 H, s), 0.64 (1 H, m, *J* = 8.1, 7.8, 3.6 Hz), −0.11 (1 H, m, *J* = 3.8, 2.7 Hz); mass spectrum, *m/e* (relative intensity) 220 (M^+, 18), 202 (4), 187 (12), 145 (8), 135 (23), 134 (71), 133 (15), 122 (15), 121 (64), 120 (28), 119 (100), 107 (17), 105 (25), 94 (14), 91 (20), 81 (13), 79 (11), 77 (12), 71 (12), 55 (10), 43 (16); mol wt calcd for $C_{15}H_{24}O$ 220.1827, found 220.1837.

Acknowledgment. We thank Mr. Francis Connor for assistance with the field work and Dr. John Schwede for identifying the alga. H. B. Wilkinson and Continental Corporation Fellowships provided to J.H.C. from the Bermuda Biological Station supported the field work. Additional support by the USDA, Forest Service, Northeastern Forest Experiment Station (for S.B.H., Visiting Fellow) and by the Schering Corporation is gratefully acknowledged.

Registry No. 2, 59700-20-8; 3, 79373-32-3; 4, 58542-82-8; 5, 79373-33-4.

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(8) Any halogenated sesquiterpenes, such as the snyderols, present in the extracts would most likely undergo solvolytic type rearrangements on the silver nitrate impregnated silica gel. That 5 is, in fact, a natural product was borne out by examination of the ^{1}H NMR and mass spectra of the sesquiterpene mixture prior to argentate chromatography. The mass spectrum revealed no halogen-containing fragment ions or any ions of mass larger than *m/e* 220. The ^{1}H NMR spectrum not only possessed signals for the geminal methyls of 5 but conspicuously lacked any signal near δ 4.05 for protons on the bromomethines of the snyderols. We thank referee II for informative suggestions in this regard.

Perchlorodihydrotrindene

Charles P. Rader* and Kenneth E. Kear

Rubber Chemicals Research Laboratories, Monsanto Industrial Chemicals Co., Akron, Ohio 44313

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The pyrolysis of hexachlorocyclopentadiene[1-4] (1) or perchlorobi-2,4-cyclopentadien-1-yl[5,6] (2) gives as a major product a solid (3, mp 344–346 °C) analyzing for C_5Cl_4 (Chart I). . The structure of 3 was originally assigned as perchlorofulvalene and subsequently revised[4] to the general perchlorodihydrotrindene structure (4), on the basis of molecular weight determination (564, boiling point elevation) and degradation to trindane (5). This paper reports mass spectral data establishing unequivocally that 3 is $C_{15}Cl_{12}$ and compelling ^{13}C NMR evidence for the structural assignment of 3. The ^{13}C resonances of 1 and 3, together with the ^{13}C–^{13}C coupling constants of 1, are also assigned.

Results and Discussion

The mass spectrum of 3 gives a molecular ion (M^+·) starting at *m/e* 600 which has an isotope cluster with relative intensities corresponding to those expected from the isotopic abundances of $C_{15}Cl_{12}$. Fragmentation ion clusters are found starting at *m/e* 565, 530, 495, 460, 425, 390, and 355. These clusters may be assigned to ions arising from the loss of one to seven Cl atoms, respectively, from the molecular ion. The intensities[7] of these ions appear to vary in a systematic manner as follows: M^+·, 8; M^+· − Cl, 43; M^+· − 2Cl, 14; M^+· − 3Cl, 100; M^+· − 4Cl, 11; M^+· − 5Cl, 43; M^+· − 6Cl, 7; M^+· − 7Cl, 27.

The relative prevalence of M^+· − 3Cl could result from the loss of three allylic chlorines from the fused ring system to give a $C_{15}Cl_9^+$ ion (6) which would then have a macrocyclic ring system with 14 π electrons, satisfying the Hückel 4*n* + 2 rule for aromatic stability. Starting at *m/e* 247.5, an interesting isotope cluster (relative intensity 13) is found. Its peaks are separated by half integral mass numbers; their multiplet relative intensities are equal to those of the *m/e* 495 ion. This is compelling evidence for assigning the *m/e* 247.5 ion as $C_{15}Cl_9^{2+}$, which could arise from the loss of an electron from $C_{15}Cl_9^+$.

