by Corey et al.[7] for a typical Wittig reaction. The methyltriphenylphosphonium bromide was obtained from the Aldrich Chemical Co. and was dried at 120 °C under vacuum overnight prior to use. The solvent (dimethyl sulfoxide) was dried over CaH_2 and distilled prior to use. To sodium hydride (0.066 mol as a 50% dispersion in mineral oil), which had been washed several times with small portions of pentane, was added 33 mL of dimethyl sulfoxide under nitrogen, and the mixture was heated at 75–80 °C with stirring for 45 min. The resulting solution was cooled in an ice–water bath and stirred, and a solution of methyltriphenylphosphonium bromide (23.60 g, 0.066 mol) in dimethyl sulfoxide (66 mL) was added dropwise with stirring over a period of 15 min. After an additional 15 min at room temperature, 3,4,4-trimethylcyclohexanone (10.00 g, 0.071 mol) was added to the ylide solution, and stirring was continued for 40 min. Distillation of the reaction mixture at 105 mm yielded a distillate, which was collected between 50 and 90 °C. The distillate was dissolved in pentane (30 mL) and washed with water (2 × 15 mL). The pentane layer was dried over anhydrous $MgSO_4$ and concentrated at reduced pressure (100 mm) to leave a residue, which on passage through a preparative GLC column (12 ft × 0.375 in. 30% SE-52 on 80–100 Chromosorb A) at 100 °C yielded 1.00 g (10%) of 3,4,4-trimethyl-1-methylenecyclohexane: ^1H NMR ($CDCl_3$) δ 0.82 (d, J = 7.0 Hz, 3 H, CH_3 at C-3), 0.84 (s, 3 H, CH_3 at C-4), 0.91 (s, 3 H, CH_3 at C-4), 0.98–2.21 (complex multiplet, 7 H, ring protons), 4.56 (partially resolved inner portion of AB, 2 H, $=CH_2$).

***cis*- and *trans*-1,1,2,4-Tetramethylcyclohexane (1 and 2).** Hydrogenation of 3,4,4-trimethyl-1-methylenecyclohexane (0.800 g, 0.006 mol) in methanol (20 mL) with 374 mg of 5% Rh on alumina catalyst at atmospheric pressure in a Parr hydrogenator was completed in 8 h. The mixture was filtered through a Celite bed in a disposable pipet. The filtrate was dissolved in pentane (30 mL), extracted with water (2 × 20 mL), and dried over anhydrous $MgSO_4$. Evaporation of the pentane at atmospheric pressure left a residue containing a mixture of 1 and 2: yield 580 mg (69%). The mixture was separated by preparative GLC on a 12 ft × 0.375 in., 30% SE-52 on 80–100 Chromosorb A, column at 90 °C. The cis isomer (60%) emerged first, followed by the trans isomer (40%): ^1H NMR ($CDCl_3$) (cis isomer, 1) δ 0.73 (s, 3 H, equatorial CH_3 at C-1), 0.78 (d, J_{HCCH} = 7.0 Hz, 3 H, CH_3 at C-2 or C-4), 0.87 (d, J_{HCCH} = 7.0 Hz, 3 H, CH_3 at C-4 or C-2), 0.88 (s, 3 H, axial CH_3 at C-1), 0.93–1.52 (complex multiplet, 8 H, ring protons); ^1H NMR (CD_2Cl_2) (trans isomer, 2) δ 0.79 (s, 3 H, equatorial CH_3 at C-1), 0.86 (d, J_{HCCH} = 6.9 Hz, 3 H, CH_3 at C-2 or C-4), 0.89 (d, J_{HCCH} = 6.9 Hz, 3 H, CH_3 at C-4 or C-2), 0.93 (s, 3 H, axial CH_3 at C-1), 1.07–1.76 (complex multiplet, 8 H, ring protons); ^{13}C NMR, see Table I. Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.54; H, 14.40 (for cis–trans mixture).

Acknowledgment. This work was supported by NSF Grant CHE80-20388.

