6′,-7′), 112.5 (C-2), 124.5, 126.3 (C-4a′,-8a′), and 151.1 and 152.0 (C-5′,-8′); IR (KBr) 3441, 2940, 2830, 1600, 1480 cm^{-1}; MS (EI) *m/z* (relative intensity) 294 (100), 261 (20), 206 (90), 189 (56); $[\alpha]_D$ −57.8° (c = 1.2); ee ≥95%. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.46; H, 7.69.

2-Methyl-2-[3′-((1′*S*,3′*S*)-1′,3′-dihydroxy-5′,8′-dimethoxy-1′,2′,3′,4′-tetrahydronaphthalenyl)]-1,3-dioxolane (7). The ketal **6** (0.1 g) was dissolved in CH_2Cl_2 (10 mL) at 20 °C, and [5,10,15,20-tetrakis(pentafluorophenyl)-21*H*,23*H*-porphine]iron(III) chloride (30 mg) was added, followed by iodosobenzene (0.156 g). The resulting reaction mixture was stirred at 20 °C for 1 h and then filtered. The filtrate was concentrated and the resulting oil purified by preparative TLC using ether as eluant to give the title compound in 60% yield: mp 138–140 °C (lit.[10] mp 141–143 °C); NMR and IR data as reported;[10] MS (EI) *m/z* 310 (6), 266 (3) relative to 205 (100); $[\alpha]_D$ +5.0° (c = 1.2, $CHCl_3$) (lit.[9] $[\alpha]_D$ +5.3° ($CHCl_3$)); ee ≥95%.

Iodosobenzene Oxidation of 2(*R*)-(−)-5,8-Dimethoxy-2-hydroxy-2-(1′-hydroxyethyl)-1,2,3,4-tetrahydronaphthalene ((−)-4). Oxidation of **4** by the procedure described above gave as the only isolable product 5,8-dimethoxy-β-tetralone (**10**), obtained in isolated yields of 60–80%, mp 96–98 °C (lit.[6] mp 97–98 °C); ^1H NMR and IR as reported.[4]

Iodosobenzene Oxidation of 1-[2′-((2′*R*)-5′,8′-Dimethoxy-2′-hydroxy-1′,2′,3′,4′-tetrahydronaphthalenyl)]ethanone (5). Treatment of **5** (100 mg) with iodosobenzene under the conditions described above for the preparation of **7** gave a complex reaction mixture, TLC analysis of which suggested the formation of the 1,3-diol **11** as only a minor product. In view of its complexity, this reaction was not investigated further.

Attempted Bromination/Solvolysis of 1-[2′-((2′*R*)-5′,8′-Dimethoxy-2′-hydroxy-1′,2′,3′,4′-tetrahydronaphthalenyl)]-ethanone (5) and 2-Methyl-2-[2′-(5′,8′-dimethoxy-2′-hydroxy-1′,2′,3′,4′-tetrahydronaphthalenyl)]-1,3-dioxolane (6). Treatment of the ketone **5** or the ketal **6** with *N*-bromosuccinimide gave only 1-[2′-(5,8-dimethoxynaphthalenyl)]ethanone (**9**), described below for reaction of **5** with NBS. A solution of **5** (0.1 g) and NBS (0.07 g) in CCl_4 (50 mL) containing one drop of 3.0 M *tert*-butyl hydroperoxide solution was refluxed under argon for 1 h. TLC monitoring of the reaction indicated the formation of a single major product, which could be isolated by filtration following reduction of the reaction volume to 5 mL. This product remained unchanged after treatment of the reaction mixture with refluxing aqueous methanol and was identified as 1-[2′-(5,8-dimethoxynaphthalenyl)]ethanone (**9**) by comparison with reported physical and spectral data:[17] mp 110–112 °C (lit.[17] mp 111–112 °C); ^1H NMR δ 2.6 (3 H, s, C-1 CH_3), 3.87, 3.90 (each 3 H, s, OCH_3), 6.65, 6.72 (2 H, ABq, C-6′,-7′ H's), 7.96 (1 H, d of d, C-3′H), 8.16 (1 H, d, C-4′H), 8.74 (1 H, d, C-1′H); MS (EI) *m/z* (relative intensity) 230 (85), 215 (100), 189 (14).

