for the sequence leading to oxime 6) of a total of 1.08 g (10.8 mmol) of ethyl acrylate in 10 mL of diethyl ether. Workup gave 2.64 g (68%) of an oil (about 75% pure as shown by GC) that was purified by distillation to give ethyl 3-(8′-fluoro-2′-naphthyl)-propanoate as a colorless liquid: HRMS m/e calcd for $C_{15}H_{15}FO_2$ (M^+) 246.1056, obsd 246.1050.

Saponification of 1.95 g of the preceding ester with aqueous 2 M NaOH yielded, after workup, 1.5 g (87%) of 3-(8′-fluoro-2′-naphthyl)propanoic acid. Recrystallization from a 19:1 (v/v) mixture of cyclohexane and 2-propanol gave white needles, mp 102.4–102.8 °C. Anal. Calcd for $C_{13}H_{11}FO_2$: C, 71.55; H, 5.08. Found: C, 71.48; H, 4.96.

Treatment of 1.13 g of the preceding carboxylic acid with about 20 g of polyphosphoric acid at 90 °C for 8 min, followed by workup, yielded 0.54 g (52%) of 9-fluoro-2,3-dihydro-1*H*-benz[*f*]inden-1-one. Recrystallization from a 19:1 (v/v) mixture of cyclohexane and 2-propanol gave material with mp 105.5–106.2 °C: ^{19}F NMR δ 11.23 (ddd, $J_{8,9}$ = 11.7 Hz, $J_{7,9}$ = 4.7 Hz, $J_{5,9}$ = 2.0 Hz). Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53. Found: C, 78.16; H, 4.66.

Treatment of 1.46 g of the preceding ketone with hydroxylamine hydrochloride and NaOH in ethanol yielded 0.85 g (54%) of 9-fluoro-2,3-dihydro-1*H*-benz[*f*]inden-1-one oxime. Sublimation[9] followed by low-temperature recrystallization from a 4:1 (v/v) mixture of ethanol and dimethyl sulfoxide gave fine white crystals, mp 235 °C dec: ^{19}F NMR (CD_3SOCD_3) δ 11.07 (ddd, $J_{8,9}$ = 12.3 Hz, $J_{7,9}$ = 4.6 Hz, $J_{5,9}$ = 1.9 Hz); ^{19}F NMR (CD_3SOCD_3, ^{1}H decoupled) δ 11.09 (s). Anal. Calcd for $C_{13}H_{10}NOF$: C, 72.55; H, 4.68. Found: C, 72.56; H, 4.74.

Analogous treatment of 96 mg of the preceding ketone with NaOH and hydroxylamine hydrochloride 95% enriched in ^{15}N (Cambridge Isotope Laboratories) yielded 60 mg (58%) of the corresponding ^{15}N oxime 7: ^{19}F NMR (CD_3SOCD_3) δ 11.07 (dddd, J_{NF} = 39.5 Hz, $J_{8,9}$ = 12.3 Hz, $J_{7,9}$ = 4.6 Hz, $J_{5,9}$ = 1.7 Hz); ^{19}F NMR (CD_3SOCD_3, ^{1}H decoupled) δ 11.10 (d, J_{NF} = 39.5 Hz).

Treatment of oxime 7 with acetic anhydride and acetic acid followed by rotary evaporation and recrystallization of the residue from a mixture of cyclohexane and toluene gave the *O*-acetyl derivative 11, mp 134.2–135.8 °C: ^{19}F NMR δ 10.83 (dddd, $J_{N,9}$ = 43.6 Hz, $J_{8,9}$ = 12.0 Hz, $J_{7,9}$ = 4.6 Hz, $J_{5,9}$ = 1.7 Hz); ^{19}F NMR (^{1}H decoupled) δ 10.89 (d, J_{NF} = 43.5 Hz); MS m/e (relative intensity) 258 (M^+, 46), 216 (100).

[^{15}N]-*O*-Acetyl-3,4-dihydro-8-fluoro-5-methyl-1(2*H*)-naphthalenone Oxime (8). Treatment of oxime 1[3] with acetic anhydride and acetic acid gave the *O*-acetyl derivative 8, mp 94.6–95.6 °C: ^{19}F NMR δ 3.45 (ddd of q, $J_{N,8}$ = 23.3 Hz, $J_{7,8}$ = 11.0 Hz, $J_{6,8}$ = 5.1 Hz, $J_{Me,8}$ = 1.2 Hz); ^{19}F NMR (^{1}H decoupled) δ 3.48 (d, J_{NF} = 23.3 Hz); MS m/e (relative intensity) 236 (M^+, 13), 194 (100).

