Et_2O/CH_2Cl_2/hexane) to give two compounds.

The minor component was found to have spectral data identical with that described above for **28** (4.5 mg, 0.03 mmol, 8.2%). The major product was identified as the cyclohexadienone **29**[5u] (35.9 mg, 0.202 mmol, 55%): mp 33 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 3 H), 1.86–1.98 (m, 2 H), 2.54–2.61 (m, 2 H), 2.66 (t, 2 H, J = 7.2 Hz), 3.09 (s, 3 H), 6.02 (s, 1 H), 6.09 (s, 1 H); IR ($CHCl_3$) 3000 s, 1675 m, 1652 s, 1600 m, 1360 m, 1245 m, 1095 s, 1030 w, 850 m cm^{-1}; mass spectrum, m/e (rel intensity) 178 M^+ (100), 163 (15), 147 (20), 135 (40) 121 (58), 119 (60), 91 (50) 43, (40); calcd for $C_{11}H_{14}O_2$ m/e 178.0994, found m/e 178.0988. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.14; H, 8.04.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8517103. The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

Evidence Supporting Two-Electron Nucleophilic Displacement in Reactions of Unhindered Alkyl Bromides and Iodides with Boron and Aluminum Hydride Reducing Agents

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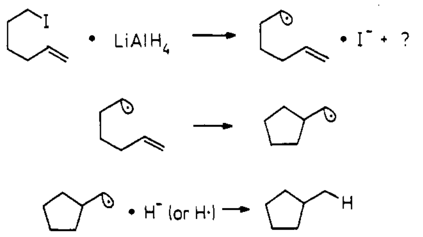
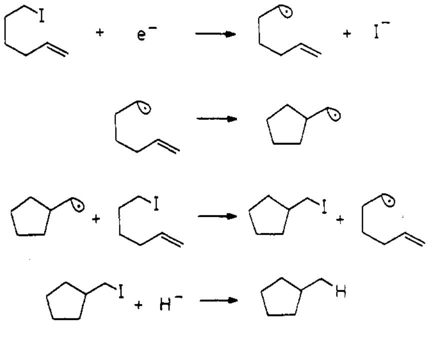
7-Bromo- and 7-iodo-2-methoxy-2-heptenenitrile were used as mechanistic probes in reactions with a variety of boron and aluminum hydride reducing agents. No radical-derived cyclized products were observed in the reductions. The reactions with these probes are best explained as conventional two-electron nucleophilic displacements of halide ion by hydride. Previous work had indicated that electron transfer (SET) from boron and aluminum hydride reducing agents to unhindered alkyl halides is not a predominant reaction, and this work supports that conclusion and sets a lower limit on the amount of SET.

The reactions of boron and aluminum hydride reducing agents with primary and secondary alkyl halides can produce hydrocarbon products. These reactions have generally been thought to occur by a conventional two-electron nucleophilic displacement of halide by hydride.[2] However, recent results with alkyl halide mechanistic probes have suggested that radicals can be formed in reactions of $LiEt_3BH$, $LiAlH_4$, and AlH_3 with simple alkyl iodides and bromides and have led to conclusions that the initial reactions involve electron transfer from the metal hydride to the alkyl halide.[3-5] In the probe studies an alkyl halide is used which, if converted to a radical, will lead to a rearranged product. The presence of rearranged reduction products thus implicates radical intermediates and by inference this has been taken as evidence of an electron transfer process. A typical reaction sequence that incorporates such an electron-transfer step is exemplified in Scheme I for reaction of the common mechanistic probe 6-iodo-1-hexene with LAH. In most probe studies quantitation of electron-transfer processes has not been attempted.

Scheme I



Scheme II



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[1] Current address: Department of Chemistry, Pohang Institute of Science and Technology, Pohang, 680 Korea.

[2] (a) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 849–856. (b) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1982**, *47*, 276–280. (c) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1983**, *48*, 3085–3091.