Acknowledgment. This work was funded by the Natural Sciences and Engineering Research Council of Canada Strategic Grant no. STRIN 041 to H.L.H.

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Dependence of Isotropic Hyperfine Coupling in the Fluoromethyl Radical Series on Inversion Angle

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Received September 25, 1990 (Revised Manuscript Received May 13, 1991)

Electron spin resonance (ESR) has proven a powerful tool in the study of organic radicals.[1] By analysis of hyperfine coupling constants (hfs), insights into hybridization, bonding, and molecular geometry may be obtained.[2] However, first-order theoretical models[3] are not always successful in describing these properties.[4] An alternative that is rapidly becoming more available to the experimental chemist is direct calculation of electronic structure and properties for comparison to experiment. Such a symbiosis of spectroscopic and computational techniques has been applied not only to radicals as simple as methyl[5] and the methane cation radical,[6] but as well to larger open-shell systems, like the 7-norbornyl radical, the cubane cation radical, and the benzene and toluene radicals and radical anions.[7,8]

The accurate ab initio prediction of isotropic hfs for open-shell molecules has been a long-standing goal for a number of investigators. While semiempirical techniques are extremely rapid, they only rarely provide results of better than qualitative accuracy.[9] Unrestricted Hartree–Fock (UHF) methods,[10] which do not take additional account of correlation effects, often give poor hfs values due, inter alia, to unrealistic spin polarizations, sometimes occurring in the core s orbitals[11] and sometimes in the valence orbitals.[12] Configuration interaction (CI) and coupled cluster (CCD) methods have proven extremely succesful for very small molecules but rapidly become unwieldly and expensive when multiple heavy atoms are present.[2d,13] We apply here a method for calculating hfs from Z-vector derived[14] MP2[15] spin density matrices that

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Table I. Energies and Predicted hfs Values for 1–4[a]

		CH_3 (1)	CH_2F (2)	CHF_2 (3)	CF_3 (4)
a_C predicted[b]	UHF	55.1	109.5	181	281
	UMP2	22.6 (32.8)[d]	72.6 (49.6)[d]	146	257
experimental[c]		38.3	54.8	149	271
a_F predicted[b]	UHF		98.8	107.4	146
	UMP2		73.7 (71.7)[d]	86.9	142
experimental[c]			64.3	84.2	142
a_H predicted[b]	UHF	−42.7	−29.9	6.92	
	UMP2	−27.6 (−25.6)[d]	−15.4 (−22.7)[d]	18.9	
experimental[c]		−25.0	−21.1	22.2	
energy[e]		−39.725 59	−138.810 02	−237.911 11	−337.016 55
r_{CH}		1.073	1.073	1.076	
r_{CF}			1.331	1.314	1.301
θ		0.0	11.1	15.8	17.6

[a] Energies are in Hartrees, hfs values in Gauss, bond lengths in angstroms, θ in degrees. [b] Calculated at either the UMP2/6-311G**//UHF/6-31G* or the UHF/6-311G**//UHF/6-31G* level. [c] Reference 20a. Signs are inferred from this and other work. [d] These values incorporate dynamic contributions from consideration of out-of-plane vibrational motion, see Tables II and III. [e] Calculated at the UMP2/6-311G**//UHF/6-31G* level.

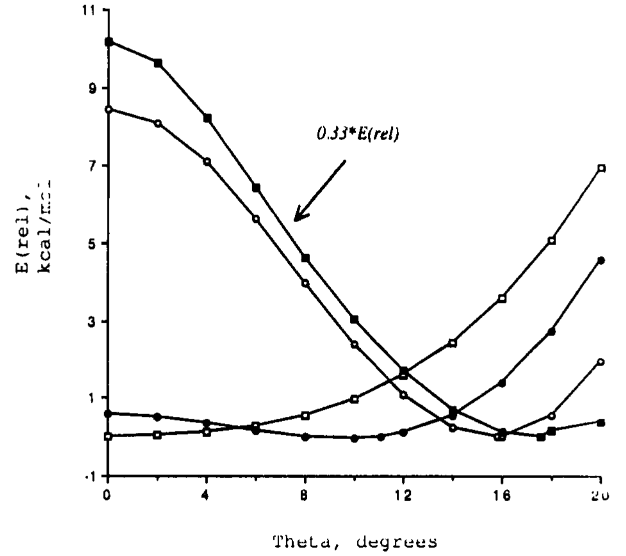


Figure 1. Relative energy vs umbrella angle θ for 1 (□), 2 (●), 3 (○), and 4 (■) calculated at the UMP2/6-311G**//UHF/6-31G* level. No comparison of energies across the isomeric series is intended. For 4, the ordinate is in units of 3.00-kcal/mol to allow for similar scaling.

