Ring-Cleavage Rearrangement of the Grignard Reagent from 2-Methylcyclobutylmethyl Chloride. Observations on Possible Radical Mechanisms of Grignard Rearrangement

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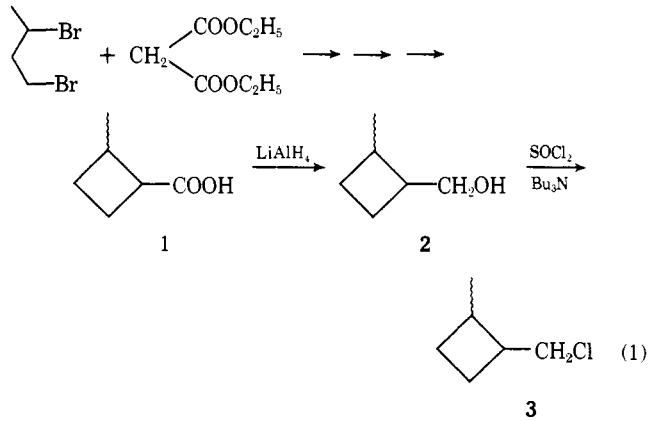
Abstract: The Grignard reagent from 2-methylcyclobutylmethyl chloride rearranges on heating to the primary Grignard **5**, in preference to secondary Grignard **6**. No cis-trans equilibration of the starting Grignard is observed. The corresponding free radical cleaves mainly to the secondary radical. The results are interpreted as eliminating the possibility of free radical mechanisms for the rearrangement of the cyclobutylmethyl Grignard reagent and, by implication, for related ring-cleavage and cyclization rearrangements of other Grignard reagents.

Kinetics of the ring-cleavage rearrangement of the cyclobutylmethyl Grignard have been reported previously.[1-3] These and other studies have been interpreted as favoring a concerted, four-center mechanism for the rearrangement, in preference to alternative radical, carbanion, and "electron-transfer" mechanisms.[1-4] An important contribution to our consideration of the mechanism of Grignard rearrangements is made by the results which we present in this paper for the Grignard reagent from 2-methylcyclobutylmethyl chloride.

Results

2-Methylcyclobutylmethyl chloride was prepared by the route shown in eq 1. Some unsaturated by-products were



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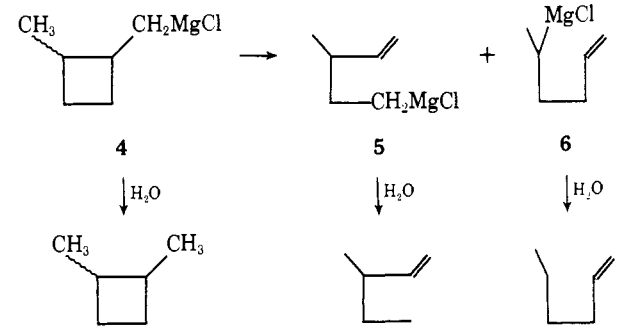
formed by elimination of the secondary bromide during the malonic ester synthesis. Since these could be largely removed by washing the chloride **3** with concentrated sulfuric acid, no attempt was made to remove them by more careful fractionation before that point. An attempt to improve the malonic ester synthesis by using sodium hydride in dimethylformamide gave major amounts of elimination. The decarboxylation produced a mixture of cis and trans isomers of **1**, as shown by gas chromatography on the methyl ester of **1**, and of **2** and **3**. The mixture of isomers was carried through the synthesis, but the individual isomers of **3**, separated by preparative GC, were studied separately. The assignment of configuration is outlined in the Experimental Section.

Hydrolysis of the Grignard reagent from either *cis*- or *trans*-**3** yielded primarily the corresponding 1,2-dimethylcyclobutane. After heating for several hours at about 60°, increasing amounts of 3-methyl-1-pentene were found in the product. Volatile materials were removed under vacuum before hydrolysis of the organometallic so that the observed products must have been derived by protolysis of organomagnesium compounds present. Therefore, this result indicates ring cleavage to yield mainly the primary Grignard reagent **5**.