The chemical evidence for the trindene ring system in 3 is very strong. Degradation of 3 with lithium and *tert*-butyl alcohol gives 5,[1] a result confirmed by us. Compound 5 has also been obtained[4] by hydrogenating 3 over plati-

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(7) All relative intensities are based on the height of the highest peak of each isotope cluster, a value of 100 being arbitrarily assigned for the M^+· − 3Cl ion.

0022-3263/81/1946-5035$01.25/0

Chart I

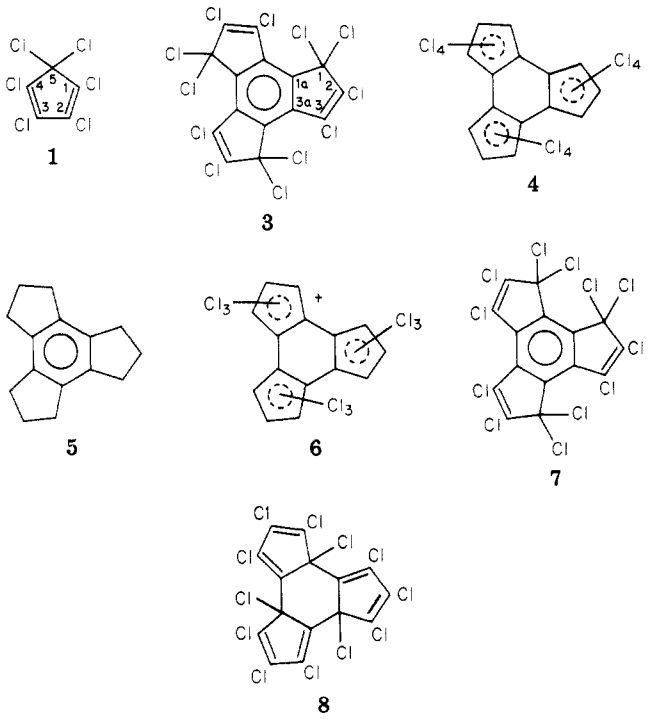

Table I. ^{13}C NMR Data for 1 and 3

compd	δ[a]	$J_{^{13}C-^{13}C}$, Hz
1	δ_1, 133.4	$J_{1,2'}$ 89.4
	δ_2, 128.5	$J_{1,3'}$ [b]
	δ_5, 81.8	$J_{1,5'}$ 55.2
		$J_{2,5'}$ 14.8
3	δ_1, 79.7	
	δ_2, 133.3	
	δ_3, 127.3	
	δ_{3a}, 134.9	
	δ_{1a}, 144.5	

[a] From tetramethylsilane as an internal standard. [b] Could not be measured from $^{13}C-^{13}C$ sidebands.

num oxide in ethanol. We have found 3 to react quite sluggishly with ethanolic silver nitrate,[8] prolonged boiling being required. Differential thermal analysis shows 3 to be stable at temperatures up to 400 °C. This stability and the high melting point of 3 suggest a flat, symmetrical molecule with the central ring aromatic. The relatively small number of infrared absorption bands (300–4000-cm^{-1} range) for a molecule this large also suggests a symmetrical molecule.

A natural-abundance ^{13}C NMR spectrum of 3 was obtained (Table I) and found to give five peaks of approximately equal intensity. Comparison of these ^{13}C data with those for 1 shows 3 to have three equivalent sp^3 carbons and 12 sp^2 carbons consisting of five groups of three equivalent carbons each. This confirms the suspected symmetry of the molecule.

Of the numerous structures which can be drawn for 3 with the dihydrotrindene ring system, only two (3 and 7) have the central ring aromatic. 3 with its C_{3h} symmetry is totally compatible with our NMR data, whereas 7 is not.

The NMR data serve to rule out the unlikely possibility of a nonaromatic central ring (i.e., with one or more exocyclic double bonds, one or two sp^3 carbons, or both). Of the possible structures with a nonaromatic central ring, only one (8) could conceivably agree with the NMR data. 8 would only be valid if the three chlorines on the central ring were syn. The steric strain resulting from bond angle distortions and nonbonded interactions are compelling reasons for rejecting 8 when the high thermal stability and symmetry of 3 are considered.

