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SYNTHESIS OF (4aR,9aS,9bR)- AND (4aR,9aS,9bS)-4a,6,6,9a-TETRAMETHYL-trans-PERHYDROINDANO[2,1-c]PYRANS

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UDC 547.659.1'665'728.2'816:542.953.2:543.422.51

$C_{(9b)}$-Epimeric (4aR,9aS)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyrans, which have the odor of ambergris, were synthesized by dehydration of the corresponding glycols. It was established that a mixture of epimeric [with respect to $C_{(3a)}$] (8aS,8bR)-5,5,8a-trimethyl-3a-ethyl-trans-perhydroindano[2,1-b]furans is formed along with a trans-perhydroindano[2,1-c]pyran derivative in the acidic dehydration of (1R,2R,7aS)-2,4,4,7a-tetramethyl-1-(2-hydroxyethyl)-2-hydroxymethyl-trans-hydrindan.

It is known [1, 2] that a number of products of the cleavage of labdane diterpenoids with the composition C_{16}-C_{18} have the odor of ambergris and are of interest to the perfume industry as substitutes for the scarce and costly ambergris derived from whales.

According to the existing concepts [2-4], the odor of ambergris is peculiar to trans-decalin derivatives that contain the I structural fragment with three axial substituents in the 2, 4a, and 8a positions and an oxygen-containing functional group attached to one of these centers (Ohloff's 1,2,4-triaxial rule).

In order to verify this rule it seemed of interest to synthesize substances with structures similar to those of the indicated decalin compounds, which, however, do not satisfy its requirements. In our opinion, derivatives of trans-perhydronaphtho[2,1-c]pyran and trans-perhydroindano[2,1-c]pyran are compounds of this sort.

In the present communication we describe the synthesis of (4aR,9aS,9bR)- and (4aR,9aS,-9bS)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyrans (II and III).

Compound II was synthesized on the basis of (1R,8aS)-Δ^2-1-(2-hydroxyethyl)-2,5,5,8a-tetramethyl-trans-octahydronaphthalene (IV) [5] (see Scheme 1). Acetylation of alcohol IV

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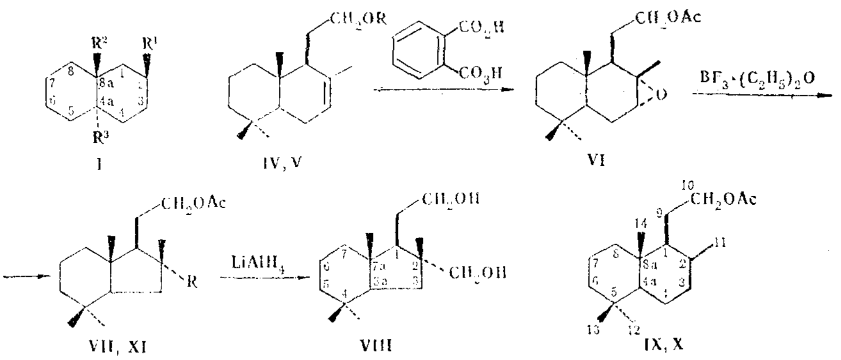
Scheme 1



IV R=H; V R=Ac; VII R=CHO; IX Δ^1; X $\Delta^{2(11)}$; XI R=CO_2H

with a mixture of acetic anhydride and pyridine gives acetate V, which is oxidized by monoperphthalic acid to (1R,8aS)-2,3-α-epoxy-1-(2-acetoxyethyl)-2,5,5,8a-tetramethyl-trans-decalin (VI). The α configuration of the epoxide ring of the latter follows from the fact [6, 7] that the β side of the molecules of compounds of this type, like acetate V, is sterically shielded. Under the influence of boron trifluoride etherate epoxy acetate VI undergoes isomerization to give (1R,2R,7aS)-2,4,4,7a-tetramethyl-1-(2-acetoxyethyl)-2-formyl-trans-hydrindan (VII). The IR spectrum of acetoxy aldehyde VII contains maxima that are characteristic for acetate and aldehyde groups, while singlet signals of four methyl groups attached to quaternary carbon atoms, the methyl group of an acetate grouping, and the proton of an aldehyde group and a triplet signal of a CH_2CH_2OAc group are present in the PMR spectrum. On the basis of the fact that the rearrangement of epoxy compounds of the cyclohexane series in acidic media with ring contraction is a stereospecific process [8, 9], the aldehyde group of acetoxy aldehyde VII has an α configuration. Reduction of acetoxy aldehyde VII with lithium aluminum hydride leads to (1R,2R,7aS)-2,4,4,7a-tetramethyl-1-(2-hydroxyethyl)-2-hydroxymethyl-trans-hydrindan (VIII) [10].

