separate NMR tube experiment, 30 mg of **3** was treated with 18.6 mg of iodine. The reaction was seen to proceed cleanly with quantitative formation of $C_6(CH_3)_5CH_2I$ and (*E*)-CHI=CH(CMe_3) and Ta(OR)$_2$I$_2$Cl: ^{1}H NMR spectrum $C_6(CH_3)_5CH_2I$ ($CDCl_3$) δ 4.41 (s, 2 H, CH_2I), 2.14 (s, 3 H, *p*-CH_3), 2.11 and 2.10 (s, 6 H each, *o*- and *m*-CH_3); (*E*)-CHI=CH(CMe_3) (C_6D_6) δ 6.41 (d, 1 H, $^3J_{HH}$ = 15.8 Hz, CHI=CH(CMe_3)), 5.73 (d, 1 H, $^3J_{HH}$ = 15.8 Hz, CHI=CH(CMe_3)), 0.68 (s, 9 H, CHI=CH(CMe_3)).

Deuteriolysis of (η^1-$C_6Me_5CH_2$)Ta($CH_2CH_2CH_2Cl$)(OR)$_2$Cl (5). To a solution of 0.5 g (0.62 mmol) of **5** in 1.0 mL of acetonitrile-d_3 was added 0.3 mL (16.6 mmol) of D_2O. After stirring for 2 h all of the reaction volatiles were distilled into a small ampoule cooled to -196 °C which contained a small amount of activated alumina. The reaction volatiles were allowed to reach room temperature and filtered into an NMR tube. ^{1}H NMR spectroscopy revealed the presence of $DCH_2CH_2CH_2Cl$. The solid remaining from the original reaction mixture was extracted with diethyl ether. The resulting solution was filtered and dried over activated alumina, and the solvent was removed under reduced pressure to yield a white, oily solid. A white crystalline solid was sublimed out at 50 °C and 10^{-3} Torr and shown by ^{1}H NMR spectroscopy to be $C_6(CH_3)_5(CH_2D)$: partial ^{1}H NMR spectrum $DCH_2CH_2CH_2Cl$ (in CD_3CN) δ 0.96 (1:2:1 triplet ($^3J_{HH}$ = 7.3 Hz) of 1:1:1 triplets ($^2J_{HD}$ = 2.2 Hz), 2 H, CH_2D); $C_6(CH_3)_5(CH_2D)$ (in $CDCl_3$) δ 2.124 (s, 15 H, CH_3), 2.106 (1:1:1 t, 2 H, $^2J_{HD}$ = 2.2 Hz, CH_2D).

Kinetics of Reaction of (η^6-C_6Me_6)Ta(OR)$_2$Cl (1) with 3,3-Dimethyl-1-butyne. A solution of 0.5 g (0.68 mmol) of **1** in 20 mL of diethyl ether was treated with a large excess (4 mL, 34 mmol, 50 equiv) of 3,3-dimethyl-1-butyne at 25 °C. The reaction was sampled at hourly intervals by withdrawing 0.5 mL of the reaction mixture, removing the solvent under reduced pressure, and dissolving the resulting solid in C_6D_6. The relative concentration of **1** in each sample was determined from monitoring the η^6-C_6Me_6 resonances by ^{1}H NMR spectroscopy. The first-order rate law $\ln [\mathbf{1}] = -kt + \ln [\mathbf{1}]_{t=0}$ is obeyed over at least 3 half-lives as a plot of $-\ln \{[\mathbf{1}]/[\mathbf{1}]_{t=0}\}$ vs t is linear (correlation = 0.9991) with k_{obsd} = 0.174 h^{-1} and $t_{1/2}$ = 3.98 h.

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Synthesis and Reactions of 5-Methylenebicyclo[2.2.0]hex-2-ene Derivatives from Hexamethyl(Dewar benzene)

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Abstract: Treatment of hexamethyl(Dewar benzene) (HMDB) with *tert*-butyl hypochlorite provides a rearranged chlorinated derivative, *exo*-6-chloro-1,2,3,4,6-pentamethyl-5-methylenebicyclo[2.2.0]hex-2-ene (**1**). Thermal rearrangement of **1** gives pentamethylbenzyl chloride (**4**); the activation energy decreases in more polar solvents, suggesting an ionic intermediate during the chloride migration and/or ring opening. The intermediate is postulated to be a delocalized carbocation that can be intercepted by nucleophiles to give substitution products. Treatment of **1** with $NaOCH_3$ in methanol gives two isomeric methoxide substitution products, **2** and **3**, in a 60:40 ratio. The structure of **2** involves the same skeletal structure and retention of stereochemistry relative to **1**; the structure of **3** indicates neighboring group participation of the transannular π bond. The rate law for the formation of **2** and **3** is first order in **1** and independent of $NaOCH_3$ concentration. A common ion rate depression is observed, added chloride ion causing a decreased rate of formation of both **2** and **3** equally, indicating reversible ionization to a common delocalized carbocation. Thermolysis of **2** gives hexamethylbenzene plus formaldehyde; NMR spectra provide evidence for a methylenecyclohexadiene intermediate, indicating that ring opening precedes loss of formaldehyde. Inclusion of basic alumina in the thermolysis of **2** diverts the reaction to formation of pentamethylbenzyl methyl ether (**5**). Thermolysis of **3** gives a complex mixture of products, including **5**.

Hexamethyl(Dewar benzene) (HMDB; 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene) has been a compound of both synthetic and theoretical interest. It is readily synthesized from 2-butyne,[1] making it the most accessible of the Dewar benzenes. The Dewar benzenes are a class of compounds that have an available reaction (aromatization) which is highly favorable thermodynamically (ΔH = -60 to -56 kcal/mol for HMDB)[2] yet relatively unfavorable kinetically, due to orbital symmetry constraints[3] (E_a = 31-37 kcal/mol for HMDB,[2,4] 23 kcal/mol for the parent Dewar benzene[5]).

