types of reactions). It should be noted, however, that this similarity does not apply in the comparison of MeOAcr/MeSAcr vs. oxy ester/thioester reactivities since the thioesters are generally somewhat more reactive than the corresponding oxy esters.[17]

Acknowledgment. This work was supported by grants from the National Institutes of Health, Public Health Service (GM 12832), and from the National Science Foundation (CHE77-24701A).

Registry No. *trans*-3-Methoxyacrylophenone, 40685-20-9; *trans*-3-(methylthio)acrylophenone, 79134-84-2; (*trans*)-3-chloroacrylophenone, 15724-86-4; piperidine, 110-89-4; morpholine, 110-91-8; propylamine, 107-10-8; glycine ethyl ester, 459-73-4; ethylenediamine H^+, 26265-69-0; 2,2,2-trifluoroethylamine, 753-90-2; methoxylamine, 67-62-9; semicarbazide, 57-56-7; cyanide ion, 57-12-5; hydroxide ion, 14280-30-9; methoxide ion, 2143-68-2; butylamine, 109-73-9.

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(17) For example, see D. J. Hupe and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 451 (1977).

Mechanistic Evidence regarding the Magnesium Halide Transformation of Cyclopropylmethanols into Homoallylic Halides

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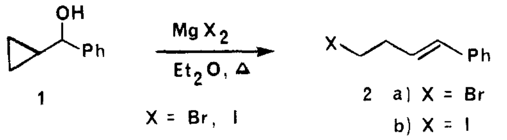
Received July 21, 1981

Cyclopropylmethanols are converted into homoallylic halides in high yield by treatment with magnesium bromide or iodide in refluxing, anhydrous diethyl ether. For uncovering of the details of the reaction mechanism, (cyclopropylphenylmethoxy)magnesium bromide (**3a**) was prepared by treatment of cyclopropylphenylmethanol (**1**) with hydridomagnesium bromide. Alkoxymagnesium bromide **3a** was stable in refluxing diethyl ether and was not changed when treated with tetrabutylammonium bromide but was transformed into 4-bromo-1-phenyl-1-butene by treatment with hydrogen bromide or magnesium bromide. These results, together with first-order kinetics for the reaction of magnesium halide with **1**, suggest a mechanism involving rapid formation of an intermediate ion pair (**4**), a magnesium oxonium bromide, which undergoes rate-determining ring opening to give homoallylic halide. A Hammett study of the reaction of substituted cyclopropylphenylmethanols with magnesium iodide provided a ρ value of −1.82, revealing substantial positive charge development on the carbinol carbon in the latter step. This investigation provides one of only a very few reported examples of Hammett studies used to probe positive charge development for a reaction carried out in anhydrous diethyl ether.

Since the early development by Julia of the hydrogen bromide promoted opening of cyclopropylmethanols as a method for the preparation of homoallylic bromides[1] and the modification by Johnson which involves intermediate formation of cyclopropylmethyl bromides,[2] this methodology has become a common route to homoallylic bromides. More recently, it has been found that cyclopropylmethanols are transformed into homoallylic bromides or iodides by treatment with the corresponding magnesium halide in refluxing, anhydrous diethyl ether.[3] The salient features of this efficient synthetic transformation can be summarized: generally, the homoallylic halide is the sole isolated product; the relative rates of reaction of the alcohols follow the order of the expected stabilities of the carbocations at the carbinol carbon; generally, the relative rates of reaction of a given alcohol with the various magnesium halides follows the order iodide > bromide > chloride, an order which parallels the relative nucleophilicities of the halides but is opposite to the probable relative acidities of the reagents; additional halide, added as tetrabutylammonium iodide, has no effect on the rate of reaction.



1

2 a) X = Br
b) X = I

(1)

Related chemistry has been reported, including the alkylation and subsequent opening of cyclopropyl ketones when treated with Grignard reagents under certain conditions,[4] an outcome which was plausibly envisioned as a ring-opening reaction of intermediate (cyclopropylmethoxy)magnesium halides (**3**).[5] Other reactions which involve use of magnesium halides to accomplish carbon–halogen bond formation together with carbon–oxygen bond cleavage include conversion of alkyl tosylates into iodides by magnesium iodide[6] and the action of the latter on propargyl acetates to give mixtures of iodides which include iodoallenes.[7] As well, the action of magnesium bromide on cyclic ethers can lead to ring opening with bromide displacement of oxygen, as in the case of oxiranes[8] or functionalized oxiranes,[9] and cyclic ethers can be effectively transformed into acyclic bromoacetates by magnesium bromide in acetic anhydride.[10]

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(1) (a) Julia, M.; Julia, S.; Guegan, R. *Bull. Soc. Chim. Fr.* **1960**, 1072. (b) Julia, M.; Descoins, C.; Risse, C. *Tetrahedron Suppl.* **1966**, *8*, 443. (c) Julia, M.; Paris, J.-M. *Tetrahedron Lett.* **1974**, 3445.