Registry No. 1, 83152-08-3; 2, 83152-09-4; 3,4,4-trimethylcyclohexanone, 40441-35-8; 4,4-dimethylcyclohex-2-en-1-one, 1073-13-8; 1,1,2-trimethyl-4-methylenecyclohexane, 83159-78-8; $Ph_3P{=}CH_2$, 3487-44-3.

Chemistry of Ambergris. 1. A Short Synthesis of (±)-δ-Ambrinol

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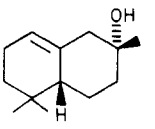
Introduction

Ambergris, a concretion formed in the intestinal tract of the blue sperm whale, has long been prized by perfumers for its unique fragrance properties. Faced with the possibility of the whales' extinction, many nations have prohibited their hunting and the importation of whale products. This has necessitated a search for synthetic ambergris compounds that may be used as substitutes in perfumery. Although α-ambrinol (1) is regarded as one



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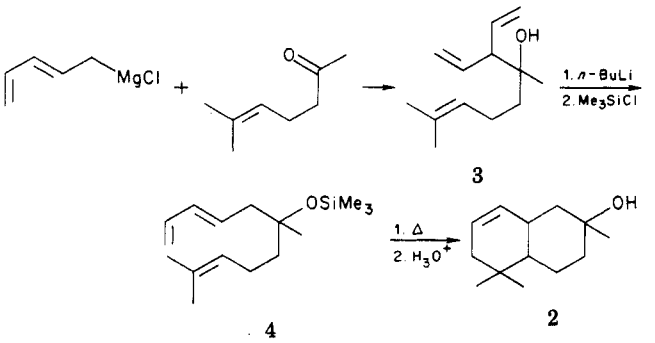
of the most important constituents of tincture of ambergris,[2] it has attracted very little synthetic attention.[3] The recent resurgence of interest in the intramolecular Diels–Alder reaction[4] prompts us to report a short synthesis of δ-ambrinol (2) from methylheptenone and pentadienylmagnesium chloride (Scheme I). Four stereoisomers of **2** were obtained, but only **2a** and **2b** have a strong ambergris odor. The assignment of stereochemistry to all four isomers necessitated an in-depth NMR study, which has demonstrated the advantages of combining ^{13}C NMR with high-field proton spectroscopy and lanthanide-induced shift techniques for stereochemical studies in hydroxydecalin systems.

Scheme I



Discussion

2,4-Pentadienylmagnesium chloride reacted smoothly with methylheptenone to give trienol **3** in 67% yield. The reaction of **3** with potassium hydride in tetrahydrofuran gave methylheptenone. However, rearrangement of the lithium alkoxide proceeded smoothly in refluxing tetrahydrofuran, providing, after quenching with chlorotrimethylsilane, the triene ether **4**.[5] The key intramolecular Diels–Alder cyclization was carried out at 220 °C in toluene to give, after hydrolysis and distillation, δ-ambrinol as a mixture of four stereoisomers, **2a–d** (ratio 5:30:10:2, re-

(1) (a) Fritzsche, Dodge and Olcott, Inc. (b) Bruker Instruments Inc.

(2) (a) Mookherjee, B. D.; Patel, R. R. 7th International Congress of Essential Oils, Kyoto, Japan, Oct 10, 1977, paper no. 136. (b) Jegou, E.; Polonsky, J.; Lederer, E.; Schulte-Elte, K. H.; Egger, B.; Ohloff, *G. Nouv. J. Chim.* **1977**, *1*, 529–531.

(3) (a) Armour, A. G.; Buchi, G.; Eschenmoser, A.; Storni, A. *Helv. Chim. Acta* **1959**, *42*, 2233–2244. (b) Strickler, H. U.S. Patent 4 163 866, 1979. Other methods of preparation involve cyclization of dihydro-γ-ionone. See: Takazawa, O.; Tamura, H.; Kogami, K.; Hayashi, K. *Chem. Lett.* **1980**, 1257–1258. Stoll, M.; Seidel, C. F.; Willhalm, B.; Hinder, M. *Helv. Chim. Acta* **1956**, *39*, 183–199.