Our original intention was to study substituted Dewar benzenes to determine the effect of substituents on the kinetics and thermodynamics of the Dewar benzene aromatization and conversely to determine the effect of the Dewar benzene system on neighboring functional group reactions. However, rearrangements are among the most common reactions of the Dewar benzene skeleton, particularly induced by electrophilic reagents.[6] Although we sought to avoid electrophilic conditions, each of the derivatives

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† Based in part upon the M.A. Theses of D. D. Ngo and M. J. Rodriguez at California State University, Fullerton.

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we have prepared has involved rearrangements, such that each of the substituted derivatives no longer include the Dewar benzene skeleton. The rearranged products incorporate functional groups at reactive positions that include various combinations of cyclobutyl, cyclopropylmethyl, allylic, and homoallylic. Of the various rearrangement reactions that are conceivable, several different types are observed in the thermal and substitution reactions.

Experimental Section

Materials. Hexamethyl(Dewar benzene) (HMDB) was prepared from 2-butyne[1a] or obtained from Aldrich Chemical Co., distilled at 38–40 °C (1 Torr), and stored at 0 °C (mp 7–8 °C) until use. *tert*-Butyl hypochlorite was prepared by chlorination of *tert*-butyl alcohol, distilled at 80 °C, stored under nitrogen at 0 °C, and freshly distilled before use.[7] Sodium methoxide stock solution was prepared by dissolution of clean sodium chunks, quickly rinsed with reagent grade methanol, into 1 L of freshly distilled methanol. The solution was filtered and sealed with a rubber septum under nitrogen. Standardization against potassium hydrogen phthalate indicated a concentration of 1.08 M immediately after preparation and 1.05 M at the conclusion of its use several months later.

Spectroscopic Methods. Infrared spectra were taken on either a Perkin-Elmer Model 399 or Model 710B and calibrated with polystyrene film. Routine proton NMR spectra were taken on a Varian Model EM-360, using internal TMS standard. Lanthanide shift experiments were carried out with tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium ($Eu(fod)_3$), purchased from Aldrich. Four different concentrations of $Eu(fod)_3$ were added, ranging from 0.02 to 0.18 mol per mol of substrate analyzed. All ^1H NMR absorptions were observed to shift linearly in proportion to the concentration of $Eu(fod)_3$ added. The shifts fell into two categories: strongly affected absorptions that were shifted between 0.5 and 1.0 ppm over the concentration range studied, and weakly affected absorptions that were shifted less than 0.3 ppm. Kinetic analyses with ^1H NMR were obtained on a Varian FT-804 instrument (located at U.C. Irvine), using $CDCl_3$ as internal standard. Carbon-13 NMR spectra were obtained on a Varian CFT-20 instrument, using TMS as internal standard and deuterium lock. Mass spectra were obtained on a Varian MAT-111 spectrometer, with calibration based upon perfluorokerosene fragmentations.

Chromatographic Methods. Thin-layer chromatography was performed on prepared plates containing 100 μm silica gel and fluorescent indicator, available from Eastman. Visualization of the Dewar benzene derivatives was particularly striking upon exposure to HCl vapor: HMDB, pink; **1**, blue; **2** and **3**, different shades of purple. Column chromatography was necessary to separate isomers **2** and **3**; occasionally compound **1** was present as well. With use of basic alumina (Woelm grade 1, 30 × 2 cm column) and petroleum ether (30–60 °C) as eluent, **2** elutes between 200 and 400 mL and **3** between 400 and 900 mL. With use of silica gel CC-7 (60 g) and 50:1 hexane:ether as eluent, **1** elutes in the first 80 mL, **2** elutes between 80 and 280 mL, and **3** elutes between 280 and 550 mL. Individual fractions are readily monitored by the TLC method described above.

Kinetic Methods (Substitution Reactions). Samples for kinetic analysis consisted of a total of 20 mL of solution, prepared in 25 × 150 mm test tubes that were thermostated in a 1-L insulated water bath held at 25.0 ± 0.1 °C. The appropiate volumes of stock $NaOCH_3$ solution, pure methanol, and any added salt (previously dissolved in methanol) were stirred together. Radical inhibitor, 4,4′-bis(2,6-di-*tert*-butylphenol) (Ethyl Corporation), was added to make a concentration of 0.01 M; this amount was shown not to affect the measured rates. After the solution had equilibrated in temperature, the appropriate volume of **1** was injected by syringe, with continued stirring, and timing was begun. Each run consisted of nine different 2-mL aliquots removed for analysis at regular time intervals. Each aliquot was pipeted into a test tube containing 2 mL of pentane and 2 mL of 0.5 M aqueous $NaHCO_3$ solution. The pentane layer was removed, concentrated by rotary evaporation at room temperature, and analyzed by NMR with 0.5 mL of $CDCl_3$ as solvent. Selected NMR absorptions were specific for quantitation of **1**, **2**, and **3**: δ 3.0 (3 H, methoxy group of **3**); δ 3.2 (3 H, methoxy group of **2**); δ 4.92 and 5.06 (2 H, vinyl hydrogens of **1**). The integration in the δ 5 region was corrected for the vinyl absorptions of **2** and **3**, based upon the concentrations calculated from the δ 3 region. All kinetic runs went to less than 10% conversion, so these were typically small but well-defined corrections to the concentration of **1**. The sum of the concentrations of **1**, **2**, and **3** was normalized to the initial concentration of **1**. There was no NMR evidence for any other products besides **2** and **3** in any run, except the run including sodium azide (see Results section).

Reaction rates were determined by the method of initial rates. Plots of the concentration of **1** vs time were linear during the first 10% of reaction, and the slope was taken to be the initial rate. Rate constants were calculated both from the initial rates and by plots of ln [**1**] vs time. The latter method gave rate constants that were consistently approximately 4% higher than the method of initial rates. The rate constants reported are the averages from the two methods.

Kinetic Methods (Thermolysis Reactions). Thermal reactions were carried out in thick-walled NMR tubes that were degassed through 3 freeze-pump-thaw cycles to an ultimate vacuum of 1 Torr and then sealed under vacuum. The samples were immersed completely in an insulated oil bath held at a fixed temperature measured to 0.1 °C. At regular intervals, the samples were removed and immersed in ice water to halt the reaction, and NMR spectra were taken. Each of the thermal reactions involved NMR spectra that were sufficiently characteristic to monitor reactants and products separately.