[3] (a) Ashby, E. C.; DePriest, R. N.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1763–1766. (b) Ashby, E. C.; DePriest, R. N.; Pham, T. N. *Tetrahedron Lett.* **1983**, *24*, 2825–2828. (c) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545–3556. (d) Ashby, E. C.; Wenderoth, B.; Pham, T. N.; Park, W.-S. *J. Org. Chem.* **1984**, *49*, 4505–4509. (e) Ashby, E. C.; Pham, T. N. *J. Org. Chem.* **1986**, *51*, 3598–3602.

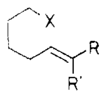
[4] For related studies, see: (a) Jefford, C. W.; Kirkpatrick, D.; Delay, F. *J. Am. Chem. Soc.* **1972**, *94*, 8905–8907. (b) Hatem, J.; Waegell, B. *Tetrahedron Lett.* **1973**, 2023–2026. (c) Chung, S.-K.; Chung, F.-f. *Tetrahedron Lett.* **1979**, 2473–2476. (d) Chung, S.-K. *J. Org. Chem.* **1980**, *45*, 3513–3514. (e) Singh, P. R.; Nigam, A.; Khurana, J. M. *Tetrahedron Lett.* **1980**, *21*, 4753–4756. (f) Singh, P. R.; Khurana, J. M.; Nigam, A. *Tetrahedron Lett.* **1981**, *22*, 2901–2904. (g) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Tetrahedron Lett.* **1981**, *22*, 3729–3732. (h) Chung, S.-K.; Filmore, K. L. *J. Chem. Soc., Chem. Commun.* **1983**, 358–360. (i) Beckwith, A. L. J.; Goh, S. H. *J. Chem. Soc., Chem. Commun.* **1983**, 905–906. (j) Hirabe, T.; Takagi, M.; Muraoka, K.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1985**, *50*, 1797–1802.

[5] Beckwith and Goh have shown that radical pathways for LAH reduction of alkyl halides are possible. However, these reactions, which occur under drastic conditions involving photolysis of solutions containing di-*tert*-butyl peroxide,[6a] do not proceed by electron transfer from LAH to the alkyl halide. It is known that trihydridoaluminum radical anion, a probable intermediate in the photochemically induced reductions, readily abstracts halogen from alkyl halides.[6b]

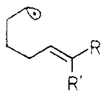
[6] (a) Beckwith, A. L. J.; Goh, S. H. *J. Chem. Soc., Chem. Commun.* **1983**, 907. (b) Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1981**, 1167–1168.

Recently, it has been shown that conventional alkyl halide mechanistic probes could provide quite misleading information. Ashby's group found that radical chain isomerization of alkyl iodide mechanistic probes could occur during metal hydride reductions.[3c,d] The reactions in a radical chain isomerization sequence are shown in Scheme II for 6-iodo-1-hexene. Steps 2 and 3 in Scheme II comprise a radical chain sequence. Recent measurements of rate constants for halogen atom transfer from an alkyl halide to an alkyl radical demonstrate that such a radical chain isomerization of an alkyl iodide probe is many orders of magnitude faster than typical S_N2 reactions, including reduction of alkyl halides by LAH, and may have appreciable chain lengths.[7a] Thus, minute amounts of radical initiation could provide substantial amounts of rearranged substitution products via Scheme II, and for previous mechanistic probe studies it is difficult to rule out radical initiation from adventitious sources. A further complicating aspect of a probe study is that a free radical might be formed from the probe following electron transfer (SET), but that radical could be trapped in a reaction that occurred faster than cyclization; this possibility has been discussed previously.[3] These facts indicate that alkyl halide probes may not provide quantitative evaluation of the extent of SET and could even provide misleading qualitative results.[7]

We recently reported the rate constants for cyclization of 5-hexenyl radicals substituted at C-1 with donor, acceptor and captodative groups.[8] If halides **1** were to react via Scheme I, then radical **2** would be formed and the subsequent cyclization to **3** would be much faster than most other probe radicals rearrange.[8] Thus, problems with trapping of free radical intermediates before rearrangement should not arise with **2**. In addition, we believed that cyclic radical **3** would be so stable that it would be incapable of abstracting halogen from **1** in a radical chain isomerization propagation step; thus, probe **1** should not rearrange via Scheme II. These two considerations suggested that halides **1** should be quite sensitive probes for electron-transfer processes and that they might provide quantitative information about the extent of an SET process. Herein we report the reactions of various boron and aluminum hydride reducing agents with 7-bromo- and 7-iodo-2-methoxy-2-heptenenitrile (**1**); our results show that no detectable amount of free radical derived products were formed and suggest that only minute amounts of SET can occur in these reactions.



