J = 6 Hz), 6.35 (d, 1 H, J = 7.7 Hz), 6.56 (d, 1 H, J = 7.7 Hz), 8.1 (m, 1 H); mass spectrum (70 eV), m/e (relative intensity) 270 (10, 213 (100), 184 (10), 170 (20).

(3) A solution of 6 mg of optically pure rugulovasine A in 0.3 mL of CF_3CO_2H (TFA) was stored for 2 h and then the NMR spectrum was recorded at room temperature. After evaporation of the TFA, 0.3 mL of $CDCl_3$ was added and the spectrum was retaken. The solution was neutralized with saturated $NaHCO_3$, extracted into $CHCl_3$, dried, and evaporated. The residue was benzoylated and checked for optical purity by the shift reagent protocol; this showed <5% racemization: NMR (TFA), 2.1 (s, 3 H), 3.0 (s, 3 H), 3.7 (br t, 2 H), 4.0 (br t, 1 H), 7.0 (d, 1 H, J = 7 Hz), 7.4 (m, 2 H), 7.5 (d, 1 H, J = 7 Hz). The same spectrum was observed when a sample of rugulovasine B or a mixture of A and B were dissolved in TFA. TFA Salt in $CDCl_3$: 2.0 (s, 3 H), 2.9 (s, 3 H), 3.5 (t, 2 H, J = 3 Hz), 3.8 (t, 1 H, J = 3 Hz), 6.9 (d, 1 H, J = 7 Hz), 7.2 (m, 2 H), 7.4 (d, 1 H, J = 7 Hz), 8.4 (s, 1 H).

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Registry No. (±)-1, 26909-33-1; (+)-1, 91465-62-2; (+)-1·HCl, 91547-42-1; (+)-1·CF_3CO_2H, 91547-43-2; (±)-2, 26909-34-2; (±)-8. 74606-95-4; (+)-8, 88668-90-0; (±)-9, 91547-44-3; (+)-9, 91424-42-9; (±)-10, 88668-91-1; (±)-10B, 91465-63-3; (±)-11, 74644-92-1; (+)-11, 74606-96-5; (±)-12, 88668-95-5; (±)-13, 91424-43-0; (±)-14, 91424-45-2; (±)-15, 91424-44-1.

Occurrence of Electron Transfer in the Reduction of Organic Halides by $LiAlH_4$ and AlH_3

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A variety of methods have been utilized to detect the occurrence of a single electron transfer pathway in the reduction of alkyl halides by $LiAlH_4$ and AlH_3, i.e., (1) product studies of reduction of cyclizable alkyl halides containing the 5-hexenyl group, (2) trapping of intermediate radicals by dicyclohexylphosphine and other trapping agents, (3) direct EPR observation of the trityl radical in the reduction of trityl bromide, and (4) stereochemical studies of the reduction of secondary halides by lithium aluminum deuteride. The extent of electron transfer was found to be a function of the solvent, the substrate, the leaving group, and the hydride reagent. For alkyl iodides, and to a much lesser extent bromides, electron transfer was found to be the major reaction pathway; however, no evidence for electron transfer was found for the corresponding chlorides or tosylates. Reduction of (+)-2-octyl iodide by $LiAlD_4$ was found to be much less stereospecific than the corresponding reduction of bromide, chloride, or tosylate, indicating intermediate radical formation in the reduction of the secondary iodide.

In recent years numerous studies concerning the reduction of organic halides by $LiAlH_4$ have appeared in the chemical literature.[1] Lithium aluminum hydride has been considered to react as a nucleophilic reagent that donates a hydride ion to substrates such as alkyl halides.[1-3] However, a variety of mechanisms, including S_N2 and radical, have been proposed to describe this reduction reaction.[4-14] For example, Brown and co-workers have reported a number of rate–structure profile studies for a series of alkyl halides and $LiAlH_4$ and have proposed an S_N2 mechanism to describe these reactions.[4-6] However, bromobenzene is readily reduced to benzene by $LiAlH_4$ under mild conditions and yet bromobenzene is not considered a likely candidate for a facile S_N2 process. On the other hand, Chung and Chung have presented evidence for radical intermediates in the $LiAlH_4$ reduction of aryl bromides based on the cyclization of vinyl *o*-bromophenyl ether.[7] Nevertheless, in our hands this reaction took place in only 3% yield after 7 days and therefore the small amount of cyclization observed over such a long period of reaction time was not considered convincing. Chung has also suggested a radical pathway for the reduction of vinyl bromides by $LiAlH_4$, based on observations of cis–trans isomerization of the styryl group.[9] The formation of radical intermediates in an electron-transfer process has also been suggested for a variety of other reactions involving organic halides and metal hydrides.[10-14] Yet, the pioneering stereochemical study of Eliel[15] which showed that $LiAlD_4$ reacted with (+)-1-chloro-1-phenylethane with inversion of configuration generally has been interpreted as convincing evidence for an S_N2 mechanism for such reactions.

Since there seems to be some confusion concerning the mechanistic pathway describing the reaction of $LiAlH_4$ with alkyl halides, we decided to study this reaction in detail. The methodology used to study the model systems involve: (1) direct spectroscopic observation of radical intermediates, (2) the use of cyclizable radical probes in the alkyl halide, (3) trapping of intermediate radicals by hydrogen donor trapping agents, and (4) reduction of optically active alkyl halides and tosylates.

With respect to direct spectroscopic observation (1), EPR was used to detect the presence of stable radical intermediates. Thus, with alkyl halides that produce stable radicals, it was possible to observe by EPR radical intermediates produced by electron transfer. In the present

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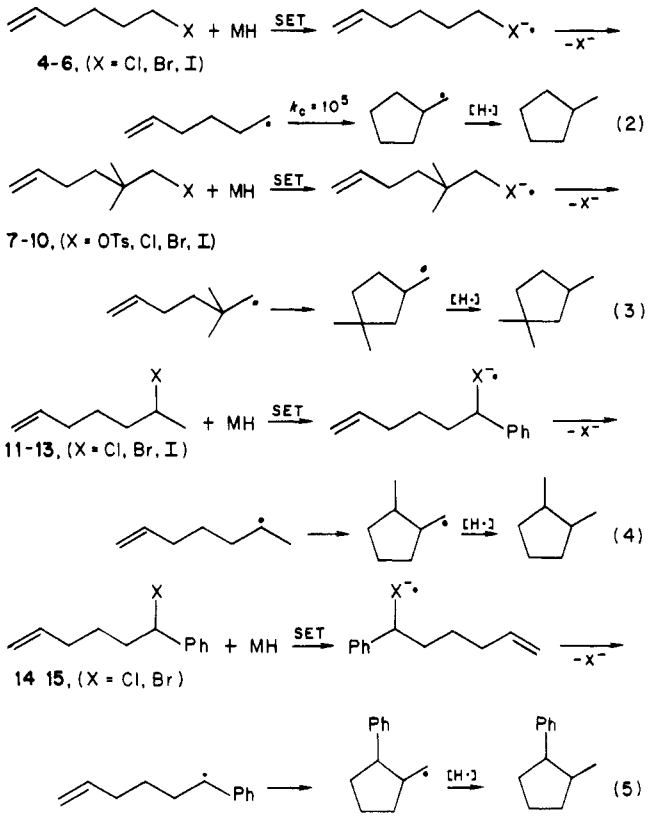
studies, reactions of metal hydrides with Ph_2CHBr (1), Ph_3CCl (2), and Ph_3CBr (3) were examined in detail (eq 1). Earlier, we reported preliminary results of our EPR

$$Ph_3CBr + MH \rightarrow Ph_3CBr^{-}\cdot + MH^{+}\cdot \rightarrow Ph_3C\cdot + Br^{-} + MH^{+}\cdot \rightarrow Ph_3CH + MBr \quad (1)$$

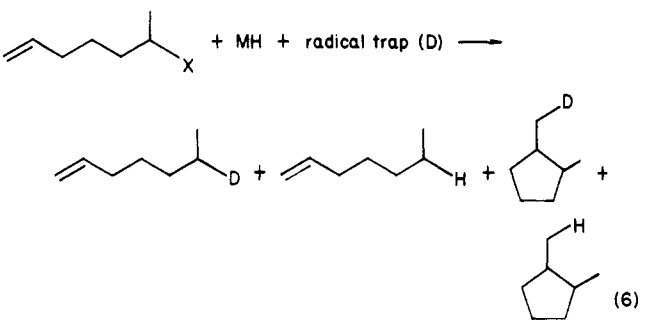
studies which indicated the occurrence of an electron-transfer process in the above systems and we now present the results of these studies in more detail.[16]

With respect to the use of cyclizable probes (2), we have studied reactions of alkyl halides containing the 5-hexenyl group with a variety of metal hydrides. Since it is known that the 5-hexenyl radical cyclizes to the cyclopentylmethyl radical,[17] alkyl halides containing the 5-hexenyl group can serve as probes for the detection of single electron transfer (SET) in the reduction by metal hydrides. Thus, if a 5-hexenyl radical, or derivative, is produced in such reactions, then the occurrence of SET is confirmed by the observation of cyclic products (eq 2–5). Earlier we reported preliminary results of studies with the alkyl halides **11–13** which indicated that reduction of alkyl iodides by $LiAlH_4$ involves a SET pathway.[18] Herein we report detailed studies of the reduction of several other cyclizable alkyl halides (**4–6**, **7–10**, and **14** and **15**).



With respect to (3), a convincing way to detect the presence of a radical intermediate is to trap the radical with a good hydrogen atom donor. Such trapping has been very informative in showing that straight chain as well as cyclic products formed on reduction of cyclizable probes have a radical precursor (eq 6).

With respect to reduction of optically active alkyl halides (4), the stereochemistry of $LiAlH_4$ reduction of alkyl halides was reexamined in the hope of further elucidating the reaction mechanism. In this connection, the cyclizable probes **14** and **15** (eq 5) were reduced in order to provide complimentary information with respect to the previous stereochemical studies by Eliel[15] using optically active (1-halophenyl)ethanes, since the steric requirements of the reaction centers should be similar. Additionally, the reduction of optically active 2-halooctanes should have steric requirements very similar to that of the secondary halides **11–13** (eq 4). Moreover, a full range of leaving groups, from tosylate to iodide, was examined in the secondary octyl system.



Experimental Section

Materials. Solvent-grade pentane, hexane, and benzene were stirred over concentrated H_2SO_4, washed with water, and dried with $MgSO_4$ under nitrogen. Reagent-grade diethyl ether (Fisher) and reagent-grade tetrahydrofuran (THF) were distilled under nitrogen from deep purple solutions of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from sodium at reduced pressure. Samples of 1-hexene, 1-heptene, cyclopentane, methylcyclopentane, *cis*- and *trans*-1,2-dimethylcyclopentane, dodecane, Ph_2CH_2, Ph_3CH, and ethylbenzene were obtained with 99% purity from Aldrich and used as received. From chemical samples a 98% purity sample of 1,1,3-trimethylcyclopentane was used as received. An authentic sample of 5,5-dimethyl-1-hexene (^1H NMR 0.88 ppm (9 H, s), 1.05–2.33 (4 H, m), 4.83–6.25 (3 H, m); mass spectrum, M^+ 112) was obtained by preparative GLC of a hydrolyzed sample of the corresponding Grignard reagent.