Synthesis of 1. Hexamethyl(Dewar benzene) (8.0 g, 50 mmol), carbon tetrachloride (150 mL), and a magnetic stirring bar were introduced into a 250-mL three-necked flask fitted with a pressure-equalizing dropping funnel, a Dewar-type reflux condenser containing ice, and a gas inlet tube. A calcium chloride tube was attached to the condenser and the apparatus was flushed with dry deoxygenated nitrogen for 2 min. Magnetic stirring was started and the flask was cooled in an ice bath for 15 min. Freshly distilled *tert*-butyl hypochlorite (5.6 g, 50 mmol) was added from the dropping funnel over a period of 15 min and stirring was continued for 1 h after the addition was completed. The reaction mixture was then stored under nitrogen in the refrigerator overnight. Removal of the solvent on a rotary evaporator at room temperature left a viscous straw-colored oil that, upon distillation under reduced pressure, yielded 4.75 g of **1** (49%): mp 19–21 °C; bp 49–50 °C (1 Torr); IR (neat) 3060 (w), 2970 (s), 2950 (s), 2930 (s), 2910 (s), 2860 (s), 1680 (w), 1660 (m), 1440 (s), 1400 (w), and 1370 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.26 (s, 3 H), 1.60 (s, 3 H), 1.63 (s, 6 H), 4.92 (s, 1 H), and 5.06 (s, 1 H); ^{13}C NMR (C_6D_6) δ 162.9 (s), 146.8 (s), 144.1 (s), 108.6 (t), 78.1 (s), 61.4 (s), 59.5 (s), 30.7 (q), 15.8 (q), 14.4 (q), 14.2 (q), and 12.7 (q); mass spectrum (*m/e*, rel intensity) M (196, 3), M + 2 (198, 1), M - Cl (161, 20). Anal. ($C_{12}H_{17}Cl$) C, H.

Synthesis of 2 and 3. A sample of **1** (2.5 g, 13 mmol) was introduced into a 200-mL round-bottom flask equipped with a magnetic stirring bar and pressure-equalizing dropping funnel. After the flask had been flushed with dry deoxygenated nitrogen, magnetic stirring was begun and a solution of sodium methoxide (1.7 g, 25 mmol) in 75 mL of absolute methanol was added through the dropping funnel over a period of 5 min. The dropping funnel was then replaced by an ice-cooled Dewar-type condenser fitted with a drying tube containing calcium chloride. The reaction mixture was stirred while being warmed in a water bath maintained at 45–50 °C for about 10 min then at room temperature for another hour. Sodium chloride separated out of the solution. Ice (20 g) was added to the mixture and stirring was continued until all the ice dissolved and the mixture became milky white. The organic material was extracted with four 30-mL portions of chloroform. The chloroform layer was washed once with 30 mL of water, dried over Type 4A molecular sieve, and then filtered. Removal of the solvent on the rotary evaporator at room temperature, followed by distillation (67–70 °C, 1 Torr) gave 1.82 g (73%) of a clear liquid. Proton NMR analysis of this liquid showed the presence of two methoxy singlets at δ 3.0 and 3.2. The oil was dissolved in 1.5 mL of 30–60 °C petroleum ether and chromatographed on a basic alumina column (grade 1, 30 × 2 cm), eluted with petroleum ether (30–60 °C). The first 200 mL of eluent were discarded. The second 180-mL fraction contained compound **2**, and the third 500-mL fraction contained compound **3**.

Compound 2: Complete removal of solvent from the second fraction on the rotary evaporator yielded 210 mg (12%) of a colorless oil: bp 67–70 °C (1 Torr); mp 3–5 °C; R_f(TLC, silica gel, C_6H_6) = 0.43; IR (neat) 3060 (m), 2980 (s), 2950 (s), 2940 (s), 2910 (s), 2860 (s), 2820 (m), 1680 (w), 1660 (m), 1450 (m), 1400 (w), 1120 (s), and 890 cm^{-1} (s); ^1H NMR (C_6H_6) δ 1.12 (s, 3 H), 1.32 (s, 6 H), 1.49 (s, 3 H), 1.51 (s, 3 H), 3.20 (s, 3 H), 4.86 (s, 1 H), 4.90 (s, 1 H); ^{13}C NMR (C_6H_6) δ 160.7 (s), 146.5 (s), 134.1 (s), 107.7 (t), 86.4 (s), 60.3 (s), 58.8 (s), 54.5 (q), 21.9 (q), 15.4 (q), 14.2 (q), 12.7 (q), 11.6 (q); mass spectrum (*m/e*, rel intensity) M (192, 1), M - CH_3 (177, 4), M - OCH_3 (161, 11). Anal. ($C_{13}H_{20}O$) C, H.

Compound 3: The third 500-mL fraction was rotary evaporated to yield 460 mg (25%) of a waxy solid: mp 58–60 °C; bp 67–70 °C (1 Torr); R_f(TLC, silica gel, C_6H_6) = 0.21; IR (neat) 3060 (m), 2970 (s), 2950 (s), 2920 (s), 2860 (s), 2820 (m), 1660 (m), 1450 (s), 1400 (m), and 870 cm^{-1} (s); ^1H NMR (C_6H_6) δ 0.92 (s, 3 H), 1.00 (s, 3 H), 1.18 (s, 3 H), 1.21 (s, 3 H), 1.30 (s, 3 H), 3.00 (s, 3 H), 4.83 (s, 1 H), and 4.96 (s, 1 H); ^{13}C NMR (C_6H_6) δ 163.9 (s), 102.6 (t), 88.9 (s), 54.1 (q),

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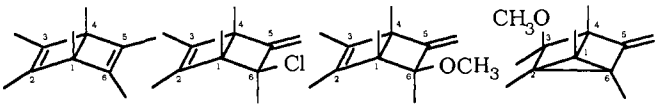
Table I. ^{13}C NMR and ^1H NMR Assignments for HMDB, **1**, **2**, and **3**[a]



