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A polar substituent effect on the ring-cleavage rearrangement of 1-arylcyclobutylmethyl Grignard reagents

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Abstract

The kinetics of the ring-cleavage rearrangements of 1-phenylcyclobutylmethylmagnesium chloride and its *p*-methyl and *p*-chloro analogs have been determined. The first-order rate constants are correlated by the Hammett equation, with $\rho = -0.47$. The results are consistent with a concerted mechanism with a cyclic transition state having significant polar character, although polar effects on the stabilities of reactant and product may also contribute. The phenyl group itself slows the reaction by a factor of 0.031, which is interpreted principally in terms of steric destabilization of the transition state.

1. Introduction

A "ring-chain" rearrangement interconverts cycloalkylmethyl organomagnesium compounds with open-chain unsaturated isomers (*e.g.* eqn. (1d), (1e)). The position of equilibrium and the rate are quite sensitive to differences in substitution and ring size. A variety of lines of experimental evidence, including substituent and solvent effects, appear to be most consistent with the concerted four-center mechanism illustrated [1,2].

In order to characterize the transition state of the reaction more completely, we should know the response of the reaction rate to polar substitution. However, earlier studies have shown that the reaction in either direction is significantly hindered by steric congestion around the reacting centers [1,3–5]. Isolation of a polar effect can most easily be attained by introducing a phenyl substituent, and varying *para* or *meta* substituents on it. In related *cyclization* reactions, this approach has been applied to probe the effect of substitution at the carbon to which the magnesium atom transfers. Not surprisingly, it was found that electron-withdrawing substitution in this position accelerates the reaction [6,7]. In recognition of this result, that carbon has been labelled δ- in transition state **2**.

The present report explores the polar effect of substitution in the position R in eqn. (1). Specifically, we have determined the rates of ring opening of 1-phenylcyclobutylmethylmagnesium chloride (**1b**) and its *p*-methyl and *p*-chloro analogs (**1a** and **1c**).

2. Results and discussion

1-Phenylcyclobutylmethanol (**8b**) was prepared by a known route [8–10] via 1-phenylcyclobutanecarbonitrile (**6b**) and 1-phenylcyclobutanecarboxylic acid (**7b**), and converted to the chloride (**9b**) by reaction with triphenylphosphine and tetrachloromethane [11]. The *p*-methyl and *p*-chloro analogs **9a** and **9c** were made similarly.

Grignard reagents **1a–1c** were prepared in THF from the corresponding chlorides and heated in sealed tubes. The occurrence of rearrangement according to eqn. (1) was inferred from the ^{13}C NMR spectra of the Grignard reagents, obtained before and after heating, and of the products **4a–4c** and **5a–5c** resulting from their hydrolysis. Kinetics of the rearrangements were studied by gas chromatographic analysis of the mixtures of hydrolysis products from samples which had been heated for appropriate time periods. Rates were measured in solutions containing all three of the substrates. In this manner, minor influences on rate resulting from variations in concentration or organometallic

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TABLE 1. Rearrangement of *p*-substituted 1-phenylcyclobutylmethylmagnesium chlorides, 115°C, tetrahydrofuran [a]

Substituent	$k \times 10^5$ (s^{-1}) [b]	k_{rel} [c]
p-CH_3 (**1a**)	3.21 ± 0.17	1.19 ± 0.05
H (**1b**)	2.70 ± 0.13	(1.00)
p-Cl (**1c**)	2.12 ± 0.07	0.79 ± 0.04

[a] Kinetics in solutions containing all three substrates in approximately equal concentration; total concentration about 1 M. [b] Average of three runs, consisting of 5 or 6 points each, from separate Grignard reagent preparations. Uncertainties are standard deviations derived from scatter within and between runs. [c] Average of rate constant ratios from three runs.

composition [1(a)] should cancel, allowing a more accurate determination of relative rates. First-order rate constants and relative rates for rearrangement of the three Grignard reagents in THF at 115°C are listed in Table 1.

Although a Hammett correlation is less informative and convincing with only three points, it may nevertheless provide a semiquantitative description of the magnitude and pattern of substituent effects on a reaction. A plot of the data in Table 1 *vs.* the standard Hammett σ [12] is quite accurately linear, and yields a ρ-value of -0.47 ± 0.01. The Hammett-Brown σ^+ correlates the data distinctly less satisfactorily. The substituent effect observed is not large, but it is clearly in the direction of increasing rate with electron-releasing substitution.

