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.

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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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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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Table I. Reaction Conditions and Product Yields for Generation of Diazomethane from Diazald and Photochemical Decomposition in the Presence of HMDB in Ether

cosolvent	Diazald (mmol)	HMDB (mmol)	mole ratio (Diazald/HMDB)	irradiation time (min)	% yield			ratios	
					1	2	3	I/C[a]	2/3[b]
EtOH	4.7	0.0		85	0.0	0.0	0.0		
none	0.0	3.1	0.0	90	0.0	0.0	0.0		
EtOH	5.0	3.1	1.6	75	1.7	3.4	1.5	2.9	2.3
EtOH	14.1[c]	4.7	3.0	260[c]	3.3	6.9	3.1	3.0	2.2
EEE[d]	7.1	4.7	1.5	110	2.7	5.1	2.3	2.7	2.2
EEE[d]	14.2[c]	3.6	3.9	205[c]	5.3	11	5.6	3.1	2.0

[a] Ratio of insertion to cycloaddition ([**2** + **3**]/**1**). [b] Ratio of allylic insertion to bridgehead insertion (**2**/**3**). [c] Total of two sequential batches. [d] 2-(2-Ethoxyethoxy)ethanol.

pellets (0.8 g, 14 mmol), deionized water (1.2 mL), diethyl ether (2.4 mL), and 2-(2-ethoxyethoxy)ethanol (4.2 mL) were placed in the reaction chamber. Diazald (1.52 g, 7.1 mmol) in 13.5 mL of diethyl ether was placed in the dropping funnel above the reaction chamber. Freshly distilled HMDB (0.76 g, 4.7 mmol) and diethyl ether (1.0 mL) were placed in the receiving flask, which was cooled in an ice/salt bath. The reaction chamber was warmed to 65 °C with a water bath, the Diazald solution was added slowly over about 6 min, the dropping funnel was rinsed with two 1-mL aliquots of ether, and the reaction chamber was maintained at 65 °C for an additional 30 min. The yellow solution in the receiving flask was photolyzed directly with a Bausch & Lomb SP-200 xenon-mercury 200-W lamp. A mirror was placed at an angle underneath the flask to maximize the light intensity and minimize irradiation of the vapor phase. During the irradiation, gas bubbles evolved and the yellow color slowly disappeared. Irradiation was continued for a few minutes past the point at which the solution turned colorless. (For typical irradiation times, see Table I.) The solution was dried over anhydrous sodium sulfate and solvent removed by rotary evaporation, leaving a single clear liquid phase. If the diazomethane is prepared with ethanol rather than 2-(2-ethoxyethoxy)ethanol, two separate liquid phases appear at this point since HMDB is immiscible with ethanol. Samples of the concentrated reaction solution were analyzed by GC/MS, and individual products were isolated via preparative gas chromatography. Since typical runs converted only about 10% of the original HMDB, product yields were enhanced for preparative runs by preparing and photolyzing a second batch of diazomethane in the same receiving flask once the first batch had been completely photolyzed.

Gas Chromatography. Analytical gas chromatography with mass spectrometric detection was carried out on a Hewlett-Packard 5995C GC/MS instrument using a 12-m cross-linked silicone gum column. Helium was the carrier gas, and the column temperature was programmed from 40 °C at the rate of 10 °C min^{-1}. Relative yields of the volatile products were calculated by comparing the total ion counts of the product peaks with the sum of all products and HMDB. Preparative gas chromatography was carried out on a Carle AGC-111 GC instrument with a 2-m column of 10% FFAP on Chromosorb W-HP (100–120 mesh). The column was baked at 200 °C overnight before each use. The most successful collection conditions employed a column temperature of 70 °C, a helium flow rate of less than 1 mL/s, and injection of a 50-μL aliquot of the concentrated reaction solution. Fractions that eluted after the large HMDB peak were collected in cooled glass ampules (4 mm × 22 cm). The fractions were rinsed out of the ampules directly into NMR tubes with a minimal amount of $CDCl_3$. In both analytical and preparative gas chromatography, three major products were observed to elute shortly after HMDB. All three of these products showed parent molecular ions of 176 (HMDB + CH_2); several other minor peaks were observed, but none showed parent molecular ions of 176. Typical retention times for the analytical GC/MS conditions described above are as follows: HMDB, 2.3 min; **1**, 3.0 min; **2**, 3.3 min; **3**, 3.5 min. Samples recovered by preparative GC were reanalyzed by GC/MS. This confirmed that the three products eluted in preparative GC in the same order as they did in analytical GC. The GC/MS analyses of the isolated products showed that they were invariably contaminated with some of the other products; typical compositions are as follows. **1**: >70% **1**, <30% **2**. **2**: >85% **2**, <15% **3**. **3**: >90% **3**, <10% **2**.

