# Rearrangement of Grignard Reagents
from 1-Aryl-4-chlorocyclohexanes

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Abstract: The rearrangement of the Grignard reagents from 1-phenyl-4-chlorocyclohexene (**1b** → **3b**) and its *p*-methyl and *m*-trifluoromethyl derivatives has been studied as an example of the intramolecular addition of a Grignard reagent to a carbon–carbon double bond. Comparison of rearrangement rates among these compounds and with the Grignard from 4-chlorocyclohexene leads to two important conclusions: (1) the aryl group *decreases* the rate of the rearrangement; and (2) the rearrangement is accelerated to a modest extent ($\rho \simeq 1.4$) by electron-withdrawing substituents. The result is most consistent with a concerted four-center addition mechanism.

Grignard reagent cyclizations (eq 1), involving intramolecular addition of the carbon–magnesium bond to an olefinic double bond, have been reported for a variety of ring sizes and systems. The reverse reaction, ring cleavage, has also been studied for three- and four-membered rings.[1-6]

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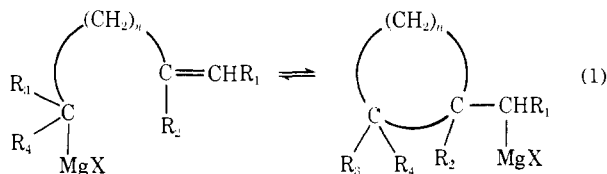
From kinetics studies of the cyclization, a pattern of substituent effects has begun to emerge. In ring closure to a five-membered ring (eq 1, $n = 3$) substitution of a methyl group on either end of the double bond (R_1 or $R_2 = CH_3$) leads to about a 1000-fold decrease in reaction rate,[4] as might be anticipated for an anionic process. However, in the cyclopropyl case (eq 1, $n = 1$), a similar decrease occurs when $R_1 = Cl$,[5] which might be expected to stabilize anionic charge inductively or by resonance. There is indication also that a phenyl group similarly located does not increase the rate, and may significantly decrease it.[6] Substantial rate decreases are also produced by $R_2 = $ methyl or phenyl.[7] It thus appears likely that the magnitude, and even the direction, of any *electronic* effect upon the cyclization may be masked by a much larger *steric* effect.

Knowledge of the electronic effect of substituents is important in a discussion of the mechanism of cyclization; the present study was undertaken to determine
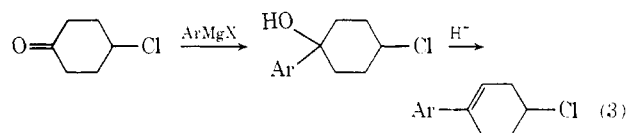
the effect of substituents at the R_1 position. To eliminate overriding steric influences, the effect of substituents on a phenyl group in this location was studied. A convenient system appeared to be the 1-arylcyclohexen-4-yl system (**1**, R = aryl). Maercker[8] has examined the case where R = H, and found that reaction occurs after "some hours" at 80°, reaching an equilibrium of about 90% **3a**. In this paper, we report results for the cases where R = phenyl, *p*-methylphenyl, and *m*-trifluoromethylphenyl (**1b–d**).
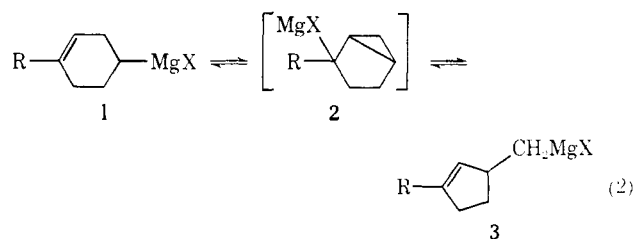
a, R = H
b, R = C₆H₅
c, R = *p*-CH₃C₆H₄
d, R = *m*-CF₃C₆H₄

Results

Compounds were prepared by the route shown in eq 3. Grignard reagents were prepared in tetrahydro-

furan, and samples were sealed in nmr tubes and ampoules for heating. After several hours heating at temperatures of 120° or higher, evidence for formation of the primary Grignard **3** appeared in the nmr spectra as a doublet for the CH_2Mg group at -0.34 ppm. On further heating, this signal increased to a maximum, and then began to decrease gradually. In the olefinic region of the spectrum, separate absorptions for the Grignard reagent and its hydrolysis product were visible, and during the extended heating period the Grignard absorption disappeared at the expense of the other. When ampoules were opened after various periods of heating, followed by hydrolysis and gas

