1,4-Anhydro-D-arabinitol (19). Sequential silylation/reductive cleavage of 0.15 g of methyl β-D-arabinopyranoside (**18**) produced 0.11 g of a mixture of **19** and **20** (see Table III). Separation on a column (1.5 × 35 cm) of AG-1X8 (200–400 mesh, OH^- form, with H_2O as eluent) gave 5.5 mg of **20** (see below) and 83 mg of **19** as a clear, colorless oil: $[\alpha]_D$ +24.6 (lit.[34] $[\alpha]_D$ +25.3) (both in absolute MeOH); ^{13}C NMR (^2H_2O) δ 64.4, 75.5, 79.6, 80.6, 88.2 [lit.[29] (^2H_2O): δ 63.2, 74.8, 78.6, 79.7, 87.2].

[2,3,5-Tri-*O*-acetyl-1,4-anhydro-D-arabinitol. ^1H NMR (C^2HCl_3): δ 2.10 (s, 3 H, OAc), 2.11 (s, 6 H, OAc), 4.01 (complex, 2 H, H-1, H-4), 4.07 (dd, *J* = 4.1, 10.9 Hz, 1 H, H-1′), 4.21 (dd, *J* = 6.8, 11.6 Hz, 1 H, H-5), 4.36 (dd, *J* = 4.5, 11.6 Hz, 1 H, H-5′), 5.04 (br d, *J* = 3.4 Hz, 1 H, H-3), 5.18 (complex, 1 H, H-2).]

1,5-Anhydro-D-arabinitol (20). Separation of the mixture of 1,4- and 1,5-anhydro-D-arabinitol (**19** and **20**, see **19** above) gave 5.5 mg of **20** as a syrup. ^{13}C NMR (^2H_2O): δ 69.8, 70.9, 71.8, 72.5, 75.5.

[2,3,4-Tri-*O*-acetyl-1,5-anhydro-D-arabinitol. ^1H NMR (C^2HCl_3): δ 2.06, 2.08, 2.12 (3 s, 9 H, OAc), 3.39 (dd, *J* = 7.6, 11.6 Hz, 1 H, H-1), 3.64 (dd, *J* = 2.3, 12.5 Hz, 1 H, H-5), 3.87 (dd, *J* = 4.5, 12.5 Hz, 1 H, H-5′), 4.03 (dd, *J* = 3.8, 11.6 Hz, 1 H, H-1′), 5.14 (complex, 2 H, H-2,4), 5.30 (complex, 1 H, H-3), ($J_{H\text{-}1,1'}$ = 11.6, $J_{H\text{-}1,2}$ = 7.6 $J_{H\text{-}1',2}$ = 3.8, $J_{H\text{-}4,5}$ = 2.3, $J_{H\text{-}4,5'}$ = 4.5, $J_{H\text{-}5,5'}$ = 12.5 Hz) (lit.[37] ($C_6{}^2H_6$): $J_{H\text{-}1,1'}$ = 11.6, $J_{H\text{-}1,2}$ = 8.2, $J_{H\text{-}1',2}$ = 4.6, $J_{H\text{-}4,5}$ = 2.2, $J_{H\text{-}4,5'}$ = 4.3, $J_{H\text{-}5,5'}$ = 12.2 Hz).]

1,5-Anhydro-2,3,4-tri-*O*-methyl-D-arabinitol (25). Compound **24** (16 mg) was treated overnight with 5 equiv of Et_3SiH and 5 equiv of TMSOTf in 0.25 mL of CH_2Cl_2 and then quenched by the addition of aqueous sodium hydrogen carbonate. Analysis of the organic layer by capillary GLC (method c) revealed a single product: GLC-CIMS (NH_3), *m/e* 177 (M + 1), 194 (M + 18); GLC-EIMS, *m/e* 176 (9.9), 117 (7.5), 114 (6.2), 101 (9.2), 88 (30.4), 85 (15.3), 75 (50.6), 58 (100), 45 (38.2), 29 (17.7).

1-(α-D-Glucopyranosyl)-2-propene (27). Sequential silylation/allyl addition [see Sequential Silylation/Reductive Cleavage (above)] of 200 mg of methyl α-D-glucopyranoside (**3**) gave 184 mg (87% yield) of white, crystalline **27**. Recrystallization from EtOH gave white crystals: mp 153–156 °C; ^{13}C NMR (^2H_2O) δ 31.4, 63.4, 72.7, 73.6, 74.9, 75.7, 77.8, 120.0, 137.1. Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 52.96; H, 7.95.