(4) (a) White, J. D.; Sheldon, B. G. *J. Org. Chem.* **1981**, *46*, 2273–2280. (b) Brieger, G.; Bennet, J. N. *Chem. Rev.* **1980**, *80*, 63–97. (c) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10–23. (d) Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 6289–6291. (e) Wilson, S. R.; Huffman, J. C. *J. Org. Chem.* **1980**, *45*, 560–566.

(5) Wilson, S. R.; Mao, D. T.; Jernberg, K. M.; Ezmirly, S. T. *Tetrahedron Lett.* **1977**, 2559–2562. Also see ref 4d. The counterion and solvent can effect the amount of fragmentation; see Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242–2244. Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett. 1978*, 3315–3318. *Ibid.*, 3319–3322.

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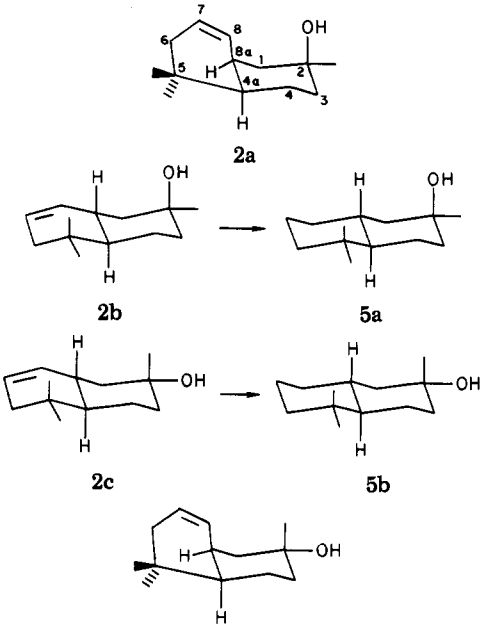
spectively) in 62% overall yield from **3**. The mixture had a strong ambergris odor. All four stereoisomers were separated by a combination of chromatographic and crystallization techniques. Interestingly, only stereoisomers **2a** and **2b** were found to have a strong ambergris odor.[6]



In both **2a** and **2b**, the axial hydroxy groups have a trans relationship to the hydrogen at C_{4a}, but **2a** is shown to have a cis-fused ring system, whereas in **2b** the rings are trans-fused. Compounds **2c** and **2d** have very weak woody odors. Hydrogenation of **2b** gave **5a**, which has a strong ambergris odor, whereas hydrogenation of **2c** gave diastereomer **5b**, which has a weak odor.[6b]

The strategy adopted for stereochemical assignment was to first establish the junction geometry and the configuration at C-2 in the two saturated systems **5a** and **5b** using ^{13}C NMR. ^{13}C shieldings in substituted decalins are known to be highly stereochemically specific, as manifested in the work of Dalling.[7] These authors showed that the chemical shift can be expressed as a sum of additive increments that take into account carbon substitution, the number of carbon substituents in the α and β positions, and various types of nonbonded interactions involving substituents in the γ and δ positions. In this manner, the ^{13}C shieldings for methyldecalins can be predicted with a high level of confidence. Although these empirical rules are strictly for methyl substituents, it is known that except for the substituted carbon, a hydroxy group produces nearly the same shielding effects as a methyl group.[8] If this approximation is used, then the chemical shifts for the two stereoisomers differing only in the configuration of C-2 may be predicted, with the exception of the C_2-methyl group, which is expected to be more highly shielded when the methyl group is axially disposed because of the 1,3-diaxial interaction with H_{8a} and $H_{4(ax)}$. The same behavior is exhibited by the cis isomers where the C-2 methyl carbon is also more shielded when the methyl group is axial.

The analysis further shows that skeletal carbons 1, 4, 4a, 6, and 8 are sensitive to the configuration at the ring junction and are more highly shielded (4–5 ppm) in the cis-fused systems.