(1) (a) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, 82, 2646 (1960); (b) M. E. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *ibid.*, 88, 1732 (1966); (c) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, 87, 5144 (1965).
(2) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, 28, 2161 (1963).
(3) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, 86, 4663 (1964).
(4) W. C. Kossa, Jr., T. C. Rees, and H. G. Richey, Jr., *Tetrahedron Lett.*, 3455 (1971); E. A. Hill, R. J. Theissen, A. Doughty, and R. Miller, *J. Org. Chem.*, 34, 3681 (1969).
(5) E. A. Hill, *J. Amer. Chem. Soc.*, 94, 7462 (1972). Please refer to this paper for additional references to cyclization and ring cleavages, and information bearing on the reaction mechanisms.
(6) (a) E. A. Hill and M. R. Engel, *J. Org. Chem.*, 36, 1356 (1971); (b) H. G. Richey, Jr., private communication.
(7) A. Maercker and K. Weber, *Angew. Chem., Int. Ed. Engl.*, 8, 912 (1969); *Justus Liebigs Ann. Chem.*, 756, 43 (1972).
(8) A. Maercker and R. Geuss, *Angew. Chem., Int. Ed. Engl.*, 9, 909 (1970).

**Table I.** Relative Rates of Rearrangement of 1-Arylcyclohexen-4-yl Grignard Reagents in Tetrahydrofuran at 122°

Aryl$_1$	Aryl$_2$	k_1/k_2[a]	r[b]	$10^7 k_1$[c]	$10^7 k_2$[c]
m-CF$_3$C$_6$H$_4$	C$_6$H$_5$	2.0 ± 0.4	0.91	13 ± 5	7 ± 3
m-CF$_3$C$_6$H$_4$	p-CH$_3$C$_6$H$_4$	6.6 ± 0.8	0.93	19 ± 3	2.7 ± 0.6
C$_6$H$_5$	p-CH$_3$C$_6$H$_4$	2.0 ± 0.4	0.94	4.1 ± 0.5	2.0 ± 0.7

[a] Determined as slope of plot of [log (fraction unrearranged)] or [fraction rearranged] for compound **1** *vs.* compound **2**. Uncertainties are standard deviations. [b] Correlation coefficient. [c] Determined from initial slopes of plots of [lot (fraction unrearranged)] *vs.* time; uncertainties estimated to reflect probable random and systematic errors.

chromatographic analysis, it was found that 1-aryl-cyclohexene was the principal product initially, with increasing amounts of 1-aryl-3-methylcyclopentene after heating. The latter increased to a maximum between 35 and 65% of the mixture of **1** and **3**, depending upon the sample, and then decreased slowly. In the case of the m-CF$_3$ derivative, samples were hydrolyzed with D$_2$O shortly after formation, and again after heating past the maximum. Mass spectrometric analysis showed 82% monodeuteration from **1d** from the early sample, but only 10 and 25% deuteration from **1d** and **3d** from hydrolysis after extensive heating. The most probable interpretation is that competitive with their equilibration, both Grignard reagents decompose to form (at least in part) the corresponding hydrocarbon. The more reactive secondary Grignard reagent is destroyed more rapidly; then, at later stages in the heating, after much of **1d** has been destroyed, there is net conversion of **3d** back to **1d**. An additional complication in the reaction was the production of substantial amounts of the corresponding biphenyls, both during Grignard formation and to a lesser extent during the heating. (Details are given in the Experimental Section.) To minimize problems arising from Grignard reagent destruction and the reversibility of the reaction, relative rates of rearrangement were compared during the initial portion of the reaction. Since it has been found that rates of Grignard rearrangements are significantly dependent upon total Grignard concentration at concentrations greater than 0.5–1 M,[3,7] experiments were conducted in solutions between 0.3 and 0.5 M. In addition, the compounds were studied in pairwise fashion in the same solution, after preliminary experiments had shown that substitution on the benzene ring produced fairly small effects. In this manner, potential differences arising from concentration or other sources would largely cancel between the compounds involved. The mixtures were analyzed by hydrolysis followed by gas chromatography to determine the relative amounts of hydrocarbon of rearranged and unrearranged structure. Relative rates in a comparison were taken as the slope of a plot of either $b/(a + b)$ or log $[a/(a + b)]$ for one compound *vs.* the other (where a = unrearranged structure and b = rearranged structure). The results are listed in Table I. Also tabulated are rate constants of individual compounds (corrected for nonquantitative Grignard formation as determined by nmr). The direct comparisons are felt to be more reliable than the rate constants. While the results lack precision, the results clearly indicate the order and magnitude of the variation in reactivity. The electron-withdrawing trifluoromethyl group accelerates the reaction rate slightly, and the methyl group produces a slight decrease. The total span of relative rates is probably about 6–7, and with some certainty, less than 10.

