Table I. Selected 100-MHz ^{1}H NMR Chemical Shifts for Individual Cis-Fused Stereoisomers 1b–d

compd	assigned stereochemistry	ppm from Me_4Si C_3-H	C_5-H	C_8-H
1b	(5*Z*,8*E*)-3-heptyl	2.78	2.66	3.66
c	(5*E*,8*E*)-3-heptyl	2.95	3.29	3.66
d	(5*E*,8*Z*)-3-heptyl	3.08	3.02	3.69

2.12 (3, s, $COCH_3$), 1.26 (10, br s, $(CH_2)_5$), 0.93 (3, br t, CH_3). This spectrum matches the data reported in the literature.[6]

3-Heptyl-5-methylpyrrolizidine (1). A solution containing 0.5 g of triketone **3** (2 mmol), 170 mg of ammonium acetate, 60 mg of potassium hydroxide, and 200 mg of sodium cyanoborohydride in 10 mL of methanol was stirred under a nitrogen atmosphere for 12 h. A slight excess of sodium borohydride was then added and the mixture was stirred for 1 h, carefully acidified with 5% HCl, and washed with ether. The aqueous solution was made basic with potassium hydroxide and extracted with ether (3 × 30 mL). The ether extracts were dried (anhydrous K_2CO_3), and the solvent was removed in vacuo to give 0.35 g (80% yield) of pyrrolizidine **1**. GLC analysis (2 m × 2 mm column packed with 10% SP-1000 on Gas Chrom Q) showed four components, **1a**, **1b**, **1c**, and **1d** in the ratio 2:14:2.2:1, which had retention times of 5.5, 7, 12.5, and 16 min, respectively, at an oven temperature of 155 °C (He carrier gas, flow rate 60 mL/min). The four components had almost identical mass spectra: mass spectrum, *m/z* (relative intensity) 223 (4), 222 (2), 208 (8), 194 (2), 180 (2), 166 (1), 152 (2), 139 (1), 138 (1), 136 (1), 125 (11), 124 (100), 110 (10), 98 (2), 97 (1), 84 (2), 82 (2), 81 (6), 69 (4), 68 (3), 67 (2), 56 (2), 55 (5), 54 (2), 43 (3), 41 (6).

Anal. Calcd for $C_{15}H_{29}N$: C, 80.65; H, 13.09; N, 6.27. Found: C, 80.63; H, 13.08; N, 6.25.

The four isomers, eluting in the order **1a**, **1b**, **1c**, and **1d**, were separated by preparative GLC (2 m × 5 mm column packed with 10% SP-1000 on Gas Chrom Q), and IR, ^{1}H NMR, and ^{13}C NMR spectra were obtained for each.

1a: IR 2780, 2700, 2640 (w), 1460, 1385, 1335, 1280, 1200, 1165, 720 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.72 (1, m), 2.31 (2, m), 1.8–1.2 (20, br m), 1.21 (3, d), 0.92 (3, br t); ^{13}C NMR (C_6D_6) δ 72.33, 60.64, 55.58, 38.83, 35.97 (2 C), 32.34, 30.58, 29.93, 26.75 (2 C), 26.49, 23.18, 22.01, 14.41.

1b: IR 2790 (w), 2690 (w), 1460, 1370, 1355, 1180, 1130, 1105, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.66 (1, m), 2.78 (1, m), 2.66 (1, m), 1.8 (4, m), 1.6–1.3 (16, m), 1.12 (3, d, *J* = 6.2 Hz), 0.88 (3, br t) (irradiation of the multiplet at δ 2.66 collapsed the doublet at δ 1.12 to a singlet, and irradiation of the doublet at δ 1.12 simplified the multiplet at δ 2.66); ^{13}C NMR (C_6D_6) δ 66.29, 64.99, 61.81, 37.46, 35.13, 32.59, 32.40 (2 C), 32.20, 30.45, 29.93, 27.33, 23.11, 22.59, 14.35.

1c: IR 1460, 1380, 1365, 1160, 1130, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.66 (1, m), 3.29 (1, m), 2.95 (1, m), 2.2–1.8 (4, m), 1.6–1.3 (16, m), 1.16 (3, d, *J* = 6.5 Hz), 0.88 (3, br t) (irradiation of the signal at δ 3.29 collapsed the doublet at δ 1.16 to a singlet); ^{13}C NMR (C_6D_6) δ 66.23, 57.59, 57.07, 38.83, 34.41, 34.15, 33.44, 32.34, 31.17, 30.58, 29.93, 27.33, 23.11, 17.66, 14.35.

