Journal of Organometallic Chemistry, 352 (1988) 263–272
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Rearrangement of the Grignard reagent from 1-methylcyclobutylmethyl bromide: origins of the methyl substituent effect

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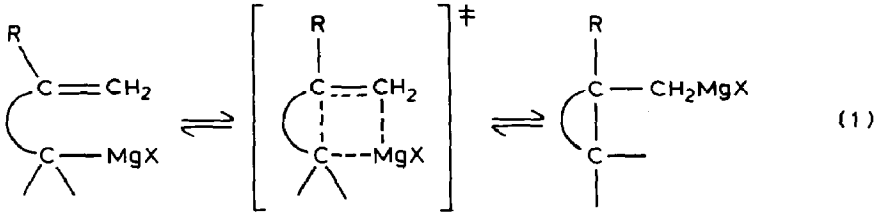
(Received May 8th, 1987; in revised form March 15th, 1988)

Abstract

1-Methyl substitution leads to a small decrease (ca. 0.45) in the rate of the ring cleavage rearrangement of cyclobutylmethylmagnesium bromide. Comparison with literature data for 3- and 5-membered rings indicates that the methyl substituent shifts the equilibrium in the direction of ring cleavage, mostly by stabilization of the double bond of the open isomer, and possibly partly by destabilization of the organometallic function of the cyclic isomer. The reaction rate is decreased in both directions, probably because of increased transition state steric repulsions.

Introduction

Cycloalkylmethyl organomagnesium compounds are interconverted with open-chain isomers in a "ring-chain" rearrangement (eq. 1) which most likely occurs via a



(1)

concerted four-center process [1]. Substantial substituent effects on the rates of these rearrangements have been observed and are summarized elsewhere [1,2]. In this study, we are specifically interested in the effect of methyl substitution ($R = CH_3$ vs. $R = H$) in eq. 1. A methyl substituent at the internal double-bond position is reported to decrease the rate of cyclization to 3- or 5-membered rings, as shown in eq. 2 and 3. In the former case [3,4], the rate of scrambling of the isotopic label (**1** ⇌ **3**) is decreased by a factor of about 10^{-2}, and in the latter [5], the cyclization is slowed by a factor of about 10^{-3}.

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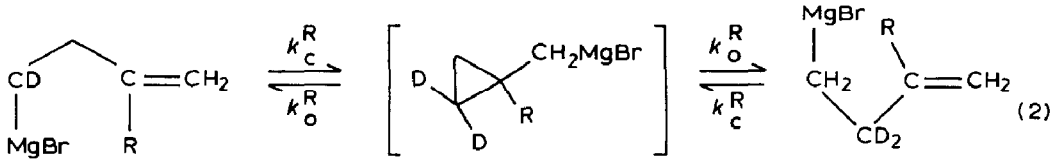
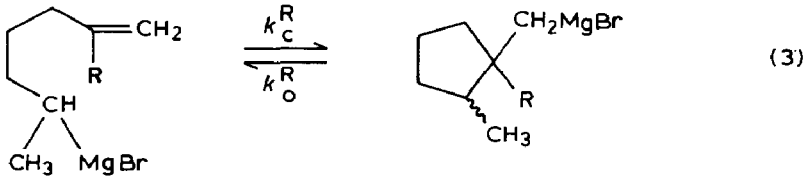


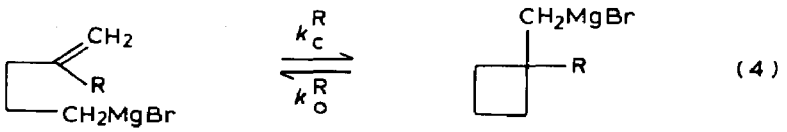
(1) (2) (3)



(4) (5)

In principle, a substituent might exert its effect on the transition state for a reaction, leaving the equilibrium constant nearly unchanged; i.e., $K^H = k_c^H/k_o^H \approx k_c^{CH_3}/k_o^{CH_3} = K^{CH_3}$, so that $k_c^{CH_3}/k_c^H \approx k_o^{CH_3}/k_o^H$. Alternatively, if the equilibrium constant ($K = k_c/k_o$) is changed by the substituent, then the rate constants in the forward and reverse directions must be affected unequally. In an idealized case, where the effect of the substituent on the transition state reflects only the fraction of reactant and product state interactions which are present at that stage, we should expect the substituent to slow the reaction in one direction and to accelerate it in the other.