Discussion

In the following discussion, we assume that the rearrangement reaction observed proceeds through the bicyclic Grignard reagent **2**. Such an assumption is consistent with the existence and ring-cleavage rearrangement of cyclopropylmethyl Grignard reagent,[1] and with recent experiments by Maercker[9] on the isotope-position rearrangement of the Grignard reagent from 5-bromo-2-pentene-5,5-d_2. Furthermore, the rate-determining process in the rearrangement is probably the cyclization to **2**, rather than its cleavage. This is consistent with our observation[3] that the 2-methylcyclobutylmethyl Grignard **4** cleaves preferentially to the primary Grignard product by a ratio of about 100:1. Furthermore, and more pertinent to the present case, Maercker[8] found that in an attempt to prepare the bicyclic Grignard **2** directly from the


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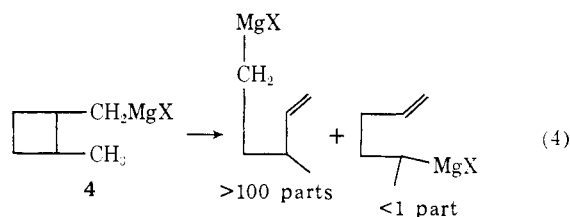
corresponding bromide, **1** and **3** were formed in a ratio of 1:5. Hence, partitioning of the intermediate is principally in the forward direction, making the first step rate determining. Finally, even if the cleavage were rate determining, its transition state should be very similar electronically to that for the closure from the cyclohexenyl reagent **1**. Therefore, substituents should affect the energies of both transition states in very similar fashion; similar conclusions about mechanism would be drawn whether ring closure or cleavage happened to be rate determining.

The first noteworthy feature of the present results is the slow rate of rearrangement of all compounds studied. Although Maercker[8] gives no rate constants for **1a**, he indicates that rearrangement occurs after "some hours at 80°."[9a] By contrast, the phenyl compound **1b** would have a half-life for rearrangement of about 350 hr at 120°. This probably corresponds to a sizable rate *decrease* produced by introduction of the phenyl group, even making suitable allowance for differences in concentration, solvent, and halogen. An opposite conclusion concerning the effect of phenyl substitution was drawn by Roberts and coworkers.

(9) A. Maercker and W. Streit, *ibid.*, 11, 542 (1972).
(9a) NOTE ADDED IN PROOF. A. Maercker and R. Geuss, *Chem. Ber.*, 106, 771 (1973), have recently published details of their work.[8] They find a rate constant at 120° in 3.5 M ether solution of about 7 × 10⁻⁴ sec⁻¹. At 80°, they find rates in dilute THF solution to be about 125-fold slower than in 3.5 M ether solution. From these, the half-life in dilute THF solution at 120° is estimated as 35 hr. We have generally found chlorides to rearrange slightly faster than bromides.

They noted that the half-life for interconversion of the aliphatic methylene groups of the allylcarbinyl Grignard **5a** was 30 hr at 27°,[1a] but that equilibrium was complete with the diphenyl derivative **5b** by the time of the first observation (5 hr at room temperature).[1b] However, from experiments on the reaction of 4-bromo-1-chloro-1-phenyl-1-butene with magnesium, it appears that the phenyl group in Grignard **5c** has, if anything, a rate-decreasing effect.[6a] Richey has also found a decrease in rate for Grignard reagent **5d**.[6b]
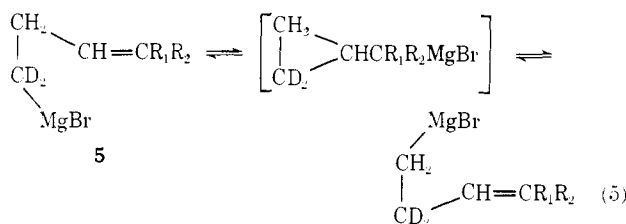
a. $R_1 = R_2 = H$
b. $R_1 = R_2 = C_6H_5$
c. $R_1 = C_6H_5$; $R_2 = Cl$ (no deuterium)
d. $R_1 = C_6H_5$; $R_2 = H$