[1-(2′,3′,4′,6′-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.03, 2.04, 2.05, 2.08 (four s, 12 H, OAc), 2.29–2.62 (complex, 2 H, H-1), 3.86 (ddd, *J* = 2.7, 5.4, 9.4 Hz, 1 H, H-5′), 4.08 (dd, *J* = 2.7, 12.1 Hz, 1 H, H-6′), 4.11 (dd, *J* = 5.4, 12.1 Hz, 1 H, H-6′), 4.28 (ddd, *J* = 4.6, 5.7, 10.8 Hz, 1 H, H-1′), 4.98 (dd, *J* = 8.8, 9.4 Hz, 1 H, H-4′), 5.09 (dd, *J* = 5.7, 9.5 Hz, 1 H, H-2′), 5.12 (ddd, *J* = 1.3, 2.7, 10.2 Hz, 1 H, H-3), 5.15 (ddd, *J* = 1.5, 2.7, 17.1 Hz, 1 H, H-3), 5.34 (t, *J* = 9.1 Hz, 1 H, H-3′), 5.75 (dddd, *J* = 6.2, 7.3, 10.2, 17.1 Hz, 1 H, H-2).]

1-(α-D-Ribofuranosyl)-2-propene (28). Sequential silylation/allyl addition of 65.3 mg of methyl α,β-ribofuranoside (**11a,b**) gave 55.0 mg (84.2% yield) of a clear, colorless oil (**28**): ^{13}C NMR (^2H_2O) δ 35.8, 64.0, 74.6, 74.7, 82.8, 83.3, 119.9, 136.8.

[1-(2′,3′,5′-Tri-*O*-acetyl-α-D-ribofuranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.04, 2.09, 2.13 (3 s, 9 H, OAc), 2.31–2.50 (complex, 2 H, H-1), 4.10 (dd, *J* = 4.7, 11.7 Hz, 1 H, H-5′), 4.22 (dt, *J* = 3.3, 7.0 Hz, 1 H, H-1′), 4.22 (ddd, *J* = 2.9, 4.8, 7.7 Hz, 1 H, H4′), 4.30 (dd, *J* = 3.0, 11.7 Hz, 1 H, H-5′), 5.07 (ddd, *J* = 1.1, 1.9, 10.2 Hz, 1 H, H-3), 5.10 (ddd, *J* = 1.8, 3.3, 17.1 Hz, 1 H, H-3), 5.27 (dd, *J* = 4.6, 7.8 Hz, 1 H, H-3′), 5.44 (dd, *J* = 3.4, 4.6 Hz, 1 H, H-2′), 5.72 (dddd, *J* = 6.9, 7.0, 10.2, 17.1 Hz, 1 H, H-2). Anal. Calcd for $C_{14}H_{20}O_7$: C, 55.99; H, 6.71. Found: C, 55.76; H, 6.55.]

1-(α-D-Fructofuranosyl)-2-propene (29). Sequential silylation/allyl addition of 206 mg of methyl β-D-fructofuranoside (**15b**) gave 151 mg (70% yield) of a mixture of **29** and **30** as a clear syrup. Complete separation of these two compounds was obtained by using a column (1.5 × 35 cm) of AG-1X8 (200–400 mesh, OH^- form) with H_2O as the eluent. Evaporation of H_2O left 75 mg of **29** and 53 mg of **30** (below) as clear syrups. For compound **29**: ^{13}C NMR (^2H_2O) δ 41.5, 63.5, 66.5, 77.6, 82.2, 82.2, 86.1, 122.1, 134.8.

[1-(1′,3′,4′,6′-Tetra-*O*-acetyl-α-D-fructofuranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.06, 2.08, 2.10, 2.11 (4 s, 12 H, OAc), 2.30 (ddt, *J* = 1.1, 7.3, 14.1 Hz, 1 H, H-1), 2.48 (ddt, *J* = 1.1, 7.3, 14.1 Hz, 1 H, H-1), 3.98 (d, *J* = 11.7 Hz, 1 H, H-1′), 4.09–4.16 (complex, 2 H, H-6′), 4.19 (d, *J* = 11.7 Hz, 1 H, H-1′), 4.36 (dt, *J* = 5.9, 9.8 Hz, 1 H, H-5′), 5.17–5.25 (complex, 2 H, H-3), 5.27 (dd, *J* = 5.3, 5.9 Hz, 1 H, H-4′), 5.40 (d, *J* = 5.3 Hz, 1 H, H-3′), 5.81 (dddd, *J* = 7.3, 7.4, 11.6, 16.6 Hz, 1 H, H-2). Anal. Calcd for $C_{17}H_{24}O_9$: C, 54.83; H, 6.49. Found: C, 54.93; H, 6.13.]

1-(β-D-Fructofuranosyl)-2-propene (30). **30** was prepared as above (see compound **29**). ^{13}C NMR (^2H_2O): δ 39.5, 64.4, 66.6, 78.3, 80.5, 83.0, 86.7, 121.4, 136.0.

