NMR and IR Binding Experiments of 1 with $(Ph_3P)_3RhClH_2$. NMR Experiment. In a flask was placed 18.4 mg (0.02 mmol) of $(Ph_3P)_3RhCl$ dissolved in 4 mL of deoxygenated benzene-d_6. To this solution was added hydrogen gas, via bubbling, for about 1 h with the solution turning a golden yellow. Compound 1 (2.4 μL, 0.02 mmol) was then added to the rhodium hydride, $(Ph_3P)_3RhClH_2$, and allowed to stir for 20 min. An aliquot was then placed in an NMR tube under nitrogen. The ^1H NMR spectra were taken on a 200-MHz FT instrument and provided downfield shifts at 8.92 (d, C-2) and 8.42 ppm (d, C-8) of 0.13 and 0.09 ppm, respectively, from the uncomplexed 1. The high-field spectra shows Rh–H signals at −8.8, −9.2, and −16.9 ppm.

IR Experiment. In a flask was placed 200 mg of $(Ph_3P)_3RhCl$ in 5-mL of dry tetrahydrofuran. Hydrogen gas was bubbled in for 1 h and the IR spectra of an aliquot was run in a solution cell (0.2 mm, NaCl windows) with a Perkin-Elmer 598 Grating IR spectrometer. This provided Rh–H stretching frequencies at 2110 (sh) and 2040 (b) cm^{-1}. Addition of 500 μL of 1 to the reaction mixture and then taking a sample for IR analysis provided Rh–H stretching frequencies at 2122 (sh) and 2065 (b) cm^{-1} consistent with a binding of 1 to the rhodium metal center, i.e., a shift of $\sim$25 cm^{-1} would be expected from other complexes of rhodium hydrides with nitrogen heterocyclic ligands.[9]

Acknowledgment. We wish to thank Dr. Heinz Heinemann of LBL for continued encouragement and support of our catalysis program. The 400-MHz ^1H NMR spectra were kindly recorded by Drs. R. Johannesen and Bruce Coxon at the NBS-NML high-field NMR facility located at NBS, Gaithersburg, MD. J. L. Tan was a DOE summer cooperative student research associate, June–Sept, 1983. This study was jointly funded by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division, and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy through the Pittsburgh Energy Technology Center under Contract No. DE-AC0 3-76SF00098.

Registry No. 1, 91-22-5; 2, 85-02-9; 3, 230-27-3; 4, 260-94-6; 5, 229-87-8; 6, 95-15-8; $(Ph_3P)_3RhCl$, 14694-95-2.

Evidence for Single Electron Transfer in the Reduction of Organic Halides by Lithium Triethylborohydride

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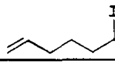
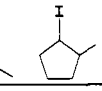
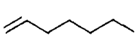
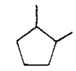
Product studies involving the reduction of cyclizable alkyl iodides and bromides, trapping of intermediate radicals by dicyclohexylphosphine, and direct EPR observation of radicals have been used to detect the occurrence of a single electron transfer pathway in the reduction of these halides by lithium triethylborohydride.

One of the most important synthetic methods in organic chemistry involves the hydrogenolysis of carbon–halogen bonds.[1] A number of different complex metal hydrides can be used for the reduction of organic halides;[2] however, the most powerful reducing agent is lithium triethylborohydride ($LiEt_3BH$), which rapidly reduces primary, secondary, allylic, benzylic, and neopentyl halides to the corresponding hydrocarbons.[3] In a recent detailed mechanistic study, Brown and Krishnamurthy proposed a S_N2 mechanistic pathway to describe the reduction of alkyl halides by $LiEt_3BH$.[4] On the other hand, we recently reported that lithium aluminum hydride ($LiAlH_4$) and aluminum hydride (AlH_3) react with organic halides (particularly iodides) in part or completely by a single electron transfer (SET) pathway.[5,6] Since the above hydrides react with alkyl bromides and iodides by SET, we were anxious to determine if $LiEt_3BH$ also reacts by a similar pathway. In this connection the following studies were carried out: (1) spectroscopic observation of a stable radical intermediate by EPR, (2) use of new alkyl halides containing a cyclizable radical probe, and (3) radical trapping reactions with dicyclohexylphosphine (DCPH).[7] The results are presented herein.

Table I. Rate-Profile Study of 0.1 M 6-Iodo-1-heptene (1) with 0.2 M $LiEt_3BH$ in THF at 0 °C

		% yield			
expt	time, min				
1	10	64	1.8	35	<1
	30	50	2.8	50	<1
	60	42	1.5	55	1.2
	120	14	1.4	87	1.5
	240	6	<1	97	2.2
2	360	5	0	94	4.3[a] (4.3)[b]

[a] This reaction was carried out from −78 °C to room temperature. [b] Cis/trans ratio of 1,2-dimethylcyclopentane.