Acknowledgment. We are grateful to the W. M. Keck Foundation and to Merck & Co., Inc. for contributions to Bryn Mawr College that enabled the purchase of a 300-MHz NMR spectrometer. We also are grateful to the Camille and Henry Dreyfus Foundation, Inc. and to PQ Corporation for contributions to Bryn Mawr College that enabled the purchase of a GC/MS system.

Registry No. 1, 137465-93-1; 5, 137465-94-2; 6, 137465-95-3; 7, 137465-96-4; 8, 137465-97-5; 9, 137465-98-6; 10a, 137465-99-7; 10b, 137466-00-3; 10c, 137466-01-4; 10d, 137466-02-5; 11, 137466-03-6; bromobenzene, 108-86-1; 3-(4-bromobenzoyl)-propanoic acid, 6340-79-0; 4-(4-bromophenyl)butanoic acid, 35656-89-4; 7-bromo-1-tetralone, 32281-97-3; 1,2,3,4-tetrahydronaphthene-1-oxime, 3349-64-2; 7-bromo-1-naphthylamine hydrochloride, 137466-04-7; 7-bromo-*N*-acetyl-1-naphthylamine hydrochloride, 137742-00-8; 7-bromo-1-naphthyldiazonium tetrafluoroborate, 137466-05-8; 7-bromo-1-fluoronaphthalene, 319-04-0; 7-(magnesiobromo)-1-fluoronaphthalene, 137466-06-9; 3-carbomethoxypropionyl, 1490-25-1; 3-(8-fluoro-2-naphthyl)-propanoic acid methyl ester, 137466-07-0; 3-(8-fluoro-2-naphthoyl)propanoic acid, 137466-08-1; 4-(8-fluoro-2-naphthyl)butanoic acid, 137466-09-2; 5-fluoro-4-oxo-1,2,3,4-tetrahydrophenanthrene, 137466-10-5; 5-fluoro-4-oxo-1,2,3,4-tetrahydrophenanthrene oxime, 137466-11-6; 2-bromo-4-fluorotoluene, 1422-53-3; ethyl 3-(5-fluoro-2-methylphenyl)propanoate, 137466-12-7; 3-(5-fluoro-2-methylphenyl)propanoic acid, 137466-13-8; 7-fluoro-4-methyl-1-indanone, 137466-14-9; 7-fluoro-4-methyl-1-indanone oxime, 137466-15-0; 3-(8-fluoro-2-naphthyl)propanoic acid ethyl ester, 137466-16-1; 3-(8-fluoro-2-naphthyl)propanoic acid, 137466-17-2; polyphosphoric acid, 137466-18-3; 9-fluoro-2,3-dihydro-1*H*-benz[*e*]inden-1-one, 137466-19-4; 8-fluoro-1,2,3,4-tetrahydro-5-methylnaphthyl oxime, 137466-20-7; 7-bromo-1-naphthylamine, 136924-78-2.

Supplementary Material Available: ^{1}H NMR characterizations (δ and J values at 300 MHz) for 30 compounds and 300-MHz ^{1}H NMR spectra for compounds 8–11 (14 pages). Ordering information is given on any current masthead page.

Reaction of Chiral Cyclopropyl Halides with SmI_2

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Reductions of (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane (7), (*S*)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (19), and (*R*)-(−)-1-fluoro-1-iodo-2,2-diphenylcyclopropane (11) with samarium(II) iodide is reported. Evidence for a samarium(III) intermediate in the reaction is presented.

Introduction

The seminal work by Kagan[1] on the use of samarium(II) iodide as a reagent for organic synthesis has generated a great deal of activity in this area.[2] In general, the reactivity of Sm(II) iodide is characterized by single electron transfer (SET) from the samarium(II) to a suitable substrate to yield an anion radical intermediate and samarium(III) ($E°_{aq}\frac{Sm^{2+}}{Sm^{3+}}$ = −1.55 V). The anion radical intermediate can dissociate into a radical and an anion or collapse to a molecular radical anion (i.e., ketyl formation from a carbonyl radical anion). The radical intermediates may undergo reaction, either in an inter- or intramolecular mode, or they may be converted to anions by electron transfer from another equivalent of samarium(II) iodide. It is in this manner that samarium(II) has been used to

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(2) For recent reviews see: Kagan, H. B. *Nouv. J. Chem.* **1990**, *14*, 453. Soderquist, J. A. *Aldrichimica Acta* **1991**, *24*, 15.

