Table I. Values for the Instantaneous Bond-Dissociation Energies (E_{IBD}) for 1,2-Dimethylenecyclobutene and Tetramethylenecyclobutane

	E_{IBD}, eV mol^{-1}	
bond[a]	eq 5	eq 6
	1,2-dimethylenecyclobutene	
C_1C_2	4.98	5.05
C_2C_3	5.32	5.20
C_3C_4	5.68	5.88
	tetramethylenecyclobutane	
C_1C_2	4.86	4.80

[a] Notation is given in Figure 3.

strained four-membered rings.

By the IMO procedure the bond overlaps (eq 1 and 2) and the deformation densities (eq 3 and 4) for 1,2-dimethylenecyclobutene and tetramethylenecyclobutane were calculated. With the values of bond overlaps and bond-deformation densities, instantaneous bond-dissociation energies were calculated by eq 5 and 6. Notation of the atoms in the molecules is given in Figure 3, and the values of both E_{IBD}'s are given in Table I.

It can be seen, from Table I, that agreement between instantaneous bond-dissociation energies calculated by unit deformation densities (eq 6) and by the bond overlaps (eq 5) is within the standard deviation error.

Established relationship 6 gives satisfactory results for covalent bonds in strained four- and five-membered rings. Also it can be said that the unit deformation density is a measure of binding power of molecular orbitals.

Registry No. Cyclobutene, 822-35-5; cyclopentadiene, 542-92-7; [2.1.1]propellane, 36120-91-9; [2.2.2]propellane, 36120-88-4; 1,2-dimethylenecyclobutene, 5291-90-7; tetramethylenecyclobutane, 3227-91-6.

Hydroboration. 72. Hydroboration–Oxidation of 1,4-Epoxy-1,4-dihydronaphthalene with and without Ring Opening

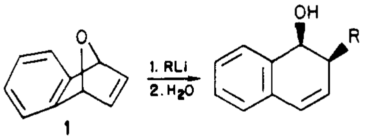
Herbert C. Brown* and J. V. N. Vara Prasad[1]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

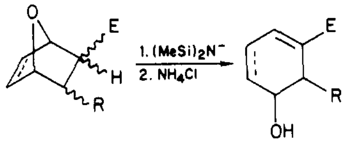
Received January 17, 1985

Recently we reported the hydroboration of heterocyclic olefins with representative hydroborating agents such as borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH) providing a highly convenient and efficient method for the synthesis of heterocyclic alcohols.[2] β-Substituted organoboranes readily undergo elimination. However, in these reactions we were able to avoid the ring cleavage by careful selection of reagent and conditions. In continuation of these studies, we selected 1,4-epoxy-1,4-dihydronaphthalene (1), an unusual heterocycle, in order to study the stability and synthetic utility of organoboranes produced in the hydroboration of the 7-oxabicyclo[2.2.1]heptene system.

There are reports in the literature that 1, on treatment with alkyllithiums, yield 1,2-dihydro-2-alkylnaphthalenes via ring opening of the initially formed addition products[3,4] (eq 1). Similarly, a base-promoted β-elimination in the 7-oxabicyclo[2.2.1]heptyl system, yielding cyclohexanols and cyclohexadienols, has been reported[5] (eq 2). Previously we reported that cyclic ethers undergo ready cleavage in the presence of lithium tri-*tert*-butoxyaluminum hydride and triethylborane.[6,7] Extension of this reaction to 1 has recently been reported to yield 1-hydroxy-1,4-dihydronaphthalene[8] (eq 3).



(1)



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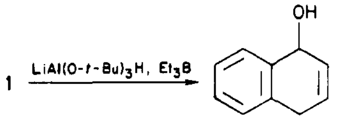
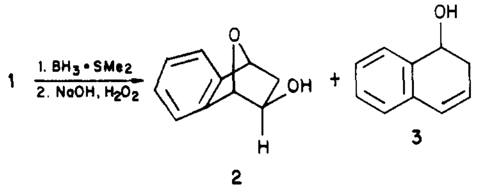


(3)

Results and Discussion

Compound 1 was hydroborated with BMS, 9-BBN, Chx_2BH, and Sia_2BH, and the products were oxidized with alkaline hydrogen peroxide. The results are shown in Table I.