1a: X = Br
b: X = I



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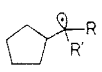


3

(R,R' = CN, OCH_3)

Results

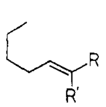
The synthesis of bromide **1a** has been reported.[8] The compound was obtained from a Wittig-type reaction as a mixture of *E* and *Z* isomers. The fact that **1a** was not isomerically pure was of no consequence because the isomeric radicals **2** have been shown to cyclize with nearly identical rates.[8] Iodide **1b** was obtained from bromide **1a** by a Finkelstein reaction and was also a mixture of isomers.

Table I. Reactions of Halide Probes 1 with Metal Hydrides

reagent	probe	conditions[a]	% yield[b] 1	% yield[b] 4
$LiBH_4$	**1a**	*i*-PrOH, 50 °C, 12 h	72	18
	1b		63	37
$NaBH_4$	**1a**	EtOH, rt, 24 h	80	14
KBH_4	**1a**	EtOH, rt, 48 h	87	3
	1b		74	13
$NaBH_3CN$	**1a**	THF, rt, 24 h	82	1
	1b		69	10
$LiBEt_3H$	**1b**	THF, rt, 1 h	11	32
		THF, rt, 3 h	0	34
$LiAlH_4$	**1a**	THF, rt, 24 h	6	60
	1b		0	98
AlH_3	**1a**	THF, rt, 24 h	100	trace
	1b		100	trace

[a] rt = room temperature. [b] Absolute yields determined by GC by comparison to an internal standard.

Two possible products from reduction of halides **1** are the reduced acyclic product 2-methoxy-2-heptenenitrile **4** and the cyclic product cyclopentylmethoxyacetonitrile **5**. Our previous results demonstrated that radical **2** cyclized to give the exocyclic radical **3** and that no detectable amount of endocyclic, six-membered ring product was formed in a radical process.[8] Authentic samples of **4** (mixture of isomers) and of **5** were available for comparison with the products from reactions of **1**.



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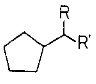

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Halides **1** were treated with various boron and aluminum hydride reagents in either alcoholic solvents or in THF. The reactions were worked up by conventional methods, and products were analyzed by capillary GC and GC–mass spectrometry. Table I contains the results; absolute yields are given. Since an authentic sample of cyclic product **5** was available for GC coinjection and mass spectral comparison, we know that to the limit of our detection capabilities (<0.1%) no cyclic product **5** was formed in any reduction reaction. The total yields of unreacted halide **1** and acyclic product **4** generally ranged from 80% to 100% with the notable exception of the $LiEt_3BH$ reaction. Halides **1** were stable to AlH_3 under the conditions of our experiments.

Michael addition of hydride to halides **1** is a potentially complicating side reaction. We typically observed small amounts of unidentified compounds in the GC traces with retention times expected for 2-methoxyheptanenitrile. In the reactions of $NaBH_3CN$, we detected a peak with a GC retention time longer than that of acycle **4** (0.1% yield from **1a** and 0.6% yield from **1b**), which displayed a mass spectrum consistent with that expected for 2-methoxyheptanenitrile.

Discussion

At room temperature or at 50 °C, radical **2** cyclizes to radical **3** more than two orders of magnitude faster than the parent radical 5-hexenyl cyclizes to cyclopentylmethyl, and the **2** → **3** rearrangement is substantially faster ($k_r = 2.5 \times 10^8$ s^{-1} at 50 °C)[8] than other radical rearrangements that have been used to probe metal hydride reductions of alkyl halides. It is known that other, slower radical rearrangements can occur in the presence of various boron and aluminum hydrides, and this fact coupled with the large k_r for **2** requires that acycle **4** could not arise from interception of radical **2** before cyclization.[9] Thus, the

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(7) (a) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 4505–4509. (b) Curran, D. P.; Kim, D. *Tetrahedron Lett.* **1986**, *27*, 5821–5824.