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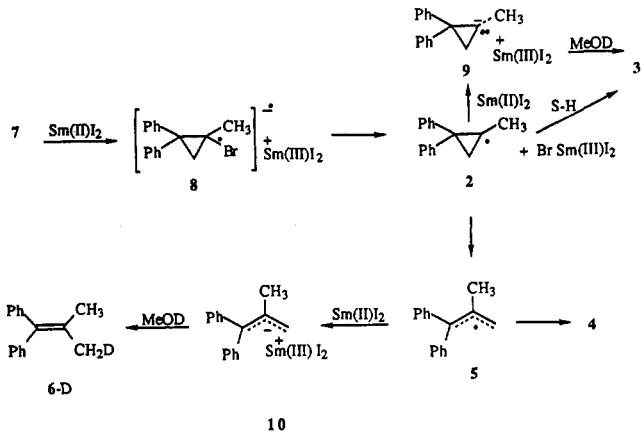
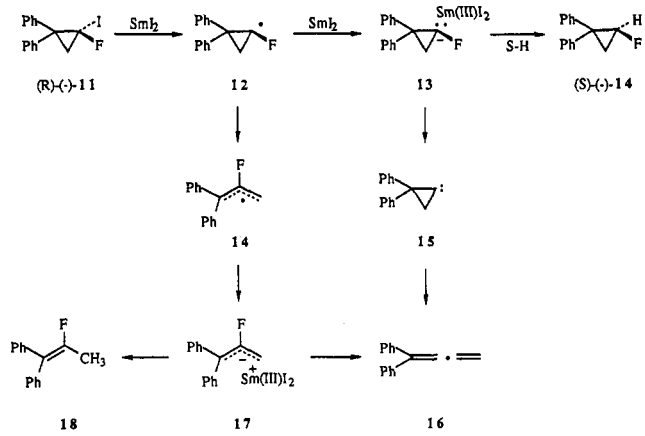
Scheme I

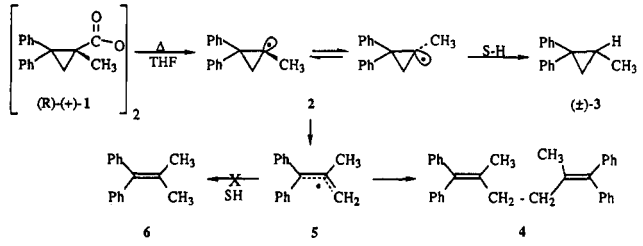


Scheme II



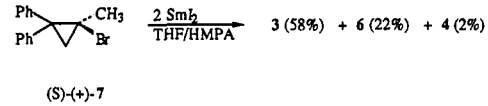
reduce organic halides,[3] carbonyls,[4] α-hydroxyl esters,[5] P–O[6] and P–Cl[7] bonds, sulfoxides,[7] and sulfones,[8] and nitro[9] compounds. Coupling reactions, both intra- and intermolecular, of the pinacolic,[10] Barbier, and Reformatski type have also been documented.[11-15]

Our interest in the cyclopropyl radical[16a-e] prompted us to investigate the use of samarium(II) iodide as another means of generating this radical. When the radical **2** was produced by thermolysis of the chiral precursor[16] (*R*)-(+)-1-methyl 2,2-diphenylcyclopropylpercarboxylate (**1**),



the resulting radical **2** abstracted a hydrogen atom from solvent (THF) to give (±)-**3**. The radical also underwent ring opening to the allyl radical **5** which coupled to yield **4** and the ratio of **3**:**4** was 1:1. As expected the allyl radical did not abstract a hydrogen atom from THF to form **6**.

When the same 1-methyl-2,2-diphenylcyclopropyl radical (**2**) was generated by treating (*S*)-(+)-**7** with 2 equiv of SmI_2 in THF/HMPA solution the product ratios were quite different. The ratio of **3**:**4** was now 29:1 and **6** was obtained as the chief minor product with the ratio of **3**:**6** being 2.5:1. Hydrocarbon **3** was essentially racemic. When the reaction was conducted in the presence of MeOD cyclopropyl hydrocarbon **3** contained at most 15% deuterium but olefin **6** contained one deuterium atom per molecule.