The products also included a small percentage of 1-hexene, derived from the secondary Grignard **6**. From unheated Grignard reagent *trans*-**4**, about 1.2% of the product was 1-hexene and, through 1 half-life of rearrangement, this increased only by about 0.6%. Thus, nearly 99% of the rearrangement yields the primary Grignard (**5**) in preference to the secondary one (**6**). A similar result was obtained with *cis*-**4**. The small amount of secondary Grignard **6** in the unheated reagent may have been a consequence of a trace of unsaturated chloride in **3** (too small to detect by NMR) or of rearrangement to **6** during Grignard *formation*.

Another significant feature in the product distribution is the lack of crossover between cis and trans isomers. In the rearrangement of *trans*-**4**, no more than 0.1% of conversion to the cis isomer occurs; no conversion from cis to trans was observed either (within somewhat wider limits of detectability).

The rates of rearrangement of *trans*- and *cis*-**4** were determined by following the composition of hydrocarbons from hydrolysis as a function of time. The rate for *trans*-**4** was determined in 1.4 *M* solution in THF; the rate for *cis*-**4** was determined in a solution which was about 0.15 *M* in *cis*-**4**, and 0.85 *M* in **7**, simultaneously with the rearrangement of **7** to **8**. The rates observed are summarized in Table I.

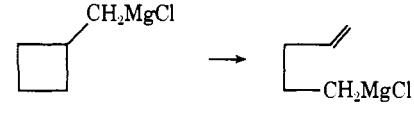


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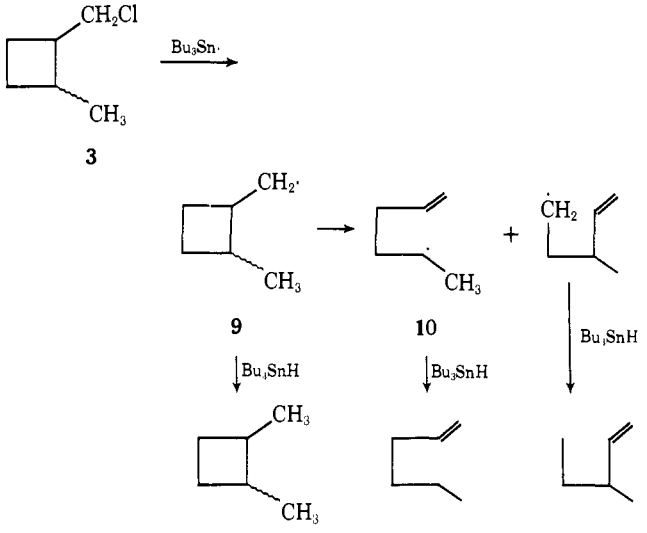
Table I. Rates of Ring-Cleavage Rearrangement of 2-Methylcyclobutylmethylmagnesium Chloride at 61.5° in THF

Compd	Concn	10^6k, sec^{-1} [a]	k_{rel}
trans-4	1.4 *M*	1.10 ± 0.02 [b]	0.36
cis-4	1.0 *M* [c]	0.93 ± 0.01 [b]	0.30
7	1.0 *M* [c]	3.09 ± 0.03 [b]	1.00
		(2.7 ± 0.1) [d]	
		(2.6 ± 0.1) [d,e]	
		(4.4 ± 0.2) [f]	

[a] Uncertainties are standard deviation in k, determined by linear least-squares analysis. [b] Determined by gas chromatography of hydrocarbon formed on hydrolysis. [c] Concentration about 0.15 *M* in *cis*-4 and 0.85 *M* in 7. [d] Determined by integration of NMR spectra. [e] Reference 3; determined at 59.6° by NMR. [f] Reference 1; determined at 61.5° by GC.