1d: IR 1460, 1370, 1175, 1148, 1130, 1098, 720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.69 (1, m), 3.08 (1, m), 3.02 (1, m), 2.1–1.8 (4, m), 1.6–1.3 (16, m), 1.14 (3, d, *J* = 6.5 Hz), 0.90 (3, br t) (irradiation of the signal at δ 3.02 collapsed the doublet at δ 1.14 to a singlet); ^{13}C NMR (C_6D_6) δ 66.29, 63.63, 52.85, 38.76, 35.45, 32.27 (2 C), 31.94, 31.68, 30.32, 29.80, 28.83, 23.96, 23.12, 14.35.

Isomer **1b** had identical GLC retention times by direct comparison and co-injection under isothermal conditions with the major component of the methylene chloride extract of *S. sp.* near *tennesseensis* (species E).

Acknowledgment. We thank W. F. Buren for species identification and Dr. R. J. Highet and Mr. E. A. Sokoloski for obtaining the nuclear magnetic resonance spectra of the isomers.

Registry No. **1a**, 74986-28-0; **1b**, 75023-37-9; **1c**, 75023-38-0; **1d**, 75023-39-1; **2**, 71525-51-4; **3**, 62619-73-2; acrolein diethyl acetal, 3054-95-3; octanal, 124-13-0; methyl vinyl ketone, 78-94-4.

^{2}H NMR Analysis of the Diastereomeric 2-Adamantanols-*4-d*

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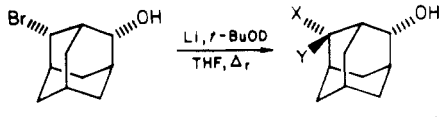
The conformational inflexibility, symmetry, and relative stability of the adamantane nucleus has made various derivatives attractive substrates for structural and mechanistic studies.[1] Stereochemical analysis of reactions of 2-substituted adamantanes, however, requires the presence of a second substituent for configurational reference. Whiting has incorporated a 5-methyl label for this purpose[2] and le Noble a 5-phenyl group.[3] Schleyer has made use of an intrinsic 1-methyl substituent.[4]

We have undertaken a group of mechanistic investigations based on ^{2}H NMR analysis of the diastereomeric 2-adamantanols-*4-d*. The isotopic label avoids the risk of steric effects likely with larger substituents[2,3] and provides for the study of related acid addition reactions. We describe here our synthetic entry into this system and establishment of a secure configurational analysis.

Cuddy, Grant, and McKervey[5] have ascertained the bromohydrin from protoadamantene and *N*-bromosuccinimide in aqueous dimethyl sulfoxide to be 4(a)-bromo-2(a)-adamantanol (**1**). We debrominated[6] purified **1** with lithium and *tert*-butyl alcohol-*d*[7] in boiling tetrahydrofuran to produce 2-adamantanol whose 15.4-MHz ^{2}H NMR spectrum in the presence of $Pr(fod)_3$ indicated the composition 83% 2(a)-adamantanol-*4(a)-d* (**2**) and 17% of the 4(e)-*d* isomer **3**. The induced (upfield) shift for the major product was markedly greater than that for the minor component, allowing epimeric assignments to be made on the basis of published pseudo-contact analyses of Eu-dispersed proton spectra of 2-adamantanol[8] and the



1 2, X = D; Y = H (83%) 3, X = H; Y = D (17%)

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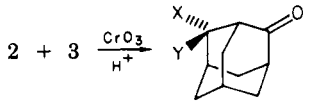
Table I. Reagent-Enhanced ^2H NMR Chemical Shifts

compd	configuration D	configuration OH	shift reagent	chemical shift, δ [a]
2	ax	ax	$Pr(fod)_3$ [b]	−7.27
3	eq	ax	$Pr(fod)_3$ [b]	−4.13
6	ax	eq	$Pr(fod)_3$ [b]	−2.70
7	eq	eq	$Pr(fod)_3$ [b]	−1.95
4	ax		$Pr(fod)_3$ [c]	−2.78
			$Eu(fod)_3$ [d]	5.75
5	eq		$Pr(fod)_3$ [c]	−0.98
			$Eu(fod)_3$ [d]	3.36
9	ex		$Pr(fod)_3$ [b]	−3.59
10	en		$Pr(fod)_3$ [b]	−2.45
12-OH	ex	ex	$Pr(fod)_3$ [b]	−9.24
13-OH	en	ex	$Pr(fod)_3$ [b]	−3.63

[a] In parts per million downfield from $(CD_3)_4Si$. [b] 15 mg of substrate and 70 mg of shift reagent in 400 μL of $CHCl_3$ containing 1% $CDCl_3$ internal reference. [c] 12 mg of substrate and 35 mg of shift reagent in 400 μL of $CHCl_3$, 1% $CDCl_3$. [d] 12 mg of substrate and 26 mg of shift reagent in 400 μL of $CHCl_3$, 0.5% cyclohexane-d_{12}.