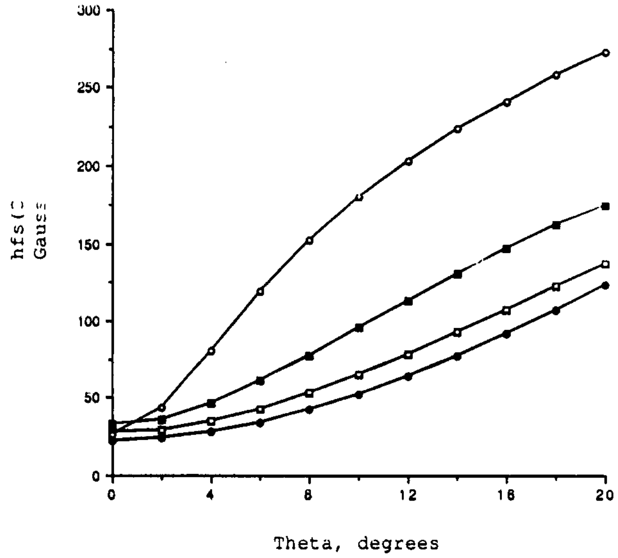
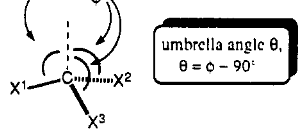


Figure 2. a_C vs umbrella angle θ for 1 (●), 2 (□), 3 (■), and 4 (○) calculated at the UMP2/6-311G**//UHF/6-31G* level.

delivers results comparable in accuracy to CI methods in a fraction of the time.[16,17]

The complete set of fluoromethyl radicals (CF_nH_{3-n}, n = 0–3) has been fully optimized at the UHF/6-31G* level.[18a] Additional electronic structure calculations were performed for each of the four radicals while stepping the umbrella angle, θ, from 0° to 20° in increments of 2°. Since it is always possible to find an axis through a central atom that makes an identical angle with each of three unique substituent atoms, θ represents only a single degree of freedom, i.e., the bond angles are otherwise unconstrained. Isotropic hyperfine coupling constants were obtained at each geometry by multiplying MP2/6-311G** derived[18b–d] Fermi contact integrals, $\rho(X)$, by the appropriate constants[19] according to the equation $a_X = (8\pi/3)gg_X\beta\beta_X\rho(X)$, where g (g_X) is the electronic (nuclear) g factor and β (β_X) is the Bohr (nuclear) magneton.[2]



1. X^1=X^2=X^3=H 3. X^1=X^2=F, X^3=H
2. X^1=X^2=H, X^3=F 4. X^1=X^2=X^3=F

Predicted and experimental[20] hfs values for 1–4, together with their equilibrium geometric and energetic data, are

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(19) $C_X = (8\pi/3)gg_X\beta\beta_X$, C_H = 1595, C_F = 1503.5, C_C = 401.5. Units are Gauss-bohr³/electron. See: Koh, A. K.; Miller, D. J. *Atom. Data and Nucl. Data Tabl.* **1985**, *33*, 235.

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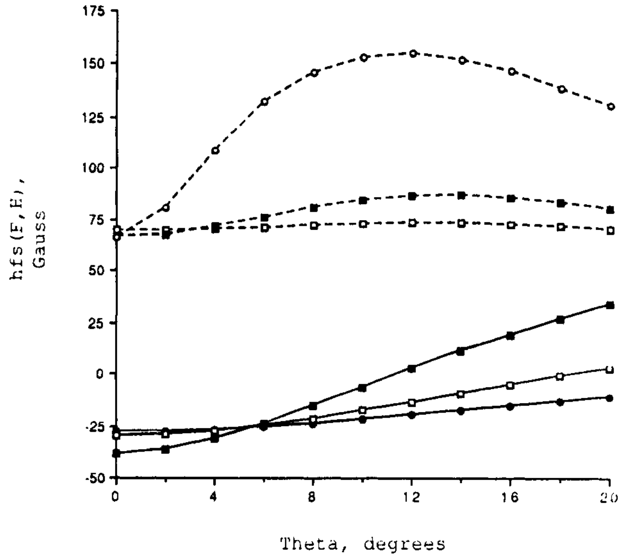