[1-(1′,3′,4′,6′-Tetra-*O*-acetyl-β-D-fructofuranosyl)-2-propene. ^1H NMR (C^2HCl_3): δ 2.10, 2.11 (two s, 6 H, OAc), 2.12 (s, 6 H, OAc), 2.32 (ddt, *J* = 1.0, 7.9, 14.4 Hz, 1 H, H-1), 2.43 (ddt, *J* = 1.3, 6.4, 14.4 Hz, 1 H, H-1), 4.14 (complex, 4 H, H-1′,6′), 4.33 (complex, 1 H, H-5′), 5.07–5.17 (complex, 2 H, H-3), 5.21 (dd, *J* = 4.2, 5.9 Hz, 1 H, H-4′), 5.38 (d, *J* = 4.3 Hz, 1 H, H-3′), 5.79 (dddd, *J* = 6.4, 7.9, 10.5, 16.8 Hz, 1 H, H-2). ^1H NMR ($C_6{}^2H_6$): δ 1.58, 1.59, 1.65, 1.66 (four s, 12 H, OAc), 2.30–2.53 (complex, 2 H, H-1), 4.13–4.20 (complex, 2 H, H-6′), 4.24 (d, *J* = 11.4 Hz, 1 H, H-1′), 4.29 (d, *J* = 11.4 Hz, 1 H, H-1′), 4.38 (complex, 1 H, H-5′), 5.1–5.5 (complex, 2 H, H-3), 5.38 (dd, *J* = 4.1, 5.1 Hz, 1 H, H-4′), 5.62 (d, *J* = 4.1 Hz, 1 H, H-3′), 5.90 (complex, 1 H, H-2).]

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Preparation and Assignment of Configuration of *cis*- and *trans*-2,3,4,4a,5,6-Hexahydro-2-naphthalenol

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The two diastereomers of 2,3,4,4a,5,6-hexahydro-2-naphthalenol (*cis*-1-OH and *trans*-1-OH) have been prepared and configurations have been established by correlation with the diastereomeric 9-methyldecalins (**8**). The correlations also establish configurations of the diastereomeric 3,4,4a,5,6,8a-hexahydro-8a-methylnaphthalenes (**2**). Configurations have also been established for the isomeric 2,3,4,4a,5,6-hexahydro-2-methylnaphthalenes (**3**) by correlation with the corresponding 2-methyldecalins.

In other projects we have investigated solvolytic and cross-coupling reactions in the 2,3,4,4a,5,6-hexahydro-2-naphthalenyl system (**1**). This paper reports the preparations and assignment of configurations of the two diastereomeric alcohols *cis*-1-OH and *trans*-1-OH.[1] The correlations involved in the structural assignments also establish configurations for the diastereomeric

(1) The cis–trans designation refers to the substituents (or hydrogens) at C-2 and C-4a.

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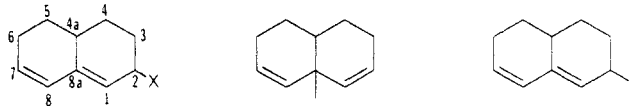
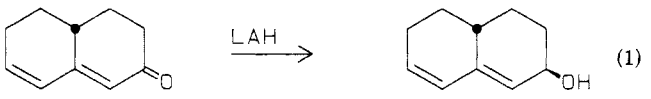
3,4,4a,5,6,8a-hexahydro-8a-methylnaphthalenes (2). In this work we have also established configurations for the isomeric 2,3,4,4a,5,6-hexahydro-2-methylnaphthalenes (3).



1 2 3

Reduction of 2,3,4,4a,5,6-hexahydro-2-ketonaphthalene (4)[2] with lithium aluminum hydride is diastereoselective and gives *trans*-1-OH with a diastereomeric purity (DP) of >95% (eq 1). The diastereomeric composition was



(1)

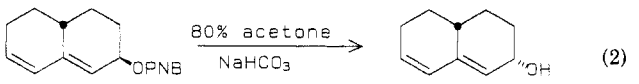
4 trans-1-OH

determined by NMR spectroscopy. Similar stereoselectivity was observed for reduction of **4** with DIBAL or sodium borohydride. The pure trans isomer was obtained from the hydride reduction product by recrystallization of the *p*-nitrobenzoate derivative (*trans*-1-OPNB) or the phenylcarbamate derivative (*trans*-1-OCONHPh).

The stereochemistry of the hydride reduction of **4** is similar to that reported for reduction of 9-methyl-$\Delta^{1(10)}$-2-octalone (**5**)[3] and $\Delta^{1(10)}$-2-octalone (**6**)[4] However, the diastereoselectivity is much higher for reduction of **4** (>20:1) than for reduction of **5** or **6** (~10:1).