In any event, interpretation of the methyl substituent effect requires that we know the magnitude of the effect on the rate in both directions (or its equivalent, on both the rate and the equilibrium). Ideally, the ring cleavage reactions of substituted and unsubstituted **2** or **5** might be compared to determine the substituent effect on ring opening. Unfortunately, cyclopropylmethyl Grignard reagents rearrange inconveniently rapidly for accurate rate studies, and the cyclization to cyclopentylmethyl Grignard reagents is essentially irreversible. Ring cleavage of cyclobutylmethyl Grignard reagents (eq. 4) is conveniently followed, but the reverse cyclization is too slow for accurate study [1]. However, it is reasonable to suppose that the methyl substituent effect on the cyclization to a four-membered ring should be comparable with those for the three- and five-membered analogs. If this is so, the methyl substituent effect ($k_o^{CH_3}/k_o^H$) derived from ring opening rates of **7a** and **7b**, taken with a methyl substituent effect = 10^{-2} to 10^{-3} on the cyclization, would allow approximation of the substituent effect (K^{CH_3}/K^H) on the equilibrium constant.

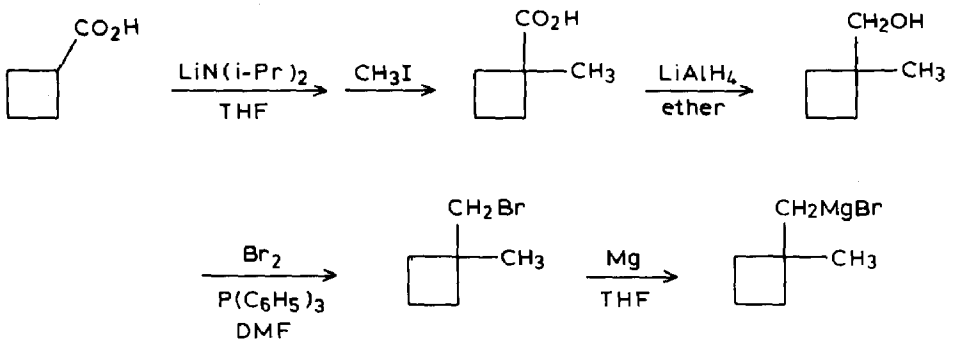


(6) (7)

(**a**, R = H ; **b**, R = CH_3)

Results and discussion

1-Methylcyclobutylmethylmagnesium bromide (**7b**) was prepared as follows:



(7b)

The unsubstituted cyclobutylmethyl bromide has been reported previously [6].

Preliminary experiments indicated that the rearrangement rate of Grignard reagent **7b** was similar to that of the unsubstituted **7a**, so the kinetics were studied using a mixture of the two. This type of organomagnesium rearrangement is known to be somewhat sensitive to the concentration and composition of the organometallic solution [1], and coupling or disproportionation side reactions in the formation of the Grignard reagent could produce different organometallic concentrations and varying amounts of magnesium bromide. However, it is expected that solution variations should affect the two reactions similarly, so that an accurate comparison of the rearrangment rates could be obtained by studying the mixture. Rates were determined by heating aliquots of the solution in sealed tubes, hydrolyzing, and analyzing the hydrocarbons so formed by gas chromatography. Similar results were obtained from the areas of the high-field proton resonances in an NMR spectrum of the Grignard reagent mixture. Results are summarized in Table 1.