Diol VIII can be obtained by a simpler method from the accessible mixture of isomeric acetates V, IX, and X [6]. The successive (without isolation of the intermediates) oxidation of a mixture of these substances with monoperphthalic acid, isomerization with boron trifluoride etherate, and oxidation with potassium permanganate in acetic acid gave a substance, the acidic part of which consists of (1R,2R,7aS)-2,4,4,7a-tetramethyl-1-(2-hydroxyethyl)-2-carboxy-trans-hydrindan (XI), which was reduced to diol VIII with lithium aluminum hydride.

Under the influence of various agents [dimethyl sulfoxide (DMSO), p-toluenesulfonyl chloride in pyridine, phosphoric acid, etc.], this diol either does not undergo dehydration or (under more severe conditions) gives a large amount of hydrocarbons. Let us note that this sort of behavior confirms the configuration at $C_{(2)}$ assigned to it and to aldehyde VII. In fact, from an examination of molecular models of diol VIII and oxide II it may be concluded that a change in the conformation of the cyclopentane ring of diol VIII, which leads to marked drawing together of the methyl group attached to $C_{(2)}$ and $C_{(7a)}$, which in turn should hinder the formation of oxide II, occurs in the production of the latter.

p-Toluenesulfonic acid in benzene proved to be the best dehydrating agent. The reaction product, which, according to data obtained by thin-layer chromatography (TLC) and gas–liquid chromatography (GLC), is a mixture of three substances and a small amount of the starting diol, was separated into three fractions by double chromatography with columns filled with silica gel.

The first and least polar fraction consisted of two substances. All attempts to separate them were unsuccessful. The IR spectrum of the mixture of these substances contains maxima that are characteristic for the tetrahydrofuran oxide ring and the gem-dimethyl group, while the PMR spectrum contains signals of four methyl groups and a $-CH_2CH_2-O$ group. Its mass spectrum in the high mass-number region contains peaks of ions with 236* (M), 221 ($M-CH_3$), 207 ($M-C_2H_5$), 191 [$M-(CH_3 + CH_2O$], and 177 [$M-(CH_3 + CH_3CHO)$].

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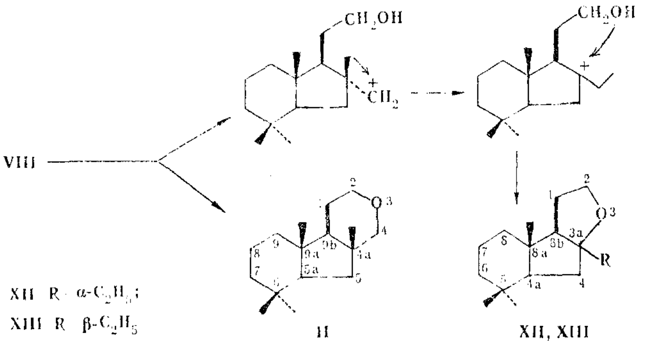
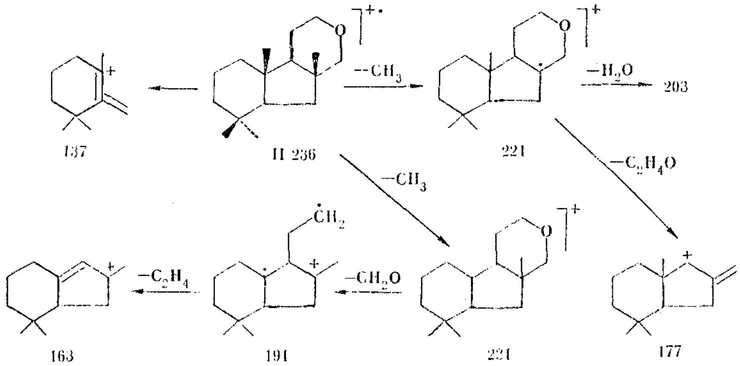
*Here and subsequently, the m/z values are given for the ion peaks.