(2) (a) Brady, S. F.; Ilton, M. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1968**, *90*, 2882. (b) Johnson, W. S.; Li, T.; Faulkner, D. J.; Campbell, S. F. *Ibid.* **1968**, *90*, 6225.

(3) McCormick, J. P.; Barton, D. L. *J. Org. Chem.* **1980**, *45*, 2566.

(4) Yovell, J.; Sarel-Imber, M.; Sarel, S. *Isr. J. Chem.* **1966**, *4*, 21p.

(5) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew.* Chem., *Int. Ed. Engl.* **1968**, *7*, 577.

(6) Gore, J.; Place, P.; Roumestant, M. L. *J. Chem. Soc., Chem. Commun.* **1973**, 821.

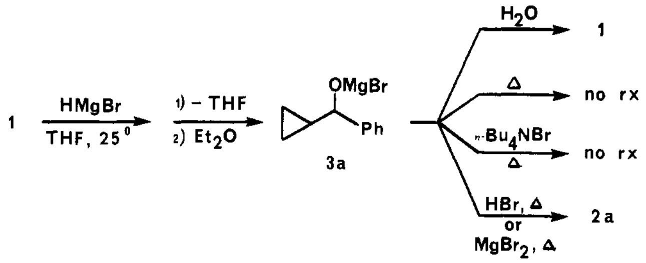
(7) Coulomb, F.; Gore, J. *J. Organomet. Chem.* **1975**, *87*, C23.

(8) Cope, A. C.; Hecht, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 4872.

(9) (a) Hudrlik, P. F.; Misra, R. N.; Withers, G. P.; Hudrlik, A. M.; Rona, R. J.; Arcoleo, J. P. *Tetrahedron Lett.* **1976**, 1453. (b) de Reinach-Hirtzbach, F.; Durst, T. *Ibid.* **1976**, 3677.

(10) Goldsmith, D. J.; Kennedy, E.; Campbell, R. G. *J. Org. Chem.* **1975**, *40*, 3571.

Scheme I



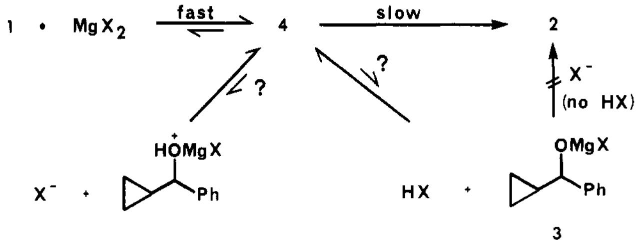
The above reports provided little firm evidence regarding mechanistic aspects, and, in fact, few mechanistic studies of this type of reaction include supporting kinetic data. To obtain such information, we carried out this investigation, seeking answers to the following questions: What intermediates are involved? What is the kinetic order of the reaction with respect to the two reactants? What is the composition of the transition state of the rate-determining step? Is significant charge developed in this transition state?

To obtain pertinent information, we took two approaches. The possible intermediate[5] (cyclopropylphenylmethoxy)magnesium bromide (**3a**) was prepared, and its relevant chemical behavior was examined. Second, a Hammett study of the reaction of substituted cyclopropylphenylmethanols with magnesium iodide was carried out. In addition to providing mechanistic evidence regarding the reaction in question, the Hammett study to probe development of positive charge provides an example carried out in anhydrous ether, of which there are very few cases reported in the literature.[11]