A reasonable charge distribution in the transition state for a concerted mechanism is illustrated in structure **2**. The logic behind this prediction is most simply described for reaction in the cyclization direction (*i.e.* the reverse of the reaction as it is written in eqn. (1)). As the polar carbon–magnesium bond approaches to add to the double bond, the pi-electrons of the double bond should be polarized by interaction with the carbon–metal dipole. If the electrophilic, Lewis-acidic nature of the metal and the nucleophilic character of the carbon are invoked to comparable extents, the alternating charge distribution shown might be expected.

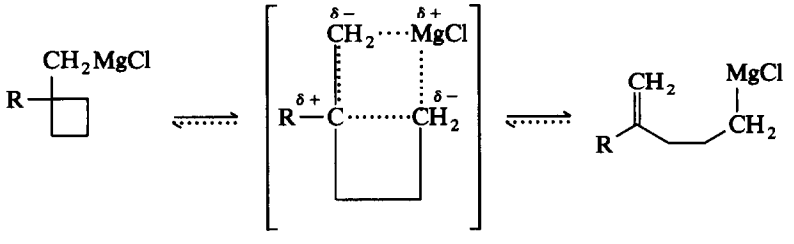
Since a partial positive charge is induced on the carbon holding the substituent R, electron-releasing substitution on this carbon should, as found, stabilize the transition state. Conversely, the previous observations in Grignard reagent cyclizations with substitution on the *opposite* end of the double bond [6,7] imply the development of partial *negative* charge in that position. The observed pattern of electronic substituent effects is, therefore, in full accord with the transition state charge distribution of **2**. By the principle of microscopic reversibility, the same transition state must be traversed in both directions of the reaction. Consequently, electron-release by the substituent R should increase the rate in both directions.

Another reaction considered to involve a cyclic mechanism with an electrophilic metal center is the hydroboration of alkenes. A transition state with a charge distribution similar to that in **2** has been formulated in that case also [13,14]. Relatively small negative ρ-values are observed for the rate of formation of hydroboration product **10** from substituted styrenes

$$ArCH{=}CH_2 + H{-}BY_2 \longrightarrow ArCH_2CH_2BY_2 + ArCH(BY_2)CH_3 \quad (2)$$

10

with a variety of reagents: BH_3 in THF [14] ($\rho = -0.5$ *vs.* σ); 9-BBN in THF [15] ($\rho = -0.49$ *vs.* σ^+); BH_2Cl in THF [16] ($\rho \approx -1.4$ *vs.* σ); thexylchloroboranemethyl sulfide [17] (*p*-methoxy corresponds to $\rho \approx -1$ *vs.* σ^+). The electrophilic nature of the metal is also evident in addition reactions of Al–Ph and Al–H bonds [18].



(1)

(a) R = *p*-$CH_3C_6H_4$; (b) R = C_6H_5; (c) R = *p*-ClC_6H_4; (d) R = H; (e) R = CH_3

TABLE 2. ^{13}C NMR shifts of non-aromatic carbons [a]

R = 1-arylcyclobutyl				
Compound	C_α	C_1	$C_{2,4}$	C_3
R–CN (6)	123.9 –124.2	39.93–40.8	34.52–34.81	16.88–17.01
R–CO_2H (7)	178.6 –182.3	51.93–52.23	32.25–32.40	16.49–16.63
R–CH_2OH (8)	70.66– 70.95	47.70–47.99	29.68–29.73	15.88–15.96
R–CH_2Cl (9)	54.44– 54.88	47.09–47.52	30.86–30.90	15.47–15.53
R–CH_3 (4)	30.41– 30.59	42.6 –42.9	34.29–34.38	15.54–15.64
R–CH_2MgCl (1)	33.4 – 33.5 [b]	50.4 –50.71	39.81–40.14	15.92–16.15
	30.8 – 30.9	49.5 –49.87	39.49–39.65	

R = 4-phenyl-4-penten-1-yl					
Compound	C_1	C_2	C_3	C_4	C_5
R–H (5)	13.70–13.80	21.22–21.43	37.32–37.55	147.35–148.8	111.39–112.73
R–MgCl (3)	7.86– 8.30	29.92–30.25	45.02–45.39	149.86–151.04	109.63–111.17

[a] Spectra of Grignard reagents in THF; other compounds in $CDCl_3$. Ranges given include *p*-CH_3, H, *p*-Cl. [b] Doubled peaks of Grignard reagents collapsed in spectra at elevated temperature.