Scheme 2



Scheme 3

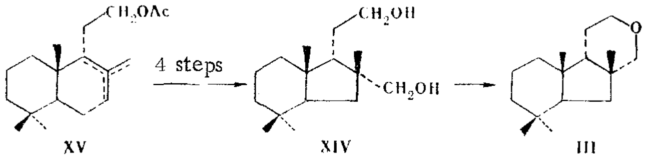


On the basis of the data enumerated above and the results of elementary analysis it was concluded that the investigated substance is a mixture of epimeric [with respect to $C_{(3a)}$] (8aS,8bR)-5,5,8a-trimethyl-3a-ethyl-trans-perhydroindano[2,1-b]furans (XII and XIII). A possible pathway for their formation is presented in Scheme 2. Compounds XII and XIII are unstable and are readily converted to less polar substances upon standing or, particularly, upon contact with acid.

The mixture of oxides XII and XIII has an intense woody-ambergris odor. This should have been expected, since the spatial orientation of the substituents attached to $C_{(2)}$, $C_{(3a)}$, and $C_{(7a)}$ in the trans-hydrindan is close to their orientation in trans-decalin compounds with general structure I.

The second fraction obtained in the chromatography of the product of dehydration of glycol VIII was an individual liquid substance. Its IR spectrum contains bands that are characteristic for the tetrahydropyran ring and the gem-dimethyl group, and signals of four methyl groups bonded to quaternary carbon atoms, a two-proton multiplet of a methylene group in the 2 position, and signals of an AB system corresponding to a methylene group in the 4 position [doublet at 3.87 ppm (A-H, J = 9 Hz) and a quartet at 3.90 ppm (B-H, J_1 = 9 Hz, J_2 = 3 Hz)] are present in the PMR spectrum; additional splitting occurs due to coupling of one proton of the AB system with the 5-H proton. The (4aR,9aS,9bR)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyran (II) structure was assigned to the investigated substance on the basis of the enumerated data. The structure was confirmed by its mass spectrum, in which the peaks of the ions with 236, 203, 191, 177, 163, 137, and 98, the possible pathway of the formation of which is indicated in Scheme 3, are the most informative.

We have previously synthesized [7] an epimer of diol VIII, viz., (1S,2R,7aS)-2,4,4,7a-tetramethyl-1-(2-hydroxyethyl)-2-hydroxymethyl-trans-hydrindan (XIV). Let us note only that it is formed via the same scheme as diol VIII from the $C_{(1)}$ epimer of epoxide VI. Like diol VIII, it can be obtained by a simplified pathway without isolation of the intermediate from a mixture of unsaturated acetates XV.



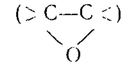
The dehydration of diol XIV with p-toluenesulfonic acid leads to (4aR,9aS,9bS)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyran (III) in good yield [11]. Its IR spectrum contains a band that is characteristic for the tetrahydropyran ring, while its PMR spectrum contains signals of four methyl groups attached to quaternary carbon atoms, a doublet of doublets of an AB system corresponding to the protons of a methylene group in the 4 position, and a two-proton multiplet of protons of a methylene group in the 2 position. Peaks of the same ions as those in the mass spectrum of oxide II are present in the mass spectrum of this compound; only their intensities differ.

Compounds II and III do not satisfy the requirements of the triaxial rule mentioned above; however, they have an intense ambergris odor.