The ring-cleavage rearrangement of the corresponding free radicals, *cis*- and *trans*-**9**, were studied by reaction of the corresponding chlorides **3** with tri-*n*-butyltin hydride in 0.02 *M* solution. In both cases, the rearranged hydrocarbon product was mostly 1-hexene so the major cleavage pathway is formation of the secondary radical **10**. From the cis

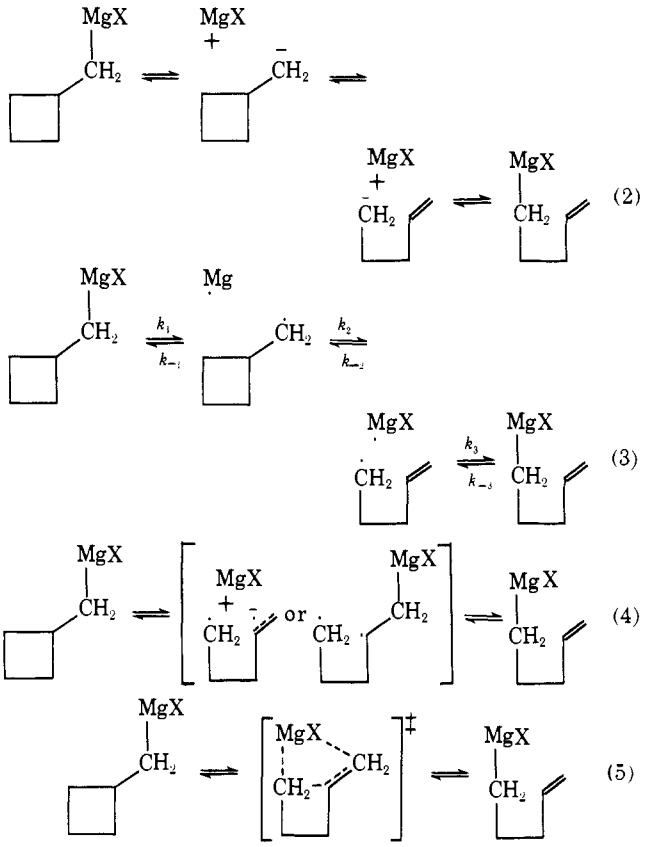


isomer, the 1-hexene comprises 98.1% of the rearrangement.

Discussion

In previous work, several mechanisms have been discussed for the cleavage rearrangement of the cyclobutylmethyl Grignard and for related processes. The most important of these are illustrated in eq 2–5. Equations 2 and 3 are stepwise processes, involving the rearrangement of an intermediate carbanion or radical, respectively, The mechanism of eq 4 is drawn by analogy with "single electron transfer" mechanisms suggested for additions to the double bond of unsaturated alcohols,[5,6] Grignard additions to carbonyl groups,[7,8] and for related rearrangements observed in the direction of ring closure.[9] In eq 5, the central structure is proposed to be a transition state rather than an intermediate of finite lifetime, although a π-complex intermediate along the reaction coordinate has been discussed.[1,10] In another publication,[4] the mechanistic evidence and its relationship to these mechanisms have been summarized in some detail, and it has been concluded that some modification of the concerted mechanism of eq 5 is most likely. We will confine our attention here to the relationship between the present results and the mechanisms of eq 3 and 4.

The critical results reported in this paper are: (a) Grignard reagents **4** cleave preferentially to yield the primary product **5** rather than the secondary product **6**; and (b) in



the course of rearrangement, extensive interconversion of *cis*- and *trans*-**4** does not occur.