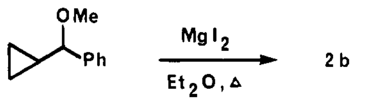
Results and Discussion

The required (cyclopropylphenylmethoxy)magnesium bromide (**3a**) was prepared by a method independent of the reaction in question. Cyclopropylphenylmethanol in anhydrous tetrahydrofuran (THF) was treated with 1 equiv of hydridomagnesium bromide.[12] After evolution of hydrogen ceased, the solvent was removed and replaced with diethyl ether, affording a solution approximately 25 mM in **3a**. Reflux of this solution for 18 h showed this alkoxymagnesium bromide to be stable to such conditions; after aqueous workup of an aliquot, GC analysis revealed the presence of **1** only (Scheme I). In addition to demonstrating the stability of **3a** in refluxing diethyl ether, this experiment showed that treatment of **3a** with water quantitatively forms alcohol **1**. Thus, the following experiments regarding **3a** were followed by GC analysis of **1** in reaction mixtures obtained after aqueous workup. To the diethyl ether solution of **3a** which contained no homoallylic halide after 18 h at reflux was added approximately 1 molar equiv of hydrogen bromide to provide an intermediate (mixture) having the same composition as that prepared by treatment of alcohol **1** with magnesium bromide. Reflux of this mixture smoothly afforded homoallylic bromide **2a**.[13] In a similar experiment, the addition of 1 equiv of magnesium bromide rather than hydrogen bromide led to complete (but slower) transformation into **2a**. These results are taken to indicate that it is not the alkoxymagnesium bromide which undergoes ring opening but rather its conjugate acid, oxonium salt **4** (X = Br). Intermediacy of such an ion also is consistent with the observed reaction (eq 2) of the methyl ether of **1** with magnesium iodide to give the corresponding homoallylic iodide (**2b**).[3] The analogous intermediate *O*-methyl magnesium oxonium ion would be expected to behave similarly to the protonated species (**4**).

Scheme II

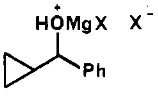


X = Br or I

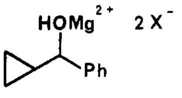


(2)

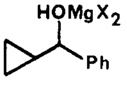
The degree of halide ionization for the intermediate magnesium oxonium species is another interesting point.[14] In addition to structure **4**, consideration must be given to the ionic species **4i**, which has no covalent magnesium–bromine bonds, and to the covalent structure **4ii**. Some literature data may be viewed as evidence against a completely covalent intermediate. First, other workers have shown that diethyl ether solutions of magnesium bromide and of ethylmagnesium bromide are electrically conducting.[15] As well, crystallographic data of hydrated magnesium bromide, crystallized from THF, suggest an ionic structure.[16] Finally, availability of ethereal oxygen to act as a ligand for the normally hexacoordinate magnesium permits replacement of the rather electronegative bromine, which can exist as ion-paired bromide. Additionally, the direct, unimolecular formation of **2** from **4ii** seems unlikely, owing to geometric constraints, although it is possible to envision ionization of **4ii** to **4** prior to transformation into **2**. The information available does not permit a distinction to be made between the two *ion pair* structures **4** and **4i**. The chemical behavior of the two should be similar, and the general mechanistic picture suggested should be the same for either. As well, evidence presented below makes an ion pair, rather than fully dissociated ions, appear to be a plausible representation for the major species.[17]



4



4i



4ii

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[11] (a) Abenhaim, D.; Henry-Basch, E.; Freon, P. *Bull. Soc. Chim. Fr.* **1970**, 179. (b) Thomas, J.; Henry-Basch, E.; Freon, P. *Ibid.* **1969**, 109. (c) Bender, D. F.; Thippeswamy, T.; Rellahan, W. L. *J. Org. Chem.* **1970**, *35*, 939. (d) Boireau, G.; Namy, J. L.; Abenhaim, D. *Bull. Soc. Chim. Fr.* **1972**, 1042.

[12] Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* **1977**, *99*, 310.

[13] Transformation into **2a** stopped at 80% completion after 20 h; this was apparently due to inaccurate measurement of HBr, since addition of more HBr in ether caused further formation of **2a**.

[14] Magnesium is generally hexacoordinate, and therefore it is presumed that diethyl ether ligands exist to complete coordination, although these ligands are not shown. Also, the question regarding degree of ionization exists not only for any intermediates in the reaction but also for the starting magnesium halide and alkoxymagnesium bromide **3a**. For simplicity, these compounds are shown as covalent, a representation which may not be entirely accurate. In any case, the degree of ionization does not affect the general conclusions drawn from the present results.

[15] Evans, W. V.; Pearson, R. *J. Am. Chem. Soc.* **1942**, *64*, 2865.

[16] Sarma, R.; Ramirez, F.; McKeever, B.; Chaw. Y. F.; Marecek, J. F.; Nierman, D.; McCaffrey, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 5289.

[17] The cited[15] conducting nature of ethereal (alkyl)magnesium bromide solutions may be taken to indicate that some dissociation of intermediate **4** (**4i**) into free ions is likely.