EXPERIMENTAL

The melting points were determined with a Kofler apparatus. The specific rotation in chloroform was measured with a Polamat S polarimeter (German Democratic Republic). The IR spectra of solutions of the compounds in CCl_4 were recorded with a Specord 711R spectrometer. The PMR spectra were recorded with Tesla BS-467 (60 MHz) and Varian XL-200 spectrometers with tetramethylsilane as the internal standard. The mass spectra were obtained with an MKh-1320 spectrometer with a system for direct introduction of the substances into the ion source at an ionizing voltage of 70 eV. Solutions of the substances in organic solvents were dried with anhydrous sodium sulfate. The petroleum ether had bp 40-60°C. The columns were filled with L40/100 μ silica gel, while LS5/40 μ silica gel (Czechoslovakian SSR) was used for thin-layer chromatography (TLC). The plates were dried for 3 days at ordinary temperatures. The spots were detected by spraying the plates with concentrated sulfuric acid with subsequent heating in the flame of a gas burner.

(1R,8aS)-Δ^2-1-(2-Hydroxyethyl)-2,5,5,8a-tetramethyl-trans-octahydronaphthalene Acetate (V). A 540-mg (5.29 mmole) sample of freshly distilled acetic anhydride was added to 245 mg (1.04 mmole) of alcohol IV [5] in 2 ml of dry pyridine, and the mixture was allowed to stand at room temperature for 2 h. It was then diluted with 15 ml of water and extracted with ether. The extract was washed successively with 10% sulfuric acid, water, sodium bicarbonate solution, and water, dried, and filtered. The ether was removed by vacuum distillation to give 251 mg (86%) of acetate V in the form of a colorless viscous liquid with $[\alpha]_D^{20}$ −10.9° (c 6.0). IR spectrum (thin layer): 820, 1670 $(>C{=}C<_H)$; 1360, 1380 $[C(CH_3)_2]$; 1745 cm^{-1} (OAc).

(1R,8aS)-2,3-α-Epoxy-1-(2-acetoxyethyl)-2,5,5,8a-tetramethyl-trans-decalin (VI). A 6-ml sample of a cooled (to 0°C) ether solution of monoperphthalic acid [12] containing 0.414 g (2.28 mmole) of the peracid was added to a cooled (to 0°C) solution of 245 mg (0.88 mmole) of acetate V in 1.5 ml of ether, and the solution was maintained at room temperature for 3.5 h until the reaction was complete. The reaction mixture was washed with 1% KOH and water, dried, and filtered, and the ether was removed by vacuum distillation. The residue (260 mg) was chromatographed with a column filled with 8.5 g of silica gel. Elution with benzene—petroleum ether (1:1) gave 190 mg (74%) of epoxy acetate VI. IR spectrum (thin layer): 1030, 1250  $(>C\underset{O}{\underbrace{-}}C<)$; 1368, 1380 $[C(CH_3)_2]$; 1745 cm^{-1} (OAc). Found: C 73.7; H 10.3%. $C_{18}H_{30}O_3$. Calculated: C 73.4; H 10.3%.

(1R,2R,7aS)-2,4,4,7a-Tetramethyl-1-(2-acetoxyethyl)-2-formyl-trans-hydrindan (VII). A 41-mg (0.29 mmole) sample of freshly distilled boron trifluoride etherate was added to a solution of 156 mg (0.53 mmole) of epoxy acetate VI in 5 ml of anhydrous benzene, and the solution was allowed to stand at room temperature for 2 h until the reaction was complete (according to TLC). Water and ether were added to the reaction mixture, the aqueous layer was separated, and the organic layer was washed successively with water, sodium bicarbonate solution, and water, dried, and filtered. The solvent was removed by vacuum distillation, and the residue (145 mg) was purified by chromatography with a column filled with 5 g of silica gel. Elution with benzene—petroleum ether (1:1) gave 71 mg (45%) of aldehyde VII with $[\alpha]_D^{20}$ +40.4° (c 4.7). IR spectrum (thin layer): 1368, 1380 $[C(CH_3)_2]$; 1724, 2720 (CHO); 1742 cm^{-1} (OAc). PMR spectrum (in CCl_4): 0.83 (6H, s), 1.1 (3H, s), 1.52 (3H, s) (2-, 4-, and 7a-CH_3); 1.92 (3H, s, OAc); 9.3 (1H, s, CHO); 3.86 ppm (2H, m, CH_2OAc). Found: C 73.8; H 10.6%. $C_{18}H_{30}O_3$. Calculated: C 73.4; H 10.3%.