5 6

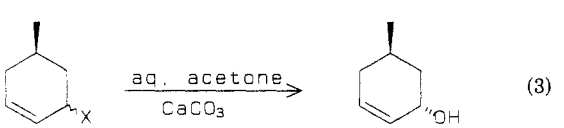
The other diastereomer, *cis*-1-OH, was obtained by solvolysis of *trans*-1-OPNB in 80% acetone containing 2 equiv of $NaHCO_3$ (eq 2). Solvent capture of the intermediate pentadienyl cation is highly diastereoselective and the initially formed product (kinetic control) is *cis*-1-OH with a DP of >96%. The *p*-nitrobenzoate derivative used for the solvolytic preparation of *cis*-1-OH was derived from the hydride reduction product of **4** and thus was mainly *trans*-1-OPNB as indicated in eq 2. We presume that the configuration of the *p*-nitrobenzoate is of no consequence in this preparation.



(2)

trans-1-OPNB cis-1-OH

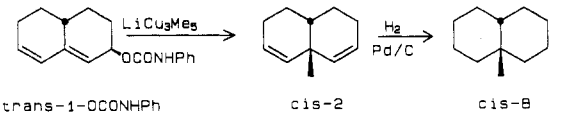
The observed stereoselectivity for capture of the pentadienyl cation generated from 1-OPNB is similar to that for capture of the 5-methyl-2-cyclohexenyl cation which gives *trans*-5-methyl-2-cyclohexenol (**7**) with a DP of -95% (eq 3).[5]



(3)

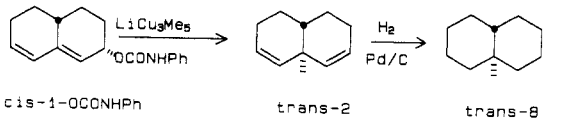
7

Configurations of *cis*-1-OH and *trans*-1-OH were established by correlation with the known[6,7] diastereomeric 9-methyldecalins (**8**) as outlined by eq 4 and 5. The first



(4)

trans-1-OCONHPh cis-2 cis-8

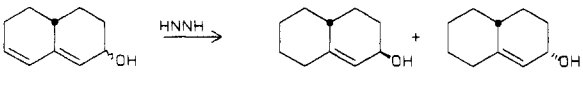


(5)

cis-1-OCONHPh trans-2 trans-8

step involves alkylation of the phenylcarbamate derivative of the alcohols by a method that results in exclusive syn-γ-alkylation.[8,9] This leads to homogeneous samples of *cis*-**2** and *trans*-**2** which in turn were reduced to the corresponding 9-methyldecalins (**8**). The latter were identified by ^{13}C NMR and IR spectral properties.[6,7]

The isomeric alcohols (1-OH) were also related to the corresponding $\Delta^{1(9)}$-octalin-2-ols (**9**). The configurations of *cis*-**9** and *trans*-**9** have been deduced from spectral properties.[4] As shown in eq 6, the disubstituted double bond in 1-OH is selectively reduced with diimide. In this experiment a mixture of 95% *trans*-1-OH and 5% *cis*-1-OH (hydride reduction product) was converted to the corresponding mixture of *cis*-**9** and *trans*-**9**. This mixture was not separated, but the chemical shift of each alkene proton of the major isomer was the same as that reported for *trans*-**9** and the alkene proton shifts for the minor component were the same as those reported for *cis*-**9**.[4] This correlation provides unequivocal confirmation of the earlier structural assignments[4] for *cis*-**9** and *trans*-**9** that were based on spectral interpretations.



(6)

1-OH trans-9 cis-9

95% trans 95% 5%

The distinguishing feature of the NMR spectra for *cis*-1-OH and *trans*-1-OH is the peak width of the α(C-2) proton. The base peak width is 24 Hz for *trans*-1-OH and 14 Hz for *cis*-1-OH. We presume that in this bicyclic system the favored conformation is the one with the proton at the ring juncture (**4a**) in a pseudoaxial position. Thus, in *trans*-1-OH the α proton is pseudoaxial and in *cis*-1-OH this proton is pseudoequatorial. Evidently the pseudoaxial–axial coupling constant in *trans*-1-OH is larger than the pseudoequatorial–axial or pseudoequatorial–equatorial coupling constant in *cis*-1-OH which results in a wider peak for *trans*-1-OH.[10]

The alcohols were converted to the diastereomeric 2,3,4,4a,5,6-hexahydro-2-methylnaphthalenes (**3**) by alkylation of the pivalate derivatives, *cis*-1-OPiv and *trans*-1-OPiv, with lithium dimethylcuprate. This alkylation is stereospecific and gives primarily the anti alkylation product. As shown in Scheme I, alkylation of