The nature of halide ion participation also has been considered. Treatment of **3a** in refluxing diethyl ether with 1 equiv of tetrabutylammonium bromide (a homogeneous solution) caused no transformation into homoallylic bromide; GC analysis after aqueous workup showed only **1** to be present. As well, addition of 1 molar equiv of tetrabutylammonium bromide during the course of a reaction between equimolar amounts of magnesium bromide and alcohol **1** had no detectable effect on the rate of the reaction, examined by using a first-order plot as described below. This result parallels that reported earlier regarding the absence of an effect of added iodide when magnesium iodide was used as the reagent to transform **1** into **2b**.[3] Nevertheless, the relative order of reactivities of the magnesium halides with cyclopropylmethanol suggests involvement of halide as a nucleophile in the rate-determining step. These facts, together with the above results regarding alkoxymagnesium bromide **3a**, can be rationalized by postulation of the *ion pair* **4** as the reactive intermediate which undergoes transformation into homoallylic halide in a rate-determining step (Scheme II). The absence of an effect due to added halide suggests that ion pair **4** undergoes little dissociation into free ions and that it is specifically the paired halide ion which participates as the nucleophile. It should be noted that the involvement of undissociated ion pairs in ring-opening[18] and other rearrangement[19] reactions of cyclopropylcarbinyl cations has been postulated by others. An additional question regarding the stereochemical relationship (syn or anti) of the entering halide and leaving hydroxymagnesium halide is not answered by these data. Either periplanar relationship would be expected to give the observed predominance of *E* isomer.

The kinetics results also provide evidence for the intermediacy of **4**. Experiments were carried out by using an equimolar mixture of alcohol **1** and magnesium halide in refluxing diethyl ether. Aliquots were analyzed by GC for starting alcohol after a normal aqueous workup. This method of following the reaction progress does not permit observational distinction between **1** and intermediates such as **3** or **4** which can form **1** upon treatment with water. Reactions of **1** with magnesium bromide and with magnesium iodide were found to follow *first-order kinetics* (up to 3 half-lives). Determination of the rate constants revealed some variability in the absolute rate of the reaction. For example, of ten experiments involving reaction of **1** with magnesium iodide, values for the rate constant varied from 2.2×10^{-3} to 3.7×10^{-3} min^{-1}, with a mean value of 2.8×10^{-3} min^{-1}, although for nine of the individual kinetic runs the correlation coefficient (r) was determined to be 0.99 or better (and 0.98 for the tenth experiment). The source of this disconcerting variability is not known, but it may be the result of traces of water present in some experiments. Addition of known amounts of water slowed the reaction markedly. In any event, it proved possible to obtain acceptably reproducible data by running kinetics experiments simultaneously in triplicate and measuring the dissappearance of reactant by GC analysis with an internal standard (hexadecane or octadecane). For the Hammett study, this approach was particularly useful, since the relevant values are not the absolute rate constants but rather the rates of reaction relative to the unsubstituted case.

The kinetic results, taken together with the conversion of **3a** into homoallylic bromide **2a** upon treatment with hydrogen bromide, provide substantiating evidence that **2a** is formed in a rate-determining, unimolecular transformation of an intermediate such as ion pair **4** (X = Br), as shown in Scheme II. Thus, the observed first-order plot for a reaction which involves both alcohol **1** and magnesium halide in the activated complex of the rate-determining step may be understood by postulating rapid and essentially complete formation of **4**, the decomposition of which follows first-order kinetics, in spite of the fact that it is composed of both reactants. It is apparent that, since intermediate **4** can form starting alcohol **1** upon aqueous workup of reaction mixture aliquots, in the kinetic experiments GC analysis of the starting alcohol actually provided a method for monitoring the concentration (and hence transformation) of **4**. The suppositon of rapid formation of intermediate **4** from alcohol **1** and magnesium bromide is reasonable: magnesium bromide generally is well-known to be relatively reactive toward oxygen functionality.[8-10] More specifically, diethylmagnesium, which presumably is a weaker Lewis acid than magnesium halide, complexes effectively in diethyl ether ($K = 6$) with oxiranes,[11d] a functionality which would be expected to provide a weaker ligand for magnesium than the hydroxyl group of **1**.