Two other factors should lead to a polar effect on the *equilibrium constant*. First, a double bond is stabilized by electron-releasing substituents because of the electronegativity of its sp^2 carbons [19,20]. In eqn. (3):

$$C_6H_5CH{=}CH{-}CH_2C_6H_4X \rightleftharpoons C_6H_5CH_2{-}CH{=}CHC_6H_4X \quad (3)$$

p-methyl and *p*-chloro stabilize and destabilize the adjacent double bond by equilibrium factors of 1.15 and 0.95, respectively [20]. Second, an electron-releasing aryl substituent should destabilize the electron-rich C–Mg group of the reactant. A very rough (and naive) estimate of this effect may be made with the benzoate ion as model for the location of the "anionic" C–Mg carbon relative to the ring. Using ionization constants of benzoic acids [21], assuming about 35% ionic character for the C–Mg bond [6,22], and ignoring solvent polarity, temperature, and any other variables, *p*-methyl and *p*-chloro effects on the stability of the reactant are estimated as factors of 0.88 and 1.19. * The *rate* will also be influenced by these two effects, to the extent that the transition state reflects the changes in bonding from reactant toward product. Both should influence the ring cleavage rate in the same sense as the proposed transition state charge distribution. It seems likely, however, that these bonding changes are not strongly developed in the transition state (*i.e.* not a "late" transition state), since the ring-cleavage is exothermic (Hammond postulate), and since substantial substituent effects were found in the cyclization reactions [6]. We conclude that, although other factors may contribute to the observed substituent effect, the results help to confirm the proposed polar character of the transition state.

The present data also provide a measure of the effect of the phenyl substituent itself on the rate of the ring-cleavage reaction. Extrapolation of the rate constant for ring-cleavage of cyclobutylmethylmagnesium chloride (eqn. (1d)) [24] to 115°C yields a value of 8.8×10^{-4} s^{-1}, and a relative rate effect of 0.031 for 1-phenyl substitution. This result is consistent with steric destabilization of a crowded cyclic transition state. Methyl has a similar effect (eqn. (1e)), decreasing the reaction rate in both directions [3–5], despite its electron-releasing polar effect. The phenyl group should also be expected to have additional electronic effects on the equilibrium and rate, whose net result may be difficult to predict. Conjugation with the double bond of the product would favor ring-cleavage *, but the electronegativity of the phenyl group should also stabilize the electron-rich C–Mg of the reactant. **

Alternative mechanisms involving initial cleavage to either a radical pair or a carbanion–magnesium ion pair may be less easily accommodated to the observed substituent effects.

^{13}C NMR data for the aliphatic carbons of the Grignard reagents and their precursors and hydrolysis

* Comparable estimates were made using Taft σ^* values for substituted benzyl groups (derived from ionization of phenylacetic acids [21]) and assuming ρ^* of about 4 for a unit charge change in R–Y ⇌ R–Z [23].

* Stabilization of about 4 kcal mol^{-1}, based on double bond isomerization [19], heats of hydrogenation (via heats of formation [25]), and heats of polymerization [26].

** A surprisingly large β-phenyl effect of approximately 1000 is reported in the mercury–magnesium exchange equilibrium between ethyl and 2-phenylethyl [27].

products are summarized in Table 2. The spectra of Grignard reagents **1** were complicated by broadening and the appearance of two signals for most of the carbons. This is probably the consequence of a decreased rate of the Schlenk equilibrium for the hindered Grignard reagent; the peaks merged and sharpened at higher temperatures. Variation of the functional group produced shift effects qualitatively consistent with published parameters for saturated carbons [28]. The α and β effects for Cl and OH in the 1-arylcyclobutylmethyl compounds were somewhat smaller than tabulated parameters, but were similar to those observed for 1-methylcyclobutylmethyl [3] or neopentyl derivatives [29]. The effect of the organomagnesium function on the shifts of the olefinic carbons of **3** (*vs.* **5**) is similar to that observed previously [3,30], and is consistent with an electrical field polarization effect [30]. There were variations in shifts of the aliphatic carbons with the aromatic substituent, but these were small, and comparable to solvent and concentration effects. Chemical shifts of the Grignard reagents were predicted usefully, though not accurately, by the equations of Leibfritz, Wagner, and Roberts [31]. The aromatic carbon shifts of **4a–4c** were similar to those of the corresponding t-butyl–Ar analogs, and were affected by the functional substituents similarly to those of 2-substituted-1-phenylethanes [30].