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(4) D'inean, E.; Loupy, A.; Maia, A.; Seyden-Penne, J.; Viout, P. *Tetrahedron* **1982**, *38*, 2923.
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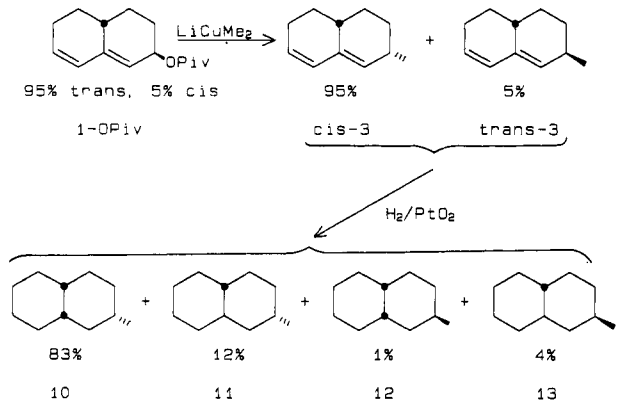
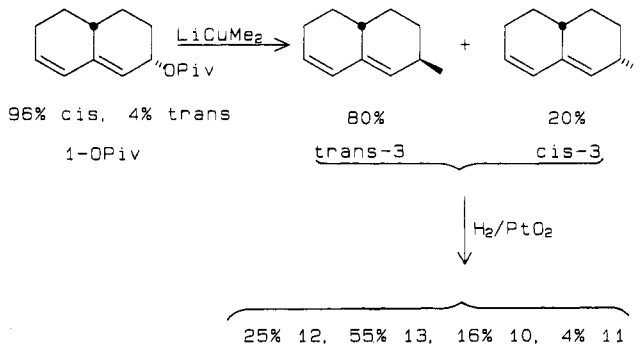
(10) Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195.

Scheme I. Correlation of *cis*-2,3,4,4a,5,6-Hexahydro-2-methylnaphthalene (*cis*-3) with *cis*-*syn*- (10) and *trans*-*anti*-2-Methyldecalin (11)



Scheme II. Correlation of *trans*-2,3,4,4a,5,6-Hexahydro-2-methylnaphthalene (*trans*-3) with *cis*-*anti*- (12) and *trans*-*syn*-2-Methyldecalin (13)



trans-1-OPiv containing 5% *cis*-1-OPiv (derived from the hydride reduction product) gives a binary mixture of 95% *cis*-3 and 5% *trans*-3. Thus in this case the reaction proceeds with complete reversal of diastereomeric configuration. None of the unconjugated alkylation product (2) was present. The configurational composition of 3 was determined by capillary GC which resolves completely a four-component mixture of the diastereomers of 2 and 3.

As shown in Scheme II, alkylation of *cis*-1-OPiv containing 4% of the trans isomer (derived from the product resulting from solvolysis of 1-OPNB) is also stereospecific (anti alkylation). However, in this case the stereospecificity is not as high as for alkylation of *trans*-1-OPiv (Scheme I). The stereochemistry for alkylation in this system (excess anti alkylation) is similar to that observed earlier for 2-cyclohexenyl[5] and acyclic systems.[11]

Configurations of *cis*-3 and *trans*-3 were established by conversion to the known 2-methyldecalins (10–13).[6,13,14] Hydrogenation over platinum oxide does not alter the configuration at C-2. Thus a mixture of 95% *cis*-3 and 5% *trans*-3 gave a mixture of 95% 10 + 11 and 5% 12 + 13 as shown in Scheme I. Similarly, as shown in Scheme II, a 80:20 mixture of *trans*-3 and *cis*-3 gave a mixture of 80% 12 + 13 and 20% 10 + 11. The four diastereomeric 2-methyldecalins (10–13) were completely resolved by capillary GC. Homogenous samples of 11 and 13 were obtained by preparative GC. However, 10 and 12 could not be separated by this method. An essentially pure sample of 10 (<2% 12) was isolated from the hydrogenation product shown in Scheme I by preparative GC. Similarly a binary mixture of 38% 12 and 62% 10 was obtained from the hydrogenation product shown in Scheme II. The diastereomeric 2-methyldecalins (10–13) were identified by their ^{1}H NMR[13] and ^{13}C NMR[6,14] spectra.

The distinguishing feature of NMR spectra for *cis*-3 and *trans*-3 is that the C-1 vinyl proton signal for *cis*-3 (δ 5.4) has a base peak width of 17 Hz as compared to a base width of 11 Hz for *trans*-3 (δ 5.3). This shows that the coupling constant is larger with a C-2 pseudoequatorial proton (*cis*-3) than with a C-2 pseudoaxial proton (*trans*-3).

Experimental Section

General Methods. Proton NMR spectra were obtained with a Brucker WP200 instrument; ^{13}C NMR spectra were obtained with a JEOLCO FX-200 spectrometer operating at 50.1 MHz. Chemical shifts for ^{13}C are referenced to the center peak of $CDCl_3$ (77.0 ppm). Mass spectra were obtained with an AE1-MS-902 high resolution instrument.