Results and Discussion

EPR Study. When $LiEt_3BH$ (0.02 M) and trityl bromide (0.02 M) were combined in THF at room temperature, a yellow color appeared immediately and the solution was shown to be EPR active. The EPR spectrum was well resolved and was identical with the EPR spectrum of the trityl radical $[Ph_3C\cdot]$[8] reported earlier[8] (eq 1). This

$$Ph_3CBr + LiEt_3BH \rightarrow [Ph_3CBr]^{-}\cdot \rightarrow Ph_3C\cdot + Br^- \quad (1)$$

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[1] Pinder, A. R. *Synthesis* **1980**, 425.

[2] March, J. "*Advanced Organic Chemistry*", 2nd ed.; McGraw-Hill: New York, 1977; p 399.

[3] Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669.

[4] Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1983**, *48*, 3085.

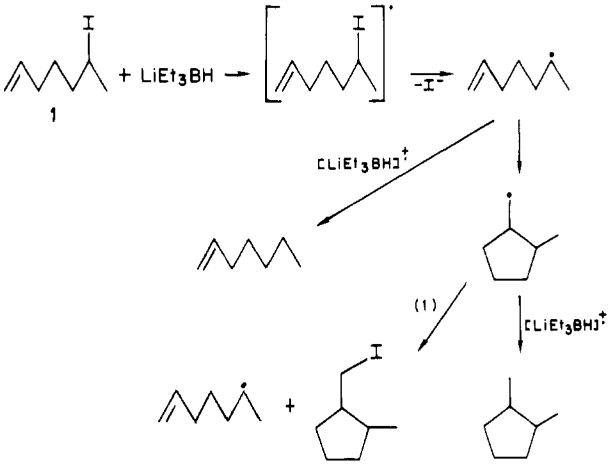
[5] (a) Ashby, E. C.; DePriest, R. N.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1763. (b) Ashby, E. C.; DePriest, R. N.; Pham, T. N. *Tetrahedron Lett.* **1983**, *24*, 2825.

[6] Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545.

[7] Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.

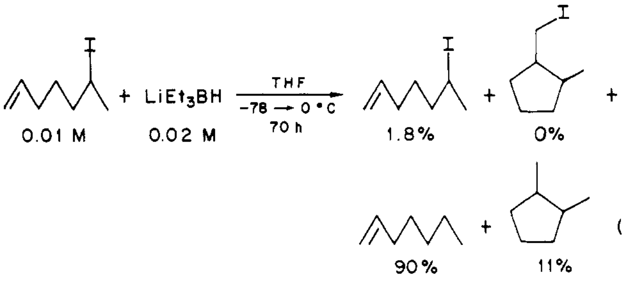
signal was not present in a solution of trityl bromide in THF in the absence of the hydride. The amount of [$Ph_3C\cdot$] was approximately 1% compared to the concentration of starting Ph_3CBr. This is the first direct (EPR spectroscopic) evidence for a radical intermediate formed on reduction of an organic halide by $LiEt_3BH$. Encouraged by this result we then studied the reduction of cyclizable alkyl halides that could be used as probes for radical intermediates.

Studies with Cyclizable Alkyl Halide Probes. First, a rate profile study of the reduction of 6-iodo-1-heptene (1) with $LiEt_3BH$ was conducted. The results are given in Table I. Two equivalents of $LiEt_3BH$ were used to reduce the iodide at 0 °C. Experiment 1 shows that after 10 min, 1.8% and after 30 min already 2.8% of the cyclized iodide is formed. The amount of cyclized reduction product, 1,2-dimethylcyclopentane, increased from less than 1% (10 min) to 2.2% after 240 min, when the reaction was nearly complete. The formation of these cyclized compounds is consistent with the formation of a radical intermediate (eq 2).



(2)

In experiment 2 (Table I), $LiEt_3BH$ was added at −78 °C to the iodide 1 in THF and the reaction mixture was allowed to warm to room temperature. In this reaction 4.3% of the cyclized hydrocarbon was formed. This shows that carrying out the reduction of 6-iodo-1-heptene (1) at a lower temperature leads to more cyclized product. It appears that the reactivity of $LiEt_3BH$ with 1 (a bimolecular process) is slowed down more than the rate of radical cyclization, giving the straight chain radical more time to diffuse from the solvent cage and cyclize (first-order process) before being trapped. To examine this point further, $LiBEt_3H$ and 1 were allowed to react at lower concentration in order to see if more cyclized products would be produced. For this reason 0.01 M 6-iodo-1-heptene (1) and 0.02 M $LiEt_3BH$ were combined at −78 °C in THF and allowed to warm to 0 °C. The results are shown in eq 3.



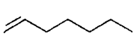
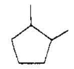
(3)

After 70 h the reaction was complete and 11% of 1,2-dimethylcyclopentane (cis/trans ratio, 4.3) was formed. This means that at lower concentration, the straight-chain radical that diffused from the solvent cage had a better chance to cyclize before hydrogen atom transfer occurs, and the cis/trans ratio indicates a radical intermediate. The formation of 4% cyclized hydrocarbon and particularly 11% at lower concentration indicates that a significant amount of reduction takes place by a SET process.