We are therefore led to assign the structure of 3 as perchloro-4,7-dihydrotrindene,[9] in clear accord with our data and those of the literature.

Proposed assignments of the five ^{13}C peaks of 3 can be made (Table I) by a comparison with the spectrum[10] of 1. To reliably assign the two sp^2 resonances of 1, we found it necessary to observe the $^{13}C-^{13}C$ sidebands. This analysis showed the sp^3 carbon to be coupled to the 133.4- and 128.5-ppm peaks with couplings of 55.2 and 14.8 Hz, respectively. Thus the coupling to the 133.4-ppm peak is through one bond and that to the 128.5-ppm peak through two.[11] The $J_{1,2}$ coupling was obtained from the two central peaks of the AB multiplet, since the two side peaks (one-sixth the intensity of the central peaks) could not be reliably observed.

The fusion of the three cyclopentadienyl rings to form 3 generates a 2.1-ppm upfield shift for the sp^3 carbon (C_1 of 3). For the two sp^2 carbons opposite the fusion, the shift of C_3 (1.2 ppm upfield) should be of the order of that of C_1, and that of C_2 (0.1 ppm upfield) should be much less. These conclusions are in accord with the very small "fusion shift" (<2 ppm) observed for the two opposite sp^2 carbons when cyclopentadiene[12] is fused to form indene.[13] The assignment of the C_{1a} and C_{3a} resonances is based on (1) our measurement of the ^{13}C resonance (132.3 ppm) of hexachlorobenzene, (2) the known effect[14,15] of an adjacent substituted sp^3 carbon on the chemical shift of an aromatic carbon, (3) comparison published spectra of cyclopentadiene,[12] indene,[13] indane,[14] furan,[15,16] benzofuran,[16] pyrrole,[16,17] and indole,[16,18] and (4) the relative insensitivity[14,19,20] of aromatic ^{13}C resonances to *o*-, *m*- and *p*-chloro substituents.

Experimental Section

Perchloro-4,7-dihydrotrindene (3) was prepared, as reported previously,[3] by heating neat hexachlorocyclopentadiene under reflux, as the temperature rose from 239 to 280 °C. Recrystallization of the crystalline product (3) from xylene gave the product: mp 344–346 °C; UV (cyclohexane) λ_{max} 268 nm (log ϵ, 4.621), 278 (4.670); IR maxima (KBr) 812, 753 (CCl), 1574, 1608 (C=C), 1020, 1199, 513 cm^{-1}.

Anal. Calcd for $C_{15}Cl_{12}$: C, 29.75; Cl, 70.25. Found: C, 29.74; Cl, 70.25.

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Mass spectral data were obtained with a CEC 21-104 mass spectrometer utilizing a direct-introduction probe and an Associated Electronics Industries high-resolution mass spectrometer (70 eV ionizing voltage) with perfluorotributylamine (mol wt 671) as a reference standard. Exact mass measurements were not made. Infrared spectra of KBr pellets of **3** were obtained with Perkin-Elmer Model 221 and 621 spectrophotometers. Ultraviolet spectra of cyclohexane (spectroquality) solutions of **3** were taken with a Cary Model 11 spectrophotometer.

^{13}C nuclear magnetic resonance spectra were obtained with a Varian CFT-20 spectrometer modified with a switchable carbon/proton probe and a frequency synthesizer/broadband amplifier. It was necessary to use chromium(III) 2,4-pentanedionate (CrAcAc, ~0.1 M) as a paramagnetic relaxation agent.[21] The shortened spin-lattice relaxation time (T_1) allowed rapid, repetitive excitation and provided an observable spectrum of **3** even though its solubility was low. The spectra were collected at ~40 °C with a 90° pulse and an ~2.9-s repetition rate, thus allowing ~5 T_1 for relaxation. For natural-abundance ^{13}C–^{13}C coupling constants for **1**, 24–72-h data acquisitions were necessary with CrAcAc as a relaxation agent. Tetramethylsilane was used as an internal standard in $CDCl_3$ solvent.

Acknowledgment. We express deep appreciation to Professor W. H. Urry and the late Dr. R. H. Campbell for securing some of the spectral data and for extremely useful discussions.

Registry No. 1, 77-47-4; 3, 79357-50-9.