***trans*-2,3,4,4a,5,6-Hexahydro-2-naphthalenol (*trans*-1-OH).** A solution of 3.50 g (23.6 mmol) of 2,3,4,5a,5,6-hexahydro-2-oxonaphthalene (4)[2] in 10 mL of dry ether was added dropwise to a cold (0 °C) stirred suspension of 350 mg (9.2 mmol) of $LiAlH_4$ in 35 mL of dry ether. The resulting mixture was stirred for 1.25 h at room temperature. Standard workup and distillation gave 3.49 g (98%) of *trans*-1-OH, bp 63–65 °C (0.02 mm), as a colorless oil which solidified on chilling to −20 °C: IR (neat) 3340 (s), 3020 (m), 2925 (s), 2860 (s), 2840 (m), 1460 (m), 1135 (m), 1040 (s), 1000 (m); NMR (δ, $CDCl_3$) 6.05 (d, 1 H, J = 9.4 Hz), 5.8 (dt, 1 H, J = 9.4, 4.2 Hz), 5.42 (s, 1 H), 4.4 (br s, 1 H), 2.0–2.3 (m, 3 H), 1.2–2.0 (m, 7 H); ^{13}C NMR (δ, $CDCl_3$) 138.7, 129.4, 128.6, 126.4, 67.8, 35.4, 32.6, 30.1, 29.1, 25.9; high resolution mass spectrum, calcd for $C_{10}H_{14}O$ m/e 150.1045, found m/e 150.1044. Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.98; H, 9.44.

The diastereomeric purity of >95% *trans*-1-OH was determined from relative peak areas of NMR signals at δ 5.57 (*cis*-1-OH) and 5.42 (*trans*-1-OH).

The above *trans*-1-OH was converted to ***trans*-2,3,4,4a,5,6-hexahydro-2-naphthalenyl *p*-nitrobenzoate (*trans*-1-OPNB)** in the usual manner.[5] After recrystallization from heptane, *trans*-1-OPNB had the following: mp 107–109 °C dec; NMR (δ, $CDCl_3$) 7.2–7.4 (m, 4 H), 6.06 (d, 1 H, J = 9.4 Hz), 5.9 (br dt, 1 H, J = 9.4, 4.2 Hz), 5.7 (br s, 1 H), 5.48 (s, 1 H), 2.1–2.5 (m, 3 H), 1.2–2.0 (m, 6 H).

***trans*-2,3,4,4a,5,6-Hexahydro-2-naphthalenyl phenylcarbamate (*trans*-1-OCONHPh)** prepared[6] from the above *trans*-1-OH and pure *trans*-1-OCONHPh was obtained in 91% yield after recrystallization from hexane: mp 105–107 °C; NMR (δ, $CDCl_3$) 7.2–7.4 (m, 4 H), 6.9–7.2 (m, 1 H), 6.59 (br s, 1 H), 6.03 (d, 1 H, J = 10.1 Hz), 5.82 (dt, 1 H, J = 10.1, 4.0 Hz), 5.4 (br s, 2 H), 2.0–2.4 (m, 3 H), 1.2–2.0 (m, 6 H); high resolution mass spectrum, calcd for $C_{17}H_{19}NO_2$ m/e 269.1411, found m/e 269.1415. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.61; H, 7.13; N, 5.13.

***cis*-2,3,4,4a,5,6-Hexahydro-2-naphthalenol (*cis*-1-OH).** A solution of 25 g (83.5 mmol) of *trans*-1-OPNB and 14 g (167 mmol) of $NaHCO_3$ in 700 mL of 80% aqueous acetone was kept at 37 °C for 28 h (>10 solvolytic half-lives). The mixture was concentrated under reduced pressure with a rotary evaporator and the residue was extracted with ether. The ether extracts were combined, shaken with brine, and dried over $MgSO_4$. Removal of the ether with a rotary evaporator and distillation of the solid residue gave 11.27 g (90% yield) of *cis*-1-OH, bp 92–94 °C (0.5 mm): IR (neat) 3350 (s), 3020 (m), 2920 (s), 2860 (m), 1440 (m), 1110 (m), 1100 (m), 1000 (s), 930 (m), 890 (m), 880 (m); proton NMR (δ, $CDCl_3$) 6.02 (d, 1 H, J = 9.8 Hz), 5.87 (dt, 1 H), J = 9.8, 4.0 Hz), 5.57 (br s, 1 H), 4.2 (br s, 1 H), 1.2–2.2 (m, 10H); ^{13}C NMR (δ, $CDCl_3$) 140.8, 130.7, 128.7, 123.3, 64.2, 36.0, 31.4, 29.9, 26.0, 25.0; high resolution mass spectrum, calcd for $C_{10}H_{14}O$ m/e 150.1045, found m/e 150.1044. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.24; H, 9.50.

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The diastereomeric purity of >96% *cis*-1-OH was determined by peak areas of NMR signals at δ 5.57 (cis isomer) and 5.42 (trans isomer).