The present results help to confirm the suggestion[6] that rearrangement in Roberts' experiments with **5b** may have occurred *during* formation of the Grignard, rather than afterward.

Two simple "extreme" mechanisms for the intramolecular Grignard addition (or its reverse, the ring opening) have been considered.[2,3,9] These involve respectively the formation of a carbanion or a radical by cleavage of the C–Mg bond, followed by addition to the double bond and reassociation to form the new C–Mg bond. These mechanisms predict different electronic substituent effects.

The effect observed for substituents on the phenyl ring in this study is relatively small. Although the results are not of the highest order of accuracy, and three points are seldom considered sufficient for a Hammett plot, it is instructive to consider the results in the context of the Hammett equation. Using established σ values[10] of $+0.43$ for m-CF$_3$ and -0.17 for p-CH$_3$, along with the rate ratio m-CF$_3/p$-CH$_3$ = 6.6, a rough ρ value of $+1.4$ is calculated. A rate ratio as large as 10 would correspond to a ρ of $+1.67$. Substantially larger ρ values are commonly observed for rates of generation of a carbanion adjacent to an aromatic ring: $\rho = +3.7$–4.0 for isotopic hydrogen exchange of substituted toluenes catalyzed by lithium cyclohexylamide,[12] and about 7 for exchange with pyrrolidine;[13] $+5.0$ for addition of living polystyrene anions to substituted styrenes;[14] $+3$ for addition of C$_2$H$_5$O$^-$ to ArC(CF$_3$)=CF$_2$;[15] $+4$ for H-exchange of ArCH(CF$_3$)$_2$;[16] $+4.4$ in Elcb elimination from ArCH$_2$CH$_2$-SOCH$_3$;[17] $+4.88$ for cleavage of ArCH$_2$Si(CH$_3$)$_3$ by

CH$_3$O$^-$;[18] $+4.63$ for rearrangement of R$_3$SiC(CH$_3$)-(Ar)OH;[11] and $+2.2$–3.0 for reaction of various organolithium compounds with ArPh$_2$CH.[19] Somewhat larger ρ values appear to be obtained for *equilibrium* formation of carbanions ($\rho = +6.9$ for acidity of ArPh$_2$CH;[20] a Brønsted α of 0.4 has been reported to relate rates and equilibria of carbanion formation for some arylmethyl compounds[21]); a ρ value of $+5$ has been obtained for radical anion formation.[22] Smaller ρ values are found for the acidity of Ar–Z–H, when the Z group is more electronegative or otherwise capable of accommodating the electron pair of the Z–H bond (ρ is $+5.3$ for ArNH$_2$ acidity;[23] 4.07 for Ar-NHPh;[24] 2.89 for ArNH$_3^+$;[25] and 2.23 for ArOH[25]). Thus, the intramolecular Grignard addition is much less sensitive to substituent effects than are reactions generating a carbanionic charge adjacent to the ring (a ρ value of 4.0 would correspond to a rate spread in the present study of a factor of about 300), and these results may be taken as evidence against carbanion addition as the rate-determining step in the rearrangement of 1 to 3. Carbanion formation by ionization from the Grignard would also appear unlikely as the rate-determining step, since this would be expected to have essentially no rate dependence upon the remote benzene ring substituents.