The nature of charge development in the transition state of the rate-determining transformation of **4** to **2** was probed by a Hammett study, which was carried out by using competition experiments. Six phenyl-substituted alcohols were examined, with the substituents being chosen to represent both meta and para substitution as well as both rate-enhancing and -retarding substituents: *p*-methoxy, *p*-methyl, *m*-methoxy, *p*-bromo, *p*-chloro, and *m*-bromo.[20] Magnesium iodide (2 mmol) was mixed with a solution containing 1 mmol each of cyclopropylphenylmethanol and a phenyl-substituted analogue together with an internal standard. The relative rates of disappearance of the corresponding ion pairs **4** (X = I) were determined by GC analysis of the corresponding starting alcohols after aqueous workup of aliquots removed from the reaction mixture at specified times. Figure 1 displays representative first-order kinetic plots, obtained by using the *p*-chloro- and *p*-methoxy-substituted alcohols. Figure 2 shows a Hammett plot of the seven values of log (k/k_0), using Brown's[21] σ^+ values, which provides a value for ρ of −1.82, indicative of substantial positive charge development in the transition state of the rate-determining step.[22] In principle, this value for ρ may reflect effects of substituents on the initial step forming ion pair **4**, as well as on its decomposition. However, any effects on the first step probably have little influence on the rates observed, since the acceptable fit of the first-order plots, taken together with the other results presented above, indicate rapid, essentially complete formation of ion pair **4**.

Few literature data exist to provide a frame of reference for evaluation of the relative magnitude of positive charge development indicated by a ρ value of −1.82 for a reaction in anhydrous diethyl ether. Perhaps the most closely related system previously reported is the diallylzinc alkylation of (substituted) styrene oxide in diethyl ether.[11a] For

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[18] Newman, M. S.; Kaugars, G. *J. Org. Chem.* **1966**, *31*, 1379.

[19] Babler, J. H.; Coghlan, M. J.; Giacherio, D. J. *J. Org. Chem.* **1977**, *42*, 2172.

[20] For each compound, the expected homoallylic iodides were isolated in good yields (67–88%). Characterizational data are given in the supplementary material.

[21] (a) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913. (b) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

[22] The linear plot using σ^+ values fits well within criteria for Hammett plots described by Jaffe:[23] the standard deviation is 0.09, and the correlation coefficient is 0.994. As expected, a plot using standard σ values[23,24] did not give a satisfactory linear fit.

[23] Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

[24] McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.

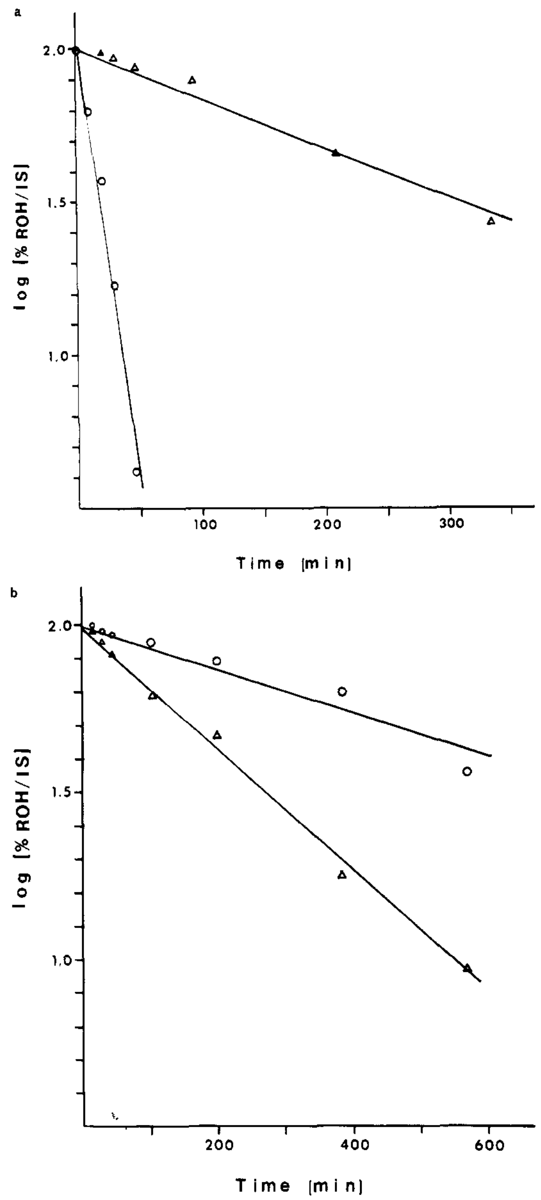

Figure 1. Representative first-order relative rate plots for the reactions of equimolar amounts of cyclopropylphenylmethanols (ROH) and magnesium iodide in refluxing diethyl ether: (a) unsubstitued (Δ) and *p*-methoxy (O) compounds, (b) unsubstituted (Δ) and *p*-chloro (O) compounds. IS is internal standard.

this reaction, which involves transfer of a *carbon* nucleophile to carbon with concomitant carbon–oxygen bond cleavage, a ρ value of −1.7 was obtained by using σ^+ values. Other Hammett studies[11] of positive charge development during reactions in anhydrous ethereal solvents concern reactions less closely related to that of eq 1, and the ρ values obtained were generally smaller, ranging from −0.4 to −0.7. Thus, it is reasonable to conclude that the present ρ value of −1.82 is indicative of substantial positive charge development, even when the possible enhancement of ρ values in less polar solvents[25] is taken into account.