In the radical mechanism of eq 3, any one of the three stages might, in principle, be rate determining. If cleavage of the Grignard to the radical pair is a rapid equilibrium, and rearrangement of the free radical is rate determining, then this is also the point at which the product is determined in an unsymmetrical case such as **4**. In that event, since the 2-methylcyclobutylmethyl radical **9** cleaves to the secondary radical **10**, secondary Grignard **6** should be the major Grignard rearrangement product. Since the opposite result is observed, this possibility is eliminated. Preferential formation of the primary Grignard might be explained within the context of the radical mechanism if either the first or third step is rate determining, In either case, the primary Grignard would be formed if the expected lower equilibrium concentration of primary radical reacts enough more rapidly than the larger concentration of secondary radical does in the third step. Either one of these circumstances implies that the radical rearrangement step must be faster than a cage recombination process ($k_2 > k_{-1}$ or $k_{-2} > k_3$, respectively). However, ring cleavage of the cyclobutylmethyl radical is not an exceptionally rapid radical process, and the reverse cyclization must be even slower. Qualitative observation of the extent of rearrangement in tri-*n*-butyltin hydride reduction (in this work) or Grignard oxygenation[11] indicates that cyclobutylmethyl radicals rearrange substantially more slowly than the 5-hexen-1-yl radical,[12,13] and this latter rearrangement is too slow to compete with cage recombination.[14,15] An additional piece of evidence that the first step is not rate determining is that the rate is insensitive to α-methyl substitution.[1,2] If the third step were rate determining, then the prior steps would be equilibria, and cis and trans isomers of **4** should have been interconverted. Again this prediction contrasts with the present results.

The mechanism of eq 4 runs into difficulty for similar reasons. If the first step is rate determining, then cleavage

toward the secondary ring carbon would again be expected. If the second step were rate determining, cis–trans equilibration of the Grignard should be observed, Again, both expectations run counter to the results reported here. Hence, we consider that both the radical and electron transfer mechanisms are demonstrated to be untenable for the rearrangement of the cyclobutylmethyl Grignard, and probably for related Grignard rearrangements.

The cis and trans isomers of **4** rearranged at similar rates, about a third as fast as the rate for the unsubstituted cyclobutylmethyl Grignard **7**. Since the rates for the methyl-substituted Grignards correspond to the cleavage of just one ring bond, a statistical correction of a factor of ½ might be applied to the unsubstituted Grignard. Thus methyl substitution, either cis or trans to the Grignard function, has little effect upon the rate, other than eliminating one direction of cleavage.

Experimental Section

Spectra were run on Varian Associates A-60 and HA-100 NMR spectrometers and Beckman IR-5 and IR-8 ir spectrometers. Gas chromatography was carried out on Varian Aerograph A90-P chromatographs, with the following columns: A, 0.25 in. × 10 ft, 20% Dow Hi-Vac silicon stopcock grease on Chromosorb W; B, 0.5 in. × 10 ft, 17% Apiezon J on Chromosorb P; C, 0.37 in. × 20 ft, 30% SE-30 on Chromosorb W; D, 0.25 in. × 10 ft, 25% Ucon polar on firebrick; E, 0.25 in. × 10 ft, 20% Carbowax 20M on Chromosorb P; F, 0.25 in. × 10 ft, 20% tricresyl phosphate on firebrick.

Elemental analyses were run by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y. Boiling points are uncorrected.

2-Methylcyclobutanecarboxylic acid (1) was prepared from diethyl malonate and 1,3-dibromobutane, followed by hydrolysis and decarboxylation, in a fashion similar to that described previously in the literature.[16,17] The latter steps were done in two ways: (1) reflux with aqueous hydrochloric acid, removal of the ethanol and aqueous acid by distillation, and finally decarboxylation with distillation of the product at about 200° and atmospheric pressure; (2) hydrolysis with concentrated aqueous sodium hydroxide, distillation to remove ethanol, followed by acidification of the hot solution with sulfuric acid, reflux (3 hr), and extraction of the product with ether.