Table 1

Rate constants for the ring opening of the Grignard reagents from cyclobutylmethyl- and 1-methylcyclobutylmethylmagnesium bromide in tetrahydrofuran solution [a]

T (°C)	k ($\times 10^5$ s^{-1}) [b]	
	Cyclobutylmethyl (**7a**) [c]	1-Methylcyclobutylmethyl (**7b**) [d]
78	0.89±0.04, 0.87±0.06	0.41±0.02, 0,39±0.02
90	3.01±0.12, 3.08±0.26	1.46±0.07, 1.43±0.04
101	9.3 ±0.3, 9.1 ±0.3	4.72±0.13, 4.63±0.11

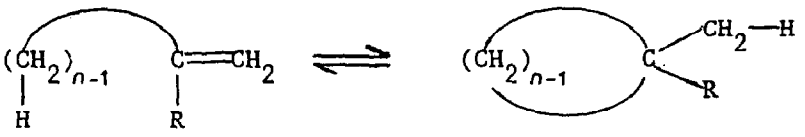
[a] Concentration about 0.5 M in each reagent. [b] First number obtained by gas chromatography technique; second number by NMR integration. Uncertainties are standard deviations from least-squares first order plots. [c] $\Delta H^{\neq} = 26.0 \pm 0.5$ kcal/mol; $\Delta S^{\neq} = -8.0 \pm 1.2$ cal/mol-deg (25.9±0.1 kcal/mol and −8.4±0.1 cal/mol-deg by NMR). [d] $\Delta H^{\neq} = 27.1 \pm 0.3$ kcal/mol; $\Delta S^{\neq} = -6.3 \pm 0.8$ cal/mol-deg. (27.5 ±0.3 kcal/mol and −5.3±1.0 cal/mol-deg by NMR).

Over the temperature range from 78 to 101 °C, the ring-opening rearrangement of 1-methylcyclobutylmethylmagnesium bromide is slower than that of the parent compound by a factor of $k_o^{CH_3}/k_o^H \approx 0.45$–$0.50$. If the methyl substituent effect on the cyclization rate is in the range of $k_c^{CH_3}/k_c^H = 10^{-2}$ to 10^{-3} (eq. 2 and 3), then the equilibrium effect $K^{CH_3}/K^H \approx 2. \times 10^{-2}$ to $2. \times 10^{-3}$. Thus, methyl substitution favors ring cleavage by a factor of 45 to 500, corresponding to 2.7 to 4.4 kcal/mol in free energy at 80 °C. The former estimate may be the better for two reasons. The cyclopropyl and cyclobutyl cyclizations are endothermic by comparable amounts, whereas the cyclopentyl is substantially exothermic; the transition states of the former two reactions are therefore more likely to have similar extents of bond formation. The cyclization to the cyclopentane ring in eq. 3 may also experience additional retardation resulting from transition state steric interactions between the two methyl groups. In either event, the decrease in equilibrium constant for cyclization is the resultant of a large decrease in cyclization rate, partially compensated by a small decrease in the rate of ring cleavage.

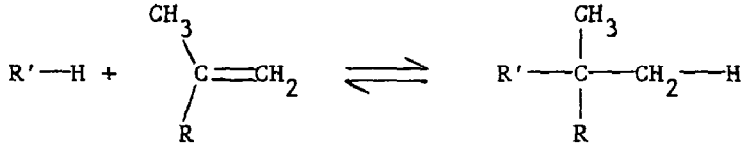
The effect of a methyl substituent on the cyclization/cleavage equilibrium constant may be dissected into its effect on the stability of the carbon skeleton and its effect on the stability of the organometallic function. The former might be approximated from thermochemical data for the corresponding hydrocarbons. Unfortunately, the heat of formation published for methylcyclobutane [7] is of doubtful validity [8], and no data are available for 1,1-dimethylcyclobutane. Scheme 1 summarizes estimates for the methyl substituent effect on $\Delta H°$ for several hypothetical inter- and intramolecular additions of a primary C–H bond to an alkene. Molecular mechanics calculations [9] provided gas-phase heats of formation for methylcyclobutane and 1,1-dimethylcyclobutane *, but it was necessary to use heats of vaporization estimated by comparisons of boiling points with other hydrocarbons to convert these to the liquid phase **. Other numbers in Scheme 1 were derived from tabulated thermochemical data [10]; values enclosed in brackets also required estimated heats of vaporization **. The liquid-phase $\Delta H°$ values appear to fall roughly in the range of $+1.5 \pm 0.5$ kcal/mol. A similar value of about 1.45 kcal/mol results from the application of Benson's method of group equivalents [11] to the intermolecular addition. The methyl substituent effect, leading to relative stabilization of the acyclic isomer, may be ascribed to the well-known stabilization of a double bond by alkyl substitution (or more correctly, the greater stabilization from branching at an sp^2 carbon than sp^3). It does not appear that specific *stabilization* of the ring by alkyl or *gem*-dialkyl substitution plays a significant role ***.