In reactions involving rate-determining radical formation adjacent to a benzene ring, small substituent effects in either direction have been observed, depending upon the nature of the radical (for instance, $\rho = +0.51$–0.6 in radical copolymerization of substituted styrenes;[26] $+0.7$ for H-abstraction from ArCH(CH$_3$)$_2$ by polystyryl radicals;[27] and small negative ρ values are observed for additions of trichloromethyl radicals[28]). The present ring substituent effects might be consistent with the radical addition, although other evidence would appear to rule it out.[3-5,2]

In an earlier publication,[3] it was proposed that the mechanism of ring cleavage of the cyclobutylmethyl Grignard reagent is a concerted process, in which migration of the magnesium occurs concurrently with bonding changes in the carbon skeleton. Such a mechanism was proposed because effects of solvent, structure, and deuterium substitution seemed inconsistent with either the radical or carbanion processes. By the principle of microscopic reversibility, the same reaction path should be involved in the reverse process, intramolecular Grignard addition, if studied for the same system under the same conditions. This same mechanism must be considered a strong prospect in similar Grignard additions, even though the particular ring system and reaction conditions may vary. Subsequent

(10) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). Somewhat more positive σ values for m-CF$_3$ have been indicated: $+0.49$ in ref 11 and $+0.47$ in ref 12b.

(11) A. G. Brook, G. E. LeGrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

(12) (a) A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964); (b) A. Streitwieser, Jr., and D. Holtz, *J. Org. Chem.*, **35**, 4288 (1970).

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(16) K. J. Klabunde and D. J. Burton, *ibid.*, **94**, 820 (1972).

(17) R. Baker and M. J. Spillett, *J. Chem. Soc. B*, 481 (1969).

(18) R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometal. Chem.*, **3**, 448 (1965).

(19) P. West, R. Waack, and J. I. Purmort, *J. Organometal. Chem.*, **19**, 267 (1969).

(20) L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 4544 (1966).

(21) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, **87**, 384 (1965).

(22) R. G. Lawler and C. T. Tabit, *ibid.*, **91**, 5671 (1969).

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(24) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).

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(26) C. Walling and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948); M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **86**, 217 (1965); M. Imoto, *ibid.*, **94**, 238 (1966).

(27) T. Yamamoto, *Bull. Chem. Soc. Jap.*, **40**, 642 (1967).

(28) M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 233, 242 (1964).

results have been consistent with this mechanism.[5] In the present study, the rate-retarding effect of phenyl substitution and the modest acceleration by electron-withdrawing groups appear to be best accounted for by the same concerted process. A steric retardation by phenyl, as well as by methyl and chlorine, would be probable in a concerted addition. The small substituent effect suggests that full carbanion formation is not involved, but rather a process which generates only fractional negative charge on the carbon adjacent to the aromatic ring. It may be significant that the observed ρ value in this study is roughly one-third that observed in carbanion-generating reactions; this is similar to the 35% ionic character for the C–Mg bond estimated from Pauling electronegativities.[29]

A further mechanistic elaboration previously suggested[3] involves metal–olefin π-complex character in the transition state. Such a complex might be an actual intermediate, following the rate-determining transition state in cleavage, or preceding it in the intramolecular addition, as shown in eq 6. Even if such a

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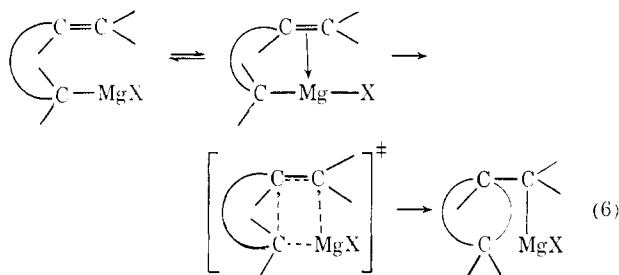
complex were not a discrete intermediate, the features tending to stabilize a complex could still be important in stabilizing the transition state, since the reaction coordinate may pass through a similar configuration. Oliver has presented evidence for intramolecular π-complex interaction in 1-buten-4-yllithium in hydrocarbon solution.[30] In the present work, we find the olefinic proton resonance signal of the Grignard reagent shifted to low field relative to the corresponding hydrocarbon, much in the same fashion as shifts observed by Oliver.

One impetus for the present work was the possibility of finding evidence for π-complex character in the transition state. This might be expected to manifest itself as a negative ρ value. For instance, ρ is -0.766 for Ag$^+$ complex formation from substituted styrenes;[31] -0.65 and -1.43 for the two modes of addition of BH$_2$Cl to styrenes;[32] -0.95 for "coordination polymerization" of styrenes.[33a] The latter two reactions are believed to involve mechanisms in which the reagent first complexes with the π electrons before rearranging, probably via a four-centered transition state, to the adduct. A ρ value of -0.619 was found for addition of dichlorocarbene to styrenes.[33b] The small positive ρ value found in the present study would probably not be inconsistent with a weak π complex as a

reaction intermediate, but provides no positive evidence for such interaction in the transition state.