NMR Spectrometry. Proton NMR spectra were taken on a Bruker AC-300 (300-MHz) or a Bruker AMX-400 (400-MHz) instrument with $CDCl_3$ as solvent and referenced to either TMS or $CHCl_3$ (7.24 δ). The presence of the other products could be detected by their NMR spectra, and the relative amounts agreed with the GC/MS analyses described above. In addition, the NMR spectra of all three products isolated from preparative GC showed two prominent peaks from an unidentified impurity at 1.54 δ and 1.26 δ.[20] The amount of this impurity, which did not appear to be detectable by GC/MS, varied from preparation to preparation and further compromised the purity of the three products. In addition, small peaks attributable to HMDB, HMB, or other products were noted in some cases.

***exo*-1,2,4,5,6,7-Hexamethyltricyclo[3.2.0.0^{2,4}]hept-6-ene (1).** The first product gave an NMR spectrum consistent with that reported in the literature.[16,17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (s, allylic hydrogens), 1.08 (s, bridgehead methyls), 0.80 (s, cyclopropyl methyls), 0.88 (d, J = 4.3 Hz) and 0.24 (d, J = 4.3 Hz, cyclopropyl hydrogens). MS: 176 (M^+, 13), 161 (100), 147 (10), 133 (28), 131 (20), 123 (18), 121 (21), 119 (31), 117 (10), 115 (16), 107 (52), 105 (33), 91 (35), 77 (26).

2-Ethyl-1,3,4,5,6-pentamethylbicyclo[2.2.0]hexa-2,5-diene (2). The structure of product **2** was assigned on the basis of the NMR spectrum, which clearly showed the diastereotopic hydrogens expected for the 2-ethyl group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (overlapping quartets, assigned to one of the diastereotopic hydrogens, with coupling to the neighboring methyl, J = 7.6 Hz, and the geminal hydrogen, J = 15.2 Hz; also noted was a small splitting to the neighboring allylic methyl, quartet, J = 1.5 Hz), 1.98 (overlapping quartets, the other diastereotopic

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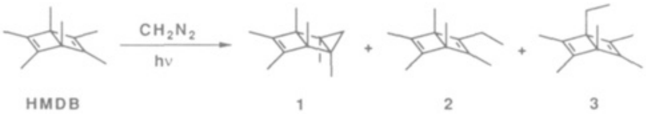
Scheme I. Products from the Reaction of Methylene with HMDB



hydrogen, coupled to the neighboring methyl, $J = 7.6$ Hz, and the geminal hydrogen, $J = 15.2$ Hz, as described for the 2.11 δ peak), 1.61 (doublet, $J < 1$ Hz, coupling to one of the diastereotopic ethyl hydrogens confirmed by a COSY spectrum) and 1.59 (singlet, six allylic hydrogens), 1.07 and 1.06 (equal singlets, bridgehead methyls), 0.97 (triplet, $J = 7.6$ Hz, methyl of ethyl group). MS: 176 (M^+, 14), 161 (100), 147 (14), 133 (16), 131 (19), 119 (19), 117 (10), 115 (11), 105 (21), 91 (22), 77 (13).

1-Ethyl-2,3,4,5,6-pentamethylbicyclo[2.2.0]hexa-2,5-diene (3). The structure of product **3** was assigned on the basis of its NMR spectrum, which clearly showed two equivalent sets of allylic methyls, weakly coupled to one another. ^1H NMR (400 MHz, $CDCl_3$): δ 1.64 and 1.59 (quartets of equal intensity, $J = 1.4$ Hz, allylic hydrogens), 1.12 (singlet, bridgehead methyl), 0.95 (triplet, $J = 7.6$ Hz, methyl of ethyl group), 1.62 (quartet, $J = 7.6$ Hz, methylene of ethyl group). MS: 176 (M^+, 14), 161 (100), 147 (17), 133 (16), 131 (18), 119 (23), 117 (9), 115 (9), 105 (20), 91 (22), 77 (16).

Results

Control Reactions. Generation and photodecomposition of diazomethane in the absence of HMDB (Table I, line 1) gave the three reported products from reaction of methylene with ether: ethyl methyl ether, ethyl *n*-propyl ether, and ethyl isopropyl ether.[21] Each of these compounds was identified by comparison of its mass spectrum with that found in the database of the GC/MS spectral library. No products that would interfere with the analysis of HMDB or its products were observed. Since there was always a great excess of ether over HMDB in all runs, it was presumed that these products were formed in all runs, although they were not routinely analyzed quantitatively.