* Molecular mechanics calculations were made using the program MMPMI (Serena Software), an augmented version of MM2 (N.L. Allinger and Y.H. Yuh, QCPE, 13 (1981) 395) adapted to Microsoft Fortran 77 by J.J. Gajewski and K.E. Gilbert. Calculated heats of formation of cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane were +6.33, −1.45, and −8.87 kcal/mol (including a conformational contribution for methylcyclobutane and torsional kinetic energy contributions added manually). The value for cyclobutane compares with a calculated value of 6.31 [9] and a tabulated experimental value of 6.79 kcal/mol [10].

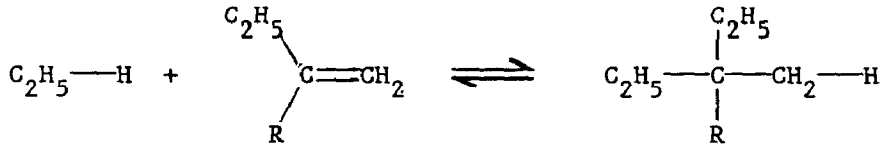
** Values used for methylcyclobutane and 1,1-dimethylcyclobutane are 6.5 and 7.2 kcal/mol respectively. Other estimates used are (kcal/mol): methylcyclopropane, $\Delta H_v° = 5.45$; 2-methyl-1-hexene, $\Delta H_f°(g) = -18.22$ [11], $\Delta H_v° = 8.33$; 2,2-dimethylheptane, $\Delta H_v° = 10.3$.



n	$\Delta H°(R=CH_3) - \Delta H°(R=H)$ (kcal/mol)
3	1.28 (l) , [0.59 (g)]
4	[2.1 (l)], 1.55 (g)
5	[1.01 (l)], 0.56 (g)



R'	ΔH ($R=CH_3$) - ΔH ($R=H$) (kcal/mol)
C_2H_5	0.76 (l) , 1.08 (g)
n-C_3H_7	1.17 (l) , 1.27 (g)
n-C_4H_9	1.74 (l) , 1.70 (g)
n-C_5H_{11}	1.48 (l) , [1.85 (g)]



$\Delta H°(R=CH_3) - \Delta H°(R=H) = 2.04$ (l) , 1.45 (g)