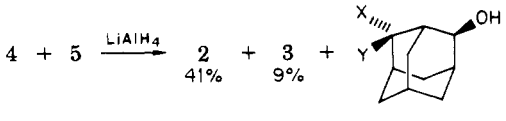
established linearity of the ^1H and ^2H chemical shift scales.[9] Jones oxidation of the **2** and **3** mixture yielded the corresponding ketones **4** and **5** in the expected 83:17



4, X = D; Y = H (83%)
5, X = H; Y = D (17%)

ratio. The comparative ^2H shifts effected in the spectrum of this ketone both by $Pr(fod)_3$ and by $Eu(fod)_3$ were in accord with the $Eu(fod)_3$-induced ^1H shifts recently reported by Lightner[10] and Wynberg[11] and co-workers for stereospecifically but dissimilarly prepared **4** and **5**, as well as those computed for unlabeled adamantanone by Demarco et al.[8c,12]

Reduction of the **4** and **5** mixture with $LiAlH_4$ regenerated alcohols **2** and **3** together with new isomers **6** and **7**, unambiguously related to **2** and **3**, respectively, by their

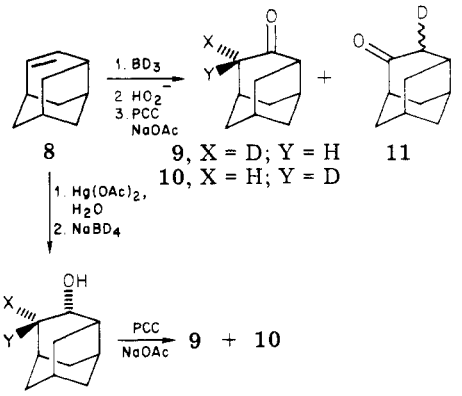


6, X = D; Y = H (42%)
7, X = H; Y = D (8%)

comparative ^2H NMR line intensities in the presence of $Pr(fod)_3$. The relative induced shifts for **6** and **7** were also consistent with the ^1H line assignments for 2-adamantanol arrived at by sophisticated pseudo-contact analyses.[8a-d]

Optimal conditions produce a nearly complete separation of the ^2H peaks of the four diastereomeric alcohols (Table I). Quantitative analysis requires a minor deconvolution of the partially overlapping signals from **6** and **7**.

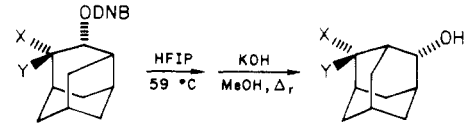
Further confirmation of the ^2H spectral identifications was achieved as follows. Deuterioboration–oxidation of protoadamantene (**8**) followed by oxidation of the resultant mixed alcohols[13] with buffered pyridinium chlorochromate[14] furnished the correspondingly labeled 4- and 5-protoadamantanones (**9** and **10**) and **11**, respectively,



8 **9**, X = D; Y = H **11**
10, X = H; Y = D

12-OH, X = D; Y = H (67%)
13-OH, X = H; Y = D (33%)

which were separated chromatographically. The spectrum of the 4-ketone with added $Pr(fod)_3$ consisted of two peaks in the ratio of 82:18, the more intense of which (upfield) could be confidently attributed to the exo-labeled epimer **9** from the known course[13] of hydroboration–oxidation[15] of protoadamantene. This information was applied in turn to analysis of the *exo*-4-protoadamantanols-*exo*- and *endo*-5-*d* (**12**-OH and **13**-OH, respectively) prepared from **8** by oxymercuration–reduction[5,13,16] using $NaBD_4$.[17] A portion of this alcohol was oxidized with pyridinium chlorochromate to **9** and **10**, whose ^2H NMR spectrum showed the label composition to be 67% exo and 33% endo, as anticipated from the relative induced shifts in the alcohol spectrum ($Z > E$). Isomerization in boiling hexafluoro-2-propanol[18] of a sample of the corresponding 3,5-dinitrobenzoates, **12**-ODNB and **13**-ODNB, followed by ester saponification was now found to yield only the two original 2-adamantanols-*4-d*, **2** and **3**, in a ratio essentially identical with that of the reactant epimers. This result can reasonably be only that of least-motion ion-pair return, i.e., inversion of configuration at the methylene-migration origin. The configurations of **2** and **3** are thus correlated with those established for **12**-OH and **13**-OH, respectively.