Aldrich's 6-chloro-1-hexene (bp 135 °C) and 6-bromo-1-hexene (bp 62 °C at 30 mmHg) were distilled from CaH_2 under nitrogen. Benzhydryl chloride (bp 126–128 °C at 0.10 mmHg), trityl chloride, and trityl bromide were obtained from Aldrich. 5-Bromo-1-pentene was obtained from Columbia Organic Co. (bp 123–124 °C, from CaH_2). Acetaldehyde (Aldrich) was distilled from P_2O_5 under N_2. Benzaldehyde (Aldrich) was distilled from CaH_2 (bp 46 °C at 6 mmHg). Dicyclohexylphosphine (DCPH) was obtained from Aldrich and distilled (bp 68–70 °C at 0.05 mmHg). Aldrich's 1,4-cyclohexadiene (bp 81–82 °C) was distilled under N_2. Deuterated dicyclohexylphosphine (DCPD) was prepared in 70% yield (98% d_1) analogous to Issleib's method for DCPH.[19] (-)-2-Octanol was purchased from Aldrich and used as received.

Solutions of $LiAlH_4$,[5] $LiAlD_4$,[20] AlH_3,[5] $HMgCl$,[21] and MgH_2[21] were prepared according to known procedures. A solution of $LiEt_3BH$ in THF was purchased from Alfa. Solutions of hydride reagents were analyzed for active hydride by hydrolysis of samples on a standard vacuum line equipped with a Teopler pump.[22] When applicable, magnesium and aluminum analyses were performed by EDTA titration.

General Procedures. Reactions were performed under nitrogen or argon at the bench with the use of Schlenk-tube techniques or in a glovebox equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone traps to remove solvent vapors. Calibrated syringes equipped with

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stainless steel needles were used for transfer of reagents. Glassware and syringes were flamed and cooled under a flow of nitrogen or argon. All melting points are corrected, and all boiling points are uncorrected. Stock solutions of reagents and reaction vessels were protected from light.

Reactions were carried out in round-bottomed flasks equipped with T-bore stopcocks attached to male 24/40 standard taper joints (allows nitrogen flush while reagents are being added or removed through the stopcock by syringe) and a Teflon-coated magnetic stirring bar. The appropriate amounts of solvents and reagents were syringed into the flask under a nitrogen or argon flush. After complete reaction, the mixture was hydrolyzed with saturated aqueous NH_4Cl solution under nitrogen atmosphere. In some cases the ether layer was separated, dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under vacuum. In other cases the organic layer was analyzed directly by an appropriate method.

Quantitative GLC analyses were obtained by using an FID detector and response-factor corrected peak areas using internal standards. Proton NMR chemical shifts are reported relative to $(CH_3)_4Si$ and quantitative N.M.R. studies were obtained by using nitromethane as the internal standard. High-resolution IR spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Mass spectra were obtained on a Varian MAT 112S and carbon–hydrogen microanalyses were conducted by Atlantic Microlabs, Inc. of Atlanta, GA. EPR spectra were recorded on a Varian E109ES.

Optical rotations were measured on either a JASCO Model 5 ORD or a Bendix-Ericsson NPL polarimeter as either neat samples or cyclopentane solutions. For gas chromatographic analyses, the following columns and conditions were used: (a) 5% OV101, 2 ft, 160 °C, 25 mL/min, dimesityl ketone (t_R = 1.37), Ph_3CH (1.000); (b) 15% TCEP + 10% Apiezon L, 25 ft, 65 °C, 40 mL/min, 1-hexene (1.00), methylcyclopentane (1.34), cyclohexene (2.27); (c) 8% Apiezon L, 25 ft, 65 °C, 30 mL/min, 1-heptene (1.00), 5,5-dimethyl-1-hexene (1.19), 1,1,3-trimethylcyclopentane (1.44); (d) same column as in (c), benzene (1.00), 1-heptene (1.14), *trans*-1,2-dimethylcyclopentane (1.26), *cis*-1,2-dimethylcyclopentane (1.67); (e) 8% Apiezon L, 4 ft, 80 °C, 40 mL/min, *n*-decane (1.00), **10** (2.67); 3,3-dimethyl(iodomethyl)cyclopentane (3.50), **6** (1.92) *trans*-2-methyl(iodomethyl)cyclopentae (3.18), *cis*-2-methyl(iodomethyl)cyclopentane (4.19); (f) same column as in (e), *n*-decane (1.00), **9** (1.13), **5** (0.81); (g) same column as in (e), 6-phenyl-1-hexene (1.30), n-$C_{12}H_{26}$ (1.00).

Preparations. 6-Iodo-1-hexene (6). Treatment of 10.0 g (51 mmol) of 6-bromo-1-hexene with 100 g of NaI in 150 mL of refluxing acetone for 2 h gave an 85% isolated yield of 6-iodo-1-hexene (**6**) upon distillation: bp 64–66 °C at 12 mmHg; n^{25}_D 1.5106; ^1H NMR (CCl_4) 1.20–2.33 ppm (6 H, m), 3.17 (2 H, t, J = 6.0 Hz), 4.77–6.20 (3 H, m); mass spectrum, m/e (relative intensity) 211 (5.1), 210 (65.8), 127 (12.7), 83 (79.7), 67 (35.4), 55 (100), 41 (77.2).

2,2-Dimethyl-5-hexen-1-ol. To the Grignard reagent prepared from 140 g of 4-bromo-1-butene and 32.0 g of magnesium chips (Ventron resublimed) in 800 mL of Et_2O was added 65.0 g of acetone (bp 56 °C from P_2O_5). After being stirred for 2 h, the mixture was quenched with aqueous NH_4Cl and extracted with Et_2O in the usual manner. After removal of Et_2O (in vacuo) the residue was treated with 650 mL of concentrated HCl at 0 °C in a separatory funnel for 20 min and extraction with 150 mL of pentane yielded 33 g of 2-chloro-2-methyl-5-hexene upon distillation from CaH_2 (bp 51 °C at 40 mmHg, ^1H NMR (CCl_4), 1.45–2.60 ppm (10 H, m, contains 6 H, s at 1.60), 4.80–6.20 (3 H, m)). The Grignard reagent from 33 g of 2-chloro-2-methyl-5-hexene and 7.0 g of magnesium was prepared in 400 mL of THF and carbonated by bubbling dry CO_2(g) through a gas dispersion tube immersed in the solution. The mixture was quenched with 15% aqueous HCl and extracted with Et_2O in the usual manner. The crude oil (38 g) obtained by evaporation of the Et_2O (in vacuo) was added to 1.2 molar equiv of $LiAlH_4$ in Et_2O at 0 °C. Workup with 15% aqueous HCl and extraction with Et_2O in the usual manner yielded 17 g of 2,2-dimethyl-5-hexen-1-ol (bp 68–69 °C at 8.0 ± 0.10 mmHg) which exhibited the following: ^1H NMR (CCl_4) 0.83 ppm (6 H, s) 0.85–2.40 (5 H, m, contains OH), 3.25 (2 H, s), 4.75–6.20 (3 H, m); IR (neat film) 3340 cm^{-1} (OH), 3070 (unsaturated C—H), 2950 (C—H), 1640 (C=C), 1470, 1360 (CH_3); n^{25}_D 1.4436; GLC purity of 98% using 24 ft, 10% TCEP on Chromasorb P at 135 °C and 40 mL/min He.

Tosylate of 2,2-Dimethyl-5-hexen-1-ol (7). In 50 mL of benzene at 0 °C were combined 1.9 g of tosyl chloride, 5.0 mL of pyridine, and 1.28 g of 2,2-dimethyl-5-hexen-1-ol. The mixture was warmed to room temperature and allowed to stir for 24 h. After filtration the mixture was distilled to yield 1.7 g (60%) of the pure product **7** which exhibited the following: bp 144–146 °C at 0.30 mmHg; ^1H NMR 0.92 ppm (6 H, s), 1.05–2.17 (4 H, m), 2.47 (3 H, s), 3.65 (2 H, s), 4.77–6.05 (3 H, m), 7.23–8.03 (4 H, m); IR 2960 cm^{-1} (unsaturated C—H), 1580 (C=C), 1410 (CH_3), 1150 (S=O); mass spectrum (CI) m/e (relative intensity) 283 (0.74), 112 (8.61), 111 (100), 110 (6.25), 69 (2.54).

1-Chloro-2,2-dimethyl-5-hexene (8). In 125 mL of CCl_4 (distilled from P_2O_5) was dissolved 40 g of Ph_3P (reagent Aldrich, dried in vacuo over P_2O_5) and 18 g of 2,2-dimethyl-5-hexen-1-ol, and the mixture was refluxed under nitrogen for 72 h. After cooling to room temperature, 500 mL of pentane was added to the mixture, which was chilled to 0 °C, followed by filtration to remove Ph_3PO. Distillation yielded 17 g of the desired product **8** (bp 62 °C at 14 mmHg) which was contaminated with approximately 10% of the starting alcohol. Preparative GLC using a 24 ft, 10% TCEP on Chromasorb P at 140 °C and 40 mL/min. He yielded analytically pure 1-chloro-2,2-dimethyl-5-hexene (**8**), which exhibited the following: ^1H NMR (CCl_4) 0.98 ppm (6 H, s), 1.21–2.25 (4 H, m), 3.35 (2 H, s), 4.80–6.18 (3 H, m); mass spectrum, 146 (7.6), 97 (20.4), 91 (21.1), 90 (20.4), 69 (8.0), 56 (81.6), 55 (100), 41 (23.0), 39 (13.8), 29 (18.8); n^{25}_D 1.4426. Anal. Calcd for $C_8H_{15}Cl$: C, 65.55; H, 10.24. Found: C, 65.65; H, 10.22.

1-Bromo-2,2-dimethyl-5-hexene (9). In a 250-mL round-bottomed flask equipped with an equalizing addition funnel and reflux condenser was placed 16 g of Ph_3P (Aldrich, dried in vacuo over P_2O_5) and 100 mL of Et_2O under dry nitrogen. The flask was cooled to 0 °C and 8.8 g of Br_2 was added through the addition funnel. The solid Ph_3Br_2 was allowed to settle, the Et_2O was decanted via cannula, and 100 mL of dry pyridine (distilled from CaH_2) was added, followed by 5.5 g of 2,2-dimethyl-5-hexen-1-ol (as prepared above). The mixture was refluxed for 20 h, cooled at 0 °C after dilution by 100 mL of pentane, and filtered to remove Ph_3PO. The mixture was concentrated on a rotary evaporator, dissolved in 300 mL of pentane, and washed with 15% aqueous HCl and then with aqueous sodium thiosulfate. Distillation of the oil (bp 68–70 °C at 14 mmHg) yielded 6.6 g of pure 1-bromo-2,2-dimethyl-5-hexene (**9**) exhibiting the following: ^1H NMR (CCl_4) 1.03 ppm (6 H, s), 1.05–2.25 (4 H, m), 3.22 (2 H, s), 4.80–6.20 (3 H, m); IR (neat film) 3050 cm^{-1} (unsat. C—H), 2950 (C—H), 1640 (C=C), 1470, 1365 (CH_3); mass spectrum, m/e (relative intensity) 192 (0.42), 190 (0.40), 137 (15.8), 135 (15.8), 111 (33.3), 97 (28.1), 81 (10.5), 69 (58.8), 55 (100); n^{25}_D 1.4665; GLC purity 98%, 24 ft, 10% TCEP at 140 °C and 40 mL/min He. Anal. Calcd for $C_8H_{15}Br$: C, 50.27; H, 7.93. Found: C, 50.51: H, 7.98.