In connection with assessment of the amount of charge development on the carbinol carbon atom and the nature of association of halide ion in 4, it is relevant to compare the above results, including the fact that the course of the reaction proceeds to give only ring-opened product, with those for other reported reactions. In particular, fully formed cyclopropylmethyl cations are well-known to give mixtures of products which reflect interconverison of cyclopropylmethyl–cyclobutyl–homoallyl cations, as in the case of the original Julia reaction.[1,26] On the other extreme, a number of substitution reactions of cyclopropylmethyl compounds take place with little or no ring opening.[26] A recently reported study of the solvolysis of a tertiary, allylic cyclopropylmethanol to give a rearranged, primary allylic acetate provides an illustrative example.[19] For this reaction, which clearly involved development of significant positive charge on the carbinol carbon, the observed strong preference for substitution without ring opening was ascribed to reaction via an intimate ion pair. Altered conditions which likely increased ion-pair separation reportedly gave rise to complete ring opening. Thus, for the present work, it seems reasonable to speculate that partial but not complete separation of ions exists for 4 and that this relationship is at least partly responsible for the preference for ring opening but absence of other skeletal rearrangement.

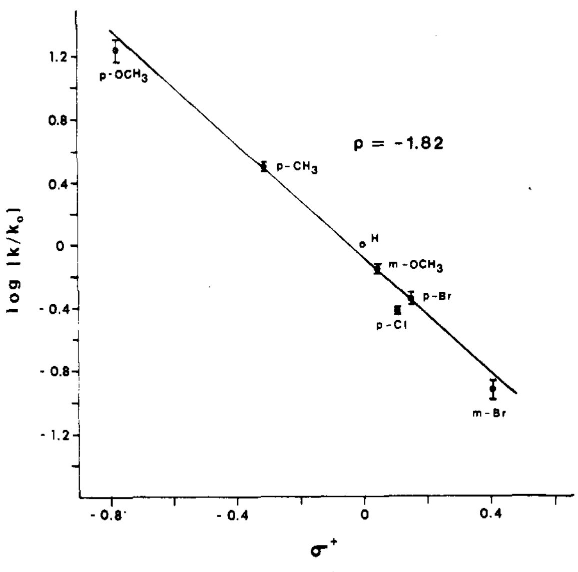

Figure 2. Hammett plot using σ^+ values for the reaction of substituted cyclopropylphenylmethanols with magnesium iodide in refluxing diethyl ether.

Conclusions

This study has shown that (cyclopropylmethoxy)magnesium bromide **3a** is stable in refluxing diethyl ether and that the previously suggested transformation of (cyclopropylalkoxy)magnesium halide into homoallylic halide is accomplished by the action of acid. Examples of this reaction previously reported[5] presumably proceeded by action of magnesium halide, formed via the Schlenk equilibrium,[27] on the (cyclopropylmethoxy)magnesium halide, a transformation which this work has shown to proceed smoothly. The reaction of cyclopropylphenylmethanol with magnesium bromide or iodide proceeds by rapid formation of an intermediate, most likely an ion pair (such as 4 or 4i) existing largely in an undissociated form,[27] which undergoes rate-determining, unimolecular transformation into 2. The transition state of this latter step involves advanced carbon–oxygen bond breaking, with consequent substantial positive charge development on the carbinol carbon, and at the same time significant carbon–halogen bond making.

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[25] (a) Buckley, A.; Chapman, N. B.; Dack, M. R. J.; Shorter, J.; Wall, H. M. *J. Chem. Soc. B* **1968**, 631. (b) Kondo, Y.; Matsui, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1037 and references therein.

[26] Breslow, R. In "Molecular Rearrangements, Part One"; de Mayo, P.; Ed.; Wiley-Interscience: New York, 1963; p 254–276.

[27] Parris, G. E.; Ashby, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 1206 and references therein.