A striking feature of the experimental data for compounds **5a** and **5b**, is the close resemblence of the shifts for corresponding carbons. The carbon shieldings, which were assigned on the basis of the residual splittings in the single-frequency off-resonance decoupled spectra and the previously discussed shielding arguments, differ by less than 2 ppm for **5a** and **5b**, with the exception of C-8a ($\Delta\delta$ = 2.4 ppm) and 2-Me ($\Delta\delta$ = 4.5 ppm). From this it can unequivocally be inferred that **5a** and **5b** possess the same junction geometry. A comparison of experimental and calculated shieldings further shows that both compounds must be trans, with the C_2-methyl group axial (**5b**) and equatorial (**5a**), respectively. The only significant discrepancies occur with C-4 and C_5-Me_{ax}, whose calculated shielding values are too large. The first deviation can be accounted for by the known γ-trans effect of −3 ppm for OH observed in substituted cyclohexanes.[9] The relative upfield shift of 4.5 ppm for C_2-Me is in excellent agreement with predictions.

Since **5a** and **5b** were obtained by hydrogenation of **2b** and **2c**, respectively, the stereochemistry of the latter two substances is therefore also established, and it follows indirectly that compounds **2a** and **2d** must correspond to the two remaining cis-linked diastereomers. In order for us to confirm their junction geometry and determine the configuration at C-2, it was necessary to resort to high-field (360 MHz) proton NMR in conjunction with lanthanide shift reagants.

Proton assignments are based upon (a) double resonance experiments, (b) chemical shifts and coupling constants, (c) lanthanide-induced shifts (LIS), and (d) spin simulation.

Although at 360 MHz the spectra of the four unsaturated compounds are largely first order, their analysis is impaired by some overlap of resonances. Paramagnetic shift reagent [$Eu(FOD)_3$] was therefore used throughout. The clue to the elucidation of the junction geometry was the identification of junction protons 4a and 8a, as well as the adjacent axial proton 1. These assignments were ascertained through extensive use of double resonance, the well-known fact that equatorial protons are less shielded than their axial counterparts, and, foremost, the angular dependence of vicinal coupling constants. The coupling of H_{4a} and H_{8a} in each compound (Table I) shows that **2b** and **2c** exhibit J values of 10.5 Hz, typical for a trans diaxial ring junction, whereas the J values of 4.5 Hz of compounds **2a** and **2b** are indicative for a cis ring junctions. These observations are consistent with the conclusions drawn from the ^{13}C NMR data for compounds **5a** and **5b**.

The configuration at C_2 was established with the aid of shift reagent experiments. In those systems in which the C_2-Me is axially disposed and the hydroxy group equatorially disposed (**2c** and **2d**), the two protons at C_1 and at C_3 experience the largest relative deshielding. If the configuration at C_2 is inverted, it is $H_{4(ax)}$, which is the most affected (**2a** and **2b**). In the case of **2a**, in addition, the ethylenic proton H_8 suffers a significant deshielding because of the close proximity of this proton to the OH resulting from the cis linkage of the junction.

Experimental Section

General. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Ether was dried over sodium ribbon. Toluene

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(7) Dalling, D. K.; Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1973**, *95*, 3718–3724.

(8) Wehrli, F. W.; Wirthlin, T. "Interpretation of ^{13}C NMR Spectra"; Heyden: Philadelphia, 1976; Chapter 2.

(9) Reference 8, Table 2.11.

was dried over 4Å molecular sieves. Chlorotrimethylsilane was distilled from calcium hydride immediately prior to use. Moisture- or oxygen-sensitive reactions were carried out in flame-dried glassware under a nitrogen atmosphere.