BMS. Compound 1 was hydroborated with BMS (3:1 mol ratio) in THF at 25 °C. The ^{11}B NMR spectrum of the reaction mixture showed a signal at δ 27.6, which, on methanolysis, transformed itself into a new signal at δ 18.3. Oxidation of the reaction mixture afforded 7-oxa-*exo*-2-benznorborneol (2) and 1-hydroxy-1,2-dihydronaphthalene (3) in a 1:5 ratio (eq 4). It should be noted that 3 is isomeric with the compound synthesized by the reaction shown in eq 3.



(4)

It appears that the latter product might have arisen from a cleavage of the organoborane initially formed. Lowering the reaction temperature to 0 °C did not avoid this cleavage. The ^{11}B NMR spectra and the product analysis after oxidation were essentially the same as in the reaction at 25 °C. However, in these two cases, only 2 mol of olefin per mol of BMS were consumed. A longer reaction time did not achieve the utilization of a third mole of olefin. However, reaction in refluxing THF (65 °C) consumed all of the olefin. The ^{11}B NMR of the reaction mixture following reaction at 65 °C for 1 h showed a signal at δ 20.2, characteristic of $B(OR)_3$ species. Oxidation of the reaction

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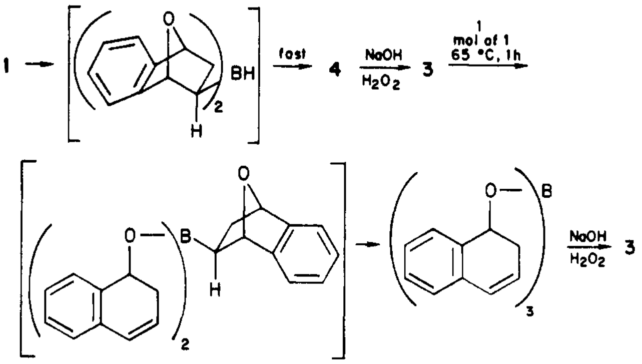
Table I. Hydroboration-Oxidation of 1,4-Epoxy-1,4-dihydronaphthalene

hydroborating agent	olefin/hydroborating agent mol ratio	solv	reactn temp, °C	reactn time, h	total yield,[a] %	product distribution,[a] mol %: 7-oxo-*exo*-2-benznorborneol	product distribution,[a] mol %: 1-hydroxy-1,2-dihydronaphthalene
$BH_3{\cdot}SMe_2$	3:1	THF	0	2	65	20	80
$BH_3{\cdot}SMe_2$	3:1	THF	25	0.25	66	16	84
$BH_3{\cdot}SMe_2$	3:1	THF	65	1	100	2	98
$BH_3{\cdot}SMe_2$	3:1	Et_2O	25	1	64	16	84
$BH_3{\cdot}SMe_2$	3:1	CH_2Cl_2	25	0.25	65	15	85
9-BBN	1:1	THF	0	12	99	[b]	99
9-BBN	1:1	THF	25	1	98	[b]	98
9-BBN	1:1	CH_2Cl_2	25	6	98	[b]	98
Chx_2BH	1:1	THF	25	1	100	100	0
Sia_2BH	1:1	THF	25	1	98	98	0

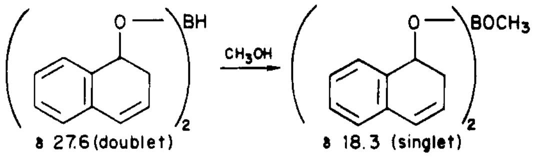
[a] By GC analysis. [b] Trace.

Scheme I



mixture afforded the homoallylic alcohol **3** in essentially quantitative yield.