2,2-Dimethyl-1-iodo-5-hexene (10). In a 250-mL flask was added 42 g of Ph_3P (0.080 mol, dried in vacuo over P_2O_5), 150 mL of benzene, 19 g of I_2 (0.075 mol), 40 mL of pyridine, and 9.8 g (0.075 mol) of 2,2-dimethyl-5-hexen-1-ol. After reflux for 24 h, the mixture was diluted with pentane (150 mL), chilled, and filtered. Distillation of the residue yielded 17.3 g (93%) of pure (98%) by GLC on 24-ft 10% TCEP, 130 °C, 40 mL/min He) 2,2-dimethyl-1-iodo-5-hexene, which exhibited the following: ^1H NMR (CCl_4) 1.05 ppm (6 H, s), 1.27–2.27 (4 H, m), 3.13 (2 H, s), 4.80–6.17 (3 H, m); bp 46 °C at 1.5 mmHg; n^{25}_D 1.5020; mass spectrum, m/e (relative intensity) 238 (1.55), 183 (2.54), 127 (2.64), 112 (2.10), 111 (22.4), 95 (4.41), 69 (100), 55 (59.5). Anal. Calcd: C, 40.35; H, 6.36. Found: C, 41.33: H, 6.66.

1-Hepten-6-ol. The title compound was prepared in 96% yield by the method of Ingold and Maeda[17] and exhibited the following: ^1H NMR 1.18 ppm (3 H, d, J = 6.0 Hz), 1.20–2.55 (6 H, m), 3.30–3.97 (2 H, 7, contains O–H), 4.80–6.17 (3 H, m); bp 74–76 °C at 23 mmHg (lit.[17] bp 61 °C at 12 mmHg).

Tosylate of 1-Hepten-6-ol. To 50 mL of pyridine at 0 °C were added 19 g of tosyl chloride and 10 g of 1-hepten-6-ol. The mixture was allowed to stand at 8 °C for 98 h. After filtration, the mixture was diluted with 400 mL of pentane, washed with dilute HCl, washed with water, dried with $MgSO_4$, and desolvated in vacuo to yield 23 g of a crude yellow oil. Purification by chromatography

on silica with ether/pentane (2–95) as eluent yielded analytically pure tosylate, which exhibited the following: ^{1}H NMR 1.08–2.20 ppm (9 H, m, contains 3 H, d, 1.80 ppm, J = 6.0 Hz), 2.38 (3 H, s), 4.37–6.05 (3 H, m), 7.20–7.78 (4 H, m); IR 3070 cm^{-1} (unsat. C—H), 2980 (C—H), 1640 (aromatic C—C), 1600 (C=C), 1490 (CH_3), 1180 (S=O); mass spectrum (CI), m/e (relative intensity) 269 (100), 213 (5.89), 193 (17.05), 187 (1.00), 173 (18.43), 157 (2.55), 135 (14.76). Anal. Calcd: C, 62.65; H, 7.53. Found: C, 62.56; H, 7.55.

6-Chloro-1-heptane (11). To 150 mL of acetone was added 10 g of LiCl and 8.0 g of the crude 6-tosyl-1-heptene. After being refluxed for 48 h, the mixture was cooled, diluted with pentane, and subjected to standard workup. Distillation yield 2.6 g (69%) of analytically pure **11**, which exhibited the following bp 70–72 °C at 81 mmHg; n^{25}_D 1.4350; ^{1}H NMR 1.40–2.32 ppm (9 H, m, contains 6 H, d, 1.55 ppm, J = 6.0 Hz), 4.02 (1 H, m), 4.78–6.05 (3 H, m); IR 3080 cm^{-1} (unsat. C—H), 2940 (C—H), 1640 (C=C), 1445, 1380 (CH_3); GLC purity 99% on 5-ft 10% OV101 at 90 °C, 40 mL/min; mass spectrum, m/e (relative intensity) 132 (0.50), 97 (7.70), 96 (26.05), 81 (70.69), 69 (13.59), 68 (10.58), 67 (24.00), 56 (20.16), 55 (77.24), 54 (100). Anal. Calcd: C, 63.38; H, 9.90. Found: C, 63.42, H, 9.94.

6-Bromo-1-heptene (12). By a procedure analogous to that used above, 6-bromo-1-heptene (**12**) was prepared in 76% yield and exhibited the following: bp 64–68 °C at 24 mmHg (lit.[17] bp 72 °C at 20 mmHg); n^{25}_D 1.4622; ^{1}H NMR 1.40–2.33 ppm (9 H, m, contains d, 3 H, 1.77 ppm, J = 6.0 Hz), 3.73–4.23 (1 H, m), 4.75–6.10 (3 H, m); IR 3080 cm^{-1} (unsat. C—H), 2960 (C—H), 1640 (C=C), 1440, 1375 (CH_3); mass spectrum, m/e (relative intensity) 178 (0.57), 176 (0.54), 97 (23.03), 81 (30.36), 55 (100); GLC purity 98% on 5-ft 15% TCEP, 120 °C, 100 mL/min. Anal. Calcd: C, 47.47; H, 7.41. Found: C, 47.55; H, 7.43.

6-Iodo-1-heptene (13). By a procedure analogous to that used above 6-iodo-1-heptene (**13**) was prepared in 78% yield and exhibited the following: bp 77–79 °C at 25 mmHg; n^{25}_D 1.5042; ^{1}H NMR 1.37–2.35 ppm (9 H, contains 3 H, d, 1.97 ppm, J = 6.0 Hz), 4.08 (1 H, m), 4.80–6.10 (3 H, m); mass spectrum, m/e (relative intensity) 224 (0.52), 97 (14.92), 57 (9.35), 56 (4.68), 55 (100), 41 (20.33); GLC purity 99% on 6-ft 10% Apiezon L, 130 °C, 60 mL/min. Anal. Calcd: C, 37.51; H, 5.86. Found: C, 37.58; H, 5.89.

6-Hydroxy-6-phenyl-1-hexene. To the Grignard reagent prepared from 36 g of 5-bromo-1-pentene and 7.5 g magnesium (Alfa, resublimed) in 300 mL of Et_2O was added 25 g of PhCHO in 50 mL of Et_2O. After 30, min, the mixture was quenched with aqueous NH_4Cl, extracted with Et_2O, and dried with $MgSO_4$. Removal of Et_2O (in vacuo) yielded 36 g (88%) of the alcohol: ^{1}H NMR: 1.04–2.23 ppm (6 H, m), 3.80 (1 H, s), 4.45 (1 H, t, J = 6.0 Hz), 4.90–6.15 (3 H, m), 7.20 (5 H, m).

6-Chloro-6-phenyl-1-hexene (14). To a 250-mL, round-bottomed flask were placed 8.0 g of the crude alcohol, 70 mL of CS_2, and 15 mL of pyridine at −50 °C under nitrogen. $POCl_3$, 15 g, was added dropwise with stirring, and the cooling bath was removed and the mixture stirred for 4 h. The mixture was poured onto ice–aqueous HCl and the organic layer was separated, washed to neutral pH, and dried with $MgSO_4$. Distillation yielded 6.2 g (69%) of **14** which exhibited the following: bp 71–73 °C at 0.10 mmHg; n^{25}_D 1.5226; ^{1}H NMR 1.27–2.37 ppm (6 H, m), 4.67–6.30 (4 H, m), 7.05–7.20 (5 H, m); IR (neat) 3060 cm^{-1} (unsat. C—H), 2950 (C—H), 1640 (C=C), 1600 (aryl C—C), 910, 695; mass spectrum m/e (relative intensity) 197 (0.23), 196 (2.32), 195 (0.81), 194 (8.26), 158 (11.63), 118 (12.49), 117 (100), 115 (28.90), 91 (58.46), 77 (8.36). Anal. Calcd: C, 74.01; H, 7.78. Found: C, 74.00; H, 7.79.

6-Bromo-6-phenyl-1-hexene (15). To a 250-mL round-bottomed flask under nitrogen were placed 8.0 g of the alcohol in 50 mL of CS_2 and 20 mL of pyridine at −50 °C. $POBr_3$, 26 g, in 50 mL of CS_2 was added dropwise with stirring and the cooling bath was removed. After being stirred for 4 h the mixture was poured onto ice–dilute H_2SO_4, and the organic layer was washed until neutral pH was obtained. Distillation afforded 8.3 g (76%) of (**15**) which exhibits the following: bp 84–86 °C at 0.10 mmHg; n^{25}_D 1.5436; ^{1}H NMR 1.30–2.42 ppm (6 H, m), 4.70–6.26 (4 H, m), 7.05–7.20 (5 H, m); IR (neat) 3060 cm^{-1}, 3030 (unsat. C—H), 2940 (C—H), 1640 (C=C), 1600 (aryl C—C), 990, 910; mass spectrum, m/e (relative intensity) 240 (0.42), 238 (0.56), 159 (24.01), 129 (11.32), 117 (93.58), 115 (34.08), 91 (100), 81 (16.95). Anal. Calcd: C, 60.26; H, 6.33. Found: C, 65.09; H, 6.65.

6-Phenyl-1-hexene. An authentic sample was obtained by reacting 0.205 g of 6-bromo-5-phenyl-1-hexene with 2.30 mL of 0.39 M $LiAlH_4$ in 3.0 mL of THF for 48 h. After quenching with water, extraction with pentane, and solvent removal in vacuo 0.135 g (96%) of an oil was obtained. Analytically pure 6-phenyl-1-hexene was obtained by preparative GLC and exhibited the following: ^{1}H NMR (CCl_4) 1.33–2.35 ppm (6 H, m), 2.67 (2 H, t, J = 6.0 Hz), 4.67–6.10 (3 H, m), 7.05-7.25 (5 H, m); I.R. (neat) 3060 cm^{-1}, 3030 (unsat. C—H) 2940 (C—H), 1640 (C=C), 1600 (aryl C—C); mass spectrum, m/e (relative intensity) M$^+$ 160. Anal. Calcd: C, 89.92; H, 10.08. Found: C, 89.88; H, 10.06.