IR spectra were obtained with a Perkin-Elmer 710B spectrophotometer. ^{1}H NMR spectra were recorded with Bruker WM-360 (360 MHz) or WM-250 (250 MHz) instruments, using tetramethylsilane as internal reference. ^{13}C NMR spectra were recorded on a Bruker WM 250 (62.9 MHz) instrument. Laboratory experiments were monitored with a 60-MHz instrument. Mass spectra were obtained with a Hewlett-Packard 5985 mass spectrophotometer. Preparative high-performance LC was carried out on a Waters Associates LC system 500. GLC analyses were obtained with a Hewlett-Packard Model 5840 or a Perkin-Elmer Sigma 2 gas chromatograph, using either a 2 or 3 m, 2-mm i.d. glass column packed with 2% Carbowax 20M on Chromosorb G, 100–120 mesh. Where indicated, percentages refer to computer-calculated peak areas without correction for response. GLC and mass spectral data were provided courtesy of the Fritzsche, Dodge and Olcott, Inc., Instrumental Laboratory.

Elemental microanalyses were performed by Industrial Testing Laboratories, Inc., St. Louis, MO. Melting points were determined with a Thomas Model 40 micro hot-stage apparatus and are uncorrected.

4,8-Dimethyl-3-vinyl-1,7-nonadien-4-ol (3). To a suspension of magnesium (35.6 g, 1.483 mol) in ether (100 mL) at 0 °C was added 1-chloro-2,4-pentadiene[10] (45.67 g, 0.44 mol) in ether (225 mL) during 2 h. The mixture was stirred at 25 °C for 45 min. Methylheptenone (50.23 g 0.405 mol) in ether (75 mL) was added to the cooled (0 °C) mixture over a 1-h period. The mixture was stirred for 17 h at 25 °C and then cooled to 0 °C, and saturated ammonium chloride solution (200 mL) was added. The ether solution was decanted from the gummy residue, the residue was washed with ether (3 × 100 mL), and the combined ethereal solutions were washed with saturated sodium bicarbonate solution (2 × 50 mL) and brine (2 × 50 mL) and dried ($MgSO_4$). The solvent was evaporated, and the residue was distilled to give 52.93 g (67% yield) of alcohol **3**: bp 72–73 °C (0.4 mm); GLC analysis indicated a purity of 96%. An analytical sample (99%) was obtained by redistillation: NMR[11] (250 MHz, $CDCl_3$) δ 1.14 (3 H, s), 1.48 (2 H, t, J = 8.4 Hz), 1.61 and 1.68 (6 H, 2 s), 1.79 (1 H, s), 2.04–2.10 (2 H, m), 2.80 (1 H, dd, J = 8.4 and 8.4 Hz), 5.06–5.17 (5 H, m), 5.78–6.0 (2 H, m); IR (film) ν_{max} 3450, 3060, 2960, 2910, 1640 cm^{-1}; MS, m/e 179, 176, 109. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.29; H, 11.06.

6,10-Dimethyl-6-[(trimethylsilyl)oxy]-1,3,9-undecatriene (4). To a cold (0 °C) solution of alcohol **3** (9.70 g, 0.05 mol) and triphenylmethane (0.150 g) in THF (300 mL) was added dropwise over 15 min n-butyllithium until a faint pink color was observed (21 mL of 2.4 M n-butyllithium in hexane required). The mixture was heated at reflux for 2.5 h and then cooled to 0 °C, and a few drops of n-butyllithium were added to restore the faint pink color. Chlorotrimethylsilane (8.15 g, 0.075 mol) was added during a 5-min period. The mixture was heated at reflux for 2.5 h and then cooled, and toluene (100 mL) was added. The solvent was evaporated under reduced pressure until the volume of the residue was about 100 mL, and solids were then removed by filtration. Addition of toluene (150 mL) and concentration were effected twice to yield about 130 mL of a solution of **4** in toluene, which was used directly in the next step. NMR analysis of the toluene solution indicated that **4** was present at the level of about 4%.