Experimental Section

Ir and nmr spectra were obtained on Beckman IR8 and Varian T-60 or HA-100 spectrometers. Elemental analyses were by the Schwarzkopf Microanalytical Laboratory. Gas chromatography was carried out on Varian Aerograph A-90-P chromatographs.

4-Chlorocyclohexanone was prepared by the method of Grewe,[34] bp 75–85° (5 mm) [lit.[34] bp 81–90° (12 mm)].

4-Chloro-1-phenylcyclohexene. A solution of phenylmagnesium chloride (54 ml, 2.42 M in tetrahydrofuran) was added dropwise to 4-chlorocyclohexanone (14.4 g, 0.11 mol) in 110 ml of dry tetrahydrofuran. After stirring for 8 hr at room temperature, the mixture was hydrolyzed, and the product was extracted into chloroform, dried, and distilled: bp 155–170° (5 mm); nmr (CCl₄) δ 7.17 (m, 5, C₆H₅), 4.1 (m, 1, CHCl), 2.93 (s, 1, OH), 2.6–1.2 ppm (m, 8, CH₂); ir (neat) 3400, 3030, 750, and 690 cm⁻¹. The product was dehydrated without further purification by refluxing for 12 hr with 2 g of p-toluenesulfonic acid in 250 ml of benzene with a Dean Stark trap. The solution was washed with aqueous sodium bicarbonate and with water, dried, and distilled to yield product in overall 45% yield: bp 160–170° (5 mm); nmr (CCl₄) δ 7.17 (s, 5, C₆H₅), 5.73 (approx. triplet, 1, $J \sim 3$ Hz, =CH), 4.00 (m, 1, CHCl), 2.36 (m, 4, allylic), and 1.93 ppm (m, 2, CH₂); ir (neat) 3030, 2940, 1670, 750, and 690 cm⁻¹.

Anal. Calcd for C₁₂H₁₃Cl: C, 74.84; H, 6.75. Found: C, 75.08; H, 6.95.

4-Chloro-1-(p-methylphenyl)cyclohexene was prepared in similar fashion, using p-tolylmagnesium bromide from 19.7 g (0.115 mol) of p-bromotoluene in THF. The intermediate alcohol, bp 160° (5 mm), was dehydrated directly to yield product in overall yield of 41%: bp 155° (5 mm); nmr (CCl₄) δ 6.74 (m, 4, aromatic), 5.43 (approx. triplet, 1, $J \sim 3$ Hz, =CH), 3.67 (m, 1, CHCl), 2.13 (m, 4, allylic), 1.96 (s, 3, CH₃), and ca. 1.7 ppm (m, 2, CH₂). The sample partially crystallized on standing in a freezer for several weeks. Recrystallization from methanol and sublimation *in vacuo* gave product of mp 40–43°.

Anal. Calcd for C₁₃H₁₅Cl: C, 75.53; H, 7.31. Found: C, 75.41; H, 7.38.

4-Chloro-1-(m-trifluoromethylphenyl)cyclohexene was prepared in similar fashion, using Grignard reagent made from m-bromobenzotrifluoride in THF. The intermediate alcohol product, bp 120–130° (5 mm), was dehydrated directly to yield product in overall yield of 62%: bp 110° (5 mm); nmr (CCl₄) δ 7.6–7.1 (m, 4, aromatic), 5.60 (approx. triplet, 1, $J \sim 3$ Hz, =CH), 3.83 (m, 1, CHCl), 2.2 (m, 4, allylic), and 1.8 ppm (m, 2, CH₂).

Anal. Calcd for C₁₃H₁₂ClF₃: C, 59.92; H, 4.61. Found: C, 59.79; H, 4.54.