HMDB 1 2 3

	skeletal carbons						methyls						methylene	methoxy
	1	2	3	4	5	6	1	2	3	4	5	6	$=CH_2$	$-OCH_3$
HMDB														
^{13}C NMR	56.0	145.0	145.0	56.0	145.0	145.0	10.0	11.0	11.0	10.0	11.0	11.0		
^1H NMR							1.08	1.60	1.60	1.08	1.60	1.08		
1														
^{13}C NMR	61.4	146.8	144.1	59.5	162.9	78.1	15.8	14.4	14.2	12.7		30.7	108.6	
^1H NMR							1.26	1.60	1.63	1.18		1.63	4.92; 5.06	
2														
^{13}C NMR	60.3	146.5	134.1	58.8	160.7	86.4	12.7	15.4	14.2	11.6		21.9	107.7	54.5
^1H NMR							1.32	1.49	1.51	1.12		1.32	4.86; 4.90	3.2
3														
^{13}C NMR	31.1	46.7	88.9	48.7	163.9	27.3	6.8	8.7	25.9	10.5		5.9	102.6	54.1
^1H NMR							1.00	0.92	1.30	1.21		1.18	4.83; 4.96	3.0

[a] Underlined values in the ^1H NMR spectra are those peaks that are strongly shifted in the presence of $Eu(fod)_3$.

48.7 (s), 46.7 (s), 31.1 (s), 27.3 (s), 25.9 (q), 10.5 (q), 8.7 (q), 6.8 (q), 5.9 (q); mass spectrum (*m/e*, rel intensity) M (192, 1), M - CH_3 (177, 5), M - OCH_3 (161, 7). Anal. ($C_{13}H_{20}O$) C, H.

Synthesis of Aromatic Analogues. Pentamethylbenzyl chloride (**4**) was prepared by chlorination of hexamethylbenzene (Aldrich) with sulfuryl chloride: mp 79–81 °C.[8] Pentamethylbenzyl methyl ether (**5**) was prepared by treatment of **4** with sodium methoxide in methanol: mp 66–67 °C.[9]

Results

Structure Determinations for 1, 2, and 3. Chlorination of HMDB with tBuOCl provides a rearranged monochlorinated derivative in about 50% isolated yield, *exo*-6-chloro-1,2,3,4,6-pentamethyl-5-methylenebicyclo[2.2.0]hex-2-ene (**1**). Table I summarizes the NMR evidence upon which the structural assignment is primarily based. The exocyclic methylene group is clearly indicated by the ^{13}C absorption at 108.6 ppm, which is a triplet (or overlapping doublets) in the spin-coupled spectrum. The exo stereochemistry of the Cl substituent is deduced from the greater deshielding effect observed on the bridgehead positions (carbons 1 and 4) compared to the transannular positions (carbons 2 and 3), relative to HMDB. Furthermore, there is strong similarity between both the IR and NMR spectra of compounds **1** and **2**, and lanthanide shift data clearly indicate that **2** has exo stereochemistry. The corresponding bromo derivative has been reported recently and gives a comparable ^1H NMR spectrum.[10]

Treatment of **1** with sodium methoxide in methanol provides a mixture of approximately equal amounts of *exo*-6-methoxy-1,2,3,4,6-pentamethyl-5-methylenebicyclo[2.2.0]hex-2-ene (**2**) and *exo*-6-methoxy-1,3,4,5,6-pentamethyl-2-methylenetricyclo-[2.2.0.$0^{3,5}$]hexane (**3**). The use of a lanthanide shift reagent greatly clarifies the location of the methoxy substituents in **2** and **3**. The absorptions most strongly affected in compound **2** are the bridgehead methyl groups and both vinyl hydrogens, as well as the methoxy group. This suggests that complexation of Eu(III) occurs with the oxygen atom, and perhaps with the π bond as well, on the exo face of the ring. With compound **3**, the lanthanide shift reagent only strongly affects one bridgehead methyl and one vinyl hydrogen, as well as the methoxy group. This suggests that complexation of Eu(III) occurs on the side of the molecule, interacting with the oxygen atom and perhaps edge-on with the π bond. Because the bridgehead methyls are primarily affected while the transannular methyls are unaffected, the substituent is identified in the exo stereochemistry. No lanthanide shift effect was observed for **1**, consistent with the reported absence of such effects for alkyl halides.[11]

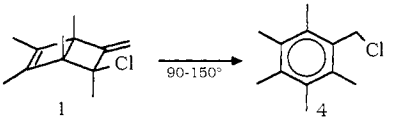
Table II. Solvent Effects on the Rate of Isomerization of **1** to **4**

solvent	*Z* value[a]	temp range, °C	E_a, kcal/mol
cyclohexane	54	120–160	23
$CDCl_3$	63	110–130	18
DMSO	71	90–110	13

[a] Kosower *Z* value, used as an indication of solvent polarity: Kosower, E. M. *An Introduction to Physical Organic Chemistry*; John Wiley: New York, 1968; p 301.

The presence of the three-membered ring in compound **3** is indicated by the three high-field absorptions in both the ^{13}C and ^1H NMR spectra. Furthermore, the location of the infrared out-of-plane bending absorption for the terminal methylene (870 cm^{-1}) is consistent with conjugation to a three-membered ring, as illustrated in a related tricyclic compound.[12]

Thermal Rearrangement of 1. Compound **1** undergoes thermal rearrangement to its aromatic isomer, pentamethylbenzyl chloride (**4**). The progress of the reaction is readily followed by NMR, using the integrated intensity of the vinyl hydrogen absorptions of **1** (δ 4.92 and 5.06, singlets, 2 H) and the benzylic hydrogen absorption of **4** (δ 4.6, singlet, 2 H). The activation energy for



the rearrangement is substantially reduced in solvents of greater polarity, as shown in Table II. In a polar solvent that is also nucleophilic (methanol), compound **1** generates a blue color, comparable to the effect of added acid on **1**. If the methanol is kept strongly basic, nucleophilic substitution rather than rearrangement takes place, as discussed in the following section. We are currently investigating conditions under which both substitution and rearrangement can be observed simultaneously.