Figure 3. a_F (dotted lines) and a_H (solid lines) vs umbrella angle θ for **1** (●), **2** (□), **3** (■), and **4** (○) calculated at the UMP2/6-311G**//UHF/6-31G* level.

collected in Table I. Figure 1 presents relative energy as a function of θ. The steady increase in equilibrium pyramidality and inversion barrier with increasing fluorine substitution is as expected.[21] Figure 2 presents MP2-derived values for a_C and Figure 3 for a_F and a_H all as functions of θ. The complete data are provided as supplementary material.

It is evident from inspection of Table I that **3** and **4** are well-described by the UMP2 method applied at their equilibrium geometries. Although there is little difference between the UHF and UMP2 predicted hfs values for **4**,[4] UHF methodology seriously overestimates a_C and a_F for **3**, while grossly *under*estimating a_H. The UMP2 correction, however, delivers excellent results.

While the relatively steep, symmetric potential wells surrounding the equilibrium structures of **3** and **4** allow vibrational motion to be effectively discounted at the experimental temperature of 77 °K, this is not the case for **1** and **2**. It is evident from inspection of Figure 1 that moderate and large amplitude ground-state vibrational motion with respect to θ is available to **1** and **2**, respectively. The significant change in hfs values for select individual atoms when averaged over these motions gives rise to the differences in Table I between the experimental and equilibrium theoretical values. The magnitude of such corrections in both single- and double-well potentials has been discussed in detail for a number of first- and second-row trihydrides.[5c]

The hyperfine couplings here may be approximated as a one-dimensional function of θ and expanded in terms of the even (by inversion symmetry) powers of θ, i.e.

$$a(\theta) = a_0 + a_2\theta^2 + a_4\theta^4 + \ldots \tag{1}$$

This assumes that contributions from the remaining normal modes, which are all higher in energy than inversion, may be ignored. The experimental hfs is then the Boltzmann-weighted average of the expectation values for the various vibrational levels, i.e.

$$\langle a(\theta)\rangle = \frac{\sum_i \langle \chi_i(\theta)|a(\theta)|\chi_i(\theta)\rangle\, e^{-E_i/k_BT}}{\sum_i e^{-E_i/k_BT}} \tag{2}$$

where the $\chi_i(\theta)$ and E_i are, respectively, the normalized eigenvectors and eigenvalues obtained from solving the one-dimensional vibrational Schroedinger equation, viz.

$$\left(\frac{\hbar}{2\mu R_0^2}\frac{\partial^2}{\partial\theta^2} + \mathrm{V}(\theta) - E_i\right)\chi_i(\theta) = 0 \tag{3}$$

Table II. Vibrational Energetics and Expectation Values for 1

vib. level	$\langle\theta^2\rangle^{1/2}$ (deg)	$\langle a_C\rangle$ (G)	$\langle a_H\rangle$ (G)	energy (cm^{-1})
0	5.8	32.8	-25.6	258.3
1	9.6	49.3	-22.6	844.8
2	11.7	61.2	-20.6	1519.4
Boltzmann average[a]	5.8	32.8	-25.6	

[a] T = 77 K.

Table III. Vibrational Energetics and Expectation Values for 2

vib. level	$\langle\theta^2\rangle^{1/2}$ (deg)	$\langle a_C\rangle$ (G)	$\langle a_F\rangle$ (G)	$\langle a_H\rangle$ (G)	energy (cm^{-1})
0	7.6	48.8	71.6	-23.0	177.0
1	10.2	64.5	72.8	-18.1	330.9
2	10.6	65.4	72.3	-17.9	701.1
Boltzmann average[a]	7.7	49.6	71.7	-22.7	

[a] T = 77 K.