(1R,2R,7aS)-2,4,4,7a-Tetramethyl-1-(2-hydroxyethyl)-2-carboxy-trans-hydrindan (XI). A solution of 55 mg (0.35 mmole) of potassium permanganate in 0.2 ml of water was added to a solution of 51 mg (0.17 mmole) of aldehyde VII in 0.3 ml of glacial acetic acid, and the mixture was allowed to stand at normal temperature for 25 min until the reaction was complete (according to TLC). A saturated solution of sodium sulfite and 5 ml of HCl solution (1:1) were added to the reaction mixture, and the precipitate dissolved. The mixture was extracted with ether, and the extract was washed with water, dried, and filtered. The ether was removed by vacuum distillation, and the residue [49 mg (94%)] was identified as acetoxy acid XI. IR spectrum: 1368, 1380 [$C(CH_3)_2$]; 1700 (COOH); 1743 cm^{-1} (OAc). PMR spectrum (in $CHCl_3$): 0.80 (3H, s), 0.85 (3H, s), 0.87 (3H, s), 1.26 (3H, s) (2-, 4-, and 7a-CH_3), 2.02 (3H, s, OAc), and 4.05 ppm (2H, t, J = 7 Hz, CH_2OAc).

(1R,2R,7aS)-2,4,4,7a-Tetramethyl-1-(2-hydroxyethyl)-2-hydroxymethyl-trans-hydrindan (VIII). A) A 40-mg (1.05 mmole) sample of lithium aluminum hydride was added to a solution of 35 mg (0.11 mmole) of acetoxy acid XI in 1 ml of absolute ether, and the mixture was allowed to stand at room temperature for 4 h until the reaction was complete. The excess lithium aluminum hydride was decomposed with ethyl acetate, and the reaction mixture was worked up in the usual manner to give 26 mg (91%) of crystalline diol VIII with mp 114-115.5°C (from petroleum ether) and $[\alpha]_D^{20}$ +8.4° (c 3.1). IR spectrum: 1368, 1380 [$C(CH_3)_2$]; 1050, 3300 (band); 3623 cm^{-1} (OH). PMR spectrum (d_6-acetone): 0.83 (3H, s), 0.86 (3H, s), 1.0 (3H, s), 1.18 (3H, s) (CH_3 attached to quaternary carbon atoms), 3.26 (2H, s, OH), and 3.58 ppm (4H, m, two CH_2OH groups).

B) A 10-mg (0.26 mmole) sample of lithium aluminum hydride was added to a solution of 12 mg (0.04 mole) of aldehyde VII in 1 ml of absolute ether, and the solution was allowed to stand at room temperature for 2 h until the reaction was complete. It was then worked up as in the preceding experiment to give 7.1 mg (75%) of diol VIII with mp 114-115°C, which was identical to the sample obtained in experiment A.

C) A 115-ml sample of a solution of monoperphthalic acid containing 7.94 (43.7 mmole) of the peracid was added to a solution of 14.56 g (52.4 mmole) of a mixture of acetates V, IX, and X in 50 ml of ether, and the mixture was maintained at room temperature for 1.5 h. It was then worked up to give 14.8 g of a mixture of oxidation products, which was dissolved in 100 ml of dry benzene. A 7.3-ml sample of freshly distilled boron trifluoride etherate was added to the solution, and the reaction mixture was allowed to stand at room temperature for 2.5 h. It was then worked up as indicated above to give 14.38 g of a mixture of substances, which was dissolved in 70 ml of glacial acetic acid. A solution of 9.1 g of potassium permanganate in 55 ml of water was added to the solution, and the mixture was stirred at room temperature for 50 min and worked up in the usual manner. The acidic part (2.87 g) was identified as acetoxy acid XI. It was dissolved in 100 ml of absolute ether, and the solution was treated with 1.47 g (38.68 mmole) of lithium aluminum hydride. The mixture was refluxed for 3 h, after which it was worked up in the usual manner to give 2.12 g (16% based on the starting mixture of acetates V, IX, and X) of diol VIII with mp 113.5-115°C (from petroleum ether).