(−)-1-Chloro-1-phenylethane (20). According to the procedure of Yamaguchi and Mosher,[23] (*R*)-(+)-PhCHOHCH$_3$ was obtained in 70% optical purity. The title compound **20** was prepared by reaction of the alcohol with $POCl_3$ in pyridine, as described by Burwell, Hart, and Shields[24] in 81% chemical yield and exhibited the following: n^{25}_D 1.5248 (lit.[24] n_D 1.5241); bp 78–80 °C at 21 mmHg (lit.[24] bp 74–75 °C at 15 mmHg): $[\alpha]^{25}$ −43.2°, neat sample, l = 0.10 cm, 57.0% optical purity (based on $[\alpha]$ 96.4° for 100% optical purity[24]).

(−)-1-Bromo-1-phenylethane (21). According to the method of Dauben and McCoy,[25] the corresponding alcohol was reacted with $POBr_3$ in pyridine to give the desired product **21** (43% yield), which exhibited the following: bp 69–71 °C at 3.0 mmHg (lit.[25] bp 86–87 °C at 11 mmHg); n^{25}_D 1.5598; $[\alpha]^{25}_D$ −55.0° for neat sample, l = 0.10 cm, 57.0% optical purity (based on $[\alpha]$ 96.4° for 100% optical purity[25]).

Optically Active 2-Halooctanes. The series of optically active 2-halooctanes (OTs, Cl, Br, I) was prepared according to the method of San Filippo and Romano.[26] For X = OTs (**16**): ^{1}H NMR 0.85–1.62 ppm (16 H, m), 2.43 (3 H, m), 4.53 (1 H, m), 7.20–7.80 (4 H, m); IR 2930 cm^{-1} (C—H), 1605 (aromatic C—C), 1455, 1370 (CH_3), 1180 (S=O); mass spectrum, m/e (relative intensity) 284 (0.21), 173 (18.41), 155 (70.02), 112 (86.01), 91 (100); $[\alpha]^{25}_D$ −7.55° for c = 0.287 g/mL in cyclopentane, 76.0% optical purity (based on $[\alpha]$ 9.93° for 100% optical purity[26]). For X = Cl (**17**): n^{25}_D 1.4240; bp 68–69 °C at 23 mmHg (lit.[26] bp 74–76 °C at 25 mmHg); $[\alpha]^{25}_D$ +27.6° for neat sample, 84.4% optical purity (based on $[\alpha]$ 31.6° for 100% optical purity[26]). For X = Br (**18**): n^{25}_D 1.4465; bp 80–82 °C at 24 mmHg (lit.[26] bp 74–76 °C at 14 mmHg); $[\alpha]^{25}_D$ +31.9° for neat sample, 73.1% optical purity (based on $[\alpha]$ 43.6° for 100% optical purity[26]). For X = I (**19**): n^{25}_D 1.4840; bp 64–66 °C at 2.0 mmHg (lit.[26] bp 54–55 °C at 1.5 mmHg); $[\alpha]^{25}_D$ +11.6° for neat sample, 18.3% optical purity (based on $[\alpha]$ 63.2° for 100% optical purity[26]).

General Procedure for Reduction of Alkyl Halides. Equimolar amounts of the desired alkyl halide and metal hydride were combined in a reaction vessel (0.1 M in each reagent) under N_2 and shielded from light in the desired ethereal solvent.[25] For EPR studies, the reagents were combined in an EPR tube under N_2. In cases where additives were employed (DCPH), the additive was added to the metal hydride, followed by addition of the appropriate alkyl halide. Control experiments showed that no reaction occurred between $LiAlD_4$ and DCPH, as determined by the constancy of the P–H stretching band at 2260 cm^{-1} in THF at room temperature. It was also found that DCPH was unreactive (as determined by GLC) toward alkyl halides in the absence of $LiAlH_4$. At the chosen time, reaction mixtures were quenched carefully with water, internal standards added, and GLC analyses performed. Deuterium incorporation was evaluated by GC–mass spectrum.

In the stereochemical studies, deuterated hydrocarbon products were isolated by repetitive preparative GLC and exhibited 98% purity by GLC. Optical rotations were measured on a Bendix-Ericsson NPL instrument with cyclopentane solvent and concentrations of products were in the range of 0.200–0.250 g/mL. Corrected rotations of products were obtained by dividing the observed rotation by the optical purity of the starting halide

(23) Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973**, *38*, 1870.
(24) Burwell, R. L., Jr.; Shields, A. D.; Hart, H. *J. Am. Chem. Soc.* **1954**, *76*, 908.
(25) Dauben, H. J.; McCoy, L. L. *J. Am. Chem. Soc.* **1959**, *81*, 5404.
(26) San Filippo, J.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514.

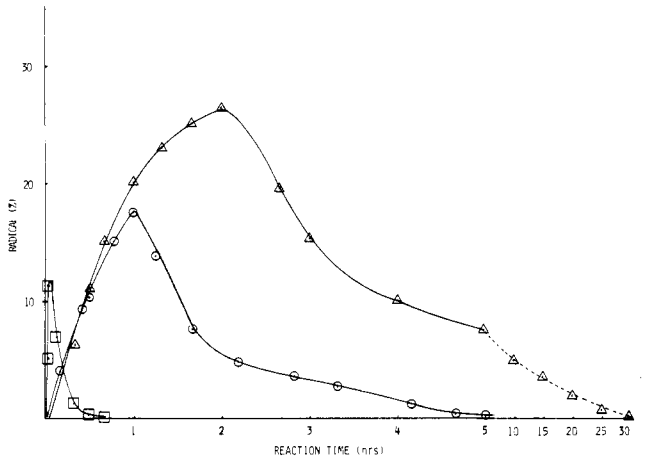


Figure 1. Formation of the trityl radical with time determined by EPR spectroscopy in the reaction of trityl bromide (3) with metal hydrides: (○) $LiAlH_4$, (□) AlH_3, (△) HMgBr.

substrate. Since the reductions of alkyl halides by $LiAlD_4$ generated lithium halide in the presence of optically active halide, the extent of racemization of the substrate by lithium halide under the reaction conditions was also measured as a control experiment in each case. Whenever possible, the optical purity of recovered alkyl halide was also measured.

Results and Discussion

EPR Studies. Various simple and complex metal hydrides (MH) such as AlH_3, MgH_2, HMgCl, HMgBr, B_2H_6, $LiAlH_4$, and $NaAlH_4$ were allowed to react with trityl halides **2** and **3** in equimolar amounts in THF at room temperature (eq 7). These reactions proceeded rapidly

$$Ph_3CX + MH \rightarrow Ph_3CH + MX \quad (7)$$
$$\mathbf{2\text{–}3};\ X = Cl, Br$$

to form a yellow-orange solution in each case, which increased in intensity with time and then slowly decreased. The reaction solutions were found to be EPR active and showed an EPR spectrum in each case consistent with that of the trityl radical[27] $Ph_3C\cdot$. This signal was not present in the solutions of the trityl halides. The rate of radical formation, but particularly its decay, was found to be dependent on the nature of the particular metal hydride employed (Figure 1).

The reduction product of these reactions is triphenylmethane (Ph_3CH) which is continuously formed during the course of the reaction (Figure 2). It is important to note that the formation of product (Figure 2) proceeds at approximately the same rate that the radical is disappearing (Figure 1). In order to determine the extent of H-atom abstraction by the trityl radical from either the metal hydride radical cation or the solvent, similar experiments were carried out using metal deuterides. In each case, a high yield of deuterium incorporation product, Ph_3CD (90%), was obtained, suggesting that hydrogen is abstracted predominantly from the metal hydride radical cation intermediate. The proposed mechanistic pathway is given in Scheme I.

The proposed pathway (Scheme I) suggests that on mixing the two reagents, one electron is transferred from the metal hydride (deuteride) to the trityl halide which subsequently produces the trityl radical. The concentration of the radical is dependent on the ease of hydrogen (deuterium) transfer from the metal hydride radical cation which is related to the reactivity of the metal hydride. Indeed, the product Ph_3CH (or Ph_3CD) is formed much

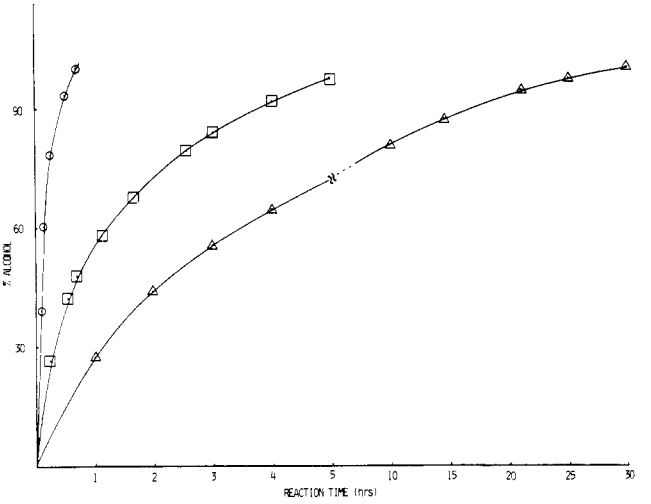
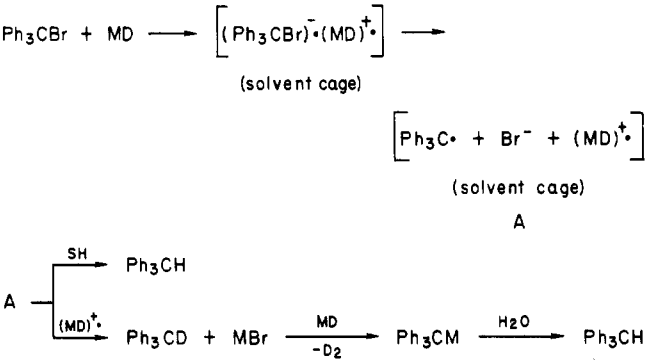


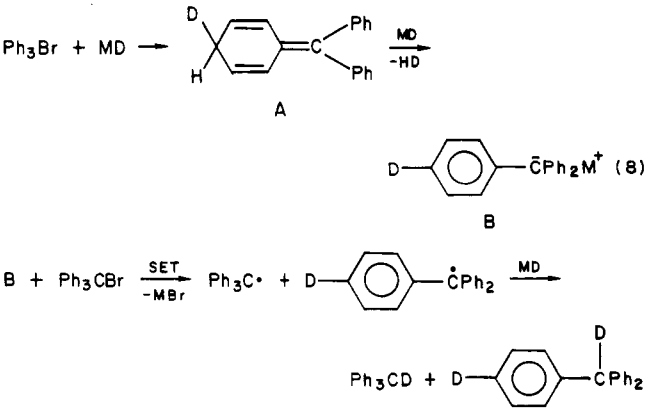
Figure 2. Formation of the reduction product (Ph_3CH) with time determined by GLC in the reaction of trityl bromide (3) with metal hydrides: (○) $LiAlH_4$, (□) AlH_3, (△) HMgBr.