Grignard reagents were prepared under nitrogen in a dried flask fused to a condenser with a side-arm gas inlet. Tetrahydrofuran used as solvent was distilled from lithium aluminum hydride under a flow of nitrogen; magnesium was a sample of sublimed magnesium received as a gift from the Dow Metal Products Co. In most cases, Grignard formation was quite slow, requiring help in initiation with a few drops of ethyl bromide, and several hours reflux. Samples were transferred by syringe to ampoules and an nmr tube, and sealed under less than an atmosphere pressure of nitrogen. After heating, tubes were opened in a "dry bag" under nitrogen, and hydrolyzed by addition of water. Magnesium salts were dissolved with dilute sulfuric or hydrochloric acid, and the hydrocarbons were extracted into methylene chloride or pentane. Products were analyzed by gas chromatography on the following columns: 10 ft × 0.25 in. 25% Ucon polar on 60–80 mesh firebrick; 10 ft × 0.25 in. 20% FFAP on 60–80 mesh Chromosorb W; 10 ft × 0.25 in. 20% poly-m-phenyl ether on 60–80 mesh Chromosorb P. Kinetic samples were analyzed on the last of these.

The nmr spectrum of the Grignard from 4-chloro-1-phenylcyclohexene had high-field absorption for the CHMg group as a broad peak at δ 0.25 ppm, an olefinic multiplet at 6.34 ppm, and aromatic absorption at 7.55–7.05 ppm. A weaker olefinic peak from the corresponding alkene was at 6.05 ppm. On heating a CH₂Mg doublet appeared at -0.23 ppm, $J = 8$ Hz. On more extensive heating, both CHMg resonances decreased, and the weaker olefinic resonance of hydrocarbon increased at the expense of that from the Grignard. A new singlet appeared at 5.31 ppm, corresponding to

(29) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 93, 98.
(30) J. P. Oliver, J. B. Smart, and M. T. Emerson, *J. Amer. Chem. Soc.*, **88**, 4101 (1966).
(31) T. Fueno, T. Okuyama, T. Deguchi, and J. Furukawa, *ibid.*, **87**, 170 (1965).
(32) D. J. Pasto and S.-Z. Kang, *ibid.*, **90**, 3797 (1968).
(33) (a) G. Natta, F. Danusso, and D. Sianesi, *Makromol. Chem.*, **30**, 238 (1959); (b) D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *J. Amer. Chem. Soc.*, **90**, 6182 (1968).

(34) R. Grewe, W. Lorenzen, and L. Vining, *Chem. Ber.*, **87**, 793 (1954).

ethylene from attack of Grignard on solvent.[35] The spectra of the other two Grignards showed similar behavior, except that the *m*-trifluoromethyl case had olefinic resonances of Grignard and hydrocarbon at 6.67 and 6.40 ppm, respectively.

Hydrolysis of the Grignard reagent from 4-chloro-1-phenylcyclohexene yielded a single major component on gas chromatography. It was collected preparatively, and the structure was confirmed as 1-phenylcyclohexene by comparison of its ir and nmr spectra with spectra of authentic samples.[36,37] A smaller peak eluted later coincided in retention time with biphenyl. Its importance increased somewhat at long heating times. With heating, a small peak of shorter retention time (originally *ca.* 1%) increased in size. The collected sample had the following nmr spectrum: δ 7.2 (m, 5, aryl), 5.80 (q, 1, $J \sim 1$ Hz, olefinic), 3.2–1.2 (m, 5), and 1.07 ppm (d, 3, $J = 6.5$ Hz, methyl). The spectrum is appropriate for the expected product, 3-methyl-1-phenylcyclopentene. For comparison, a mixture of 3-methyl-1-phenylcyclopentene and 4-methyl-1-phenylcyclopentene was prepared by addition of phenylmagnesium chloride to 3-methylcyclopentanone, followed by dehydration as described above for other syntheses.[38] Gas chromatography failed to give sufficient resolution of the components for a preparative separation, but did indicate very slight separation into components. The retention time coincided with that of the component from the Grignard hydrolysis. The nmr spectrum was also generally similar to that of the Grignard hydrolysis product, but showed differences in intensity in the 3.2–1.2 ppm range. These are consistent with the presence in the mixture of 4-methyl-1-phenylcyclopentene, which should lack nonallylic methylene absorption in the vicinity of δ 1.6 ppm, and which is also an expected dehydration product.