Experimental Section

The following instrumentation and chromatographic materials were used. GC: Varian-Aerograph Model 2400 with flame-ionization detectors; packed, 4% OV-17 or OV-101 on high-performance Chromosorb G (100/120 mesh); $^1/_8$ in. × 6 ft glass column. NMR: Varian T-60 spectrometer; Me_4Si as an internal standard. IR: Perkin-Elmer 237-B grating infrared spectrometer. UV: Cary Model 14 spectrophotometer. TLC: Merck $HF_{254/366}$ silica gel; I_2 visualization. Column chromatography: Merck PF_{254} silica gel 60. Melting points (uncorrected): Thomas-Hoover apparatus. Elemental analyses were performed by Galbraith Laboratories.

Anhydrous diethyl ether was prepared by reflux over sodium benzophenone ketyl, followed by distillation of the required amount directly into reaction flasks.

Magnesium halide solutions in anhydrous diethyl ether were prepared as previously described.[3] Concentrations were determined by EDTA titration.

Cyclopropylphenylmethanol (1) was prepared in 96% yield from cyclopropyl phenyl ketone by reduction with $LiAlH_4$.[28] Chromatographic and spectral data are given in the supplementary material.

(Cyclopropylphenylmethoxy)magnesium Bromide (3a). To 4.9 mL (1.0 mmol) of HMgBr in THF[12] under Ar was added 0.154 g (1.0 mmol) of alcohol 1. The mixture was stirred until H_2 evolution ceased, at which time the solvent was removed under reduced pressure, and then under Ar 40 mL of anhydrous diethyl ether was added, providing a solution approximately 25 mM in **3a**.

Stability and Reactions of (Cyclopropylphenylmethoxy)magnesium Bromide (3a) in Diethyl Ether. Diethyl ether solutions of **3a** were prepared as described above and treated in the following manners.

A 40-mL (1.0 mmol of **3a**) solution was refluxed 18 h, at which time an aliquot was removed. After a standard aqueous workup, GC analysis (OV-101, 50 °C rising to 200 °C at 10 °C/min) showed only alcohol 1 (retention time 11.4 min) to be present.

To the above solution after an 18-h reflux was added 323 mg (1.00 mmol) of $(n\text{-}Bu)_4NBr$, and refluxing was continued an additonal 29 h, at which time an aliquot was removed. After a standard aqueous workup, GC analysi again showed only alcohol 1 to be present.

A 40-mL (0.5 mmol of **3a**) solution containing ca. 0.4 mmol of HBr was refluxed for 20 h, at which time an aliquot was removed. After a standard aqueous workup, GC analysis (OV-101, 50 °C rising to 200 °C at 10 °C/min) showed the presence of a mixture of alcohol 1 and homoallylic bromide **2a** (retention times 17.5 and 18.8 min, *Z*/*E* isomers in a 2:98 ratio) in a ratio of ca. 1:4.

A 40-mL (0.5 mmol of **3a**) solution containing 1.0 mmol of $MgBr_2$ was refluxed for 43 h. GC analysis of aliquots, after a standard aqueous workup, periodically removed showed a steady increase in amount of conversion into homoallylic bromide **2a**, which was complete after 43 h.

Substituted cyclopropylphenylmethanols were prepared by addition of cyclopropylmagnesium bromide to the appropriate substituted benzaldehyde (Aldrich Chemical Co.). A general procedure follows. To 1.00 g (41.2 mmol) of Mg was slowly added with stirring at 0 °C under Ar 4.52 g (37.4 mmol) of bromocyclopropane[29] in 20 mL of THF. The resulting mixture, cooled in an ice bath, was stirred for 60 min after the addition was complete. To the resulting solution of cyclopropylmagnesium bromide was added over 10 min 18 mmol of a substituted benzaldehyde in 20 mL of THF. After the reaction mixture was stirred 16 h at 25 °C, 10 mL of 1.9 M aqueous NH_4Cl solution was added dropwise. Following extraction with diethyl ether (2 × 50 mL), a standard aqueous workup, drying ($MgSO_4$), and concentration, the desired alcohol was purified by column chromatography (typically, 1.2 g on 100 g of silica gel, using 3:7 diethyl ether–pentane). Yields varied from 64% to 83%. Characterizational data, given in the supplementary material, agreed with literature data.[30] Satisfactory combustion analytical data were obtained for those alcohols (*m*-bromo, *m*-methoxy) not previously reported.