Scheme I



more rapidly from $LiAlH_4$ or $NaAlH_4$ compared to AlH_3 or HMgBr. Again, the amount of deuterium incorporation (when M–D is employed) is dependent on the reactivity of the metal hydride. Thus, high deuterium incorpporation product (Ph_3CD > 90%) is observed in the reaction of $LiAlD_4$ with Ph_3CBr. The small amount of Ph_3CH formed in this reaction can be explained either by abstraction of hydrogen from the solvent or an alternative route involving a further reaction of Ph_3CD with MD, resulting in the formation of Ph_3CM which upon hydrolysis forms Ph_3CH. Indeed, a slow gas evolution (H_2 or D_2) is observed when the above reaction mixture is allowed to stand for a long period of time and the amount of deuterium incorporation product decreases with time.

An alternative mechanistic scheme which should be considered for the reduction of Ph_3CBr by metal hydrides (or deuterides) is shown in eq 8. Thus, it may be suggested



(27) Adam, F. C.; Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 2057.

Table I. Reaction of Benzhydryl Halides with $LiAlH_4$ in THF at Room Temperature

Ph_2CHX	time	temp, °C	% yield Ph_2CH_2	% yield $Ph_2CHCHPh_2$	product ratio
Cl	0.5 h	RT	3.0	no trace	
Cl	1 h	RT	3.5	no trace	
Cl	20 h	RT	20	no trace	
Cl	91 h	RT	53	no trace	
Cl	168 h	RT	96	no trace	
Br	1.2 min	0	3.4	11	3.4
Br	2.3 min	0	4.3	24	3.6
Br	11 min	0	9.0	36	4.0
Br	30 min	0	22	78	3.5
Br	60 min	0	22	78	
Br ($LiAlD_4$)	60 min	0	29 (100% d_1)	68	
Br ($LiAlD_4$ + 5DCPH)	60 min	0	52 (72% d_1)	51	
Br (AlH_3)	120 min	RT	2.6	71	

that Ph_3CBr undergoes a conjugate reduction by MD to produce compound A, which can be deprotonated by MD to produce the anion B. A carbanion such as B should be able to transfer an electron to Ph_3CBr, which would produce the intermediate trityl radical. However, this mechanistic suggestion is not supported by the available data. First of all, most (90%) of the product in the reaction of Ph_3CBr with $LiAlD_4$ is Ph_3CD, as determined by GLC, NMR, and mass spectral analyses. Thus, if a conjugate reduction process were involved, one would expect substantial dideuterated reduction product in the reaction of $LiAlD_4$ with Ph_3CBr, but no such dideuterated product could be found by mass spectral or NMR analysis. Also, the EPR spectrum of the intermediate radical in the reaction of $LiAlD_4$ with Ph_3CBr is consistent with the trityl radical and not a deuterated radical. Hence the conjugate reduction process (eq 8) is not supported by the data and, therefore, the most reasonable explanation of the mechanism of the reduction of Ph_3CBr by $LiAlD_4$ is given in Scheme I.

Although trityl halides are rather unusual alkyl halides, at least it has been demonstrated by a direct spectroscopic method that a carbon radical is produced as an intermediate upon reaction of an organic halide with metal hydrides. Presumably, the observance of trityl radicals in these reductions is a consequence of the longer lifetime of such relatively stable radical intermediates. Indeed, no EPR-active species could be detected in the metal hydride reductions of other typical alkyl halides such as those employed in the cyclizable probe studies. Nevertheless, the EPR studies presented herein are valuable in that they demonstrate, by direct spectroscopic observation of free radicals, the occurrence of electron transfer in reductions of organic halides.

Although Singh and co-workers[11] reported that the reduction of benzhydryl chloride in THF at 0 °C produces diphenylmethane and dimer products in 25% and 42% yields, respectively (eq 9)

$$Ph_2CHX + LiAlH_4 \xrightarrow[0\ °C]{THF} Ph_2CH_2 + Ph_2CHCHPh_2 \quad (9)$$

in 35 min, we found reduction to be much slower (only 3% diphenylmethane and no dimer) under the same conditions (Table I). We did observe the complete reduction of benzhydryl chloride, but only after 168 h; however, no dimer was observed. Therefore, unlike Singh, we have no evidence of a radical product formed in this reaction. On the other hand, we did find that benzhydryl bromide is readily reduced under the same conditions (THF, 0 °C) employed for benzhydryl chloride reductions. Furthermore, dimer is formed as the major product, indicating the intermediate formation of a radical. The data in Table I further shows that reduction of benzhydryl bromide by $LiAlD_4$ results in the formation of reduction product which is 100% d_1. In addition, the same reaction in the presence of dicyclohexylphosphine (DCPH), a hydrogen-atom donor, resulted in the trapping of the benzhydryl radical precursor of the dimer as evidenced by a decrease in the amount of dimer with a concurrent increase in the amount of diphenylmethane formed as well as by a decrease in the amount of deuterium incorporation in the diphenylmethane product. Since AlH_3 is a byproduct in the reduction of these halides by $LiAlH_4$, a reaction was carried out between benzhydryl bromide and AlH_3 in THF. In this case, the reaction was much slower than in the case of $LiAlH_4$ although the product is nearly entirely dimer (Table I). It is clear that AlH_3 is an even better one-electron donor than $LiAlH_4$ or is a poorer hydrogen atom donor to the intermediate radical and that the reaction with AlH_3 proceeds essentially completely by an SET pathway. However, because of the slowness of the reaction of benzhydryl bromide with AlH_3, compared to $LiAlH_4$, it seems that the formation of AlH_3 as a byproduct in the $LiAlH_4$ reaction cannot be used as the reason for the SET behavior of $LiAlH_4$. Furthermore, the product ratio in the reaction with $LiAlH_4$ is essentially constant throughout the reaction. If dimer formation was a result of AlH_3 byproduct, the ratio of products (dimer/Ph_2CH_2) would have been much smaller at the beginning of the reaction. Therefore, these results indicate that benzhydryl bromide, but not chloride, is reduced by $LiAlH_4$ by a SET pathway.

Reduction of benzyl iodide and *n*-octyl iodide by $LiAlH_4$ in THF was carried out in order to determine if dimer product is formed (eq 10 and 11). In each case no dimer

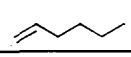
$$PhCH_2I + LiAlD_4 \xrightarrow[RT]{THF} \overset{30\ min}{PhCH_3\ (98\%\ d_1)} + PhCH_2CH_2Ph \quad (10)$$
$$97\% \qquad 0.0\%$$

$$n\text{-}C_8H_{17}I + LiAlD_4 \xrightarrow[RT]{THF} \overset{30\ min}{n\text{-}C_8H_{18}\ (99\%\ d_1)} + n\text{-}C_{16}H_{34} \quad (11)$$
$$95\% \qquad 0.0\%$$

product was observed, thus providing no evidence for an SET process. The absence of dimer, of course, does not prove that electron transfer is not involved in these reactions since the resulting radicals, if formed, would not be expected to be as stable as benzhydryl radicals and not as likely to form dimer.

Studies with Cyclizable Alkyl Halide Probes. The reduction of the 6-halo-1-hexenes **4** (X = Cl), **5** (X = Br), or **6** (X = I) by various metal hydrides was carried out, and the results are given in Table II. In every case reduction by $LiAlH_4$ of **4**–**6** gave 1-hexene as the only product. No

Table II. Reduction of 6-Halo-1-hexenes 4–6 by Metal Hydrides in THF at Room Temperature

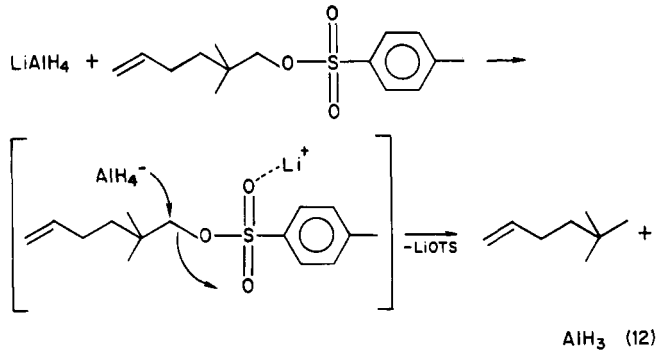
expt	substr	hydride	time, h	% yield[a]	
					
1	4 (X = Cl)	$LiAlH_4$	168	51	0.0
2	5 (X = Br)	$LiAlH_4$	24	97	0.0
3	5	AlH_3	24	26	0.0
4	6 (X = I)	$LiAlH_4$	1	95	0.0
5	6	$LiAlD_4$	1	95 (100% d_1)	0.0
6	6	AlH_3	24	29	7.1
7	6	MgH_2	24	72	0.71
8	6	HMgCl	24	32	0.70
9	6	$LiEt_3BH$	1	52	0.0
10	6	$Li(Bu^tO)_3AlH$	24	8.0	0.0
11	6	$LiAlH_4$[b]	1	98	0.0
12	6	$LiAlH_4$[b]	1	92	0.0
13	6	$LiAlD_4$[b]	1	95 (100% d_1)	0.0

[a] Recovered substrate accounts for material balance in expts 1, 3, 6, and 10. Yields were determined by GLC. [b] In expt 11, the solvent is HMPA and in exp 12, and in 13 the solvent is Et_2O.

trace of methylcyclopentane was found in any reduction by $LiAlH_4$, even in the presence of HMPA (Table II, expt 11). Also, deuterium incorporation in the product was quantitative as shown in the reaction of $LiAlD_4$ with **6** in either THF or Et_2O solvent (Table II, expts 5 and 13). These data show that reduction of the 6-halo-1-hexenes by $LiAlH_4$ is best described as a polar S_N2 process or else, if radical species are involved, the collapse to product must be substantially faster than the cyclization of the probe. With respect to the latter possibility, it is interesting that the less reactive hydrides AlH_3, MgH_2, and HMgCl produce small amounts (0.71–7.1%) of methylcyclopentane on reaction with **6**, as shown in expts 6–8. The formation of methylcyclopentane nevertheless indicates that **6** reacts with the less reactive hydride reagents, at least to some extent, by a process involving radical intermediates.

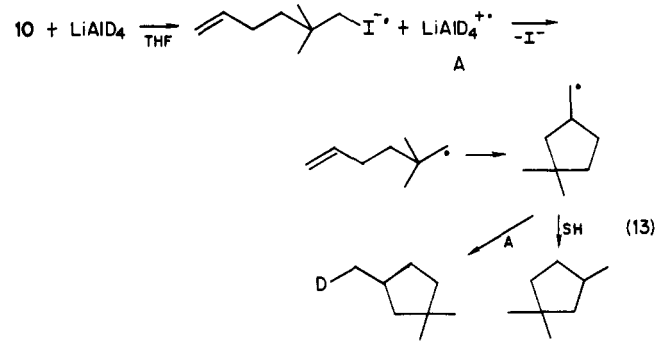
Since it is possible that any 5-hexen-1-yl radical formed in the reduction of **4–6** may be converted to product at a rate faster than that of the probe cyclization, it was decided to examine the metal hydride reduction of the 1-halo-2,2-dimethyl-5-hexenes **7–10**. In the case of SET, the bulky neooctenyl radical should be less reactive toward hydrogen abstraction from either the metal hydride radical cation or solvent and hence a better opportunity to observe cyclization of the probe would exist. In addition, the steric hindrance of the neopentyl-type group should raise substantially the activation energy for an S_N2 process more so than an electron-transfer process. Thus, for sterically hindered systems it is possible than an electron-transfer pathway is more favorable energetically[28] than an S_N2 pathway, whereas, for a less sterically hindered substrate, the reverse would be true. The results of the reduction of **7–10** by metal hydrides are given in Table III. For **7** (X = OTs), the only hydrocarbon product, 5,5-dimethyl-1-hexene, is produced in low yields (11% in Et_2O) and 1.8% in THF, expts 1–2) in 96 h. The observation of only straight-chain product and the solvent effect (Et_2O > THF) indicate no evidence for a SET process in the reduction of the tosylate **7**. A polar process is suggested in which the coordination of Li^+ to the tosyl oxygen enhances the transfer of hydride (eq 12).