Triene **4** was prepared as above on a 0.01-mol scale, except that after reaction with chlorotrimethylsilane, the solvent was evaporated, hexane was added, and the mixture was filtered. The solvent was evaporated, and the residue was Kugelrohred (bath temperature 130 °C, 0.3 mm) to give 2.366 g (98% yield) of triene **8**, 99% pure (E/Z ratio; 9:1) according to GLC analysis. Decoupling experiments reveal that J_{3-4} is 15.1 Hz, indicating trans geometry. Distillation of more than a few grams of triene **8** resulted in lower yields due to polymerization: NMR[11] (250 MHz, $CDCl_3$) δ 0.14 (9 H, s), 1.22 (3 H, s), 1.41–1.51 (2 H, m), 1.63 and 1.70 (6 H, 2 s), 2.06 (2 H, dt, J = 8.5 and 7.5 Hz), 2.27 (2 H, d, J = 7.5 Hz), 4.96–6.12 (2 H, m), 5.71 (1 H, dt, J = 15.1 and 7.5 Hz), 6.07 (1 H, dd, J = 15.2 and 10.3), 6.34 (1 H, dt, J = 16.7 and 10.3 Hz); IR (film) ν_{max} 2950, 1650, 1600, 1460, 1360 cm^{-1}; MS m/e 201, 200, 199, 131, 73, 69; UV λ_{max} (hexane) 229 nm (calcd. 222) (ε 14 100). Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 72.14; H, 11.28.

Thermal Reaction of 6,10-Dimethyl-6-[(trimethylsilyl)oxy]-1,3,9-undecatriene (4). A solution of triene **4** (prepared from 0.05 mol of alcohol **3** as described above) in toluene (1.1 L) and sodium carbonate (10 g) were charged into a stainless-steel Parr reactor. The reactor was evacuated and purged with nitrogen. The reactor was heated at 220 °C for 20 h. After the reactor was cooled, solids were removed by filtration, the solvent was evaporated, and the residue was stirred with 95% ethanol (350 mL), water (30 mL), and 2 N hydrochloric acid solution (20 mL) at 25 °C for 10 h. Solvent was evaporated under reduced pressure until the volume of the residue was about 100 mL, and water (300 mL) was added. The organic product was extracted with hexane, and the extracts were washed with saturated sodium bicarbonate solution and then with brine and dried (Na_2SO_4). The solvent was evaporated, and the residue was distilled to give 6.01 g (62% yield based on alcohol **3**) of δ-ambrinols (**2**), bp 86–97 °C (0.7 mm). GLC analysis showed 10% of isomer **2a**, 60% of **2b**, 20% of **2c**, and 4% of **2d**.

The mixture of δ-ambrinols was chromatographed on a Waters Prep Pak-500/silica column (eluant: hexane/ethyl acetate, 23:3). The best fractions were combined and rechromatographed. Analytical samples were obtained by crystallization from hexane (except for isomer **2b**). The purity of each stereoisomer was determined by GLC analysis.

1,2,3,4,4aβ,5,6,8aβ-Octahydro-2β,5,5-trimethyl-2α-naphthalenol (2a): mp 43–45 °C; 99% pure; IR (melt) ν_{max} 3585, 3475, 2965, 1645, 1445, 1385, 1365 cm^{-1}; MS, m/e 194, 176, 161. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.34; H, 11.04.

1,2,3,4,4aβ,5,6,8aα-Octahydro-2β,5,5-trimethyl-2α-naphthalenol (2b): bp 90–91 °C (0.9 mm); 100% pure; IR (film) ν_{max} 3340, 2960, 1650, 1460, 1380, 1360 cm^{-1}; MS, m/e 176, 161. Anal. ($C_{13}H_{22}O$). Found: C, 80.13; H, 11.27.

1,2,3,4,4aβ,5,6,8aα-Octahydro-2α,5,5-trimethyl-2β-naphthalenol (2c): mp 101–102 °C: >99% pure; IR (CCl_4) ν_{max} 3600, 3330, 2950, 1645, 1460, 1380, 1360 cm^{-1}; MS, m/e 194, 179, 176, 161. Anal. ($C_{13}H_{22}O$). Found: C, 80.16; H, 11.38.

1,2,3,4,4aβ,5,6,8aβ-Octahydro-2α,5,5-trimethyl-2β-naphthalenol (2d): mp 82–83 °C; 99% pure; IR (melt) ν_{max} 3300, 2960, 1645, 1440, 1375, 1360; MS, m/e 194, 179, 176, 161. Anal. ($C_{13}H_{22}O$). Found: C, 80.14; H, 11.33.