Scheme I represents our interpretation of the experimental observations. We suggest that the initial reaction between bromide (*S*)-(+)-**7** and samarium(II) iodide involves a single electron transfer from samarium(II) into the carbon–bromine antibonding σ* orbital to give the anion-radical samarium(III) diiodide **8** which collapses to cyclopropyl radical **2** and samarium(III) bromodiiodide. As expected of this radical intermediate,[16] it can partition itself by reacting with solvent (THF) to yield hydrocarbon **3** which is racemic[16] or it can undergo ring opening to form allyl radical **5**. That is what is usually observed when radical **2** is formed in solution.[15] However, under the conditions of this reaction, containing a molar excess of samarium(II) iodide, both radicals **2** and **5** can undergo further reduction to form anions **9** and **10**. The observation that the cyclopropyl hydrocarbon contained only ~15% deuterium when the reaction is carried out in the presence of MeOD would indicate that **2** reacts with solvent to abstract a hydrogen atom or undergoes ring opening before it is further reduced by samarium(II) iodide. The allyl radical **5** undergoes reduction by samarium(II) iodide to yield **10** at a rate faster than the coupling of **5** to yield dimeric product **4**. The allyl anion samarium(III) iodide **10** is quenched by MeOD when the latter is included in the reaction mixture to yield **6**, which possesses one deuterium atom per molecule.

To gain further insight into the nature of the samarium(III) iodide–cyclopropyl bonding in the postulated structure **9** an attempt was made to prepare this intermediate. Thus, (*S*)-(+)-**7** was treated with *tert*-butyllithium to yield the corresponding optically stable 1-lithio-2,2-diphenylcyclopropane[17] which was converted to **9** by addition of 1 equiv of samarium(III) triiodide. The reaction mixture then was treated with dimethoxyethane (DME) in order to decompose any unreacted lithium reagent. Subsequent treatment of the reaction mixture

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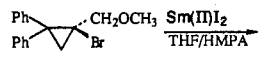
(15) Molander, G. A.; Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8236.
(16) (a) Gawronska, K.; Gawronski, J.; Walborsky, H. M. *J. Org. Chem.* **1991**, *56*, 2193. (b) Walborsky, H. M.; Collins, P. C. *J. Org. Chem.* **1976**, *41*, 940. (c) Walborsky, H. M.; Chen, J.-C. *J. Am. Chem. Soc.* **1971**, *93*, 671. (d) Walborsky, H. M.; Chen, J.-C. *J. Am. Chem. Soc.* **1970**, *92*, 7573. (e) For reviews pertaining to the cyclopropyl radical see: Walborsky, H. M. *Tetrahedron*, **1981**, *37*, 1625. Boche, G.; Walborsky, H. M. *Cyclopropane Derived Reactive Intermediate*, John Wiley & Sons: New York, 1990.
(17) Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *84*, 3283.

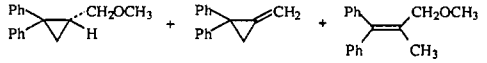
with MeOD revealed that **9** was also decomposed by the DME since **3** did not contain any detectable deuterium. The optical purity of (*R*)-(−)-**3** formed was 56%, 78% overall retention of configuration. Had the lithium reagent not reacted with samarium(III) triiodide the configuration would have been completely retained. That **9** was indeed formed was also indicated by ^{7}Li NMR (see Experimental Section). After **9** was formed in THF alone and the reaction mixture was allowed to remain at 0 °C for 2.5 h, quenching with MeOD gave **3** with 72% retention of configuration containing ~38% deuterium. If the reaction mixture was kept at 0 °C for 18 h before quenching with MeOD hydrocarbon **3** did not contain deuterium and the retention of configuration was reduced to 52%. This would indicate that **9** reacts slowly with THF and that it slowly racemizes in solution. Samarium(III) intermediates have been implicated by Kagan in the Barbier reaction[2,3,10] and by Molander in the sequential coupling reaction.[10] We view **9** as a contact ion pair.