The reaction of $LiAlH_4$ with 1-chloro-2,2-dimethyl-5-hexene (**8**) was examined (expts 3–4); however, no reduction products could be observed even in HMPA. The reduction of **9** by $LiAlH_4$ proceeded very slowly but produced nearly equal amounts of 5,5-dimethyl-1-hexene (9.8%) and 1,1,3-trimethylcyclopentane (7.5%) over a period of 480 h. Clearly, these data indicated that a substantial portion of the reaction pathway involves the development of radical character sufficient for cyclization of the probe to occur. Detailed interpretation of such probe cyclization will be discussed below in the studies of the reactions of the iodo compound **10**. Note that AlH_3 was found to be completely unreactive toward **9** in THF.



AlH_3 (12)

The reduction of 2,2-dimethyl-1-iodo-5-hexene (**10**) by a variety of metal hydrides was examined (Table III, expts 7–16). Reaction of **10** with $LiAlH_4$ in THF (expts 7–8) gave a high yield of 1,1,3-trimethylcyclopentane with only a small amount of 5,5-dimethyl-1-hexene formed. Experiment 9 indicates from the percentage of deuterium incorporation in the products that a source of hydrogen other than that originating from the metal hydride is involved in the reduction of **10**. The deuterium incorporation study and the extent of cyclization reflected in the product strongly suggest the occurrence of radical intermediates, which can cyclize and abstract a hydrogen atom from either the solvent or the metal hydride (eq 13). In Et_2O,



(13)

the reaction of $LiAlH_4$ with **10** is considerably slower but gives only 1,1,3-trimethylcyclopentane as product (36%, expt 14). Also, the less reactive hydrides of aluminum and magnesium (expts 10–12) give mostly cyclic hydrocarbon product, but these reactions are very slow. No reaction between **10** and $NaBH_4$ could be detected in diglyme.

Next, we expanded the scope of these studies by examining the reductions of the secondary halides (6-halo-1-heptenes) **11–13**. The results are given in Table IV. Note that the order of reactivity as a function of leaving group is I > Br > Cl. More importantly, the major product of reduction of **13** (X = I) is 1,2-dimethylcyclopentane (mixture of cis and trans) but only small amounts (5% or less) of cyclic product are formed in the reduction of **12** (X = Br) by $LiAlH_4$ or AlH_3. Once again, reduction of **13** by $LiEt_3BH$ gave a much different product distribution than reduction by $LiAlH_4$ (expt 4), in that 91% 1-heptene was obtained from $LiEt_3BH$ whereas $LiAlH_4$ gave 19% 1-heptene and 80% 1,2-dimethylcyclopentane. In addition, it is well-known that the formation of 1,2-dimethylcyclopentane with a 2.3:1 cis to trans ratio is indicative of radical

(28) Kochi, J. K. "Organometallic Mechanism and Catalysis"; Academic Press: New York, 1978; pp 430–435.

Table III. Reduction of 2,2-Dimethyl-1-halo-5-hexenes 7–10 by Metal Hydrides at Room Temperature

expt	substr	hydride	solvent	time, h	% yield[a]	
1	7 (X = OTs)	$LiAlH_4$	Et_2O	96	11	0.0
2	7	$LiAlH_4$	THF	96	1.8	0.0
3	8 (X = Cl)	$LiAlH_4$	THF	48	0.0	0.0
4	8	$LiAlH_4$	HMPA	48	0.0	0.0
5	9 (X = Br)	$LiAlH_4$	THF	480	9.8	7.5
6	9	AlH_3	THF	480	0.0	0.0
7	10 (X = I)	$LiAlH_4$	THF	24	3.4	81
8	10	$LiAlH_4$	THF	48	2.5	96
9	10	$LiAlD_4$	THF	48	5.5 (65% d_1)	89 (57% d_1)
10	10	AlH_3	THF	54	0.0	25
11	10	HMgCl	THF	54	0.0	0.40
12	10	MgH_2	THF	54	2.1	34
13	10	$LiAlH_4$	Et_2O	24	0.0	36
14	10	$LiAlH_4$	HMPA	24	3.5	95
15	10	$NaBH_4$	diglyme	480	0.0	0.0

[a] In expts 1–7, 10–13, and 15 material balances are accounted for by recovered substrate. Yields were determined by GLC.

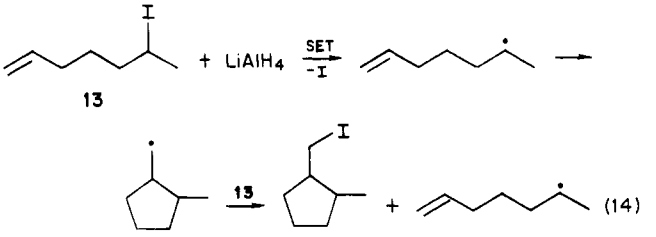
Table IV. Reduction of 6-Halo-1-heptenes 11–13 by Metal Hydrides at Room Temperature

expt	substr	hydride	time, h	% yield[a]	
1	11 (X = Cl)	$LiAlH_4$	48	2.5	0.0
2	12 (X = Br)	$LiAlH_4$	96	91	2.2
3	12	AlH_3	96	65	5.2
4	13 (X = I)	$LiAlH_4$	4	19	80
5	13	AlH_3	72	0.0	93
6	13	$LiEt_3BH$	48	91	1.5

[a] Recovered alkyl halide accounts for the material balance in expts 1 and 3.

cyclization.[29] Thus, the observation of predominantly cis cyclic products would be highly suggestive of[29,30] the occurrence of a SET pathway in the reaction of **13** with $LiAlH_4$ and AlH_3. However, further studies gave some very interesting results.

Table V provides data on the reduction of **13** with both $LiAlH_4$ and AlH_3 in THF. The purpose of these studies was to provide a reaction profile of the reactions with particular emphasis on the cis/trans ratio of the cyclized hydrocarbon (1,2-dimethylcyclopentane) formed in the reaction. It was our surprise to find that the starting iodide **13** cyclized rapidly to (2-methylcyclopentyl)methyl iodide during the reactions with both $LiAlH_4$ and AlH_3, and therefore much of the product formed was a result of direct reduction of the cyclized iodide. The cis/trans ratio of the cyclized iodide and cyclized hydrocarbon formed from the reactions of AlH_3 with **13** was constant (3.9 and 4.2, respectively). On the other hand, the cis/trans ratio of cyclized hydrocarbon formed from $LiAlH_4$ was relatively constant with an initial value of 2.1 which increased slightly with time as the amount of cyclized hydrocarbon formed from the cyclized iodide (cis/trans ratio = 5.8–8.7) increased. It seems that in the reduction of **13** with $LiAlH_4$, a somewhat different process of cyclizing **13** to the iodide is in operation compared to the reaction with AlH_3. In any event the cis/trans ratio of cyclized hydrocarbon formed on reaction of $LiAlH_4$ with **13** is close to the value of 2.3 and 2.8 found in reactions involving a radical intermediate.[29,30] The reaction of **13** with $AlCl_3$ was carried out (expt 3) in an attempt to determine if the observed cyclization to the cyclized iodide could be the result of a carbonium ion intermediate; however, no reaction was observed. The isomerization of **13** to its cyclic isomer can be visualized as a radical-chain process which is initiated by SET from $LiAlH_4$ or AlH_3, as in eq 14.



(14)

In order to test the possibility of a radical-chain process, 1.0 mol of **13** was allowed to react with 0.1 mol of $LiAlH_4$ in THF. The data in Table VI provide evidence that the cyclized iodide intermediate (formed in 70% yield after 70 h) is produced by a radical-chain process.

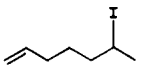
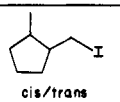
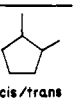
In view of the results obtained from studies with the secondary iodide **13**, the reaction profiles of AlH_3 and $LiAlH_4$ with 2,2-dimethyl-1-iodo-5-hexene (**10**) in THF were obtained and are given in Table VII. Note that in the reaction with $LiAlH_4$, no 3,3-dimethyl-1-iodomethylcyclopentane is detected, probably because the cyclic iodide is substantially less sterically hindered than the neopentyl group of **10** and therefore more reactive toward $LiAlH_4$ than **10**. Once again, it is clear that AlH_3 can readily induce cyclization of the starting iodide to the cyclic isomer which can then be reduced to the hydrocarbon by a mechanism very similar to one described for **13** (eq 14).

To complete the scope of our studies concerning the reductions of cyclizable alkyl halides, we next examined the reduction of the 6-halo-6-phenyl-1-hexenes **14** and **15** by $LiAlH_4$ in THF. The only product when X = Cl or Br is 6-phenyl-1-hexene and therefore no evidence of SET was obtained for these reactions. Unfortunately, 6-iodo-6-phenyl-1-hexene could not be prepared as a stable compound and, hence, a full range of leaving groups could not be examined for these benzylic cyclizable alkyl halides.

Having obtained evidence of radical intermediates in the reductions of cyclizable alkyl iodides, next we sought to obtain additional information by utilizing a trapping agent to trap the intermediate radicals. In particular, since Kuivila[31] has shown that dicyclohexylphosphine (DCPH)

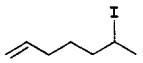
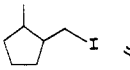
(29) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 613.
(30) Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711.
(31) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.

Table V. Rate Profile Studies of the Reaction of 6-Iodo-1-heptene 13 with $LiAlH_4$, AlH_3, and $AlCl_3$ in THF at Room Temperature[a]

			% yield			
expt	reagent	time, min		 cis/trans		 cis/trans
1	$LiAlH_4$	10	48	28 (5.8)	16	6 (2.1)
		20	19	40 (7.2)	19	18 (2.0)
		60	1	27 (8.7)	18	44 (2.5)
		120	0	9	20	67 (2.8)
		260	0	<1	19	80 (3.5)
2	AlH_3	10	70	28 (3.7)	<1	<1
		20	50	41 (4.1)	<1	3.5
		60	21	61 (3.9)	<1	11 (4.2)
		240	<1	69 (3.8)	<1	21 (4.2)
3	$AlCl_3$	23 h	98	0	0	0

[a] All reactions carried out were 0.1 M in both hydride and halide.