1,2,3,4,4aβ,5,6,7,8,8aα-Decahydro-2β,5,5-trimethyl-2α-naphthalenol (5a). A mixture of **2b** (0.582 g, 0.003 mol), ethanol (15 mL), and 5% platinum on carbon (0.05 g) was shaken under a hydrogen atmosphere (40 psi) at 25 °C until hydrogen uptake ceased. Filtration, evaporation of solvent, and Kugelrohr distillation (bath temperature 130 °C, 0.3 mm) gave 0.581 g (99%) of alcohol **5a**, which was 95% pure as indicated by GLC analysis. Chromatography on silica gel, followed by Kugelrohr distillation, gave material that was 97% pure: IR (film) ν_{max} 3355, 2940, 1460, 1380, 1365 cm^{-1}; MS, m/e 196, 181, 178, 163. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.36; H, 12.45.

1,2,3,4,4aβ,5,6,7,8,8aα-Decahydro-2α,5,5-trimethyl-2β-naphthalenol (5b). Alcohol **2c** (0.388 g, 0.002 mol) was hydrogenated as above. After evaporation of solvent 0.392 g (100%) of material was obtained, which according to GLC analysis contained one major component (95%). Crystallization from petroleum ether (35–60 °C) gave alcohol **5b**, mp 85–86 °C, which was 98% pure according to GLC analysis: IR (CCl_4) ν_{max} 3500, 3350, 2940, 1460, 1380, 1370 cm^{-1}; MS, m/e 196, 181, 178, 163. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.53; H, 12.41.

Registry No. (±)-**2a**, 83152-99-2; (±)-**2b**, 83153-00-8; (±)-**2c**, 83153-01-9; (±)-**2d**, 83153-02-0; **3**, 83153-03-1; (±)-(*E*)-**4**, 83153-04-2; (±)-(*Z*)-**4**, 83153-07-5; (±)-**5a**, 83153-05-3; (±)-**5b**, 83153-06-4; 1-chloro-2,4-pentadiene, 40596-30-3; 6-methyl-5-hepten-2-one, 110-93-0.

Supplementary Material Available: Experimental and calculated ^{13}C shieldings in the four stereoisomers of 2-

(10) Spangler, C. W. *Tetrahedron* **1976**, *32*, 2681–2684.

(11) We thank Dr. Michael Motto, Natural Products Laboratory, FD&O Inc., for recording this spectrum.

hydroxy-2,5,5-trimethyldecalin (Table I), ^{1}H NMR chemical shifts and coupling constants (Table II), a drawing illustrating the shielding of the axial methyl group in **5b** (Figure 1), and the 360-MHz ^{1}H NMR spectrum of **2c** with various amounts of shift reagent added (Figure 2) (4 pages). Ordering information is given on any current masthead page.

Poly(ethylene glycols) as Soluble, Recoverable, Phase-Transfer Catalysts

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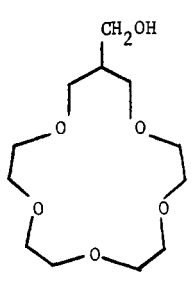
Poly(ethylene glycols) (PEG's) of molecular weights from 1500 to 6800 g/mol can be quantitatively precipitated from benzene, acetone, acetonitrile, methanol, or methylene chloride by addition of ethyl ether. This property offers the possibility of designing various soluble but recoverable materials such as catalysts and synthetic intermediates. Other work has shown that glymes and PEG's can act as phase-transfer catalysts (PTC's),[1-7] presumably operating by the same mechanism as crown ethers. However, the potential recoverability of these catalysts has not been described. A soluble, recoverable PTC provides an interesting alternative to the popular practice[8-12] of immobilizing PTC's on insoluble polymer backbones. In the present paper we describe the attachment of crown ethers to PEG's and examine the utility of PEG and PEG crown as soluble, recoverable PTC's.