Nucleophilic Substitution on 1. In methanolic $NaOCH_3$ solution, **1** undergoes nucleophilic substitution to form two methoxy

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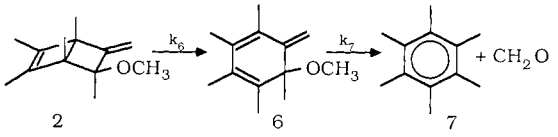
Table III. Observed Initial Reaction Rates and Product Composition for Conversion of **1** to **2** and **3** (Methanol Solvent, 25.0 °C)

run no.	[1], M	[$NaOCH_3$], M	other salts	rate, $\times 10^{-6}$ M s^{-1}	2:3, %
1	0.10	0.05		9.3	55:45
2	0.10	0.09		9.5	62:38
3	0.10	0.10		9.8	60:40
4	0.10	0.12		9.3	61:39
5	0.10	0.20		9.3	63:37
6	0.10	0.40		9.7	60:40
7	0.06	0.10		6.0	61:39
8	0.08	0.10		7.9	66:34
9	0.12	0.10		11.8	59:41
10	0.14	0.10		13.8	66:34
11	0.10	0.10	0.06 M NaCl	8.6	64:36
12	0.10	0.10	0.10 M NaCl	7.7	61:39
13	0.10	0.10	0.16 M NaCl	6.9	58:42
14	0.10	0.10	0.10 M $NaClO_4$	10.9	53:47
15	0.10	0.10	0.10 M NaBr	9.9	58:42
16	0.10	0.10	0.10 M NaI	9.8	58:42
17	0.10	0.10	0.05 M NaN_3	5.3[a]	71:29
18	0.10	0.10	0.10 M NaN_3	4.1[a]	72:28
19	0.20	0.20[b]	0.10 M $AgNO_3$	(very fast)	10:90

[a] Observed rate of formation of (**2** + **3**); additional new products were observed in this case. [b] KOH.

Scheme I



2 6 7

derivatives (**2** and **3**) in a ratio very close to 60:40 for nearly all of the reaction conditions listed in Table III. The rates of formation of these products were determined under a variety of conditions. Initial rates are independent of $NaOCH_3$ concentration (runs 1–6) and are directly proportional to the concentration of **1** (runs 3, 7–10). The presence of added NaCl causes a common-ion rate depression (runs 3, 11–13). Addition of an inert electrolyte, $NaClO_4$, causes a small rate increase (run 14), which we attribute to the normal salt effect. Addition of halide anions (Br^-, I^-) that are better nucleophiles and better leaving groups than Cl^- causes no significant effect on the rate (runs 15 and 16). Addition of NaN_3 depresses the rate of formation of the usual products (runs 17 and 18), slightly shifts the product mixture further in favor of **2**, and causes the formation of new, unidentified products.

Nucleophilic substitution of **1** can also be carried out with methanolic $AgNO_3$. In this case (run 19) the reaction is extremely rapid, and the product ratio strongly favors compound **3** (approximately 10:90 for products **2**:**3**).

Thermolyses of Methoxy Derivatives 2 and 3. Compound **2** undergoes thermal elimination to form as the ultimate products hexamethylbenzene (**7**) and formaldehyde. Hexamethylbenzene is isolated as a crystalline product upon completion of the reaction, while formaldehyde is identified on the basis of formation of its characteristic product with dimedone.[13] The thermolysis of compound **2** was carried out in C_6D_6 solution at temperatures in the range 110–130 °C. During the thermolysis, an intermediate was detectable having the following proton NMR spectrum (δ): 1.30 (s, 3 H), 1.70 (s, 6 H), 1.82 (s, 6 H), 2.90 (s, 3 H), 5.30 (s, 1 H), 5.54 (s, 1 H). Structure **6** was assigned on the basis of these spectral data (Scheme I).

Table IV and Figure 1 illustrate the conversion of **2** to **6** and then to **7** as a function of time and temperature. The relative percentage composition of the reaction mixture was determined by integration of strong, characteristic NMR absorptions for each compound: **2** (δ 3.2, singlet, 3 H), **6** (δ 2.9, singlet, 3 H), and **7** (δ 2.2, singlet, 18 H). The constancy of the total proton count

(13) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley: New York, 1967; p 266.

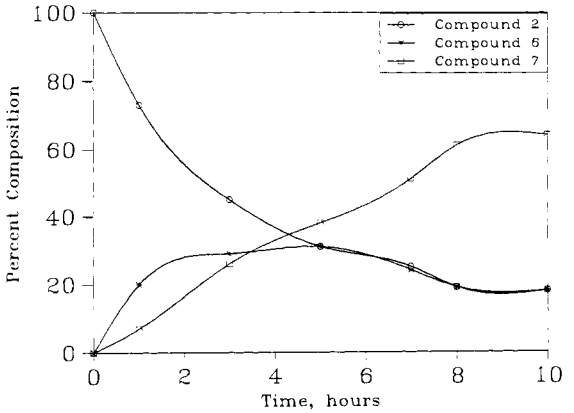


Figure 1. Thermolysis of **2** at 110 °C in C_6D_6.

Table IV. Observed Product Ratios during the Thermolysis of **2** (C_6D_6 Solvent)

	product ratios (2:6:7)		
time, h	110 °C	120 °C	130 °C
0	100:00:00	100:00:00	100:00:00
0.33		80:16:04	66:27:07
0.67		65:25:10	49:32:19
0.83			40:32:28
1.00	73:20:07	57:27:16	32:32:36
1.17			24:27:49
1.50		48:27:25	19:24:57
2.0		34:30:36	
2.5		30:28:42	
3.0	45:29:26	23:19:58	
3.5		23:16:61	
5.0	31:31:38		
7.0	26:24:50		
8.0	20:20:60		
10.0	18:18:64		
k_6, s^{-1}	5.1×10^{-5}	1.31×10^{-4}	3.0×10^{-4}
k_7, s^{-1}	7.0×10^{-5}	1.81×10^{-4}	4.3×10^{-4}

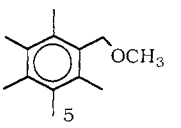
$E_{a6} = 27$ kcal/mol; $A_6 = 1.6 \times 10^{11}$ s^{-1}
$E_{a7} = 28$ kcal/mol; $A_7 = 4.1 \times 10^{11}$ s^{-1}

was confirmed for each spectrum of the product mixture, as were the relative ratios based on other peaks in the spectrum.