In all cases, the product was a mixture of cis and trans isomers. This was shown by gas chromatography of either the methyl ester (columns C and D) or of the reduction products (as described below). These were present in different preparations in a ratio between 5:1 and 1:1, the major isomer having the shorter retention time. The larger ratios were obtained in preparations utilizing acid hydrolysis of the diester, with extended periods of heating during removal of the hydrochloric acid and subsequent decarboxylation. The observation of an isomer mixture is in contrast with earlier reports in which the derivative of a single isomer, characterized either as cis or trans, was isolated,[17,18] but consistent with other reports.[19,20] NMR spectra of the methyl esters of *trans*- and *cis*-**1**, separated by GC, were obtained: (trans) δ 3.63 (s, 3, OCH_3), 2.6 (m, 2), 2.05 (m, 4), and 1.12 ppm (d, 3, J = 6.0 Hz, CH_3); (cis) δ 3.64 (s, 3, OCH_3), 3.0 (m, 2), 2.1 (m, 4), and 1.01 ppm (d, 3, J = 6.7 Hz, CH_3).

The product obtained in these preparations was shown by NMR and GC to contain small amounts of unsaturated by-products, formed by elimination of the secondary bromine. In a malonic ester synthesis attempted using sodium hydride as base in dimethylformamide solution, unsaturated products were much more important.

2-Methylcyclobutylmethanol (2) was prepared by reduction of either **1** or its methyl ester with lithium aluminum hydride in ether.[20,21] The product was again a mixture of trans and cis isomers, with the trans isomer eluted first (GC, columns C, D, and E). Samples separated preparatively had the following NMR spectra in CCl_4: (trans) δ 3.7 (s, 1, OH), 3.45 (d, 2, J = 5 Hz, CH_2OH), 1.95 (m, 4), 1.5 (m, 2), and 1.06 ppm (d, 3, J = 5.5 Hz, CH_3); (cis) δ 3.51 (m, 2, CH_2OH), 3.25 (s, 1, OH), 2.45 (m, 2), 2.0 (m, 2), 1.6 (m, 2), and 1.02 ppm (d, 3, J = 6.5 Hz, CH_3). The multiplet for the α-methylene group of the cis isomer could be analyzed at either 60 or 100 MHz as the AB part of an ABX spectrum, yielding the parameters: $\Delta\nu$ = 0.14 ppm; J_{AB} = 10.5 Hz; J_{AX}, J_{BX} = 7.6, 6.4 Hz. The ir spectra of both isomers showed appropriate OH stretching absorption at 3300 cm^{-1} but differed considerably in appearance in the CO stretching region (1000–1050 cm^{-1}).

2-Methylcyclobutylmethyl Chloride (3). Thionyl chloride (18 g, 0.15 ml) was added dropwise with stirring over a period of 1 hr to a solution of **2** (14 g, 0.14 mol) and tri-*n*-butylamine (26 g, 0.14 mol) in 300 ml of anhydrous ether maintained at 0°. The solution was allowed to warm to room temperature over 3 hr, and most of the ether was distilled at slightly reduced pressure. The temperature was then raised to 110° over about 3 hr, with distillation of product from the reaction flask under aspirator vacuum. Redistillation yielded 9.4 g of product, bp 124°. Unsaturated impurities could be removed by extracting with sulfuric acid, washing, drying, and distilling. Gas chromatography (columns A–E) showed that the product consisted mainly of two components in a ratio depending upon that of the sample of **1** used in the synthesis. NMR spectra of the separated isomers were obtained in CCl_4: (trans) δ 3.44 (d, 2, J = 6.1 Hz, CH_2Cl), 2.07 (m, 4), 1.54 (m, 2), and 1.10 ppm (d, 2, J = 5.8 Hz, CH_3); (cis) δ 3.45 (m, 2, CH_2Cl), 2.6 (m, 2), 2.05 (m, 2), 1.65 (m, 2), and 1.06 ppm (d, 2, J = 6.7 Hz, CH_3). The α-methylene multiplet of the cis isomer at either 60 or 100 MHz could be fit reasonably well to the AB part of an ABX spectrum, with $\Delta\nu \sim 0.09$ ppm, $J_{AB} \sim 10.5$ Hz, and $\frac{1}{2}|J_{AX} + J_{BX}| \sim 7.4$ Hz.