(8) Park, S.-U.; Chung, S.-K.; Newcomb, M. *J. Am. Chem. Soc.* **1986**, *108*, 240–244.

formation of any **4** at all is quite significant since the only source of **4** was conventional two-electron nucleophilic displacement of halide from **1** by hydride or a cage reaction sequence not involving free radicals. Based only on mass balances of **1** and **4**, the minimum amount of nucleophilic displacement in the reactions of $LiBH_4$ and $LiAlH_4$ with iodide **1b** is 100% and 98%, respectively, and for several other reactions nucleophilic displacement must be the major reaction.

To restate the point made in the preceding paragraph, because radicals like 5-hexenyl and 1-methyl-5-hexenyl can form at least 1% of cyclized product in the presence of metal hydrides, regardless of the mechanistic details, any radical **2** produced in our reactions must have cyclized (>99%) to radical **3**.[9] Thus, the absence of cyclic product **5** in the reductions of **1** indicates that radical **3** (and, by implication, radical **2**) was not formed in these reactions. This is not a superficial conclusion. In the solvent–reagent systems we studied, the fastest reactions possible for a simple, unstabilized primary radical with a molecule are halogen atom transfer from the alkyl halide, hydrogen atom transfer from the alkyl halide, hydrogen atom transfer from the solvent, and possibly reduction of the radical by metal hydride.[13] The only reactions of a simple radical in our system which are faster than those noted are radical–radical reactions which should occur with diffusion limited rate constants but which, because of low radical concentrations, are not observed. Now, for the case of stabilized radical **3**, all bimolecular radical–molecule reactions should be slowed appreciably relative to those of simple radicals, but it is reasonable to assume that the set of radical–molecule reactions given above will still be the fastest radical–molecule reactions available to **3** and that these reactions should have similar *relative* velocities to one another. There are now the two following possibilities: (1) any radical **3** formed reacted mainly by radical–molecule reactions which should have produced a detectable amount of **5** or (2) radical **3** is so stable that it did not react in radical–molecule reactions but accumulated to an appreciable concentration such that any radical **3** formed reacted mainly by radical–radical reactions which should have produced detectable amounts of **5** via disproportionation. Thus, cyclic product **5** would be expected *if* radical **3** had been formed, and the absence of cyclic product **5** indicates that very little if any **3** was formed in the reactions we studied.

We observed only slight reactions of the probes with AlH_3 under our conditions. While the absence of reaction provides poor evidence for a mechanistic conclusion, it should be noted that simple alkyl iodide probes exhibited radical chain isomerizations when treated with AlH_3 with rates about the same as those observed when the probes were treated with $LiAlH_4$.[3c] We conclude that those AlH_3 isomerizations resulted almost entirely from radical chain processes and that the propagation step with the captodative stabilized radical **3** is not possible.

Conclusion

The use of halides **1a** and **1b** as mechanistic probes for reactions of boron and aluminum hydrides with alkyl halides indicates that SET from the reducing agent to the halide to give a free radical is not an important process for these unhindered primary halides. These reductions are best explained as conventional nucleophilic displacements of halide by hydride. This conclusion is in general accord with the results of previous studies of unhindered alkyl halide probes,[3] but our work sets a lower limit on the extent of SET.

Our previous results[7] demonstrated that very small amounts (ca. 0.1 mol % or less) of radical initiation could result in the observed amounts of rearranged reduced products when other mechanistic probes were employed in hydride reductions, and it is reasonable to suspect that in previous studies only limited amounts of SET occurred even when substantial amounts of rearranged reduction products were detected. Indeed, one must be concerned with the possibility that adventitious impurities or side reactions can be responsible for initiation of radical chain isomerization processes in reactions of any alkyl halide probe with boron or aluminum hydride reducing agents.