The rate constant for conversion of **2** to **6** was determined at low conversions in the usual manner of initial rates. The conversion of **6** to **7** was more complex, since it is both formed and consumed during the reaction. The rate constants were determined during the portion of the reaction for which the concentration of **6** was maximal and hence relatively constant. The observed rate of formation of **7** in this region is also maximal, approximately constant, and directly proportional to the concentration of **6** according to eq 1. Thus k_7 was estimated from the slope of the curve of [7] vs t at the point of maximum concentration of **6**.

$$d[7]/dt = k_7[6] \quad (1)$$

Thermal rearrangement of compound **2** in the presence of basic alumina diverts intermediate **6** to the formation of its aromatic isomer pentamethylbenzyl methyl ether (**5**). Thermal rearrangement of compound **3** gives a much more complex mixture of products, but **5** can be observed in the product mixture as a minor component.

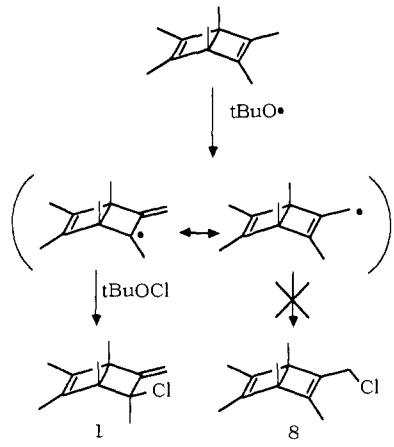


5

Discussion

Synthesis of 1. The Dewar benzene skeleton is susceptible to ring opening and rearrangement reactions. This is particularly

Scheme II



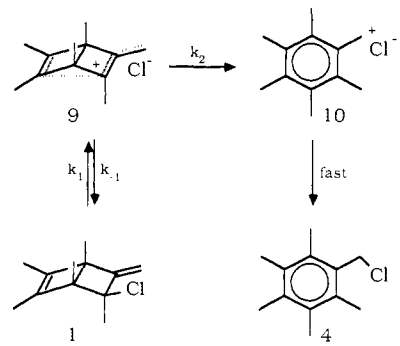
true of hexamethyl(Dewar benzene) (HMDB), with its electron-donating substituents, and especially in the presence of electrophilic reagents or Lewis acid catalysts.[6] We carried out the chlorination of HMDB using *tert*-butyl hypochlorite in CCl_4, which is generally understood to be a free radical chain substitution process.[14] The sole product isolated (**1**) shows only an allylic rearrangement and no evidence for any of the more deep-seated rearrangements typical of electrophilic reagents. Thus we believe that the conversion of HMDB to **1** is a simple free radical chain substitution reaction, as shown in Scheme II.

The radical intermediate of Scheme II has also been prepared by low-temperature photolysis of di-*tert*-butyl peroxide in the presence of HMDB.[15] In those studies, the radical was characterized by its EPR spectrum, and it was noted to be remarkably stable, giving no evidence for ring-opening to the corresponding benzyl radical, even up to 100 °C.

The preference for formation of the tertiary allylic chloride (**1**) over the possible primary structure (**8**), which would have retained the Dewar benzene skeleton, can be attributed to both kinetic and thermodynamic factors. For allylic radicals with both primary and tertiary termini, the tertiary position generally is more favorable kinetically, attributed to a higher free electron density, while the primary position generally leads to the more stable product having the more highly substituted π bond.[16] In this particular case, however, product **1** is expected to be more stable because the π bond is exocyclic rather than confined to a four-membered ring. The strain energy of methylenecyclobutane has been calculated to be 1.7 kcal/mol less than that of 1-methylcyclobutene.[17] Thus both kinetic and thermodynamic arguments point to a preference for the rearranged allylic product. In fact, we have not succeeded in carrying out a substitution reaction of HMDB that retains the basic Dewar benzene skeleton as in **8**. Nevertheless, compound **1** undergoes a fascinating variety of rearrangement and substitution products, which is the major body of work reported in this paper.

Thermal Rearrangement of 1. Thermal rearrangements of Dewar benzene derivatives generally provide the corresponding aromatic isomers as the sole products.[1c,2-5] An early interest in these rearrangements was the question of whether an excited state of the aromatic product could be formed, based on the high exothermicity and high activation energy of the process. We found no evidence for excited state formation during the thermal rearrangement of HMDB to hexamethylbenzene,[18] while others have

Scheme III



$$\text{rate} = (k_1k_2/k_{-1})[\mathbf{1}] \qquad (2)$$

detected a small fraction of the aromatization reaction that leads to excited triplet states.[19,20]

Compound **1** similarly undergoes rearrangement to its aromatic isomer, **4**, at temperatures comparable to those that isomerize HMDB. However, this aromatization reaction involves both a ring opening and a chlorine migration, and the steps could presumably come in either order or occur synchronously. The strong effect of solvent polarity on the observed activation energy of isomerization of **1** (see Table II) suggests that ionization, or at least charge dispersal, is a crucial part of the reaction during or prior to the rate-determining step. We believe the overall evidence best supports a mechanism in which reversible ionization of chloride ion precedes rate-determining opening of the cyclobutene ring, followed by reattachment of chloride (Scheme III).

Although step 2 is rate-determining, increased solvent polarity favors the overall reaction primarily by increasing k_1. The existence of a cationic intermediate such as **9** is supported by the isolation of products from nucleophilic trapping, as discussed in the following section. In those experiments, a common-ion rate depression is observed, indicating that the ionization is reversible. Nucleophilic trapping products from cation **10** have not been observed, although the appropriate choice of solvent and temperature may allow observation of aromatization competitive with nucleophilic substitution. If the mechanism consisted of ring opening preceding the chlorine migration, an intermediate cyclohexadiene would be formed. We have found no evidence for such an intermediate during this rearrangement reaction. In contrast, such an intermediate is readily detected by NMR in the thermal rearrangement of **2**.

Nucleophilic Substitution Products from 1. Although **1** undergoes facile aromatization in polar solvents, it is possible to divert the reaction to nucleophilic substitution in methanol. Such reactions can be followed conveniently at room temperature, well below the temperatures required for aromatization of **1**. The substitution products (**2** and **3**) are formed with the complete exclusion of aromatic products, which further reinforces the notion that ionization of **1** is a much more facile process than ring opening.