Stereochemical Correlation. Assignments of cis and trans isomers to the series of 2-methylcyclobutyl derivatives is based on, and confirmed by, a variety of evidence. (1) A sample of the methyl ester of **1**, originally of isomer ratio of 1.7:1 in order of elution, was heated at reflux for several hours with 2 *M* sodium methoxide. The mixture was converted almost entirely to the isomer of shorter retention time, which was therefore presumed to be trans. (2) The isomer of the methyl ester of **1** which was assigned cis stereochemistry had an NMR spectrum in agreement with that reported for the cis isomer, as synthesized by two alternative routes.[22] (3) A mixture of isomers of ratio about 5:1 was carried through steps leading eventually to a similar mixture of *trans*- and *cis*-1,2-dimethylcyclobutanes. Separated samples of the two chlorides (**3**) were also converted to the dimethylcyclobutanes, and the trans isomer of the methyl ester of **1** was reduced to *trans*-**2**. Throughout the conversion, trans isomers had shorter GC retention times than cis isomers. (4) The α-methylene protons of *cis*-**2** and *cis*-**3** were magnetically nonequivalent, while those of the trans isomers appeared as a simple doublet. (5) In the NMR spectra, the methyl groups of cis isomers of **2, 3,** 1,2-dimethylcyclobutane, and the methyl ester of **1** all appeared at slightly higher field than those of the corresponding trans isomers. Also, the tertiary ring hydrogens of the trans isomers showed an upfield shift relative to the cis isomers. These effects may be explained by a shielding effect of the adjacent cis grouping. Another consistent trend noted was a variation in the apparent coupling constant of the 2-methyl substituent. It was consistently smaller in the trans isomer (ca. 5.5 Hz) than in the cis (ca. 6.5 Hz).

Grignard Reagent from 3. Grignard reagents were prepared on a small scale in tetrahydrofuran from samples of **3** of varied isomeric composition. Hydrolysis of the Grignard reagent and gas chromatography (column B; after addition of isooctane and washing with ice-water to remove tetrahydrofuran) showed that there were two major components. These were isolated and characterized as follows: *trans*-1,2-dimethylcyclobutane [NMR (CCl_4) δ 1.9 (m, 4), 1.4 (m, 2), and 1.02 ppm (unsym d, 6, $J \sim 5$ Hz, CH_3); ir (gas) 2910, 1460, 1385, 1332, 1245, 1100, 975, 900 cm^{-1}]; *cis*-1,2-dimethylcyclobutane [NMR (CCl_4) δ 2.35 (m, 2), 2.0 (m, 2), 1.55 (m, 2), and 0.97 ppm (unsym d, 6, J = 6.4 Hz, CH_3); ir (gas) 2910, 1465, 1390, 1345, 1225, 1110, 1030, 960, 880 cm^{-1}]. The shorter GC retention time of the trans isomer is expected from the difference in boiling points reported (trans, 56.8–56.9°; cis, 66.3–67.1°).[23]

A sample of Grignard reagent was heated for 125 hr at 60° in a sealed tube. Hydrolysis yielded a mixture of hydrocarbons, again including *cis*- and *trans*-1,2-dimethylcyclobutane, but with a new major component identified as 3-methyl-1-pentene by comparison of its NMR[24] and ir[25] spectra with published spectra. Additional minor components (<3%) present in the hydrolysis products of

both heated and unheated Grignard reagents were identified as 1-hexene and *cis*- and *trans*-2-hexene. They were identified by comparison of NMR and ir spectra and GC retention times with those of authentic samples. These resulted at least partly from unsaturated impurities in the halide from which the Grignard reagent was prepared.

More detailed studies were carried out on Grignard solutions prepared from individual isomers of **3** separated by preparative gas chromatography (columns B and C).