Experimental Section

General. Reactions were performed in oven-dried flasks under nitrogen using syringe-transfer techniques. ^1H NMR spectra were measured on a Varian EM-390; chemical shifts are reported relative in internal Me_4Si. GC analyses were performed on a Hewlett-Packard (HP) 5790A series gas chromatograph equipped with a capillary injector and a flame ionization detector using a 25 m BP-1 (Scientific Glass Engineering) fused silica column; signal integration was achieved by using a HP 3390A integrator. GC–mass spectra data were obtained by using a HP 5790A series gas chromatograph with a HP 5970A series mass selective detector; a 25-m cross-linked 5% phenylmethylsilicone-coated fused silica column (HP) was used. IR spectra were recorded on a Perkin-Elmer Model 297 spectrophotometer. THF was distilled from potassium–benzophenone immediately before use. Ethanol and isopropyl alcohol were reagent grade and were used as obtained. Commercial hydride reducing agents were purchased from Aldrich Chemical Co. Standardized solutions of $LiAlH_4$ in THF and solutions of AlH_3 in THF were prepared by the method of Krishnamurthy and Brown.[2a]

The preparation and characterizations of 7-bromo-2-methoxy-2-heptenenitrile (**1a**), 2-methoxy-2-heptenenitrile (**4**), and cyclopentylmethoxyacetonitrile (**5**) have been reported.[8]

7-Iodo-2-methoxy-2-heptenenitrile (1b). To a stirred solution of **1a** (1.06 g, 4.86 mmol) in 35 mL of dry acetone was added potassium iodide (1.62 g, 10 mmol). The mixture was stirred for 24 h at room temperature. The reaction mixture was subjected to a conventional extractive workup (ether/water). The organic phase was dried ($MgSO_4$), and the solvent was distilled in vacuo. The residue was purified by chromatography on silica gel (1% ethyl acetate in hexanes elution) to give 0.9 g (70%) of a mixture of isomers of **1b** as an oil: ^1H NMR ($CDCl_3$) δ 5.45 (1 H, t, J = 7.5 Hz), 3.70 and 3.60 (3 H, 2 s), 3.50 (2 H, t, J = 6 Hz), 2.2 (2 H, m), 2.0–1.4 (4 H, m); GC–mass spectrum; *m/e* (relative in-

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(9) In fact, boron and aluminum hydrides apparently react only slowly with alkyl radicals. Russell and Guo found that $NaBH_4$ did not react appreciably with 5-hexenyl, and they set the rate constant for this reaction at $<1 \times 10^4$ M^{-1} s^{-1} at 30 °C.[10] Similarly, LAH reduction of a radical is slow. In the photoinduced radical reduction of neophyl chloride by LAH, Beckwith and Goh found that neophyl radical partially rearranged (21% rearrangement) in the presence of (initially) 1.0 M LAH in ether at room temperature.[6a] From the recently reported kinetic study of the neophyl rearrangement,[11a] we calculate a rate constant for this rearrangement of ca. 900 s^{-1} at 25 °C; we have adjusted Frnaz's data by a factor of 1.2 to incorporate the new rate constant reported for reaction of neopentyl radical with n-Bu_3SnH,[11b] which is a more appropriate model reaction than that used by Franz. Thus, assuming that the mean concentration of LAH in the Beckwith and Goh study was 0.8 M, the LAH trapping reaction of neophyl occurred with a rate constant of ca. 4000 M^{-1} s^{-1}. This trapping value is actually an upper limit because it is quite close to the expected value for reaction of neophyl with THF[12] and may be close to the rate constant for reaction of neophyl with solvent ether.

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(12) Newcomb, M.; Park, S.-U. *J. Am. Chem. Soc.* **1986**, *108*, 4132–4134.

(13) Approximate rate constants at 50 °C are 2×10^6 M^{-1} s^{-1} for iodine atom transfer from primary RI,[7] 6×10^2 M^{-1} s^{-1} for bromine atom transfer from primary RBr,[7] $<3 \times 10^3$ M^{-1} s^{-1} for β-hydrogen atom transfer from RI or RBr,[7] 6×10^3 s^{-1} (pseudo-first order) for hydrogen atom transfer from solvent THF[12] and presumably similar rate constants from solvent ethanol and isopropyl alcohol. Reactions of radicals with $NaBH_4$ and with LAH are slow.[9]

tensity) 265 (9.7) (M^+), 138 (9), 106 (70), 96 (100), 55 (55); IR (film) 2210, 2230 cm^{-1}.