Another system studied[16a] was (*R*)-(−)-1-fluoro-1-iodo-2,2-diphenylcyclopropane (**11**). The stereochemistry of the chiral 1-fluoro-2,2-diphenylcyclopropyl radical[12] has been previously investigated, and the extent of retention of configuration was shown to be dependent on the radical trap employed.[16a] It was, therefore, of interest to establish how good samarium(II) iodide was as a radical trap. In this case, the second equivalent of samarium(II) iodide would trap the radical by transferring an electron to it, resulting in the formation of **13**, the fluoro analogue of **9**. Under the conditions of the experiment the fluorocyclopropyl hydrocarbon, (*S*)-(−)-**14**, was obtained in 55% yield and an optical purity of ~95% with overall retained configuration. Thus, samarium(II) iodide can be classified as an excellent radical trap toward **12**, equivalent to tri-*n*-butyltin hydride. The high optical purity of (*S*)-(−)-**14** indicated that **13** is the precursor of **14**, presumably by reaction with solvent. The reaction of **12** with solvent, to any large extent, to yield **14** is deemed unlikely since it has been shown that extensive racemization is observed when this occurs.[16a]

The origin of byproduct allene **16** (formed in 18% yield) is not clear. The α-elimination of fluorosamarium(III) diiodide to yield a carbene intermediate **15** which can collapse to allene is one possibility. An alternative is ring opening of radical **12** to allyl radical **14** which when trapped by Sm(II) iodide would yield **17**. The latter would be expected to undergo β-elimination to form **16**. We cannot distinguish between these two possibilities. The small amount of olefin **18** formed (1%) is probably due to quenching of **17**.



(S)-(+)-19



(+)-20 21 22

Reaction of (*S*)-(+)-**19** with Sm(II) iodide resulted, as expected, in the expected formation of racemic **20** (50% yield) by way of a radical intermediate similar to the one formed in the reaction of (*R*)-(+)-**1** under the same conditions. Of significance is the formation of **21** (16% yield) which would be expected if a Sm(III) ion-pair intermediate were involved.[18] Formation of a minor product, olefin **22** (2% yield), is analogous to the formation of **18** from (*R*)-(−)-**11**.

(18) Webb, J. L.; Mann, C. K.; Walborsky, H. M. *J. Am. Chem. Soc.* **1970**, *92*, 2042.

Experimental Section

Samarium diiodide (solution in THF) was purchased from Aldrich. *tert*-Butyllithium was titrated before use. THF was dried by refluxing and distilling from sodium–potassium alloy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 300-MHz apparatus. IR spectra were recorded on a Perkin-Elmer model 257 spectrophotometer. Optical rotations were measured at the 546.1-nm mercury line on a Bendix-Ericson Model 987 ETL/NPL polarimeter equipped with a Bendix Model DR-1 digital display. Radial chromatography separations were performed with Merck silica gel 60 PF_{254} by using Harrison Research Chromatotron Model 7924T. Preparative GC were performed on Varian Aerograph Model 700 gas chromatograph with 15% SF-96 on chromosorb W as a stationary phase.

Reaction of Samarium Diiodide with Cyclopropyl Halides. Samarium diiodide (2 mmol, 20 mL of 0.1 M solution in THF) was added to a solution of 1 mmol of the appropriate cyclopropyl halide in THF (25 mL) and HMPA (1 mL) at ambient temperature. The reaction mixture decolorized after a few minutes, and stirring with continued for an additional 2 h. The reaction mixture was diluted with water and extracted with hexane. The organic layer was separated, dried over magnesium sulfate, filtered, and evaporated to dryness. The oily residue was separated using radial chromatography (elution with pentane) and/or preparative gas chromatography (170 °C).

(*S*)-(+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane[17] **(7)** yielded the following products.

1-Methyl-2,2-diphenylcyclopropane[17] **(3)** (120 mg (58%)). NMR: δ 0.92 (d, J = 6 Hz, 3 H), 1.12 (dd, J = 4.8, 6 Hz, 1 H), 1.25 (dd, J = 4.2, 6 Hz, 1 H), 1.59–1.70 (m, 1 H), 7.05–7.35 (m, 10 H). IR (neat): 3051, 3016, 2943, 2919, 2794, 1592, 1488, 1440, 1027, 760, 696, 605 cm^{-1}. MS: M^{+}, 208. $[\alpha]^{25}_{Hg}$ 0° (c 1, $CHCl_3$).

1,1-Diphenyl-2-methylpropene[18] **(6)** (45 mg (22%)). NMR: δ 1.78 (s, 6 H), 7.05–7.45 (m, 10 H). MS: M^{+}, 208.