Dehydration of Diol VIII. A solution of 400 mg (1.57 mmole) of diol VIII and 152 mg (0.97 mmole) of p-toluenesulfonic acid in 20 ml of dry benzene was refluxed in a Dean—Stark apparatus for 3 h, after which the reaction mixture was cooled, diluted with ether, washed successively with water, sodium bicarbonate solution, and water, dried, and filtered. The solvent was removed by vacuum distillation, and the residue (365 mg) was chromatographed with a column filled with 8 g of silica gel. Elution under slight pressure [13] with ethyl acetate—petroleum ether (7:93) gave the following three fractions (in the order of increasing polarity): 1) 214 mg; 2) 60 mg (according to GLC and IR spectroscopy, a mixture of unsaturated alcohols, which was not further investigated); 3) 90 mg (starting diol VIII). Fraction 1 was rechromatographed with a column filled with 12 g of silica gel; elution with ethyl acetate—petroleum ether (1:19) gave 131.6 mg (46% based on the unchanged starting diol) of a mixture of two substances (according to GLC, Tsvet-106 chromatograph, glass column l 1 m, d 3.5 mm, 5% SE-30 on Chromaton H-AW-DMCS, V_{He} 50 ml/min, t_{col} 150°C, t_{vap} 220°C, flame-ionization detector). IR spectrum: 1368, 1380 [$C(CH_3)_2$]; 1053, 1098 cm^{-1} (tetrahydrofuran ring). PMR spectrum (in $CDCl_3$): 0.81-0.89 ppm (four singlet signals, the intensity of which corresponds to four methyl groups) and 3.71 ppm (multiplet signal of 2-H protons). Mass spectrum*: 236 (M^+, 9), 223 (13), 222 (82), 221 (100), 208 (9), 207 (56), 204 (4), 203 (5),

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*The peaks of ions with intensities ⩾3% of the maximum peak are presented (the intensities are given in parentheses).

192 (4), 191 (12), 189 (4), 179 (6), 177 (16), 165 (5), 163 (11), 161 (3), 152 (4), 151 (8), 149 (4), 139 (5), 138 (10), 137 (46), 136 (11), 135 (6), 133 (5), 125 (7), 124 (16), 123 (58), 122 (6), 121 (12), 120 (3), 119 (7), 112 (3), 111 (17), 110 (28), 109 (34), 108 (6), 107 (17), 105 (9), 98 (10), 97 (51), 96 (12), 95 (50), 94 (8), 93 (20), 92 (3), 91 (13), 94 (38), 83 (12), 82 (18), 81 (47), 80 (6), 79 (21), 78 (3), 77 (11), 71 (7), 70 (7), 69 (39), 68 (10), 67 (42), 66 (3), 65 (6), 57 (6), 56 (6), 55 (44), 54 (5), 53 (16), 51 (3), 43 (14). Found: C 80.7; H 11.9%. $C_{16}H_{28}O$. Calculated: C 81.2; H 12.0%. Subsequent elution gave 81.3 mg (28% based on the unchanged starting diol) of (4aR,9aS,9bR)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyran (II) in the form of a viscous colorless liquid with $[\alpha]^{20}_{D}$ −24.5°(c 6.0). IR spectrum: 1372, 1389 [$C(CH_3)_2$]; 1052, 1078, 1098 cm^{-1} (tetrahydropyran ring). PMR spectrum (in $CDCl_3$): 0.83 (9H, s, 4a-, 9a-, and axial 6-CH_3), 0.88 (3H, s, equatorial 6-CH_3), 3.35 (2H, M, 2-H), 3.87 (A-H, d, J = 9 Hz), and 3.90 ppm (B-H, q, J_1 = 9 Hz, J_2 = 3 Hz) (R-H). Mass Spectrum: 236 (M^+, 30), 222 (21), 221 (100), 207 (3), 205 (3), 203 (10), 193 (10), 192 (4), 191 (7), 190 (5), 189 (10), 180 (7), 179 (7), 178 (13), 177 (69), 176 (4), 175 (7), 165 (7), 164 (3), 163 (18), 162 (3), 161 (11), 153 (3), 152 (8), 151 (16), 150 (4), 149 (9), 148 (3), 147 (11), 145 (3), 139 (8), 138 (13), 137 (44), 136 (21), 135 (17), 134 (4), 133 (15), 131 (3), 126 (4), 125 (13), 124 (23), 123 (34), 122 (12), 121 (31), 120 (5), 119 (17), 117 (4), 115 (3), 112 (4), 111 (12), 110 (16), 109 (57), 108 (11), 107 (31), 106 (5), 105 (21), 103 (3), 99 (16), 98 (72), 97 (63), 96 (13), 95 (25), 94 (11), 93 (27), 92 (4), 91 (26), 85 (14), 84 (11), 83 (22), 82 (24), 81 (25), 80 (7), 79 (28), 78 (5), 77 (21), 71 (7), 70 (5), 69 (41), 68 (17), 67 (41), 66 (4), 65 (8), 57 (11), 56 (7), 55 (44), 54 (4), 51 (5), 50 (3), 45 (4), 44 (3), 43 (23). Found: C 80.9; H 12.0%. $C_{16}H_{28}O$. Calculated: C 81.2; H 12.0%.