In pure methanol, **1** gradually develops a blue color and a complex mixture of products forms. Since nucleophilic substitution by methanol evolves acid, we expect that acid-catalyzed rearrangements occur under these conditions. Reactions under these conditions were not studied further; rather we maintained basic conditions and followed the kinetics and products that resulted. Although all of the work reported here used methanolic sodium methoxide, we did observe that other bases accomplished the same effect. Inclusion of 2,6-dimethylpyridine in methanol also converted **1** to the same pair of products, **2** and **3**, in the usual ratio. Since the rate of the reaction is independent of methoxide concentration, we believe that the base simply functions to neutralize the acid that would be generated in the solvolysis reaction. We

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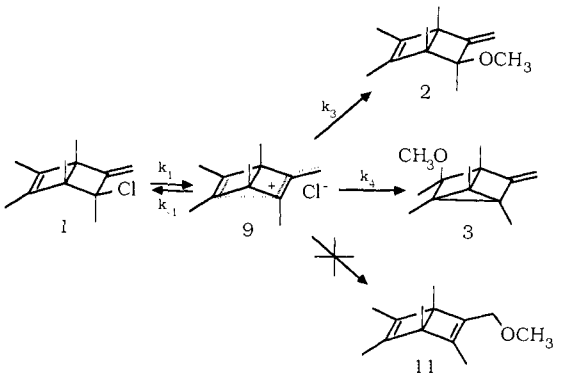
Scheme IV



have not attempted to distinguish whether methanol or methoxide is the active product-forming nucleophile in this reaction. The difficulties of making such differentiations has been described for buffered solvent systems.[21]

The position of the chloride functional group in **1** is unusual in that it can be described as a tertiary cyclobutyl chloride that is also allylic with respect to the exocyclic π bond and homoallylic with respect to the transannular π bond. Each of these systems undergoes characteristic cationic rearrangements.[22] The two products observed, **2** and **3**, are exactly analogous to those formed from nucleophilic substitution on the 5-norbornenyl system, which represents a homoallylic system.[22] Thus it appears that interactions with the transannular π bond are most important in determining the substitution products from **1** (Scheme IV). The transannular interaction in **9** leads to 2,6 σ bonding, which is distinctly different from the transannular interaction initiated by electrophilic additions to HMDB, in which a 1,6 σ bond shift occurs.[6a]

As in the formation of **1**, discussed earlier in conjunction with Scheme II, the absence of a primary allylic derivative (**11**) can be attributed to both kinetic and thermodynamic arguments. These effects minimize the apparent significance of the exocyclic π bond in the overall reaction.

The product ratio of **2** to **3** is consistent under a variety of conditions, indicating that the cation intermediate (**9**) partitions between the two possible substitution products essentially independent of reaction conditions.

Nucleophilic Substitution Kinetics of 1. The rate law for conversion of **1** to **2** and **3** is first order in **1** and independent of $NaOCH_3$ concentration, consistent with the mechanism of Scheme IV with step 1 rate-determining.

The initial reversible ionization steps are the same as those in the thermal rearrangement mechanism (Scheme III). In methanol, ionization is particularly favorable because the solvent is highly polar. Once formed, the intermediate cation (**9**) has the opportunity either to react with nucleophile (Scheme IV) or to undergo ring opening (Scheme III). Around room temperature, ring opening is very slow, so addition of nucleophile predominates under these conditions. The addition of an inert electrolyte (0.10 M $NaClO_4$) increases the rate somewhat, consistent with the normal salt effect on S_N1 reactions.[23] Furthermore, the addition of excess leaving group (0.10 M NaCl) decreases the rate, consistent with the common ion effect on S_N1 reactions.[24]

Application of the steady-state approximation for **9** leads to the rate law

$$\text{rate} = \frac{k_1(k_3 + k_4)[\mathbf{1}]}{(k_{-1}[Cl^-] + k_3 + k_4)} \qquad (3)$$

The relative rate constant for ionic recombination (k_{-1}) compared to product formation ($k_3 + k_4$) can be evaluated by plotting the [Cl^-] dependence (Table III, runs 3, 11–13) as a rearranged form of the rate law

$$(\text{rate})_0/(\text{rate}) = 1 + \{k_{-1}/(k_3 + k_4)\}[Cl^-] \qquad (4)$$

$$\text{slope} = \{k_{-1}/(k_3 + k_4)\} = 2.6$$

Rate constants k_3 and k_4 are taken to include the solvent nucleophile concentration. The solvent nucleophile can be considered to be either methanol or methoxide. If methanol is the nucleophile competitive with Cl^-, where [CH_3OH] = 24 M, then Cl^- is 62 times more reactive than CH_3OH toward cation **9**. If methoxide is the product-forming nucleophile, where [CH_3O^-] = 0.10 M, then Cl^- is 0.26 times as reactive as CH_3O^- toward cation **9**. These relative reactivities are in the usual order of S_N2 nucleophilicities expected for CH_3O^-, Cl^-, and CH_3OH.[25] S_N1 nucleophilicities generally follow the same order, although the magnitudes of the relative nucleophilicities vary significantly depending upon the structure and stability of the carbocation under consideration.[21]

Addition of comparable concentrations of NaBr or NaI did not cause a rate depression; in fact, they caused no significant effect on the rate at all (Table III, runs 3, 15, 16). Since Br^- and I^- are better nucleophiles than Cl^-, it is likely that they do react rapidly with cation **9**; however, these reactions produce alkyl halides of even greater solvolytic reactivity than **1**. The bromo derivative has been isolated and found to be unstable at room temperature.[10] Thus the reaction is not truly reversed when a reactive halide displaces chloride; since the resultant alkyl halide reacts even more rapidly than **1**, the overall reaction rate is unaffected. In addition, the product ratio is unaffected, again indicating that a free cation (**9**) is the reactive precursor to products **2** and **3**.