1,1,6,6-Tetraphenyl-2,5-dimethyl-1,5-hexadiene (4) (2%) which was identified by NMR and compared to an authentic sample.[16] NMR: δ 1.62 (s, 6 H), 2.24 (s, 4 H), 7.00–7.25 (m, 20 H).

(*R*)-(−)-1-Fluoro-1-iodo-2,2-diphenylcyclopropane[16a] **(11)** yielded the following products.

(*S*)-(−)-1-Fluoro-2,2-diphenylcyclopropane[16a] **(14)** (117 mg (55%)). NMR δ 1.57 (dd, J = 6.3, 11, 7 Hz, 1 H), 1.79 (ddd, J = 3.2, 7.0, 22.8 Hz, 1 H), 5.01 (ddd, J = 3.2, 6.3, 65.4 Hz, 1 H), 7.15–7.45 (m, 10 H). IR (neat) 3051, 3021, 1594, 1489, 1441, 1427, 1362, 1155, 1122, 1045, 1004, 989, 748, 698 cm^{-1}. $[\alpha]^{25}_{Hg}$ −19.5° (c 0.56, $CHCl_3$, ee = 95%).[16a]

1,1-Diphenylallene[16b] **(16)** (34 mg (18%)). NMR: δ 5.24 (s, 2 H), 7.10–7.40 (m, 10 H). MS: M^{+}, 192.

1,1-Diphenyl-2-fluoropropene (18) (1%) was identified by NMR and comparison with an authentic sample.[16a] NMR: δ 2.04 (d, J = 18 Hz, 3 H), 7.20–7.40 (m, 10 H).

(*S*)-(+)-1-Bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane[18] **(19)** yielded the following products.

1-(Methoxymethyl)-2,2-diphenylcyclopropane[18] **(20)** (120 mg (50%)). $[\alpha]^{25}_{Hg}$ 0°. NMR: δ 1.28–1.36 (m, 2 H), 1.88–1.98 (m, 1 H), 3.06–3.18 (m, 2 H), 3.24 (s, 1 H), 7.10–7.45 (m, 10 H). IR (neat) 3050, 3016, 2915, 2867, 2805, 1593, 1488, 1440, 1164, 1105, 749, 697 cm^{-1}. MS: M^{+}, 240.

1-Methylene-2,2-diphenylcyclopropane[18] **(21)** (33 mg (16%)). NMR: δ 1.85 (m, 2 H), 5.58 (m, 1 H), 5.88 (m, 1 H), 7.15–7.25 (m, 10 H). MS: M^{+}, 206.

1,1-Diphenyl-2-(methoxymethyl)propene (22) (5 mg (2%)). NMR: δ 1.83 (s, 3 H), 3.25 (s, 3 H), 3.90 (s, 2 H), 7.05–7.50 (m, 10 H). MS: M^{+}, 240.

Reaction of Samarium Diiodide with 1-Bromo-1-methyl-2,2-diphenylcyclopropane in the Presence of MeOD. The experiment was conducted according to the general procedure described above, using THF–HMPA solvent system containing 2 equiv of MeOD which had been added prior to the samarium diiodide. Usual workup followed by radial chromatography gave the mixture of the two main products: 1-methyl-2,2-diphenylcyclopropane (**3**) and 1,1-diphenyl-2-methylpropene (**6**) (4:1). This

mixture was further analyzed in order to assess the extent of deuterium incorporation. The ^1H NMR spectrum was virtually identical with the spectra of the authentic samples, thus indicating that the cyclopropane derivative contains at least 80% the C-H compound. In the ^{13}C NMR spectrum two signals for the CH_3 carbons of 1,1-diphenyl-2-methylpropene (δ 22.60, 22.85, lower intensity, split) were found. GC-MS analyses gave M = 209 for 1,1-diphenyl-2-methylpropene (at least 80% of deuterium) and mass 208 (100) and 209 (35) for 1-methyl-2,2-diphenylcyclopropane (up to 15% of C-D compound).