(a) Trans Isomer. The Grignard reagent was prepared under dry nitrogen from 0.94 g of chloride and 0.23 g of sublimed magnesium[26] in 5 ml of THF (distilled from lithium aluminum hydride under a slow stream of nitrogen). Volatiles were pumped to a trap under high vacuum and replaced by fresh solvent. Titration for base gave a concentration of 1.4 *M*. Samples of Grignard reagent were transferred to ampules and sealed under nitrogen. The ampules were heated in a bath at 61.5° for appropriate periods of time. They were opened in a "dry bag" under nitrogen, fitted with an adapter which permitted volatiles to be removed under vacuum, and then hydrolyzed by addition of *n*-butyl alcohol. Volatile products were then distilled to a trap and analyzed by gas chromatography (columns A, B, and F). A first-order rate plot of log {[dimethylcyclobutane]/([dimethylcyclobutane] + [3-methyl-1-pentene])} vs. time was made, assuming equal sensitivity for the two components. A small amount of 1-hexene was present in the hydrolysis product. This was initially about 1.2% of the total hydrocarbon product, and increased slightly during the period of heating. The rate of increase of 1-hexene was 0.013 ± 0.002 of the rate of increase of 3-methyl-1-pentene. No evidence for unsaturation was apparent in the NMR spectrum of the chloride used, but as little as 1 or 2% might not be detected. A trace component in the hydrolysis product had a GC retention time equal to that of *cis*-1,2-dimethylcyclobutane. During the period of heating, it appeared to decrease from about 0.14 to 0.10% of the total product.

One sample of Grignard reagent was prepared in greater than 50% concentration in THF. The product from hydrolysis without further heating was over half rearranged. The hydrocarbons of rearranged structure were 3-methyl-1-pentene and 1-hexene in about equal amounts.

(b) Cis Isomer. A Grignard reagent was prepared by reaction of a mixture of 0.13 g (1.1 mmol) of cis-**3** and 0.62 g (5.9 mmol) of cyclobutylmethyl chloride with 0.21 g of magnesium in 7 ml of THF. Volatiles were removed by pumping under high vacuum and replaced with fresh solvent. The concentration was about 1 *M*. The Grignard reagent was transferred by syringe to ampules and to two NMR tubes, which were sealed under nitrogen. Ampules were heated for various periods at 61.5° and hydrolyzed as indicated above. Analysis for C_5 and C_6 components was carried out by GC on columns A and F. Rearrangement of the cyclobutylmethyl Grignard was also monitored by integration of the NMR spectrum after various periods of heating, using the high-field doublet and triplet for initial and rearranged Grignard reagent, respectively. Rate constants were evaluated as above.

As with the trans isomer, small amounts of a component with the same retention time as 1-hexene were present in the hydrolysis products from all samples of the Grignard reagent. The amount of 1-hexene varied erratically between 2.5 and 3.5% of the major products. *trans*-1,2-Dimethylcyclobutane was not detected, but analysis of the gas chromatographs indicates that it could have been present in amounts up to about 5% of the amount of 3-methyl-1-pentene. Another minor component made up between 1 and 2% of the total.

Reaction of 3 with Tri-*n*-butyltin Hydride. Solutions in benzene were prepared using separated isomers of **3**, about 0.02 *M* each in the chloride and tri-*n*-butyltin hydride. A trace of azobis(isobutyronitrile) was added. The solutions were placed in Pyrex tubes, degassed under vacuum, and sealed. Tubes were heated for 44 hr at 80°, opened, and analyzed by gas chromatography on columns B and D. The hydrocarbon product from the cis isomer had the composition: 3-methyl-1-pentene, 1.5%; 1-hexene, 82.5%; and *cis*-1,2-dimethylcyclobutane, 16%. The total hydrocarbon yield was 87%. From the trans isomer, the total yield was 85%. 1-Hexene, the major rearrangement product, comprised 59% of the total; 3-methyl-1-pentene was probably less than 5%, with *trans*-1,2-dimethylcyclobutane making up the remainder.

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(25) "Infrared Spectral Data", American Petroleum Institute, Research Project 44, No. 622, 707.
(26) We are indebted to the Dow Metal Products Company for a gift of sublimed magnesium. Results summarized in ref 4 indicate that magnesium purity has only a modest effect upon rates of Grignard rearrangement reactions.