During the reaction at 25 °C, the ^{11}B NMR signal at δ 27.6, a doublet in the coupled spectrum, can be attributed to either a R_2BH or a $(RO)_2BH$ species. Since the reaction mixture on methanolysis showed a new signal at δ 18.3, singlet, characteristic of the $B(OR)_3$ species, the signal at δ 27.6 is attributed to the $(RO)_2BH$ species **4** (eq 5). The

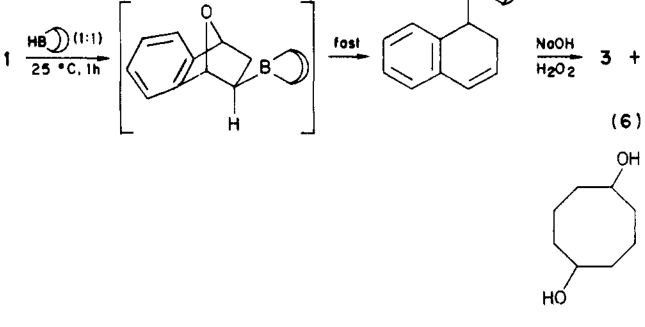


(5)

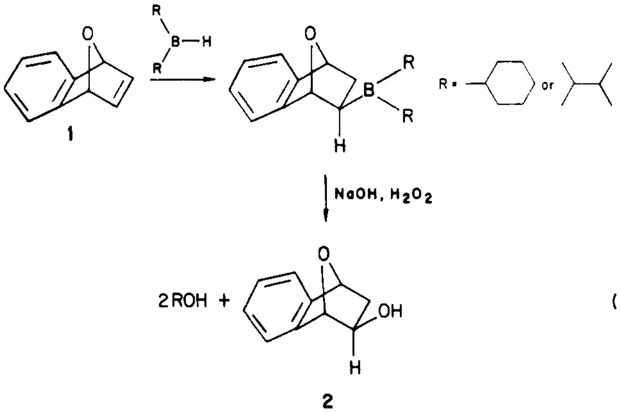
hydroboration of olefin **1** with BMS in a 3:1 mol ratio at 25 °C in Et_2O or CH_2Cl_2 yielded results similar to those in THF. The results are summarized in Scheme I.

9-BBN. The olefin **1**, on treatment with 9-BBN (1:1 mol ratio) in THF at 25 °C, followed by oxidation, affords the homoallylic alcohol **3** in quantitative yield. A similar reaction at 0 °C was slow and required 12 h for completion. The reaction of **1** with 9-BBN at 25 °C in methylene chloride required nearly 6 h. In all of these cases the ^{11}B NMR spectrum before oxidation showed a signal at δ 57.9, characteristic of a R_2BOR species. The results are summarized in Scheme II.

Scheme II



Chx_2BH. The olefin **1**, on treatment with Chx_2BH (1:1 mol ratio) in THF at 25 °C, afforded the trialkylborane, which, on oxidation, gave exo alcohol **2** in quantitative yield (eq 7, R = cyclohexyl).



(7)

Sia_2BH. In this case also, as with Chx_2BH, the reaction at 25 °C yielded the clean trialkylborane, which readily oxidized to the exo alcohol **2** in quantitative yield (eq 7, R = siamyl).

Mechanism. Although the primary objective of this study was synthetic, it is of interest to consider a simple interpretation of the results in terms of the reaction mechanism.

Organoboranes containing electronegative substituents in the β-position readily undergo elimination.[9-19] Study of the hydroboration of substituted cyclic olefins has revealed that such eliminations in cyclic derivatives follow two distinct courses.[12,19] In the case where the substituent is a strong leaving group (X = Cl, Br, I, OTs), the reaction involves a trans elimination catalyzed by bases, even THF (eq 8).

On the other hand, where the substituent is not a strong leaving group but possesses good donor properties (X =

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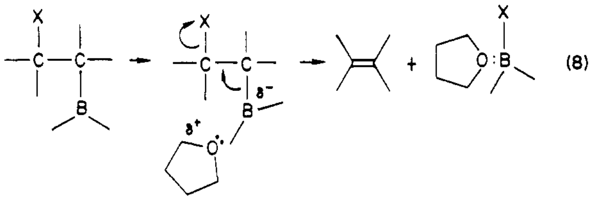
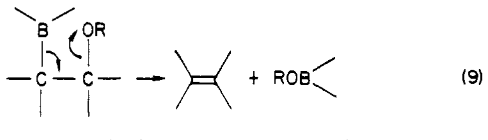


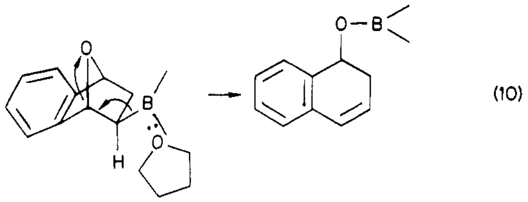
(8)

OR, OAc), the reaction involves a facile cis elimination (eq 9).