Table VI. Reaction of 6-Iodo-1-heptene (13) with $LiAlH_4$ in 1:0.1 Ratio in THF at Room Temperature[a]

	% yield			
time, h				
1	52	38	3.1	3.5
4	26	59	3.2	9.0
70	19	70	2.4	9.4

[a] 0.1 M iodide and 0.01 M $LiAlH_4$ were used.

can be utilized as a trapping agent for alkyl radical intermediates (eq 15), the ability of DCPH, deuterated di-

$$RX + e^- \rightarrow R\cdot + X^- \xrightarrow{\text{DCPH}} RH \qquad (15)$$

cyclohexylphosphine (DCPD), and also cyclohexadiene to trap any intermediate radicals in the reduction of alkyl halides was examined. Note that in order to observe such trapping of radical intermediates, both $LiAlD_4$–DCPH and $LiAlH_4$–DCPD combinations were used followed by an examination of the extent of deuterium incorporation in

Table VII. Profile of Reactions of 2,2-Dimethyl-1-iodo-5-hexene (10) with Hydride Reagents in THF

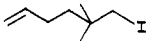
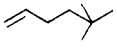
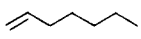
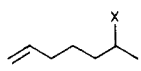
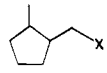
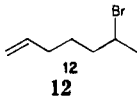
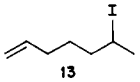
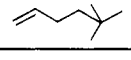
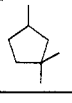
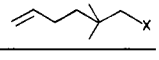
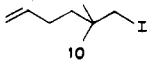
			% yield			
expt	reagent	time, h				
1	$LiAlH_4$	2	96	0.0	0.0	2.0
		5	73	0.0	2.0	24
		8	63	0.0	2.0	54
		24	20	0.0	2.0	75
2	AlH_3	2	83	5.0	0.0	5.0
		5	77	6.0	0.0	7.0
		8	75	16	0.0	12
		24	57	18	0.0	20

Table VIII. Effect of Trapping Agents on the Reduction of Alkyl Halides in THF at Room Temperature[a]

					% yield			
expt	halide	reducing agent	additive	time, h				
1	 12	$LiAlD_4$		48	91 (98% d_1)	2.2	4.5	0
2	12	$LiAlD_4$	10 DCPH	48	89 (98% d_1)	2.8	3.0	0
3	 13	$LiAlH_4$		1	18	44	1	27
4	13	$LiAlH_4$	1 DCPD	1	44 (24% d_1)	41 (19% d_1)	<1	4
5	13	$LiAlD_4$		1	32 (100% d_1)	13 (34% d_1)	27	28
6	13	$LiAlD_4$	1 DCPH	1	28 (12% d_1)	63 (8% d_1)	0	<1
7	13	$LiAlD_4$	1 DCPD	1	24 (100% d_1)	70 (65% d_1)	0	8
8	13	$LiAlD_4$		1	37 (97% d_1)	7 (38% d_1)	59	<1

					% yield		
expt	halide	reducing agent	additive	time, h			
9	 10	$LiAlD_4$		48	7.5 (65% d_1)	91 (57% d_1)	0
10	10	$LiAlD_4$	10 DCPH	1.5	6.0 (28% d_1)	73 (31% d_1)	20

[a] All reactions carried out were 0.1 M in both hydride and halide.

the products. The reduction of several cyclizable alkyl halides by $LiAlH_4$ and $LiAlD_4$, both in the presence and absence of trapping agents, were conducted and the results are given in Table VIII. Control experiments demonstrate that the alkyl halides employed were recovered quantitatively (by GLC) from THF solutions of DCPH and 1,4-cyclohexadiene and that no reaction occurred between $LiAlH_4$ and the trapping agents, as determined by infrared spectroscopy (ν_{Al-H} = 1685 cm^{-1}, ν_{Al-D} = 1225 cm^{-1}, ν_{P-D} = 1645 cm^{-1}, ν_{P-H} = 2660 cm^{-1}) and hydrogen analysis. From expts 1 and 2 it is clear that the reduction of the bromide **12** by $LiAlD_4$ is unaffected even by the presence of a ten-fold excess of DCPH, which indicates that no radicals are formed which can be trapped by DCPH. A comparison of the data from expts 3 and 4 show that more straight-chain radical is being trapped (18% to 44%) when DCPD is present at the expense of the cyclized iodide (27% to 4%). Further 24% d_1 for straight chain and 19% d_1 for cyclized hydrocarbon in expt 4 show that these compounds have a radical precursor that can be trapped by DCPD. The low d_1 content indicates that the radical intermediate can also be trapped by $LiAlH_4$ and solvent.

A comparison of the results of expts 5–7 further reveal the radical nature of the reaction. Comparison of expts 3 and 5 show that the reaction of $LiAlD_4$ with **13** is slower than the reactions with $LiAlH_4$, indicating that either $LiAlD_4$ is a poorer one-electron donor toward **13** or that abstraction of deuterium atoms from $LiAlD_4^{+\cdot}$ is the rate-determining step. Once again it is clear from expt 6 that the d_1 content of the straight-chain hydrocarbon (12% d_1) and the cyclized hydrocarbon (8% d_1) is due to the fact that the precursor of both of these compounds is the corresponding radical. The results of expt 7 show that DCPH and not solvent is the trapping agent for the straight-chain hydrocarbon that was observed in expt 6 although the cyclized hydrocarbon radical is trapped by $LiAlD_4^{-\cdot}$, DCPH, and solvent (expts 5 and 7). Experiment 8 shows that cyclohexadiene is not as good a radical trap as DCPH but nevertheless does trap the radical involved in the radical-chain process since very little cyclized iodide is formed compared to the same reaction in the absence of cyclohexadiene (expt 5). Experiments 9 and 10 provide information about the reduction of **10**. Compared to **13**, the reduction of **10** by $LiAlD_4$ involves the formation of considerably more cyclized hydrocarbon (91% compared to 13%) and the low d_1 content of both the straight-chain and cyclized hydrocarbon indicate a radical precursor for both products. The results of expt 10 indicate that DCPH is a very effective radical trap for the straight-chain hydrocarbon and that the cyclized hydrocarbon is trapped by $LiAlD_4$, DCPH, and solvent.

Comparison of the data from expts 3–4 and 5–6 show that DCPD and DCPH exert an accelerating effect on the reductions of **13** by $LiAlH_4$ and $LiAlD_4$, respectively. When **13** was allowed to react with $LiAlH_4$ and DCPD, DCPH was formed to exactly the same extent that DCPD was lost (determined by IR spectra). This indicates that when deuterium abstraction takes place, DCP· then can abstract hydrogen from solvent (THF) in addition to providing the opportunity for a radical-chain process (steps 3 and 4) which could indeed speed up the reaction (Scheme II).

Upon consideration of all of the studies of the reduction of cyclizable alkyl halides, it is clear that reduction of alkyl iodides can proceed by a pathway different from the major pathway of reduction for chlorides or bromides. Thus, there is no evidence for the intermediacy of radicals in the reduction of alkyl tosylates or chlorides; therefore, the

Scheme II

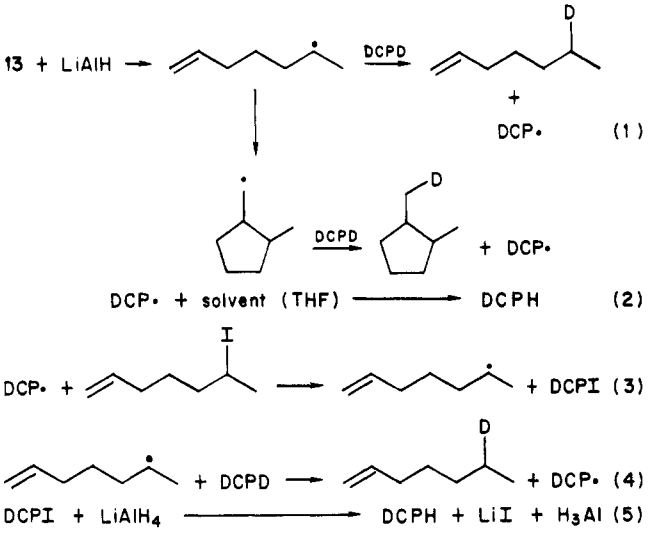


Table IX. Reduction of 2-Halooctanes by $LiAlD_4$ in THF

				2-deuteriooctane	
expt[a]	% opt purity	time, h	% yield	obsd[c] $[\alpha]^{25}_D$	corr. $[\alpha]^{25}_D$
1	(−)-OTs, 77.1	240	73	−0.66°	−0.85°
2	(+)-Cl, 87.4	720	52	+0.78°	+0.89°
3	(+)-Br, 73.1	48	85	+0.78°	+0.93°
4	(+)-I, 14.0	4	98[b]	+0.020°	+0.14°

[a] Experiments 1, 3, and 4 were conducted at 25 °C; expt 4 was performed at 50 °C. [b] (+)-2-Iodooctane recovered after 48% reduction was 37% racemized. Racemization of (+)-2-iodooctane by LiI under similar conditions was negligible. [c] Limits of precision are ±5%.

known data is consistent with an S_N2 pathway. However, the present studies show that alkyl bromides to a small extent are reduced by an SET process but mainly are reduced by a S_N2 process. Since alkyl chlorides and bromides are not as good electron acceptors as iodides, it is not surprising that the reduction of alkyl chlorides and bromides proceeds by a different mechanistic pathway than iodides. However, for iodides, it is clear that alkyl radicals are significantly involved in the reduction process. From the reaction profile studies, it seems that AlH_3 and $LiAlH_4$ rapidly cyclize an alkyl iodide such as 6-iodo-1-heptene, by a radical-chain process involving iodine atom transfer (Scheme III). Of course the cyclized iodo compound can then by reduced to the hydrocarbon by $LiAlH_4$ or AlH_3, either by a simple S_N2 attack or by a radical process. The rate acceleration by DCPH can be a consequence of trapping the radicals via a H-atom transfer instead of via an I-atom transfer when no DCPH is present, or simply by generation DCP· in the reaction which itself can react with the alkyl halide in a radical-chain process. Thus, it seems that the reduction of alkyl iodides such as **10** or **13** involves the production of radical intermediates in a chain process which appears to be initiated by electron transfer from $LiAlH_4$ or AlH_3 as depicted in Scheme III.