Hydrolysis products from the other two Grignard reagents showed a similar pattern, except that the *m*-trifluoromethyl compound appeared to rearrange somewhat more rapidly, and show a greater maximum degree of rearrangement, while the *p*-methyl compound rearranged less readily. Spectra of products were quite similar to their analogs in the unsubstituted phenylcyclohexenyl system. It was found that in mixed runs involving the *m*-trifluoromethyl compound as one component, the yield of biphenyl from the other component (*p*-methyl or unsubstituted phenyl) was particularly high (15–20% before heating), although *m*-trifluoromethylbiphenyl was never great (2–3%); biphenyl yield in the absence of trifluoromethyl compounds was low (3–4%). An

(35) E. A. Hill, *J. Org. Chem.*, 31, 20 (1966).

(36) C. J. Pouchert, "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., Inc., 1970, p 428.

(37) An nmr spectrum of authentic 1-phenylcyclohexene was kindly supplied by Mrs. A. Napiorkowski of the Aldrich Chemical Co.

(38) We acknowledge the assistance of Mr. M. Schwiesow who carried out this preparation.

authentic sample of *m*-trifluoromethylbiphenyl[38,39] was prepared for gas chromatographic comparison.

Additional evidence of proton abstraction by Grignard reagent under vigorous and extended heating was provided by hydrolysis of the Grignard reagent with D_2O. 1-(*m*-Trifluoromethylphenyl)cyclohexene, isolated from an unheated sample of Grignard reagent, was found by mass spectrometric analysis to be 82% monodeuterated. However, after 48 hr at 125–130°, only 10% of this component was deuterated, and the hydrolyzed rearrangement product, 3-methyl-1-(*m*-trifluoromethylphenyl)cyclopentene, was 25% monodeuterated.[40]

Kinetics. Grignard solutions were prepared from mixtures of two halides in approximately equal concentration, with total concentration of Grignard about 0.3–0.5 *M*. Grignard solutions were analyzed after hydrolysis by titration for total base and for magnesium. With Grignard reagent mixtures including the *m*-CF₃ compound, the magnesium titration gave values about 20% higher than the total base, suggesting the likelihood of some disproportionation process occurring during Grignard formation. Samples were heated in sealed tubes for appropriate periods of time in a bath controlled to $122 \pm 0.3°$. After hydrolysis, samples were analyzed by gas chromatography for the hydrocarbon corresponding to both rearranged and unrearranged Grignard reagents. Equal detector response of isomers was assumed. In the comparison of *p*-methyl with *m*-trifluoromethyl, the gas chromatographic separations were completely clean and led to the most reliable relative reactivities; in the other two comparisons, there were some near coincidences of retention times that required a resolution of partially overlapping peaks. Most gas chromatographic analyses were done in duplicate, with good agreement between duplicate determinations.

First-order plots [log (fraction unrearranged) *vs.* time] were curved. Such behavior is anticipated if destruction of Grignard is competitive with rearrangement. Rough initial rates were determined from these plots. In earlier runs carried further to completion, the fraction of rearranged hydrolysis product reached a maximum, and then decreased with further heating. Relative rates were obtained as the slope of a plot for one compound *vs.* the other in a comparison run of either (fraction rearranged) or log (fraction unrearranged). These plots were linear, within the limits imposed by scatter in the data, and gave substantially identical slopes and statistical parameters. Slopes, standard deviations, and correlation coefficients were evaluated by an unweighted least-squares analysis.

(39) C. K. Bradsher and J. B. Bond, *J. Amer. Chem. Soc.*, 71, 2659 (1949).

(40) We gratefully acknowledge the help of Professor D. R. Dimmel of Marquette University with mass spectra. Spectra were run on a CEC 21-1036 spectrometer.

Anchimeric Assistance in Photobromination of Alkyl Halides

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Abstract: Anchimeric assistance approaching 10^3 in magnitude is observed in photobromination of alkyl bromides. This is attributed to bromine assistance in the transition state with the requirement of an antiperiplanar arrangement of the bridging bromine and the hydrogen being abstracted by a bromine atom. Also, the activation energy is lower and activation entropy more negative than for the photobromination of alkanes as required by the bridging mechanism. Alkyl chlorides and fluorides do not show an anchimeric assistance effect. Conditions are described for photobromination with constant bromine concentration (bromostasis) and complete scavenging of hydrogen bromide.

There have been a number of studies on the influence of an electronegative substituent on the rate of hydrogen abstraction by halogen atoms. Generally,

electronegative substituents deactivate, the effect attenuating with separation of the reaction site and substituent.