Reactions of Halides 1 with Metal Hydrides. The following general procedure was used. To a solution of 0.1 mmol of metal hydride in 0.5 mL of solvent was added a solution of 0.1 mmol of substrate and 10 mg of dodecane (standard) in 0.5 mL of solvent via syringe. After the appropriate amount of time, the reaction mixture was treated with water and worked up by a conventional extractive method, and the product mixture was analyzed by GC.

Acknowledgment. We thank the donors of Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for financial support.

Single-Electron-Transfer Pathway in the Coupling of Cyclopropenyl Cations with Organometallic Reagents

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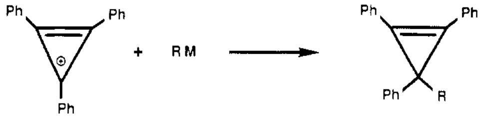
Received February 2, 1987

Treatment of diphenylmethylcyclopropenylium perchlorate with various Grignard reagents produced substituted cyclopropenes in excellent yield. Alkyl and vinylic Grignard reagents react at the methylated carbon atom. The substantial increase in formation of the 1,3-diphenyl-substituted isomer when allylic or benzylic Grignard reagents are used can be attributed to the involvement of a single-electron-transfer (SET) mechanism. The cyclopropenyl radical prefers to localize the odd electron on the phenylated carbon, thereby accounting for the preferential formation of the 1,3-diphenyl-substituted isomer. Reduction of the cyclopropenyl cation with activated magnesium metal leads to four products that have been identified as the unsymmetrical bicyclopropene dimer, a Dewar benzene derivative, and *o*- and *m*-dimethyltetraphenylbenzene The thermal and triplet-sensitized behaviors of the bicyclopropene and Dewar benzene systems were investigated and were found to give rearranged dimethyltetraphenylbenzenes. Mechanisms to explain these results involve rearrangement of a series of radical cation, prismane, and diradical intermediates.

Strained organic molecules have always fascinated organic chemists[1] as well as theoreticians.[2] Three-membered rings have attracted special attention because of severe enforced bond angle deformation and cyclopropene is of particular interest in this context.[3] Cyclopropene itself was first prepared some 60 years ago,[4] but, despite its unusual structure, the molecule received minimal attention until the late 1950s.[5] Two factors led to a resurgence of interest with this highly strained ring system. First, developments in carbene chemistry led to a new and convenient synthesis of cyclopropene derivatives.[6] Secondly, it was realized that the cyclopropenyl cation obeyed the Hückel $[4n + 2]$ π rule.[7] Since the initial preparation of a cyclopropenyl cation,[7] many aryl, alkyl and heteroatomic substituted derivatives of this simplest cyclic aromatic system have been synthesized.[8] Of particular interest are the intrinsic stability of the parent ion and the relative stabilities of its substituted derivatives. On the pK_{R+} scale,[9] it is clear that arylcyclopropenyl cations are generally less stable than alkyl-substituted varieties,[9-11] while the latter are less stable than dialkylaminocyclopropenyl cations.[8]

A variety of cyclopropenes can be readily prepared and their application as synthons in natural product synthesis has raised considerable interest in recent years.[12-16] For some time our group has been interested in the thermal and photochemical transformations of variously substituted cyclopropenes.[17] We have found that a variety of substituted cyclopropenes can be readily prepared by treating variously substituted cyclopropenyl cations with Grignard reagents according to the general procedure of Breslow and co-workers.[9] In spite of the synthetic utility of this reaction, the mechanistic details of the process are still not well-understood. We report here the results of our studies, which provide evidence for an electron-transfer component in the coupling of cyclopropenyl cations with various organometallic reagents.



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Results and Discussion

Electron-transfer mechanisms are increasingly being invoked to describe the reactions of alkylmetal compounds with organic substrates.[18] Recent work by Ashby[19] as well

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[17] For a review, see: Padwa, A. *Org. Photochem.* **1979**, *4*, 261.

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