The above *cis*-1-OH was converted to ***cis*-2,3,4,4a,5,6-hexahydro-2-naphthalenyl phenylcarbamate (*cis*-1-OCONHPh)** which was purified by recrystallization from hexane. Pure *cis*-1-OCONHPh, obtained in 98% yield, has the following: mp 102–105 °C; NMR (δ, $CDCl_3$) 7.2–7.5 (m, 4 H), 7.0–7.1 (m, 1 H), 6.61 (br s, 1 H), 6.06 (d, 1 H, J = 9.7 Hz), 5.90 (br s, 1 H), 5.60 (br s, 1 H), 5.33 (br s, 1 H), 2.0–2.4 (m, 3 H), 1.2–2.0 (m, 6 H); high resolution mass spectrum, calcd for $C_{17}H_{19}NO_2$ m/e 269.1411, found m/e 269.1416. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.93; H, 7.15; N, 5.14.

Correlation of the Diastereomeric 2,3,4,4a,5,6-Hexahydro-2-naphthalenyl Phenylcarbamates (1-OCONHPh) with the Diastereomeric 9-Methyldecalins (8). This correlation involves two transformations, regio- and stereospecific syn-γ-methylation of 1-OCONHPh with $Li_2Cu_3(CH_3)_5$[9] followed by hydrogenation of the intermediate 3,4,4a,5,6,6a-hexahydro-8a-methylnaphthalenes (**2**) to **8**. Product compositions were determined by capillary GC (61 ft, UCON LB-550-X).

A. Conversion of *cis*-1-OCONHPh to *cis*-2. A solution of "$Li_2Cu_3Me_5$" in ether was prepared by addition of 8.2 mL of 1.70 M ethereal MeLi to a cold (−30 °C) suspension of 1.60 g (8.40 mmol) of CuI in 10 mL of dry ether. The solution was stirred at −30 °C for 5 min and warmed to 0 °C after which this homogeneous solution was added to a solution of 750 mg (2.78 mmol) of *cis*-1-OCONHPh in 10 mL of dry ether. The reaction mixture was stirred at 0 °C for 2 h and then at room temperature overnight. The reaction was quenched with 4 mL of saturated aqueous NH_4Cl. The resulting mixture was filtered and the aqueous layer was extracted with ether. The combined extracts were washed with 5% HCl, saturated $NaHCO_3$, and saturated brine and dried over $MgSO_4$. The solvent was removed by fractionation and the alkylation product separated from polar impurities by rotary TLC (pentane/2 mm silica gel plate). Removal of the solvent gave 320 mg (78%) of ***cis*-3,4,4a,5,6,8a-hexahydro-8a-methylnaphthalene (*cis*-2)** shown to be diastereomerically pure by capillary GC: IR (neat) 3020 (m), 2960 (s), 2930 (s), 2870 (s), 2840 (m), 1465 (m), 1460 (m), 1440 (m), 1370 (m); NMR (δ, $CDCl_3$) 5.56 (dt, 2 H, J = 9.9, 3.5 Hz), 5.39 (dt, 2 H, J = 9.9, 1.9 Hz), 1.9–2.2 (m, 4 H), 1.4–1.8 (m, 5 H), 1.07 (s, 3 H); high resolution mass spectrum, calcd for $C_{11}H_{16}$ m/e 148.1252, found m/e 148.1253.

In the same way, *trans*-1-OCONHPh was converted to ***trans*-3,4,4a,5,6,8a-hexahydro-8a-methylnaphthalene (*trans*-2)** in 83% yield. Capillary GC showed this product to be diastereomerically pure: NMR (δ, $CDCl_3$) 5.62 (dt, 2 H, J = 9.8, 2.0 Hz), 5.48 (dt, 2 H, J = 9.8, 3.3), 2.0–2.2 (m, 4 H), 1.4–1.7 (m, 5 H), 0.93 (s, 3 H); high resolution mass spectrum calcd for $C_{11}H_{16}$ m/e 148.1252, found m/e 148.1253.

B. Conversion of Diastereomeric 3,4,4a,5,6,8a-Hexahydro-8a-methylnaphthalenes (2) to the Corresponding 9-Methyldecalins (8). Hydrogenation of 301.6 mg of the above *cis*-**2** in 6 mL of dry ether over 50 mg of 10% Pd/C at 40 psi resulted in quantitative conversion to *cis*-9-methyldecalin (*cis*-**8**). Capillary GC of the reaction product showed the *cis*-**8** to be diastereomerically pure. A homogeneous analytical sample was isolated by preparative GC (4 ft × $^1/_4$ in., Carbowax on Chromasorb P, 130 °C) and identified as *cis*-**8** by the IR[9] and ^{13}C NMR spectra[8]: proton NMR (δ, $CDCl_3$) 1.1–1.8 (m, 17 H), 0.96 (s, 3 H); high resolution mass spectrum, calcd for $C_{11}H_{20}$ m/e 152.1566, found m/e 152.1566.