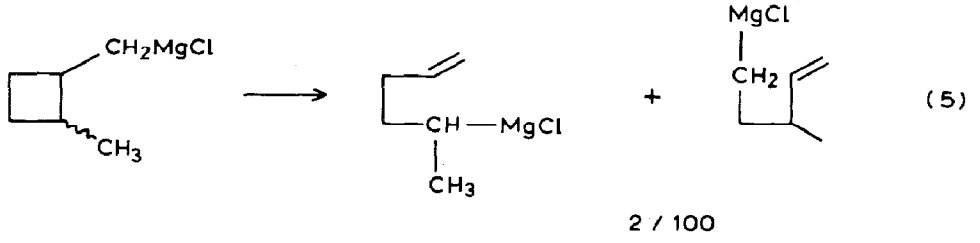
Scheme 1

*** The "*gem*-dimethyl stabilization" of rings has been attributed largely to increased numbers of *gauche* interactions which destabilize the open-chain isomers or precursors [12]. There is some uncertainty concerning thermodynamic evidence for the stabilization of small rings by substitution. Cyclopropanes with cyano, amino, or *gem*-dimethyl substitution do not appear to be stabilized to an experimentally significant extent [13]. An apparent stabilization of cyclobutanes with ethyl, cyano and amino substituents (all ~ 2.0 kcal/mol) is reported, but it has been suggested that the apparent inconsistency may result from an incorrect heat of formation for cyclobutane itself [14]. The quantum-mechanically calculated effect of methyl substitution on cyclopropane is small [15]. Using published thermochemical data [10] along with the molecular mechanics estimates noted above, the increments to liquid-phase $\Delta H_f°$ for the addition of the second (geminal) methyl substituent are as follows: cyclopropane, −8.37; cyclobutane, −8.12; cyclopentane, −8.24; and butane, −8.61 kcal/mol. It thus appears unlikely that the methyl substituent has any specific ring-stabilizing effect on the cyclizations of eqs. 2–4.

The methyl substituent may also make an entropic contribution favoring ring cleavage. From tabulated entropies [11], it appears that the methyl substitution (methylcyclopentane → 1,1-dimethylcyclopentane) increases the entropy by 6.0 cal/mol-deg (eliminating the effect of ring symmetry), while the substitution (1-butene → 2-methyl-1-butene) increases the entropy by 7.3 cal/mol-deg. A similar comparison may be drawn from the relevant group increments [11] for replacement of tertiary sp^3 CH vs. internal olefinic CH by C–CH_3: 5.2 and 7.6 cal/mol-deg. At 80 °C, a methyl effect of 2.0 cal/mol-deg corresponds to about 0.7 kcal/mol in free energy.

It is quite possible that methyl substitution in cyclobutylmethylmagnesium bromide may additionally influence the equilibrium by destabilization of the organometallic function. In the series ethyl–propyl–isobutyl–neopentyl, the organolithium is destabilized relative to the corresponding iodide by 0.4 to 0.9 kcal/mol per β-methyl group [16], and Cram assigns a pK_a difference of about 0.5 per β-methyl group in the corresponding hydrocarbons [17]. However, a difference of only 0.3 kcal/mol was reported in a magnesium–mercury exchange between ethyl and isobutyl [18]. If the experimental methyl substituent effect on the cyclization equilibria of eq. 2–4 is on the order of 2.5 kcal/mol or more, and the effect on the carbon skeleton may be assigned a value of approximately 2.2 kcal/mol, then β-methyl destabilization of the organomagnesium function may also make a significant contribution.

The observation that methyl substitution retards the reaction in both directions implies that the transition state is destabilized by some factor present in neither reactant nor product (or present to a lesser degree than in the transition state). It is likely that the retarding effect of methyl substitution is steric in nature, a consequence of increased congestion around the reacting carbon atoms. It has previously been suggested that the preferred direction of cleavage of 2-methylcyclobutylmethyl Grignard reagents (eq. 5) results as much from a transition state steric effect as from the relative stabilities of the products [19]; and the cyclization-cleavage rearrange-



ment of the 3,3-dimethylcyclobutylmethyl Grignard reagent likewise appears to be slowed in both directions by steric hindrance in the transition state [20].

In some earlier studies of ring-cleavage rearrangements of substituted cyclobutylmethyl Grignard reagents, it was necessary to estimate the substituent effect on rate because relevant data for cyclobutylmethylmagnesium bromide itself in THF were not available. By extrapolating or interpolating from current results, more reliable estimates of substituent effects may now be made. In particular, 2-phenyl substitution [21] produces an estimated rate increase in the range of 40–1000 at temperatures of 25–40 °C, and 3,3-dimethyl substitution [20] is estimated to decrease the rate by a factor of 5 at 100 °C. These are not meaningfully different from earlier estimates.