The reduced mass, μ, may be obtained from the inverse G matrix element[22] for the out-of-plane bending coordinate,[23] and R_0 is the equilibrium CH or CF bond length. The potential function V is obtained from a polynomial fit to the total electronic energy (Figure 1) truncated in this case after the quartic term. Numerical solution[24] of eq 3 then affords the requisite eigenvectors and energy eigenvalues for eq 2. Tables II and III present the results from these calculations.

Chipman[5d] has earlier performed just such an analysis for **1** employing a sextic potential. His value of 5.7° for $\langle\theta^2\rangle^{1/2}$, which by its deviation from the equilibrium value of θ gives some indication of the importance of vibrational motion, agrees closely with that obtained here. Chipman also noted that contributions to the experimental hyperfine coupling from vibrational states above the lowest were negligible at the experimental temperature (77 K); that is also observed here, as expected. The improvement in predicted hfs for **1** is considerable, especially for a_C where out-of-plane bending accounts for 10.2 G.

Unlike **1**, the more shallow, anharmonic potential for **2** allows a ca. 6% contribution from the first excited vibrational level. Again, a sizable deviation of $\langle\theta^2\rangle^{1/2}$ from the equilibrium θ is noted. While the difference is not as large in magnitude as that for **1**, it occurs in a region where both a_C and a_H change rapidly as functions of θ. This gives rise to a decrease of 23 and 7.3 G in the predicted values for a_C and a_H, respectively. A significant improvement in comparison to experiment is again noted. While the predicted a_F moves in the proper direction, it still remains 7.4 G too high. It may be that consideration of other normal modes would correct this, although the good

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[21] Bent, H. A. *Chem. Rev.* **1968**, *68*, 587.

[22] Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1955. (b) Herzberg, G. *Infrared and Raman Spectra*; D. Van Nostrand: Princeton, 1945.

[23] For an XYZ$_2$ molecule with Y the central atom, $\mu^{-1} = {}^{1}/_{3}m_{\mathrm{X}^{-1}} + {}^{2}/_{3}m_{\mathrm{Z}^{-1}} + 3m_{\mathrm{Y}^{-1}}$, Lindeman, L. P.; Wilson, M. K. *J. Chem. Phys.* **1956**, *24*, 242.

[24] (a) Truhlar, D. G. *J. Comp. Phys.* **1972**, *10*, 123. (b) Quantum Chemistry Program Exchange, QCPE no. 203.

agreement in a_F found for 3 and 4 suggests that the CF stretch is unimportant. It is more likely that these small discrepancies arise from θ being only an approximation, albeit a good one in the small angle limit, to the true inversion normal-mode coordinate for 2.

In both cases, it is again noteworthy that *UHF-derived hfs values* are significantly too high for carbon and fluorine and too low for hydrogen (Table I) and would remain so even after vibrational correction. Indeed, for a_C of 1 and a_H of 2, agreement with experiment would become still more poor!

A final item of interest is the effect of increasing fluorine substitution on the angular dependence of the hfs values. Although a_C monotonically increases with increasing θ for the entire fluoromethyl series, a decrease in the *rate* of increase at high θ is noted for 2–4, i.e., the curves have a point of inflection. This effect becomes more pronounced with each subsequent fluorine addition.

At a given θ, the increase in the magnitude of a_C with increasing fluorine substitution is consistent with the expected redistribution of more s character to the nonbonding SOMO and more p character to the C–F bonding orbitals.[21] Consideration of the dependence of the fluorine and hydrogen hfs values on θ provides an interesting insight into the SOMO hybridization. The monotonically increasing values of a_H with increasing θ imply enhanced contribution (in a bonding sense) of hydrogen s AO's to the SOMO. It is interesting that incorporation of fluorine s AO's into the SOMO appears to be avoided as rigorously as possible. Thus, a_F in 2 and 3 only increases very slightly (relative to a_C and a_H) as the planar radical pyramidalizes. On the other hand, a_H increases at a rate determined by the number of hydrogen atoms that may contribute to the SOMO—the fewer atoms, the more contribution per atom, and the greater the sensitivity of a_H to θ. It is especially noteworthy that in 4, where with pyramidalization delocalization of spin to the highly electronegative fluorine atoms can no longer be as effectively avoided, a_F responds much more dramatically to increasing θ. Finally, as with a_C, an inflection at high θ, which goes so far as to cause the curves to pass through a maximum, is observed for a_F.