The crown ethers (hydroxymethyl)-16-crown-5 (**1**), (hydroxymethyl)-19-crown-6 (**2**), and diaza-18-crown-6 (**3**)



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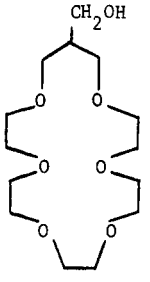
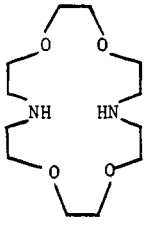


2



3

Table I. Partitioning of Polyethers between Equal Volumes of Water and Methylene Chloride and between Water and Benzene at 25 °C

ether	% in organic phase	
	CH_2Cl_2 [a]	C_6H_6 [b]
15-crown-5	68	
18-crown-6	75	
PEG-1000	80	
PEG-6800	75 (99) [b]	0.1

[a] Measured by HPLC beginning with a 5% (w/w) solution in water. Results are accurate within 3%. [b] Measured by using ^{14}C-labeled PEG and scintillation counting, starting with 0.25 mM PEG in water.

Table II. Phase Transfer of Metal Picrates from Water into Methylene Chloride[a]

PTA	[PTA] g/100 mL of soln	[PTA] M × 10^3	% in CH_2Cl_2 [b] Na picrate	% in CH_2Cl_2 [b] K picrate
none			0.7	0.7
15-crown-5	0.013	0.58	1.5	1.7
18-crown-6	0.015	0.56	2.4	17.3
PEG-1000	0.047	0.47	2.0	8.2
	0.181	1.81	3.9	14.5
PEG-6800	0.242	0.36	4.7	20.8
	0.181	0.27	3.6	19.2
5-3400	0.181	0.50		18.8
6-3400	0.181	0.49		18.1

[a] Aqueous potassium picrate and sodium picrate were 0.0954 and 0.085 mM, respectively. [b] Error limits ±0.1% for sodium picrate and ±0.5% for potassium picrate.

were attached to a PEG of molecular weight 3400 or 6800 g/mol as shown in eq 2 and 3. To indicate the molecular

$$\text{PEG–CH}_2\text{OH} + \text{TsCl} \xrightarrow[\text{NaH}]{\text{CH}_2\text{Cl}_2} \text{PEG–CH}_2\text{OTs} \quad (1)$$

$$\underset{\mathbf{1, 2}}{\text{ROH}} + \text{PEG–CH}_2\text{OTs} \xrightarrow[\text{C}_6\text{H}_6]{\text{NaH}} \text{PEG–CH}_2\text{OR} \quad \begin{matrix}\mathbf{5},\ \text{R} = 1\\ \mathbf{6},\ \text{R} = 2\end{matrix} \quad (2)$$

$$\underset{\mathbf{3}}{\text{R}_2\text{NH}} + \text{PEG–CHO} \xrightarrow[\text{CH}_3\text{OH}]{\text{NaCNBH}_3} \underset{\mathbf{7}}{\text{PEG–CH}_2\text{NR}_2} \quad (3)$$

weight of the polymer backbones, we will use notation of the type **5**-3400, where the number after the hyphen denotes the PEG molecular weight.

Preparation of the PEG tosylate has been reported by Mutter.[13] However, upon repeating this procedure, we found by HPLC analysis that extensive chain cleavage and molecular weight reduction had occurred. The NaH–TsCl method (eq 1) gave product with no chain cleavage. The crown alcohols **1** and **2** were prepared by the method of Tomoi et al.[14] We found it was critical in following this method that (a) the reaction of glycol and 3-chloro-2-(chloromethyl)-1-propene be conducted by very slow (24–48 h) addition of reagents, (b) potassium hydride rather than sodium hydride be used in the preparation of methyl-19-crown-6, and (c) the water solubility of the alcohols be considered in the hydroboration of the methylene crowns.

Compounds **5**–**7** are readily soluble in benzene, acetonitrile, methylene chloride, and acetone, so phase-transfer

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