3. Experimental details

Proton and ^{13}C NMR spectra of isolated compounds were obtained in $CDCl_3$ solution on a Bruker WM250 spectrometer; chemical shifts are relative to internal tetramethylsilane. In Grignard reagent solutions, a small amount of C_6D_6 was added for a lock, and ^{13}C shifts were measured relative to the THF resonance which appears at 25.85 ppm under these conditions; when it was identifiable, C_6D_6 appeared within 0.1 ppm of 128.00 ppm. ^{13}C assignments were assisted by off-resonance decoupling and by the use of additive parameters [28,30,31]. Data are summarized in Table 2. Routine gas chromatograms were obtained on a Varian A90P chromatograph, using an 8 ft × 1/4 in column of 20% Ucon 50-HB-280 on 60–80 mesh Chromosorb W. For the analysis of Grignard reagent hydrolysis products, a Hewlett-Packard 5890 GC was used, equipped with a cross-linked methyl silicone capillary column (25 m × 0.25 mm). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Boiling and melting points are uncorrected. Tetrahydrofuran was dried by distillation from sodium benzophenone under nitrogen. Magnesium used for Grignard reagent preparations was Reade RMC-4 (99.98%).

3.1. 1-Phenylcyclobutylmethyl chloride (9b)

1-Phenylcyclobutanecarbonitrile (**6b**) was prepared from phenylacetonitrile and 1,3-dibromopropane with sodium hydride (50% dispersion in mineral oil) in DMSO, following a procedure of Butler and Pollatz [8]. Distillation through a 10-cm Vigreaux column yielded 60.5% of colorless liquid, b.p. 103–117°C/3.2 Torr (lit. [8] b.p. 120–122°C/7 Torr). The nitrile was hydrolyzed with potassium hydroxide in 2-hydroxyethyl ether, as described by Lyle and Lyle [9], to give 1-phenylcyclobutanecarboxylic acid (**7b**) in 75% yield, m.p. 107–108°C (toluene) (lit. [8] m.p. 107–108°C). 1-Phenylcyclobutylmethanol (**8b**) was prepared by reduction of the acid with an excess of lithium aluminum hydride in ether. The colorless crystalline product was isolated in 87% yield, m.p. 59–60°C (toluene) (lit. [10] m.p. 60°C).

A solution of 9.3 g (57.4 mmol) of **8b** and 19.0 g (72.4 mmol) of triphenylphosphine in 20.5 ml of CCl_4 was kept at room temperature for 48 h. The solution was chilled to 0°C, diluted with 10 ml petroleum ether to precipitate triphenylphosphine oxide, and then filtered through filter cell; the precipitate was washed with petroleum ether. The solvent was removed under vacuum and the product (50% yield) was distilled using a Hickman-type molecular still (60°C/0.45 Torr). Anal. Found: C, 72.84; H, 7.12, $C_{11}H_{13}Cl$ calc.: C, 73.13; H, 7.25%.

3.2. 1-(4-Methylphenyl)cyclobutylmethyl chloride (9a)

The same sequence was followed: 1-(4-methylphenyl)cyclobutanecarbonitrile (**6a**), 46% yield, b.p. 105–114°C/2.25 Torr (lit. [10] b.p. 93°C/0.3 Torr); 1-(4-methylphenyl)cyclobutanecarboxylic acid (**7a**), 69% yield (toluene, and sublimed, 120°C/0.35 Torr), m.p. 116–117°C (lit. [10] m.p. 115–116°C); 1-(4-methylphenyl)cyclobutylmethanol (**8a**), 97% yield, m.p. 28–29°C (lit. [10] m.p. 29–30°C); **9a**, reaction time 7 d, 68% yield, b.p. 98–99°C/1.75 Torr. Anal. Found: C, 74.31; H, 8.01. $C_{12}H_{15}Cl$ calc.: C, 74.03; H, 7.77%.