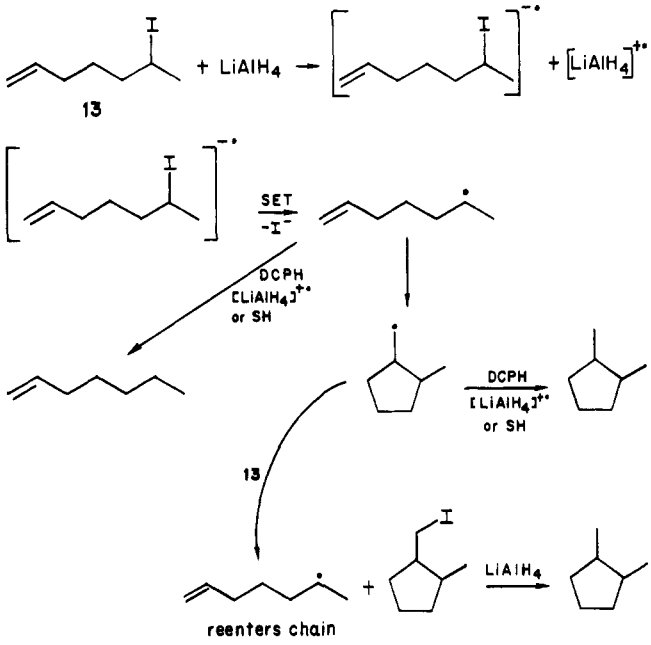
Reduction of Optically Active Halides. An important reason for studying the 6-halo-1-heptenes as radical probes in metal hydride reduction is that a stereochemical probe having similar steric requirements about the reaction center is available. Thus, the secondary octyl halides can be utilized as stereochemical probes since these compounds can be prepared optically pure. Of course, inversion of configuration has been associated with an S_N2 process and the comparison of the results of the $LiAlD_4$ reduction of thee 6-halo-1-heptenes and the $LiAlD_4$ reduction of the

Table X. Reduction of (-)-1-Halo-1-phenylethanes 20 and 21 by $LiAlD_4$ in THF

expt	substrate, % optical purity	temp, °C	time, h	(-)-deuteriophenylethane % yield obsd	$[\alpha]^{25}_D$	corr. $[\alpha]^{25}_D$
1	20 (X = Cl), 41.5	48	24	72[a]	-0.27°[c]	-0.70°
2	21 (X = Br), 57.0	25	4	92[b]	-0.48°	-0.84°

[a] Recovered 20 exhibited 39.5% optical purity. [b] Racemization of 21 by LiBr in THF was negligible under similar conditions. [c] Limits of precision are ±5%.

Scheme III



optically active *sec*-octyl halides should provide a detailed mechanistic picture for the reduction of secondary halides. Since the reduction of 6-iodo-1-heptene (13) by $LiAlH_4$ produces a large amount of cyclized product, indicative of a radical intermediate, one might reasonably expect the stereospecificity for the $LiAlD_4$ reduction of (+)-2-iodooctane to result in complete racemization or at least produce a product that is substantially less active than that observed for the reduction of the corresponding bromide, chloride, and tosylate. The reduction of the *sec*-octyl halides 16–19 (X = OTs, Cl, Br, I) by $LiAlD_4$ were conducted in THF solvent and the results are given in Table IX. Since the absolute configuration and maximum rotation of optically pure 2-deuteriooctane are not available, one can only compare the corrected rotations of the 2-deuteriooctane as a function of the leaving group. From expts 1–3 of Table IX it is seen that the value of corrected $[\alpha]^{25}_D$ for the deuteriooctane varies from -0.85° (X = (-)-OTs) to +0.89° (X = (+)-Cl) to 0.93° (X = (+)-Br); however, these values are essentially equal within experimental error. Thus, it has been shown that for X = OTs, Cl, and Br, $LiAlD_4$ reduction of these 2-halooctanes proceeds with the same degree of stereospecificity. However, the corrected $[\alpha]^{25}_D$ +0.14° for X = I and, hence, the reduction of (+)-2-iodooctane proceeds with substantially less stereospecificity than the reduction of the other 2-halooctanes.

Thus, upon consideration of the stereochemical data for the reduction of the secondary octyl halides in conjunction with the studies of the secondary cyclizable halides 11–13, it seems clear that $LiAlH_4$ reduction of the secondary tosylates and chlorides are best described as predominantly polar S_N2 processes, completely devoid of radical intermediates. In the case of X = Br there is a competition involving S_N2 and SET processes with the S_N2 process strongly predominating. On the other hand, when X = I, it seems clear that a predominant SET process is in operation involving radical intermediates, as described in Scheme III.

Table XI. Effect of Impurities on the Reduction of 6-Iodo-1-heptene (13) by $LiAlH_4$ in THF[a]

expt	additive	reagent	% yield	
1	none	$LiAlH_4$	42	53
2	iron, 10 ppm[b]	$LiAlH_4$	45	52
3	iron, 150 ppm[b]	$LiAlH_4$	41	58
4	none	$LiAlH_4$[c]	40	55

[a] All reactions were carried out at room temperature for a period of 48 h. [b] An appropriate aliquot of a standard solution of $FeCl_3$ in THF was added to the substrate just prior to the addition of $LiAlH_4$. [c] A sample of $LiAlH_4$ was recrystallized 3 times from benzene–THF solvent.

To complete our stereochemical studies, we examined the reductions of the 1-halo-1-phenylethanes 20 and 21 by $LiAlD_4$ and the results are given in Table X. Eliel[15] had demonstrated previously that the chloride 20 is reduced with predominant inversion and this result is reproduced in expt 1. The reduction of the bromide 21 also proceeded with a high degree of inversion. Hence, it seems that secondary benzylic chlorides and bromides are reduced by $LiAlD_4$ by an S_N2 pathway devoid of radical species. Unfortunately, similar studies could not be carried out on the iodide since we were not able to prepare a stable sample of the iodide.

Purity of Solutions of $LiAlH_4$. Since it is possible that trace amounts of transition metals may catalyze an electron-transfer process,[32] several experiments were conducted in order to evalute the effect of trace impurities on the reduction of 13 by $LiAlH_4$. Thus, reactions of 13 with $LiAlH_4$ were conducted by doping solutions of 13 in THF with $FeCl_3$ just prior to the addition of $LiAlH_4$, and the results are given in Table XI. Note that the presence of 10 or even 150 ppm of iron caused no change in either the product yield or isomeric distribution (expts 1–3, Table XI). Furthermore, the product yield and isomeric distribution of a reaction of 13 and $LiAlH_4$ that was recrystallized from THF–benzene several times was identical with that obtained from the reaction using a standard solution of $LiAlH_4$ (expts 1 and 4). Thus, it seems unlikely that transition-metal catalysis is an important feature of the $LiAlH_4$ reduction of compounds such as 13.

Conclusion

A variety of methods have been utilized in order to evaluate the occurrence of an electron transfer pathway for the reduction of organic halides by main-group metal hydrides. Direct spectroscopic observation of the trityl radical by EPR was made in the reduction of trityl bromide by $LiAlH_4$. The reduction of a series of alkyl halides containing a cyclizable radical probe was also examined

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and it appears that tosylates and chlorides are reduced entirely by an S_N2 pathway. In the case of alkyl bromides, it appears that S_N2 and SET are in competition, with S_N2 being strongly favored except when a very stable radical such as the trityl radical is produced. However, for alkyl iodides it appears that SET is the major reaction pathway for reduction by $LiAlH_4$ and AlH_3. Further detailed studies have shown that $LiAlH_4$ and AlH_3 are both responsible for the observed electron transfer phenomena. Studies of reductions of optically active halides are consistent with the results of the cyclizable probe studies in that a high degree of inversion in the product is observed for tosylates, chlorides and bromides. However, the reduction of 2-iodooctane by $LiAlD_4$ proceeds with much less stereospecificity than reduction of the other 2-halooctanes, indicating the presence of radical intermediates in this reaction.

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Registry No. **4**, 928-89-2; **5**, 2695-47-8; **6**, 18922-04-8; **7**, 89745-98-2; **8**, 76695-77-7; **9**, 56068-49-6; **10**, 77400-57-8; **11**, 15661-92-4; **12**, 38334-98-4; **13**, 13389-36-1; **16**, 27770-99-6; **17**, 16844-08-9; **18**, 1191-24-8; **19**, 1809-04-7; **20**, 3756-41-0; **21**, 3756-40-9; Ph_2CHCl, 90-99-3; Ph_2CHBr, 776-74-9; $LiAlH_4$, 16853-85-3; $LiAlD_4$, 14128-54-2; AlH_3, 7784-21-6; MgH_2, 7693-27-8; HMgCl, 22106-77-0; $LiEt_3BH$, 22560-16-3; $Li(t\text{-}BuO)_3AlH$, 17476-04-9; iron, 7439-89-6.

On the Sulfur–Nitrogen Bonding Character of *N*-Arylsulfilimines

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The S–N bonding character of *N*-arylsulfilimine was investigated by X-ray structure determination and X-ray photoelectron spectroscopy (XPS). The crystals of sulfilimine I are monoclinic, space group $A2/a$, in a unit cell of dimension a = 16.726 Å, b = 25.877 Å, c = 5.676 Å, γ = 118.29°. The positions of hydrogen atoms were also determined. The data of structure determinations and XPS suggest that the $d\pi$–$p\pi$ interaction between the sulfur and the nitrogen is not important, but the *N*-arylsulfilimines are stabilized by other factors with the resonance interaction of the *p*-nitrophenyl moiety, i.e., the strong interaction through the σ bond between the sulfur and the nitrogen and the hyperconjugative effect. The multipeak structure due to shake up transition was observed in N 1s peaks of the nitro group of *N*-arylsulfilimines and it was found that there is a correlation between the energy separation of doublets and the resonance interaction of the aryl ring.

Introduction

The bonding character in sulfilimines has been studied by a number of investigators.[3] However, the problem of the exact bonding character in sulfilimine remains uncertain, because it is extremely difficult to determine the degree of contribution of many factors such as electron-withdrawing effect of substituents, $d\pi$–$p\pi$ interaction, etc.[4] The ability of the sulfur atom to stabilize an adjacent negative charge remains a interesting phenomenon. For example, Epiotis et al. reported the hyperconjugative stabilization associated with the interaction of the carbon lone pair orbital with the antibonding σ orbital of an adjacent sulfur; the enhanced stability of a carbanion adjacent to sulfur is dominated by the n_C–σ^*_{SH} stabilizing interaction and not by $d\pi$–$p\pi$ conjugation.[5,6] In addition, the contribution of the hyperconjugative effect related to n_C–σ^*_S interaction for the stability of sulfonium ylides was discussed by the Fava group[7] and the Heathcock group.[8] On the other hand, Streitwieser et al. concluded by ab initio SCF–MO calculations that the sulfur of thiomethyl anion stabilizes carbanions by polarization rather than by d orbital conjugation.[9] We have also reported a stabilizing effect, which we termed the electron displacement effect, in the N^+–N^- bonding of aminimides which do not have d orbital available.[10] This effect means that the electron cloud of the σ bond between N^+ and N^- in aminimide lies closer to the quaternary nitrogen (N^+) and consequently, the electron density of the anionic nitrogen (N^-) decreases and the aminimide is stabilized. We also found evidence that the anionic nitrogen of the carbonyl stabilized sulfilimine is stabilized by the electron displacement effect.[11] On the other hand, as the ability of *N*-aryl substituent to stabilize the anionic nitrogen is very different from that of the carbonyl group or the sulfonyl group, the bonding character of stable *N*-arylsulfilimines has been studied by several physical measurements and chemical reactivities.[12]

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