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Stereospecific Formation of Equatorial Diacetylimides from the Stereoisomers of Six-Membered Carbocyclic Amines

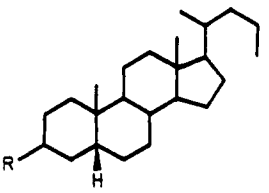
Mark M. Green* and M. Vairamani

Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201

We report here that in varied six-membered carbocyclic primary amines, diacetyl imide derivatives could only be obtained from the equatorial stereoisomers.

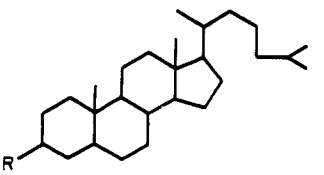
Reduction of the oxime derivatives of 3-oxocholane[1] (series **1**, Chart I), 3-oxocholestane[2] (series **2**), and 4-*tert*-butylcyclohexanone (series **3**) utilizing lithium aluminum hydride for the steroids and catalytic hydrogenation for the cyclohexane served to produce the mixtures of isomeric amines. After acylation with acetic anhydride and pyridine, chromatography yielded two extremely easily separable materials. In each case (series **1–3**) the faster moving material was shown by mass spectrometry, proton NMR, and elemental analysis to be the imides, which were isolated as pure substances (**1a–3a**).[3] Similar analysis indicated the slower moving material to be, in each case (series **1–3**), a mixture of the epimeric acetyl amides. Further acetylation of these mixtures produced more of the previously encountered imides (**1a–3a**) and, after a single crystallization, the isomerically pure amides of the axial amine in each case (**1b–3b**).

Chart I



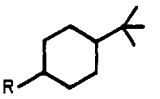
series 1

1a, R = (3α)-N(COCH$_3$)$_2$
b, R = (3β)-NH(COCH$_3$)
c, R = (3α)-NH(COCH$_3$)



series 2

2a, R = (3β)-N(COCH$_3$)$_2$
b, R = (3α)-NH(COCH$_3$)
c, R = (3β)-NH(COCH$_3$)
d, R = (3α)-NCO
e, R = (3β)-NCO



series 3

3a, R = *trans*-N(COCH$_3$)$_2$
b, R = *cis*-NH(COCH$_3$)
c, R = *trans*-NH(COCH$_3$)

In each case the imides **1a–3a** could be easily hydrolyzed in alcoholic NaOH to yield the isomerically pure equatorial acetyl amides **1c–3c**.

In the cholestanes[2] and the *tert*-butylcyclohexanes[4] the epimeric amides are known materials.[2,4] In the cholanes we characterized the epimeric amides here as well as the imides which have not been previously reported in any of these systems.

In another attempt to prepare the axial imide we subjected **1b** and **3b** to refluxing acetyl chloride. Evaporation of the solvent yielded a solid material in which no imide could be detected by proton NMR (absence of a signal near δ 2.4[3]) or by thin-layer chromatography (no spot near the positions for **1a** and **3a** in each case). We also subjected 3α- and 3β-isocyanatocholestane (**2d** and **2e**) to refluxing acetic anhydride.[5] The equatorial isomer (**2e**) yielded a mixture of the amide **2c** and the imide **2a** in low yield and a great deal of tar while the axial isocyanate **2d** gave only the amide **2b** in a similar low yield.

Our inability to isolate an axial imide in all three systems could arise from an insuperable kinetic barrier or from a highly unfavorable equilibrium. The imide of 3β-aminocholestane (**2a**) does yield a mixture of **2a** and the amide **2c** in refluxing acetic anhydride–pyridine which favors the imide (**2a**). This is consistent with reports that imides and amides can equilibrate.[6] Earlier work has shown that the acetyl imide could not be isolated from tertiarybutyl amine and that the yield of imide compared to amide decreases with increasing steric size of the *N*-alkyl group.[7] Equilibrium processes could explain the formation of the amide **2b** from the axial isocyanate **2d** in refluxing acetic anhydride. The reagent, present in large excess as the solvent, could contain enough acetic acid to supply the necessary protons. Although the imide **2a** is formed from the equatorial isomer **2e**, the amide **2c** is also isolated here. The proposed mechanism of imide formation from isocyanates[8] could not lead to amide, but others have also

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(8) See ref 3a pp 347–348 and references therein.

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