(4aR,9aS,9bS)-4a,6,6,9a-Tetramethyl-trans-perhydroindano[2,1-c]pyran (III). A 10-mg (0.06 mmole) sample of p-toluenesulfonic acid was added to a solution of 220 mg (0.87 mmole) of diol XIV [7] (mp 90-91°C) in 10 ml of dry toluene, and the solution was refluxed in a Dean—Stark apparatus for 4 h. It was then worked up as indicated in the preceding experiment, and the residue (200 mg) was chromatographed with a column filled with 8 g of silica gel. Elution with benzene—petroleum ether (1:9) gave 167 mg (82%) of (4aR,9aS,9bS)-4a,6,6,9a-tetramethyl-trans-perhydroindano[2,1-c]pyran with mp 50.5-52°C (from methanol) and $[\alpha]^{20}_{D}$ −23.5° (c 2.8). IR spectrum: 1098, 1114 (tetrahydropyran ring); 1375, 1390 cm^{-1} [$C(CH_3)_2$]. PMR spectrum (in CCl_4): 0.84 (6H, s, 6-CH_3); 1.03 (3H, s) and 1.19 (3H, s) (4a- and 9a-CH_3); 2.97 (A-H, d, J = 10 Hz) and 3.34 ppm (B-H, m, 2-H_2). Mass spectrum: 236 (M^+, 14), 221 (13), 203 (3), 193 (3), 192 (3), 191 (10), 189 (3), 180 (3), 178 (3), 177 (22), 163 (12), 161 (5), 151 (3), 149 (7), 147 (7), 139 (9), 138 (19), 137 (36), 136 (27), 135 (15), 134 (3), 133 (17), 126 (5), 125 (5), 124 (15), 123 (31), 122 (14), 121 (27), 120 (5), 119 (17), 112 (7), 111 (9), 110 (12), 109 (31), 108 (14), 107 (31), 106 (7), 105 (22), 99 (31), 98 (100), 97 (31), 96 (24), 95 (44), 94 (19), 93 (30), 92 (6), 91 (31), 85 (14), 84 (5), 83 (30), 82 (31), 81 (42), 80 (13), 79 (31), 78 (6), 77 (24), 71 (7), 70 (14), 69 (37), 66 (4), 65 (15), 57 (29), 56 (15), 55 (42), 54 (7), 52 (4), 51 (8), 50 (7), 49 (3), 48 (3), 45 (7), 44 (7), 43 (31). Found: C 81.5; H 12.1%. $C_{16}H_{28}O$. Calculated: C 81.2; H 12.0%.

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