3.3. 1-(4-Chlorophenyl)cyclobutylmethyl chloride (9c)

The same sequence was followed: 1-(4-chlorophenyl)cyclobutanecarbonitrile (**6c**), 61% yield, b.p. 111°C/2 Torr (lit. [10] b.p. 169–170°C/20 Torr); 1-(4-chlorophenyl)cyclobutanecarboxylic acid (**7c**), 73% yield, m.p. 89–90°C (toluene, and sublimed) (lit. [10] m.p. 89–90°C); 1-(4-chlorophenyl)cyclobutylmethanol (**8c**), 74% yield, m.p. 56–57°C (toluene) (lit. [10] m.p. 55–56°C); **9c**, reaction time 2.5 d, 64% yield, b.p. 95–105°C/0.75 Torr. Anal. Found: C, 61.21; H, 5.58. $C_{11}H_{12}Cl_2$ calc.: C, 61.42; H, 5.62%.

3.4. Preparation and handling of Grignard reagents; kinetics

Grignard reagents were prepared under a positive pressure of dry nitrogen in a flask fused to a reflux condenser and side-arm gas connection. An excess of magnesium turnings was activated by treatment with a few drops of 1,2-dibromoethane in 2 ml of THF; the resulting solution was drawn off by syringe and the turnings were washed with a small portion of THF. The halide (4–15 mmol) was added in one portion in the volume of THF required for a 1 M solution, and the mixture was heated to reflux until reaction occurred. In some instances the reaction was subjected to ultrasound. The solution was transferred via syringe, in a counterflow of nitrogen, to a 10 mm NMR tube (for qualitative observations) or to several dried, nitrogen-filled tubes (for kinetics). These were partially evacuated and sealed, heated in a thermoregulated bath for appropriate periods of time, and refrigerated until analysis by NMR or hydrolysis. The tubes were opened and hydrolyzed (HCl) in a nitrogen-filled glove bag, and the solutions extracted (CH_2Cl_2) and dried (Na_2SO_4). Grignard reagent solutions for kinetics were prepared from an approximately equimolar mixture of the chlorides, in a total concentration of about 1 M. Three separate preparations and rearrangement kinetics runs were made, consisting of five or six tubes each.

Preliminary studies by ^{13}C NMR established the presence and nature of the rearrangement. Sealed samples of the individual Grignard reagents were examined initially, and after periods of heating which had led to rearrangement to an extent of 75% or more. Spectra were also obtained after hydrolysis, and for the individual hydrolysis products **4a–4c** and **5a–5c** after preparative GC. Spectra are summarized in Table 2. Both the formation of the Grignard reagents and their rearrangement were found to be quite clean. In the initial solutions, there was up to 5% of "hydrolysis" product, but no evidence for the presence of dimer or other side-product in the Grignard reagent formation. At most, one or two spurious resonances, of intensity no greater than 5% of the known components, might be seen. Resonances of the rearranged Grignard reagent appeared in the heated solutions, along with much weaker signals of "hydrolysis" products (formed by attack on solvent); otherwise there was no indication of any other process in competition with the rearrangement. Spectra of the hydrolyzed solutions were similarly uncomplicated. The solutions used in the kinetics were superior to those in the qualitative study.

Gas chromatograms of the solutions from hydrolysis were run at an initial temperature of 70°C for 10 min and then programmed at 4° min^{-1}. All peaks for **4a–4c** and **5a–5c** were separated with near base-line resolution, and no additional components were noted Since the reaction occurs without significant side reaction, the concentration of reactant is proportional to the fraction of unrearranged Grignard reagent, **1**/(**1** + **3**). This fraction was set equal to the corresponding ratio of hydrolysis products **4**/(**4** + **5**); peak areas were measured as height × (width at half-height), and equal sensitivity within isomeric pairs was assumed. In several instances, replicate ratios were found to agree within 2%. Rate constants, listed in Table 1, were calculated from the slopes of first order plots of ln (fraction unrearranged) *vs.* time, using an unweighted least squares routine. No point deviated more than 0.056 (fraction rearranged) from the plots, and the average deviation was 0.015. Correlation coefficients ranged from 0.9958 to 0.9997. Tabulated uncertainties in the rate constants are the larger of standard deviations within the runs or from the mean of three runs. Relative rates and their uncertainties in Table 1 were calculated from the mean rate constants of the individual compounds. Quite similar values were obtained using a variety of alternative approaches which compared extents of reaction in individual heated samples or the rate constants in each run, but with very little change in either the values or apparent precision.

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