Experimental

Boiling points are uncorrected. NMR spectra were obtained on Varian Associates EM-360L and CFT-20 and a Bruker WM-250 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane; in Grignard reagent solutions, the ^{13}C shifts were established relative to C_6D_6 at 128 ppm. ^{13}C NMR assignments were assisted by off-resonance decoupling or DEPT experiments; multiplicities given are for the off-resonance decoupled spectra, and shifts shown in parentheses are estimated from the hydrocarbon skeleton using additive parameters [22–24] or model compounds. Mass spectra were obtained on a Hewlett-Packard 5985 gas chromatograph mass spectrometer with electron impact or methane chemical ionization, using a capillary column, 0.25 mm ID × 30 m, 0.25 μm coating of 6% diphenyl/94% dimethylpolysiloxane. Gas chromatography was on Varian A90-P3 chromatographs with columns of: A. 1/4″ × 5′, 10% Ucon 50-HB-2000 on 60–80 mesh firebrick; B. 1/4″ × 10′, Dow Corning silicone grease on 60–80 mesh firebrick; C. 1/4″ × 10′, 25% tricresyl phosphate on 60–80 mesh Chromosorb P. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Tetrahydrofuran and ethyl ether were dried by distillation from sodium benzophenone under nitrogen. Dimethylformamide was dried by treatment with BaO for 1–2 days, refluxing for 24 h with 5–10 g/l of chlorotriphenylsilane, and distillation twice at about 5 torr [25]. Water content of solvents was determined by Karl Fischer titration using a Labindustries Aquametry Apparatus.

Magnesium used for Grignard reagent preparation was turned from a sample of sublimed magnesium received as a gift from the Dow Metal Products Company.

Cyclobutylmethyl bromide was prepared from cyclobutylmethanol by the procedure previously described for 1-cyclobutylethanol [26]. From cyclobutylmethanol (12 g, 0.14 mol), triphenylphosphine (48 g, 0.18 mol) and bromine (13 ml, 0.18 mol) in dried dimethylformamide (120 ml), cyclobutylmethyl bromide (14.6 g, 71%) was obtained as a colorless liquid, b.p. 40 °C (12 torr) [lit, [6] b.p. 132–134 °C (760 torr)]; IR(neat) 2833, 2770, 1429, 1355, 1244 and 1149 cm^{-1}; ^1H NMR ($CDCl_3$); δ 3.36 (d, 2, *J* 7 Hz, CH_2Br), 2.66 (m, 1, CH), 1.85 ppm (m, 6, CH_2); ^{13}C NMR ($CDCl_3$); δ 39.1 (t, CH_2Br, 42.0), 37.7 (d, CH, 41.8), 27.3 (t, $2CH_2$, 27.1), 17.1 ppm (t, CH_2, 18.4).

1-Methylcyclobutylmethyl bromide

1-Methylcyclobutanecarboxylic acid was prepared in 88% yield as described by Beckwith and Moad [27]; ^1H NMR ($CDCl_3$); δ 11 (s, 1, CO_2H), 1.73–2.62 (m, 6, CH_2), 1.50 ppm (s, 3, CH_3); ^{13}C NMR ($CDCl_3$): δ 185 (s, CO_2H), 43.35 (s, *C*), 31.55 (t, $2CH_2$), 23.72 (q, CH_3), 15.24 ppm (t, CH_2); mass spectrum (EI, 15 V): *m/e* (intensity) 115(3), 114(*m*, 8), 113(7), 100(5), 99(62), 97(9), 96(16), 87(8), 86(100), 73(11), 71(11), 70(12), 69(79), 68(34), 58(21); (CI): 115(*m* + 1, 52), 97(100), 86(7), 69(83).

The acid was reduced in 86% yield with lithium aluminum hydride to yield 1-methylcyclobutylmethanol; b.p. 50–60 °C (12 torr) [Lit. [27] b.p. 70–71 °C (32 torr)]; IR (neat) 3225, 2830, 1429, 1350, 1026 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.01 (t, 1, *J* 5 Hz, OH), 3.47 (d, 2, *J* 5 Hz, CH_2OH), 1.77 (m, 6, CH_2), 1.11 ppm (s, 3, CH_3); ^{13}C NMR ($CDCl_3$): δ 71.02 (t, CH_2OH, 70.8), 40.05 (s, *C*, 40.9), 29.69 (t, $2CH_2$,

30.0); 24.12 (q, CH_3, 24.5), 14.86 ppm (t, CH_2, 14.9); mass spectrum (EI, 15 V): *m/e* (intensity) 100(0.2), 99(0.2), 85(3), 83(5) 82(10), 72(32), 71(46), 69(8), 67(16), 58(10), 57(100); (CI): 101(0.2), 100(*m*, 1.4), 99(2), 84(7), 83(100), 81(6), 73(3), 72(5), 71(4), 57(5), 55(11).