4-Bromo-1-phenyl-1-butene (2a) and 4-iodo-1-phenyl-1-butene (2b) were prepared and characterized as previously reported.[3]

Substituted 4-Iodo-1-aryl-1-butenes. The six phenyl-substituted homoallylic iodides were prepared on a 2-mmol scale by using the described[3] procedure. Reactions were allowed to proceed to completion, as determined by GC. In each case, the expected homoallylic iodide was the only product observed. The *E*/*Z* isomeric ratios were greater than 95:5. Characterizational data are contained in the supplementary material.

Kinetics Experiments. Reactions were carried out by using 1 mmol each of (substituted) cyclopropylmethanol and magnesium halide in anhydrous diethyl ether containing 0.6 mmol of an internal standard (either hexadecane or octadecane) under an Ar atmosphere, and the mixture was kept at reflux by a heating bath held at 50 °C. At specified time intervals, 1.0-mL samples were removed by syringe, and, after a standard aqueous workup and dilution, the relative amounts of starting alcohol and internal standard were determined by GC.

The Hammett study kinetics experiments were carried out as described above, with a small modification: 1 mmol each of 1 and phenyl-substituted 1 were mixed with 2 mmol of MgI_2, added by syringe to the refluxing ether solution to initiate the reaction, in a total volume of 60 mL of diethyl ether. The 1-mL aliquots were washed twice with 1 mL of aqueous 10% sodium thiosulfate solution, dried ($MgSO_4$), and diluted with diethyl ether prior to GC analysis. Rate constants for the reactions were calculated by using the equation $\ln([ROH]/[IS]) = -kt + \ln([ROH]/[IS])_0$, where [ROH]/[IS] is the amount of starting alcohol relative to the internal standard, as determined by GC, and linear regression and statistical analyses were carried out. For the individual rate plots of the reactions using substituted arylcyclopropylmethanols, the correlation coefficients ranged from 0.97 to 0.98 with most being 0.98. For the Hammett plot using σ^+ values to give a ρ value of −1.82, the standard deviation was calculated to be 0.09, and the correlation coefficient *r* was found to be 0.994.

The effect of added bromide on the rate of reaction of alcohol 1 with $MgBr_2$ was determined by carrying out a rate experiment as described above, except that after the first three aliquots had been withdrawn (extending over ca. 0.5 half-life), 1.0 mmol of $(n\text{-}Bu)_4$ NBr was added. No change in the slope of the first-order rate plot was observed.

Acknowledgment. We thank Professors R. P. Hanzlik and R. K. Murmann for valuable discussions. Support to D.B. in the form of a Dorothy V. Nightingale Summer Research Fellowship is appreciated.

Registry No. 1, 1007-03-0; *m*-Br-1, 79134-92-2; *p*-Br-1, 70289-39-3; *p*-Cl-1, 18228-43-8; *m*-CH_3O-1, 79134-93-3; *p*-CH_3O-1, 6552-45-0; *p*-CH_3-1, 6552-46-1; (*E*)-**2a**, 7515-41-5; (*Z*)-**2a**, 73611-78-6; (*E*)-*m*-Br-**2b**, 79134-94-4; (*Z*)-*m*-Br-**2b**, 79134-95-5; (*E*)-*p*-Br-**2b**, 79134-96-6; (*Z*)-*p*-Br-**2b**, 79134-97-7; (*E*)-*p*-Cl-**2b**, 79134-98-8; (*Z*)-*p*-Cl-**2b**, 79134-99-9; (*E*)-*m*-CH_3O-**2b**, 79135-00-5; (*Z*)-*m*-CH_3O-**2b**, 79135-01-6; (*E*)-*p*-CH_3O-**2b**, 79135-02-7; (*Z*)-*p*-CH_3O-**2b**, 79135-03-8; (*E*)-*p*-CH_3-**2b**, 79135-04-9; (*Z*)-*p*-CH_3-**2b**, 79135-05-0; **3a**, 79135-06-1; cyclopropyl phenyl ketone, 3481-02-5; cyclopropylmagnesium bromide, 23719-80-4; *m*-bromobenzaldehyde, 3132-99-8; *p*-bromobenzaldehyde, 1122-91-4; *p*-chlorobenzaldehyde, 104-88-1; *m*-methoxybenzaldehyde, 591-31-1; *p*-methoxybenzaldehyde, 123-11-5; *p*-methylbenzaldehyde, 104-87-0.

Supplementary Material Available: Characterizational data for 1 (GC, NMR), the six phenyl-substituted analogues of 1 (GC, NMR), and the six phenyl-substituted 4-iodo-1-aryl-1-butenes (GC, NMR, IR) (2 pages). Ordering information is given on any current masthead page.

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