Addition of NaN_3 as an irreversible competitive nucleophile leads to formation of additional, unidentified products and a decrease in the rate of formation of the normal products (Table III, runs 17 and 18). In this case, we consider that the rate of formation of the cation intermediate is essentially unchanged, but the intermediate has been partially diverted to new products, diminishing the rate of formation of the usual products. These experiments indicate that the cation intermediate can be diverted to nonsolvolytic products by a suitably powerful nucleophile. If the rate depression is analyzed as was the common ion rate depression (eq 4), the relative rate constant for N_3^- attack on **9** is 13.7 times greater than the forward reaction to products, or N_3^- is 330 times more reactive than CH_3OH toward cation **9** or 1.4 times more reactive than CH_3O^- toward **9**. In the presence of NaN_3, the ratio of the solvolysis products is shifted slightly to further favor **2** (the **2**:**3** ratio is 72:28 rather than approximately 60:40). This could be caused by partial blockage of the transannular position by azide anion, leading to preferred solvent addition at the original site of the leaving group (product **2**).

Addition of $AgNO_3$ causes the most pronounced effect on the product distribution, with the **2**:**3** ratio reversing completely to favor **3** by 90:10. This effect can be readily explained by a nearly complete blockage of the front side of the ring by the newly formed AgCl, while leaving the transannular position unaffected and open to solvent attack. As a synthetic approach, this represents the most convenient method to prepare **3**, which is ordinarily the minor solvolysis product.

Thermal Rearrangement of 2. In the thermolysis of **2**, the intermediate methylenecyclohexadiene (**6**) is detectable during the reaction by its characteristic NMR spectrum, and it can be observed to convert to the final aromatic product, hexamethylbenzene (**7**), as indicated in Table IV. The conversion of **2** to **6** corresponds to a four-electron electrocyclic ring-opening reaction that presumably proceeds in the orbital-symmetry-forbidden disrotatory sense, analogous to the ring-opening reactions of the Dewar benzenes. The conversion of **6** to **7** is a symmetry-allowed

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retro-ene reaction, involving hydrogen transfer from the methoxy group to the incipient benzylic position with elimination of formaldehyde. Both steps involve comparable activation energies (27–28 kcal/mol), but the second step has a significantly higher *A* factor. Thus intermediate **6** only builds up to about 30% in the reaction mixture, as illustrated in Figure 1.

Intermediate **6** is also unstable in the presence of alumina at room temperature, which converts it to its aromatic isomer, pentamethylbenzyl methyl ether (**5**). This conversion amounts to a 1,3 shift of the methoxy group, which would require either acid or base catalysis.

Comparison of Ring-Opening Reactions. Chloro derivative **1** and methoxy derivative **2** are structurally analogous, and both undergo thermal rearrangement to aromatic products in approximately the same temperature range. However, they follow remarkably different mechanistic pathways to aromatization. The primary difference between **1** and **2** is the presence of a good leaving group in **1** and the absence of a good leaving group in **2**. Thus **1** undergoes initial ionization, while **2** undergoes initial ring opening.

Compound **1** has a readily dissociable leaving group and initiates reactions by dissociation of Cl^-. Those reactions include nucleophilic substitution and thermal ring opening of the cation intermediate. The ring-opened cation intermediate from **1** has achieved aromatic stabilization, and the subsequent product is aromatic isomer **4**. Compound **2**, on the other hand, does not have a readily dissociable leaving group and this contributes to a somewhat greater thermal stability. Compound **2** undergoes its ring-opening reaction at higher temperatures, but yields a product (**6**) that is still not aromatic; a further reaction is required to achieve aromaticity, in this case, to hexamethylbenzene by elimination of formaldehyde.

The relative ease of disrotatory cyclobutene ring openings has been correlated by Hückel MO considerations, in particular including the Dewar benzene system and the effects of benzannelation and bismethylenation.[26] The effect of two exocyclic methylene groups lowers the observed activation energy,[27] as do unsymmetrical halogen substitution patterns.[5] Our derivatives (**1** and **2**) include a single exocyclic methylene and a single electron-withdrawing substituent, thus also representing an unsymmetrical substitution pattern. The observed activation energies for **1** and **2** are lower than that of HMDB: HMDB, 37 kcal/mol;[4] **2**, 27 kcal/mol; **1**, 23 kcal/mol. In fact the data for **1** represent the ring opening of cation **9**, also a methylene-substituted unsymmetrical cyclobutene.

Compound **3** does not include a cyclobutene structure, and its thermal rearrangement is much more complex and has not been studied fully. Higer thermolysis temperatures are required (above 150 °C) and the product mixture apparently includes a variety of products. Compound **5** is clearly detectable as one of the minor products.

Radical Cation Chemistry. Compounds containing strained rings often undergo even more facile ring openings and rearrangements when they undergo one-electron oxidation to their radical cations.[28] This has been demonstrated for HMDB, which undergoes rapid isomerization to hexamethylbenzene via a radical cation chain reaction.[29] Earlier, we have reported that **1** and **2** undergo rapid ring-opening reactions subsequent to photoinduced electron transfer at room temperature.[30] The two reactions differ significantly in that the two methylenecyclohexadiene ring-opening products have different stabilities. Compound **2** gives **6**, which is stable at room temperature and is directly observed in the NMR spectrum with appropriate CIDNP polarization. Compound **1**, on the other hand, gives **4** as the only observable product. The pattern of the CIDNP effects clearly indicates that **4** had a methylenecyclohexadiene precursor, which was unstable at room temperature and rapidly underwent a 1,3 chlorine migration. Further, it was demonstrated from the CIDNP spectrum that the chlorine migration takes place in the ground state rather than as the radical cation. Thus the lability of the chloride leaving group again causes a significant difference in reactivity between the analogous chloro and methoxy derivatives.

Conclusions

Hexamethyl(Dewar benzene) can be converted to rearranged substitution products **1**, **2**, and **3**. The formation of chloro derivative **1** is a free radical substitution, and the formation of **2** and **3** is solvolytic nucleophilic substitution. Like HMDB, each of the rearranged substitution products undergoes a thermal ring-opening reaction that leads utlimately to an aromatic product. Because these are rearranged derivatives, each requires more than one step to arrive at an aromatic product. For **1**, the thermal reaction involves ionization and chloride migration as well as ring opening, yielding **4**. For **2**, the ring opening is followed by elimination of formaldehyde to yield hexamethylbenzene.

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