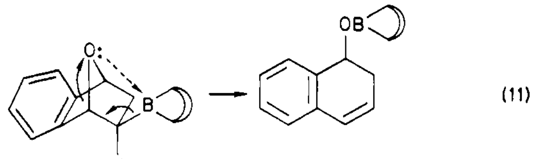
(9)

In the case of the hydroboration of **1**, we observed that the reaction is not catalyzed by THF. Therefore, the ring opening cannot involve the trans pathway (eq 10).



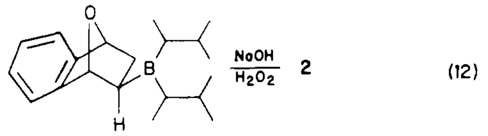
(10)

Indeed, the cis pathway (eq 11) provides a simple explanation for the observed phenomena. Those hydroborating agents that involve a relatively exposed boron atom can readily achieve coordination of the 7-oxa substituent to boron, leading to the facile elimination observed.



(11)

On the other hand, those derivatives (Chx_2B and Sia_2B) that have the boron atom surrounded by bulky substituents find it difficult to achieve coordination of the 7-oxa substituent to boron (eq 12). Such derivatives persist and are readily oxidized to the hydroxy compound **2**.



(12)

Conclusion

The formation of either exo alcohol **2** or homoallylic alcohol **3** from olefin **1**, depending upon the hydroborating agents used, demonstrates the complementary nature of these hydroborating agents. For preparation of the ring-opened compound **3**, this procedure is superior to the literature method.[20] The overall reaction of **1** with BMS or 9-BBN is almost equivalent to the monohydroboration–oxidation of naphthalene, a reaction that cannot be achieved directly. Moreover, hydroboration with Chx_2BH or Sia_2BH, followed by oxidation, provides a convenient route to compound **2**, which has not been previously described in the literature.

Finally, consideration of the different steric requirements of the hydroborating agents provides a simple explanation why hydroborations with BMS and 9-BBN result in ring opening, whereas hydroboration with Chx_2BH and Sia_2BH do not.

Experimental Section

The reaction flasks and other glass equipment were stored in an oven at 150 °C overnight and assembled in a stream of dry nitrogen gas. Syringes were assembled and fitted with needles while hot and cooled in a stream of dry nitrogen gas. Special techniques used in handling air-sensitive materials are described in detail elsewhere.[21]

Spectra. ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The chemical shifts are in δ relative to $BF_3{\cdot}OEt_2$. ^1H NMR (90 MHz), ^{13}C NMR (80 MHz), IR, and mass spectra were recorded on Perkin-Elmer R-32, Varian FT-80A, Perkin-Elmer 137, and Finnegan GC/mass spectrometers, respectively.

GC Analyses. All GC analyses were carried out with a Hewlett-Packard 5750 chromatograph using 9 ft × 0.125 in. columns packed with 10% Carbowax 20M on Chromosorb W (100–120 mesh).

Materials. Borane–methyl sulfide (BMS), 9-borabicyclo-[3.3.1]nonane (9-BBN), and 1,4-epoxy-1,4-dihydronaphthalene were purchased from the Aldrich Chemical Co. BMS and 9-BBN were estimated according to the standard procedure.[21] Tetrahydrofuran (THF) was distilled over benzophenone ketyl and stored under nitrogen atmosphere in an ampule. Dicyclohexylborane[22] and disiamylborane[2] were prepared according to the literature procedures.