Attempted Preparation of 1-Methyl-2,2-diphenylcyclopropylsamarium(III). *tert*-Butyllithium (1 mmol; pentane) was added dropwise, with stirring, to a solution of (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane (7) (140 mg, 0.5 mmol, ee = 81%) in THF at -90 °C. The reaction mixture was stirred for 0.5 h and injected to a suspension of samarium triiodide in THF (prepared in situ from stoichometric amounts of samarium and iodine at -50 °C). After the reaction mixture was allowed to reach 0 °C (2 h) it was treated with 0.5 mL of DME and, after 0.5 h, quenched with MeOD. The reaction mixture was diluted with pentane (50 mL) and washed with water. The organic layer was separated and dried over magnesium sulfate and the solvent removed under reduced pressure. The oily residue was purified by radial chromatography (elution with pentane) to give 88 mg (85%) of 1-methyl-2,2-diphenylcyclopropane (3). The ^1H NMR spectrum was identical with that of an authentic sample (no deuterium incorporation). $[\alpha]^{25}_{Hg}$ -85° (*c* 1, $CHCl_3$, ee = 57%),[16] 78% retention of configuration.

The experiment described above was repeated starting with the (*S*)-(+)-7 (ee = 91%). The reaction mixture was kept at 0 °C for 18 h and then quenched with MeOD. No significant amount of deuterium could be found by ^1H NMR. $[\alpha]^{25}_{Hg}$ 62° (*c* 0.18, $CHCl_3$, ee = 47%) 52% retention of configuration.

^7Li NMR Experiment (Chemical Shifts Related to Lithium Iodide Solution in Water). 1-Methyl-2,2-diphenylcyclopropyllithium in THF was prepared in an NMR tube, and 5% of benzene-d_6 was added (for locking purposes). ^7Li NMR was taken at 104 MHz (Bruker 270-MHz apparatus). δ 0.5 LiBr, 2.1 broad, cyclopropyllithium derivative. Samarium triiodide suspension in THF was then added, and the NMR spectrum was taken again after 0.5 h. The broad signal at 2.1 completely disappeared.

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Reinvestigation of a Criticized Mechanistic Probe Study of Metal Hydride Reductions of Alkyl Halides

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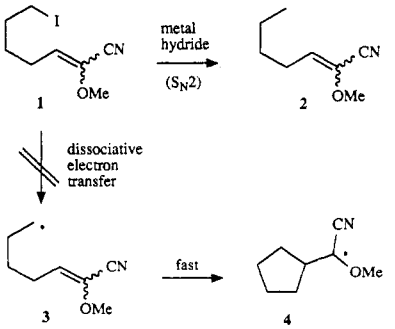
Published claims that $LiAlH_4$ promotes isomerizations of either 7-iodo-2-methoxy-2-heptenenitrile (1) or 2-methoxy-2-heptenenitrile (2) and the speculations resulting from these claims have led to new studies of reactions of 1 and 2. Highly isomerically enriched samples of 1 and 2 were prepared, and the equilibrium populations of isomers for both 1 and 2 were determined by iodine-mediated equilibrations. Reactions of isomerically enriched samples of 1 and 2 as well as mixtures of isomers with $LiAlH_4$ demonstrated that $LiAlH_4$-induced isomerizations did not occur. Absolute yields of product 2 from reactions of 1 with limited amounts of $LiAlH_4$ did not agree with previously reported results. Reactions of 2 with limited amounts of $LiAlH_4$ resulted in selective destruction of 2 with (*Z*)-2 reacting faster than (*E*)-2. On the basis of these facts and the fact that speculations regarding radical intermediates from reactions of 1 with $LiAlH_4$ are inconsistent with known kinetic values for radical reactions, the published criticisms of a study employing 1 as a probe for radical formation in reactions with metal hydrides are found to be without merit.

The use of mechanistic probes to implicate reactive intermediates and suggest the details of reaction pathways is of unquestioned utility. In studies of potential electron-transfer reactions of alkyl halides, a variety of radical probes have been applied, and the results of these studies have demonstrated unequivocally that radical intermediates are produced in many reactions; extensive pioneering studies by Ashby's group are perhaps best recognized in this regard.[2] However, one must remain aware of the shortcomings of probe studies that are product oriented; the implication of a specific reactive intermediate produced under a given set of conditions can provide inferences concerning the reaction mechanism, but establishing the mechanism is often considerably more difficult and usually requires detailed studies to verify that suggested pathways are kinetically competent. In the case of

Scheme I



potential electron-transfer reactions of alkyl halides, probe studies can be seriously compromised by radical chain isomerizations of the alkyl halide that converts, for example, 5-hexenyl iodides to cyclopentylmethyl iodides in a process unrelated to the reaction of interest. The caveat is that small amounts of radical initiation from any of a

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(2) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.

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