Irradiation of a solution of HMDB in ether (without diazomethane present) under conditions that simulated typical reaction conditions (Table I, line 2) did not lead to any significant change in the observed GC/MS analyses.

Reaction of Methylene with HMDB. Photodecomposition of diazomethane in the presence of HMDB gives rise to three products that can be clearly identified as methylene adducts with HMDB by their parent molecular ions at 176 ($C_{13}H_{20}$). The three products elute after HMDB and are formed in a characteristic ratio under a variety of reaction conditions (the ratio of **1**:**2**:**3** is roughly 1:2:1; see Table I). The products were shown to be the reported cycloaddition product (**1**) and the two unreported but expected insertion products (**2** and **3**) (Scheme I).

Discussion

The reaction conditions were designed to generate methylene in a singlet state, and the observed products are those that would be expected for the reaction of singlet methylene with HMDB. The insertion reactions produce the major products with very little selectivity displayed toward the two types of C–H bonds available. The ratio of products **2**:**3** (2.0–2.3) is only marginally greater than the ratio of the abundance of hydrogens on allylic or bridgehead methyl groups. This is consistent with the low selectivity in C–H insertions generally observed for singlet methylene, whereby allylic C–H bonds show reactivity essentially equal to that of nonallylic C–H bonds.[22]

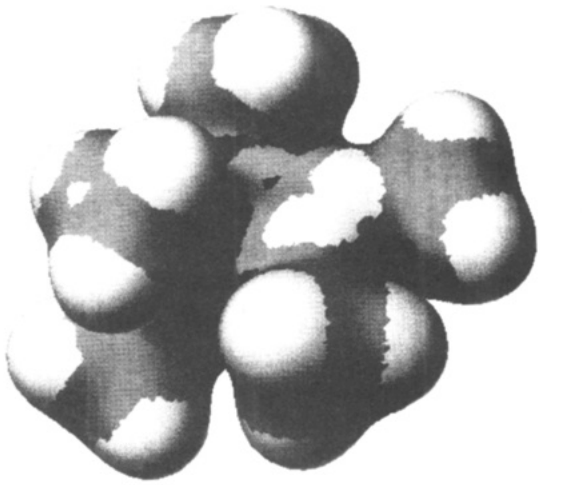


Figure 1. Electron-density model of HMDB (Tektronix CAChe system running MOPAC version 5.10). The shading indicates the relative gradient of the electron-density contour (darker represents a lower gradient at the contour boundary).

Cycloaddition to a π bond, giving rise to **1**, produces only about 25% of the total product. This is a relatively low ratio, compared, for example, to neat liquid *cis*-2-butene, which gives nearly 50% cycloaddition products under comparable reaction conditions.[23] Calculated as reactivity per C=C bond versus reactivity per C—H bond, HMDB shows a reactivity ratio of about 3:1 (from Table I, the total I/C of about 3 can be normalized by 18 C—H bonds and two C=C bonds to give a cycloaddition:insertion ratio of about 3). Most aliphatic alkenes show a cycloaddition: insertion ratio of about 6–9.[22] The low reactivity of the π bond of HMDB is probably caused by steric hindrance of the methyl groups, illustrated by a model of the electron density in Figure 1.

The possibility of a C–C insertion reaction at the unusually long central bond of HMDB was not detected. The product of such a reaction would have a norbornadiene structure and would be expected to be stable under the reaction conditions. The steric hindrance of the bridgehead methyl groups appears to be very significant around the central C–C bond (see Figure 1).

It was also of interest to determine whether the C–H insertion products, which are still Dewar benzenes, showed any unusual reactivity that could be related to the excess energy released in the reaction. A minor product was detected with a very long retention time (just after HMB) and a mass spectrum consistent with ethylpentamethylbenzene. Its yield was about 5–10% of the small HMB impurity, which is consistent with its formation by direct reaction of methylene with HMB rather than decomposition of either **2** or **3**.

Acknowledgment. This work constituted the senior thesis of S.D.R. at Reed College. The 400-MHz NMR spectra were obtained at Portland State University with the expert assistance of Professor David H. Peyton.

Abbreviations: HMB, hexamethylbenzene; HMDB, hexamethyl(Dewar benzene) (1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene).

Supplementary Material Available: ^1H NMR spectra (400 MHz) of compounds **1** and **2** (2 pages). Ordering information is given on any current masthead page.

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