12-ODNB, X = D; Y = H
13-ODNB, X = H; Y = D

2, X = D; Y = H (68%)
3, X = H; Y = D (32%)

The mixture of alcohols **2** and **3** constitutes a redundantly double-labeled substrate for 2-adamantyl stereo-

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chemical studies, while the 12-OH and 13-OH mixture provides the means for related investigations of 4-protoadamantyl derivatives.

Experimental Section

General. Melting points are uncorrected. ^{2}H NMR spectra were obtained at 15.4 MHz, using a Varian XL-100-15 Fourier-transform instrument with proton decoupling. Overlapping signals were quantitatively deconvoluted by means of a du Pont Model 310 curve resolver with the assumption of Lorentzian line shapes. GLC analyses were performed on a Varian Model 920 gas chromatograph, employing the following columns: (A) 20 ft × 0.25 in. 20% SE-30 on acid-washed DMCS-treated Chromosorb W; (B) 6 ft × $^1/_8$ in. Carbowax 20M on acid-washed DMCS-treated Chromosorb W.

2(a)-Adamantanol-*4(a)-d* and -*4(e)-d* (2 and 3). An oven-dried 250-mL three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and nitrogen atmosphere was charged with 920 mg (3.97 mmol) of 4(a)-bromo-2(a)-adamantanol (1),[5] 46.0 g (533 mmol) of *tert*-butyl alcohol-*d*,[7] and 150 mL of anhydrous tetrahydrofuran. After addition of 2.00 g (433 mmol) of finely cut lithium wire (prewashed in hexane) at room temperature, the stirred mixture was heated under reflux for 16 h, cooled, and poured into 500 mL of ice water. Extraction with ether, drying over $MgSO_4$, and solvent removal left a brown solid, which was recrystallized from hexane at −78 °C to give 485 mg (3.2 mmol, 80%) of white powder: mp (sealed tube) 259–263 °C (lit.[11] mp 258–260 °C); mass spectrum, *m/e* 153 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.3–2.3 (m, 14 H), 3.9 (m, 1 H), as expected.[19] The ^{2}H NMR spectrum consisted of two largely overlapping peaks near δ 1.89, which were fully resolved by the introduction of $Pr(fod)_3$ as recorded in Table I; the ratio of signals at δ −7.27 (**2**) and −4.13 (**3**) was 83:17.

2-Adamantanone-*4(a)-d* and -*4(e)-d* (4 and 5). Alcohol mixture **2** and **3** was oxidized to the corresponding ketones, **4** and **5**, using Jones reagent as reported by Numan and Wynberg:[11] mp (sealed tube) 253–255 °C (lit.[11] mp 254–256 °C); mass spectrum, *m/e* 151 (M^+); ^{1}H NMR as expected;[20] ^{2}H NMR as in the text and Table I.

Four Diastereomeric 2-Adamantanols-*4-d* (2, 3, 6, and 7). Ketones **4** and **5** were reduced with $LiAlH_4$ in ether in the usual manner[21] to give the four isomeric labeled alcohols. The dispersed ^{2}H NMR spectrum, Table I, consisted of four absorptions. The peak assignments for **2** (41%) and **3** (9%) were made from the spectrum of the precedent twofold alcohol mixture, while those for **6** (42%) and **7** (8%) followed from matching intensities with the signals from **2** and **3**, respectively.

4-Protoadamantanone-*exo-5-d* and -*endo-5-d* (9 and 10). Protoadamantene[5] (**8**) (268 mg, 2.00 mmol) was deuterioborated and oxidized, using an excess of deuterioborane in tetrahydrofuran (Alfa) as described for the hydroboration by Boyd and Overton.[13] The resulting crude mixture of 4- and 5-protoadamantanols was dissolved in 5 mL of dry methylene chloride and added to a stirred solution of 426 mg (1.98 mmol) of pyridinium chlorochromate (Aldrich) and 536 mg (3.94 mmol) of sodium acetate in 10 mL of methylene chloride at room temperature. After 2 h the mixture was filtered through Florisil, and the solvent was removed by rotary evaporation, leaving a yellow solid crude product, which was established by GLC (column A, 150 °C) to consist of 67% 4-protoadamantanone and 33% 5-protoadamantanone. The 4-ketone (50 mg, 0.33 mmol) was isolated by preparative TLC:[13] mp (sealed tube) 212–214 °C (lit.[13] mp 210–212 °C); ^{2}H NMR, Table I and text.