1-Methylcyclobutylmethanol (4.0 g, 0.040 mol), triphenylphosphine (15 g, 0.06 mol) and dried dimethylformamide (30 ml) were heated at 55 °C for 0.5 h and bromine (5.0 ml, 0.092 mol) was added over 45 min, with the temperature maintained at 55 °C. After heating to reflux for 0.5 h, volatiles were distilled at 2 torr to a trap cooled to −78 °C. Water was added, and the organic layer was separated, dried ($MgSO_4$) and run through an alumina column, using pentane as eluent. The product was purified by distillation to yield 3.47 g (54%); b.p. 40 °C (12 torr); IR(neat 2833, 1770, 1429, 1355, 1244, and 1149 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.44 (s, 2, CH_2Br), 1.86 (m, 6, CH_2), 1.25 ppm (s, 3, CH_3); ^{13}C NMR ($CDCl_3$); δ 46.46 (t, CH_2Br, 46.1), 39.66 (s, C, 40.3), 31.84 (t, $2CH_2$, 31.2), 25,49 (q, CH_3, 25.7), 13.94 ppm (t, CH_2, 14.9); mass spectrum (EI, 15 V): *m/e* (intensity) 164(0.7), 162(m, 0.7), 136(97), 134(100), 122(42), 120(43), 83(20), 69(57), 67(7), 56(13), 55(92); (CI): 164(4), 163(2), 162(4), 161(2), 137(2), 136(10), 135(2), 134(10), 84(6), 83(100), 81(4), 55(6). Anal. Found: C, 44.23; H, 6.89. $C_6H_{13}Br$ calc: C, 44.19; H, 6.80%.

Preparation and manipulation of Grignard reagents

Grignard reagents were prepared in dried THF under nitrogen, in a flask sealed to a condenser with a side-arm above the condenser for attchment to an inert gas or vacuum line. Magnesium (25% excess) was introduced into the flask and dried by gentle flame heating under nitrogen. Solvent and bromide were then introduced by syringe. In some instances where reaction did not start spontaneously within 10 min, the reaction was initiated by sonication in the water-filled bath of a Bransonic Model B-12 ultrasound laboratory cleaner, by addition of a few chips of magnesium previously activated by reaction with methyl iodide in THF, or by addition of a trace of ethyl bromide. Reaction mixtures were refluxed 1 h after initiation. Portions were transfered under a flow of nitrogen by syringe into nitrogen-filled NMR or sample tubes, and then sealed under a slight negative pressure. Sample tubes had a ground joint such that, after cracking open in a dry bag, they could be fitted to an adapter for attchment to a vacuum system. Volatiles were pumped to a trap, fresh solvent was added, the reagent was hydrolyzed by addition of water, and the volatile solvent and hydrolysis products were vacuum-transferred to a trap for GC analysis or spectroscopic investigation.

Preparation and rearrangement of the Grignard reagent from 1-methylcyclobutylmethyl bromide

A Grignard reagent, **7b**, was prepared from the bromide (1.4 g, 7 mmol) and sublimed magnesium (0.22 g, 9 mg-at) in 5 ml of THF. The proton NMR spectrum of the Grignard reagent had a singlet at −0.10 ppm, and hydrolysis produced a single monomeric hydrocarbon (GC, Column B). After heating, the proton NMR spectrum had a new triplet at −0.57 ppm (*J* 7 Hz), and the hydrolysis product had an additional GC component. The ^{13}C NMR spectrum was obtained for the Grignard reagent before and after heating, and also after hydrolysis of both solutions. A set of resonances which disappeared either after heating or on hydrolysis was assigned to 1-methylcyclobutylmethylmagnesium bromide: δ 42.25 (*C*