Hydroboration with BMS. In a 25-mL flask equipped with a septum inlet, magnetic stirring bar, and connecting tube leading to a mercury bubbler was placed 1.44 g (10 mmol) of 1,4-epoxy-1,4-dihydronaphthalene in 4.2 mL of THF. To it was added 0.37 g (2 mmol) of tridecane (internal standard), followed by 0.37 mL (3.3 mmol) of BMS (8.98 M), added dropwise via syringe. The reaction was followed by ^{11}B NMR. After 15 min, the reaction mixture was cooled to 0 °C and oxidized, using 10 mL of 3 N sodium hydroxide and 3.8 mL of hydrogen peroxide. The reaction mixture was stirred at 25 °C for 5 h. The aqueous phase was saturated with 5 g of anhydrous potassium carbonate. A small amount of the organic phase was dried over 4-Å molecular sieves and analyzed by GC. The percentages of the products were calculated by using appropriate correction factors. The results are summarized in Table I. 1-Hydroxy-1,2-dihydronaphthalene undergoes aromatization under the GC analysis conditions. It occurred during our attempts to isolate the product by preparative GC or during GC/mass spectral analysis. The product could be successfully isolated by distillation under reduced pressure (see following procedure).

Hydroboration with 9-BBN. In the usual experimental setup were placed 1.44 g (10 mmol) of 1,4-epoxy-1,4-dihydronaphthalene and 0.37 g (2 mmol) of tridecane. To it 23.8 mL of 9-BBN in THF (0.42 M) was added dropwise under magnetic stirring at 25 °C. The reaction was followed by ^{11}B NMR. After the reaction was complete, the reaction mixture was oxidized with 10 mL of 3 N sodium hydroxide and 3.8 mL of hydrogen peroxide. The contents were kept at 25 °C for 5 h. The reaction mixture was saturated with anhydrous potassium carbonate. The organic layer was concentrated by evaporating THF, and the residue was taken in 20 mL of diethyl ether and washed with 2 × 20 mL of water. The organic phase was kept over anhydrous magnesium sulfate and subjected to GC analysis.

In another experiment, 1-hydroxy-1,2-dihydronaphthalene was isolated and characterized by spectra. 1-Hydroxy-1,2-dihydronaphthalene: bp 101–103 °C (0.5 mm); $n^{20}{}_D$ 1.5955; IR (neat) 3386, 3039, 2939, 1638, 1601, 1447, 1278, 1037, 857, 784; ^1H NMR ($CDCl_3$) δ 7.1 (m, 5 H), 6.5–5.8 (m, 2 H), 4.7 (t, 1 H), 2.9 (s, exchangeable with D_2O, 1 H), 2.5 (m, 2 H).

Hydroboration with Chx_2BH and Sia_2BH. The reactions were done as described for 9-BBN. 7-Oxa-*exo*-2-benznorborneol

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2: mp 102–104 °C; IR (KBr) 3405, 3012, 2937, 1457, 1321, 1284, 1268, 1211, 1000, 980, 905, 854, 833, 750, 653; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 4 H), 5.45 (d, 1 H), 5.2 (s, 1 H), 4.1 (m, 1 H), 1.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 146.72, 141.78, 127.37, 126.76, 120.66, 118.96, 86.18, 78.7, 72.68, 39.98; mass spectrum, CI, *m/e* 163 (M + 1, 22%), 145 (100%), 118 (15%), 117 (9%), EI, *m/e* 133 (2%), 119 (7%), 118 (100%), 103 (2%), 90 (12%). Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.76; H, 6.28.

Acknowledgment. We gratefully acknowledge support from the National Institutes of Health (Grant GM 10937-22) in this research.

Registry No. 1, 573-57-9; 2, 96898-07-6; 3, 37480-22-1; BMS, 13292-87-0; 9-BBN, 280-64-8; Chx_2BH, 1568-65-6; Sia_2BH, 1069-54-1.