In addition to providing insight into the conformational sensitivity of hfs constants in methyl radicals substituted with electron-withdrawing groups, this investigation demonstrates the potential of the MP2 approach for calculation of isotropic hyperfine coupling. We have obtained results of similar quality for molecules containing one or more of several atoms from the first two rows of the periodic table.[16a,b] The high accuracy, reasonable speed,[25] and ready availability of code[17,24] for this technique should be particularly useful to those researchers seeking cogent relationships between structure and spectroscopy.

Acknowledgment. Funding for this work was provided under projects 1C162622A553I and 1L161102A71A. I am deeply indebted to Professor Don Truhlar for generously providing insight and advice.

Registry No. 1, 2229-07-4; 2, 3744-29-4; 3, 2670-13-5; 4, 2264-21-3.

Supplementary Material Available: Optimized singly constrained geometries (UHF/6-31G*) and energies and hfs values (UMP2/6-311G**//UHF/6-31G*) for all structures (4 pages). Ordering information is given on any current masthead page.

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(25) As a benchmark, calculation of the MP2 Fermi contact integrals for a single CF_3 geometry required ca. 7000 cpu s on a Stardent Titan equipped with two P2 processors.

Reactions of Methylene with Hexamethyl(Dewar benzene)[†]

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Received October 16, 1990

Introduction

Hexamethyl(Dewar benzene), 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene (HMDB), has been of interest both theoretically and experimentally since it is a prototypical example of a molecule that is thermodynamically unstable (ΔH = −56 to −60 kcal/mol for conversion to hexamethylbenzene, HMB[1,2]), yet is kinetically stable (E_a = 35–37 kcal/mol,[1-5] corresponding to less than 1% conversion to HMB after 2 days at 100 °C).[6] The thermodynamic instability reflects both the ring strain of HMDB and the aromatic stabilization of HMB. The kinetic stability is attributed to the constraints of orbital symmetry, which dictate that the allowed ring opening should be conrotatory, while the geometric necessity is a disrotatory ring opening.[7] The central C–C bond of HMDB is 163 pm, claimed to be the longest C–C single bond on record.[8]

HMDB undergoes a number of reactions with electrophiles[9-12] and free radicals,[13] most commonly involving rearrangements of the carbon skeleton. Reactions of HMDB with carbenes or carbenoids have been reported in a few cases. Reaction with dichlorocarbene apparently begins with a cycloaddition product, which undergoes subsequent rearrangement and elimination, as well as a second cycloaddition.[14,15] Metal-catalyzed decompositions of diazomethane presumably give rise to carbenoids, which in the presence of HMDB give the simple single- or double-cycloaddition products, assigned the exo stereochemistry.[16,17] The C–H insertion reactions that are typical of free carbenes have not been observed in reactions with HMDB.

This research project was undertaken in order to determine the products of reaction of HMDB with free methylene. Beyond the opportunity to observe C–H insertion products from HMDB, several intriguing possibilities from such a reaction come to mind. Typical C–H insertion reactions of methylene are highly exothermic; thus such a reaction would be a means of injecting an additional 80–90 kcal/mol of internal energy into HMDB, with unknown consequences. For example, could the exothermicity of the C–H insertion reaction help initiate the ring opening? In addition, we believed that the unusually long C–C bond in HMDB would be an appropriate candidate for a carbene C–C insertion reaction, which has never been observed before.[18]

Experimental Section

Materials. HMDB (Aldrich) was distilled at 58–61 °C (25 Torr) and stored under nitrogen at −15 °C. HMB, Diazald, and 2-(2-ethoxyethoxy)ethanol were obtained from Aldrich and used as received. Anhydrous diethyl ether was from EM Science.

Generation and Reaction of Methylene with HMDB. An Aldrich Mini-Diazald apparatus was used to generate diazomethane in the standard manner.[19] A detailed account of an ethanol-free preparation is described below. Potassium hydroxide

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[†] Dedicated to Professor Joseph F. Bunnett on the occasion of his retirement.

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0022-3263/91/1956-5232$02.50/0