42.75), 40.64 (2 CH_2, 39.1), 33.10 (CH_3 34.0), 28.45 (CH_2Mg, 28.1) and 14.17 ppm (CH_2, 14.8). New Grignard reagent resonances which appeared on heating and disappeared on hydrolysis were assigned to rearranged Grignard reagent: δ 148.11 (=C, 148), 108.18 (=CH_2, 108), 47.79 (γ-CH_2, 44.3), 29.10 (β-CH_2, 27.6), 22.60 (CH_3, 22.3), and 7.76 ppm (CH_2Mg, 7.6). Additional resonances, which were comparable in intensity to the organomagnesium reagent peaks and were unchanged on heating or hydrolysis, were assigned to the hydrocarbon dimer; after hydrolysis, this remained as non-volatile residue when the hydrolysis products were vacuum transferred to a cold trap; ^{13}C NMR ($CDCl_3$): δ 38.5 (s, C, 35.9), 36.81 (t, -CH_2CH_2-, 36.4), 33.30 (t, 4CH_2, 32.4), 26.21 (CH_3, 26.9) and 14.96 ppm (t, 2CH_2, 14.8); mass spectrum (CI): 166 (*m*, 3), 165(9), 151(3), 139(4), 138(12), 123(21), 111(12), 110(19), 109(71), 98(4), 97(46), 96(9), 95(88), 85(11), 84(8), 83(100), 81(17), 71(13), 70(3), 69(50), 68(7), 67(7), 57(14), 55(14); (EI, 70 V): 166(0.3), 151(0.2), 138(5), 123(8), 110(11), 109(12), 96(13), 95(100), 82(13), 81(24), 69(11), 68(50), 67(19), 55(27), 53(7). The volatile monomeric hydrolysis products had ^{13}C NMR spectra in agreement with published values; 1,1-dimethylcyclobutane ($CDCl_3$ + THF): δ 35.87 (C), 34.84 (2CH_2), 29.22 (CH_3), and 14.78 ppm (CH_2) [28]; 2-methyl-1-pentene ($CDCl_3$ + THF): δ 146.04 (=C), 110.17 (=CH_2), 40.58 (CH_2), 22.32 (CH_3), 21.36 (CH_2), 13.89 ppm (CH_3) [29].

Kinetics

A Grignard reagent was prepared by reaction of a mixture of 1.00 g (6.7 mmol) of cyclobutylmethyl bromide and 1.10 g (6.7 mmol) of 1-methylcyclobutylmethyl bromide with 0.44 g (18 mg-at) of magnesium in 15 ml of THF. Samples of Grignard reagent (ca. 0.5 ml each) were sealed into sample and NMR tubes as described above. Kinetics of rearrangment were followed by two independent methods. Hydrolysis products from sample tubes which had been heated for various periods of time were analyzed for methylcyclobutane, 1-pentene, 1,1-dimethylcyclobutane and 2-methyl-1-pentene by gas chromatography (column B). With the assumption of equal thermal conductivity detector sensitivity for isomeric hydrocarbons, semilogarithmic first order rate plots were made of the fraction unrearranged vs. time. Areas were measured by planimetry, by cutting and weighing, and as the product of height and width. It was also possible to integrate NMR resonances of the protons α- to the magnesium. Triplets for the two rearranged Grignard reagents coincided, but were distinct from the singlet and doublet resonances of the unrearranged species. Areas were most accurately determined by planimetry and by cutting and weighing. Semilogarithmic first order rate plots were made of the fraction of each unrearranged species in the mixture vs time. Rate constants and activation parameters were evaluated by weighted least squares analyses of the first order rate and Eyring plots, respectively.

Acknowledgment

We acknowledge the assistance of F. Laib with NMR and mass spectra, and the advice of Dr. Suzanne Wehrli on NMR spectroscopy, and preliminary experiments by Richard Pariza and Stephen Andruski.

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