***exo*-4-Protoadamantanol-*exo-5-d* and -*endo-5-d* (12-OH and 13-OH).** These labeled alcohols were prepared in 70% yield by the oxymercuration–reduction of 268 mg (2.00 mmol) of protoadamantene[5] (**8**) with 638 mg (2.00 mmol) of $Hg(OAc)_2$ and then 500 mg (11.9 mmol) of $NaBD_4$ (Alfa), using the procedure described by Schleyer and co-workers[16] for the undeuterated alcohol. The product was recrystallized from hexane at −78 °C: mp 202–203 °C (lit.[16] mp 203–206 °C); mass spectrum *m/e* 153 (M^+); ^{2}H NMR, Table I and text. The NMR peak assignments were made by oxidation of a sample of the mixed alcohols to the corresponding ketones, **9** and **10**, whose spectrum had been analyzed as described in the text. The oxidation of 200 mg (1.30 mmol) of 12-OH and 13-OH was effected in 91% yield by using buffered pyridinium chlorochromate as employed in the synthesis of **9** and **10** via hydroboration (see above).

***exo*-4-Protoadamantyl-*exo-5-d* and -*endo-5-d* 3,5-Dinitrobenzoate (12-ODNB and 13-ODNB).** The alcohol mixture 12-OH and 13-OH was converted to the 3,5-dinitrobenzoates in 70% yield by using the procedure described by Schleyer and co-workers[16] for preparation of the undeuterated esters: mp 141–143 °C (lit.[16] mp 142–144 °C); ^{1}H NMR as expected.[16]

Isomerization–Saponification of Dinitrobenzoates 12-ODNB and 13-ODNB to Alcohols 2 and 3. A solution of 157 mg (0.50 mmol) of dinitrobenzoate mixture 12-ODNB and 13-ODNB in 10 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (Columbia, distilled from BaO immediately before use) containing 59 mg (0.55 mmol) of 2,6-lutidine (Aldrich) was boiled under reflux under nitrogen for 5 days. The solvent was evaporated under vacuum, 50 mL of 20% methanolic potassium hydroxide was added, and the solution was refluxed for 12 h. The bulk of the methanol was removed by rotary evaporation, and the residue was poured into 500 mL of water and extracted with ether. The ether extract was washed with water and dried ($MgSO_4$). Rotary evaporation left a white solid, indicated by GLC (column B, 150 °C) to be only 2-adamantanol. Sublimation (0.5 mm) gave 65 mg (0.43 mmol, 85%) of **2** and **3**: mp (sealed tube) 257–259 °C (lit.[11] mp 257–260 °C, dideuterated); ^{2}H NMR, Table I and text.

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Registry No. **1**, 33782-47-7; **2**, 75081-60-6; **3**, 75081-61-7; **4**, 75081-62-8; **5**, 75081-63-9; **6**, 75081-64-0; **7**, 75109-23-8; **8**, 29844-85-7; **9**, 75031-70-8; **10**, 75109-24-9; **12-OH**, 75031-71-9; **12-ODNB**, 75031-72-0; **13-OH**, 75081-65-1; **13-ODNB**, 75082-08-5; *tert*-butyl alcohol-*d*, 3972-25-6; 4-protoadamantanone, 27567-85-7; 5-protoadamantanone, 31517-40-5; 2-adamantanol, 700-57-2.

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Complexation of Arenediazonium Ions by Crown Ethers: A CNDO/2 Study

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In 1975, Haymore, Ibers, and Meek[1] reported the preparation of a solid one-to-one complex of benzenediazonium hexafluorophosphate with the cis-anti-cis isomer of dicyclohexano-18-crown-6. The infrared spectrum of this complex, in which the diazonio group neck of the aryldiazonium ion is inserted into the collar of the crown ether,[2] provided the first example of a benzenediazonium ion complex in which ν(NN) of the cation increased upon complexation (from 2285 cm^{-1}, uncomplexed, to 2317 cm^{-1}, complexed). Subsequently, this unusual infrared spectral shift upon complexation has been confirmed for solid

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