Hydrogenation of the above *trans*-**2** by the same method resulted in quantitative conversion to ***trans*-9-methyldecalin (*trans*-8)** shown to be diastereomerically homogeneous by capillary GC. The IR[9] and ^{13}C NMR[8] spectral properties of an analytical sample (preparative GC) were the same as reported for *trans*-**8**: proton NMR (δ, $CDCl_3$) 0.9–1.8 (m, 17 H), 0.82 (s, 3 H); high resolution mass spectrum, calcd for $C_{11}H_{20}$ m/e 152.1566, found m/e 152.1565.

Alkylation of 2,3,4,4a,5,6-Hexahydro-2-naphthalenyl Pivalate (1-OPiv) with Lithium Dimethylcuprate. The cuprate was prepared by adding 2 equiv of ethereal MeLi to a cold (−20 °C) suspension of CuI in dry ether. Immediately following, a cold (−20 °C) ethereal solution of 1-OPiv was added and the reaction was allowed to warm to room temperature. All reactions were carried out under a positive pressure of dry nitrogen. After about 8 h the reaction was quenched by addition of saturated NH_4Cl. The precipitate was removed by filtration and washed well with ether. The ether extracts were combined, shaken with 5% HCl, 10% NaOH, and saturated brine, and then dried over $MgSO_4$. After removal of the solvent by fractionation, the alkylation products were isolated by rotary TLC (pentane, 2 mm silica gel).

In a typical experiment a solution of 350 mg (1.5 mmol) of *trans*-1-OPiv (DP >95%) in 10 mL of ether was added to 3 mmol of preformed $LiCuMe_2$ in 10 mL of ether. After workup and rotary TLC, 195 mg (88% yield) of a 95:5 mixture of *cis*-**3** and *trans*-**3** was obtained. This binary mixture had the following: IR (neat) 3050 (m), 2920 (s), 2860 (s), 1460 (m), 1010 (w), 860 (m); NMR (δ $CDCl_3$) 6.00 (d, 1 H, J = 9.5 Hz), 5.7 (br dt, 1 H, J = 9.5, 4.2 Hz), 5.40 (br s, 0.95 H), 5.29 (s, 0.05 H), 2.0–2.4 (m, 4 H), 1.1–1.8 (m, 6 H), 1.0 (d, 2.9 H, J = 7.0 Hz), 0.98 (d, 0.1 H, J = 7.0 Hz); mass spectrum, calcd for $C_{11}H_{16}$ m/e 148.1252, found m/e 148.1253. The diastereomeric composition was determined by capillary GC (61 ft, UCON LB-550-X).

A similar experiment with *cis*-1-OPiv (DP > 96%) gave an 86% yield of a 20:80 mixture of *cis*-**3** and *trans*-**3**. This binary mixture had the following: IR (neat) 3020 (m), 2960 (s), 2930 (s), 2860 (s), 2840 (m), 1470 (m), 1020 (m), 870 (m), 760 (m); NMR (δ $CDCl_3$) 6.00 (d, 1 H, J = 9.5 Hz), 5.70 (br dt, 1 H, J = 9.5, 4.2 Hz), 5.4 (br s, 0.2 H), 5.29 (br s, 0.8 H), 2.0–2.4 (m, 4 H), 1.1–1.8 (m, 6 H), 1.00 (d, 0.6 H, J = 7.0 Hz), 0.98 (d, 2.4 H, J = 7.0 Hz); high resolution mass spectrum, calcd for $C_{11}H_{16}$ m/e, 148.1252, found m/e 148.1253.

Correlation of *cis*- and *trans*-2,3,4,4a,5,6-Hexahydro-2-methylnaphthalenes (*cis*-3 and *trans*-3) with the Diastereomeric 2-Methyldecalins (10–13). A mixture of 95% *trans*-**3** and 5% *cis*-**3** in acetic acid was hydrogenated over PtO_2 at 45 psi for 1 h. The hydrogenation product was found to be 83% **10**, 12% **11**, 1% **12**, and 4% **13** by capillary GC. Homogeneous samples of **11** and **13** and **10** containing 1% **12** were obtained from the above mixture by preparative GC (4 ft × $^1/_2$ in. 20% Carbowax on Chromasorb P, 140 °C). The proton[13] and ^{13}C NMR spectra[8,14] were the same as those reported earlier.

Hydrogenation of a mixture of 20% *trans*-**3** and 80% *cis*-**3** gave a mixture of 16% **10**, 4% **11**, 25% **12**, and 55% **13**. Preparative GC gave a 1.6:1 mixture of **12** and **10**. This composition was determined by capillary GC and confirmed by ^{13}C NMR spectroscopy.[8,14]

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