The Structure of Tetrahydrobinor-S (Pentacyclo[8.4.0.0^{2,6}.0^{3,8}.0^{9,13}]tetradecane) Based on C–C Connectivity Two-Dimensional NMR Study

V. V. Krishnamurthy, Joseph G. Shih, and George A. Olah*

The Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

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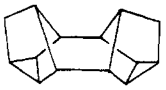
Diamantane, the second member of the adamantanoid hydrocarbons, became readily available after a convenient high-yield preparation was reported independently by Schleyer[1] and McKervey.[2] The chemistry of this interesting cage hydrocarbon and its derivatives has been extensively studied since then. The preparation involves acid-catalyzed rearrangement of the isomeric pentacyclic hydrocarbon tetrahydrobinor-S. Tetrahydrobinor-S is the product of hydrogenation of binor-S[3,4] (1) (heptacyclo[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane) over PtO_2 in AcOH at 40 atm H_2 pressure.[1,2] Hydrogenation of binor-S, in principle, can give rise to four products (**2**–**5**) corresponding to the hydrogenolysis of the cyclopropane rings in various fashion.



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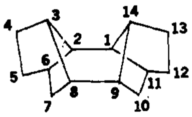

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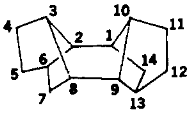

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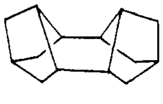

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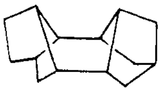

5

In fact only one product is formed when binor-S is hydrogenated with H_2 over PtO_2 catalyst. However, the structure of tetrahydrobinor-S remained elusive. Structures **4** and **5** can be ruled out on the basis of the ^{13}C NMR[5,6] spectrum. The ^{13}C NMR spectrum shows seven carbon resonances at $\delta_{^{13}C}$ 49.8 (d), 39.3 (d), 37.8 (d), 37.0 (d), 32.4 (t), 32.2 (t), and 24.1 (t). Structure **4** (C_{2h} symmetry) should have five carbon resonances, while structure **5** (C_1 symmetry) should have 14 carbon resonances. Thus, these two structures obviously will not fit the observed ^{13}C spectrum. However, both structure **2** (C_s symmetry) and structure **3** (C_2 symmetry) contain seven distinct carbons of the same general type in accord with the observed ^{13}C spectrum. The significant difference between structures **2** and **3** is that **2** is achiral while **3** is chiral. On the basis of molecular mechanics calculation Schleyer et al. suggested **3** as the structure of the compound.[5]

We now wish to report our study using carbon–carbon connectivity 2D (CCC2D) NMR spectroscopy[7] unequivocally proving the structure of tetrahydrobinor-S to be **3**, i.e. pentacyclo[8.4.0.0^{2,6}.0^{3,8}.0^{9,13}]tetradecane.

Results and Discussion

The carbon–carbon connectivity 2D NMR developed by Freeman et al.[7] and the later modifications of the technique[8,9] are based on the INADEQUQTE[10] pulse sequence (see Experimental Section for the details of the pulse sequence). The INADEQUATE pulse sequence generates a double quantum coherence in molecules containing two scalar coupled ^{13}C spins. The CCC2D NMR experiment uses the frequency of the double quantum coherence itself as the criterion for connectivity. The double quantum coherence, generated by the $90°-\tau-180°-\tau-90°$ sequence, is allowed to "evolve" during the evolution period at the double quantum frequency, which is the sum of the resonance frequencies of the coupled spins (measured with respect to the transmitter frequency). A proper choice of τ ($\approx 1/4J_{CC}$, where J_{CC} is the one-bond ^{13}C–^{13}C coupling constant) would generate double quantum coherence only from molecules containing two scalar coupled ^{13}C spins adjacent to each other. After two-dimensional Fourier transformation, a spectrum is obtained with the conventional carbon-13 satellite lines in the F_d dimension and the corresponding double quantum frequencies in the F_e dimension (see Experimental Section for details).

An examination of structures **2** and **3** reveals that the two molecules differ in their connectivities. In fact, if **2** were the correct structure, one would predict two double quantum frequencies each for the methylene carbons (C_4, C_5, and C_7) and for two of the four methine carbons (C_1 and C_8) as they each are attached to two other "nonequivalent" carbons. However, the other two methine carbons (C_3 and C_6) are attached to three nonequivalent carbons, and thus one would observe three double quantum frequencies for each of these two CH's. In contrast in structure **3**, all the methine carbons are attached to three nonequivalents carbons, and thus each one should show three double quantum frequencies. For the methylenes, as in structure **2**, one would predict two double quantum

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