It is also possible that the straight-chain hydrocarbon is at least partially formed by a radical process. This possibility can be investigated if the hydrogen atom donor is employed in the reaction and hydrogen atom transfer is substantially faster than cyclization of the probe. In order to investigate this possibility, some reactions with the radical trap dicyclohexylphosphine (DCPH) and deuterated dicyclohexylphosphine (DCPD) were conducted, and the results are given in Table II. The experiments were carried out with a reducing agent:trapping agent: iodide ratio of 2:2:1. By comparing experiment 1 to 2, it is clear that more cyclized hydrocarbon is formed when DCPH is added. Experiment 2 shows that the deuterium incorporation of the cyclized hydrocarbon is 0% when the reduction of 1 with $LiEt_3BD$ is carried out in the presence of DCPH, which indicates that all cyclized radicals formed during the reaction (outside of the solvent cage) were trapped by DCPH or THF. No trapping could be observed during the formation of the uncyclized hydrocarbon (100% d_1), and thus it appears that all of the straight-chain product is formed in the solvent cage by a rapid radical coupling process or by an S_N2 process. On the other hand, the use of deuterated dicyclohexylphosphine (DCPD) as a trapping agent (experiment 4) leads to a different result. When reduction of 1 with $LiEt_3BH$ was carried out in the presence of DCPD, 13% deuterium incorporation of the uncyclized hydrocarbon was observed. This means that at least 13% of the straight chain hydrocarbon in experiment 4 must have been formed by an electron-transfer process. The implication is that $LiEt_3BH$ is a better one electron donor than $LiEt_3BD$. It is also possible that a radical chain process is involved. In experiment 4 with DCPD as donor, the cyclized radical has a longer lifetime and can abstract iodine from 1, which then can be trapped by DCPD. The deuterium incorporation for the cyclized product is only 41% (experiment 4) because DCPD is not as efficient a radical trap as DCPH in experiment 2 (deuterium isotope effect). The cyclized hydrocarbon can only be formed by a radical process and 41% d_1 indicates that nearly 60% of the radical intermediate was trapped by THF or $LiEt_3BH$.

Comparison of the data from experiments 1 and 2 (Table II) show that DCPH exerts an accelerating effect on the reduction of 1 by $LiEt_3BD$. When 1 was allowed to react with $LiEt_3BH$ and DCPD, DCPH was formed to the same extent than DCPD was lost (determined by IR spectros-

Table II. Effect of DCPH and DCPD on the Reduction of 6-Iodo-1-heptene (1) by $LiEt_3BD$ and $LiEt_3BH$ in THF at Room Temperature[a]

				% yield	
expt	reagent	additive	time, h		
1	$LiEt_3BD$		2	90 (98% d_1)	1[b]
2	$LiEt_3BD$	DCPH	2	90 (100% d_1)	13[c] (0% d_1)
3	$LiEt_3BH$		2	98	2.4
4	$LiEt_3BH$	DCPD	2	86 (13% d_1)	15[c] (41% d_1)

[a] 0.1 M halide and 0.2 M reducing agent and radical trap were used. [b] Recovered alkyl halide accounts for the material balance in expt 1. [c] Cis/trans ratio was 3.8:1.

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

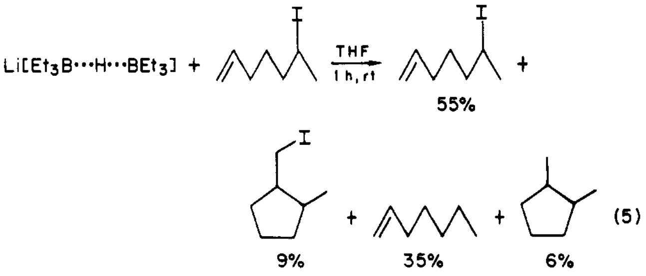
copy). Recently we reported the same phenomena on reaction of 1 with $LiAlH_4$ as the reducing agent.[6] This result indicates when deuterium abstraction takes place, DCP· is formed which then can abstract hydrogen from the solvent (THF) in addition to providing the opportunity for a radical chain process (steps 3 and 4, Scheme I) which indeed can speed up the reaction.

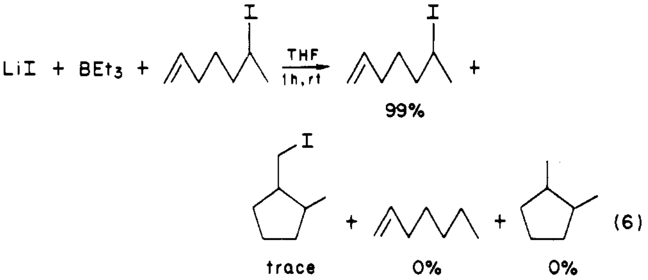
The preferential cis cyclization during the reduction of 6-iodo-1-heptene (1) (Table II, cis/trans ratio = 3.8; Table I, experiment 2, cis/trans ratio = 4.3:1) is additional evidence for an electron-transfer process since it is known that orbital symmetry control leads to a favored cis cyclization of radicals involving the 6-heptene-2-yl system.[9] Additionally, 6-bromo-1-heptene was also reduced with $LiEt_3BH$, but even in the presence of DCPD no cyclized products could be detected which means that this bromide is reduced probably by a exclusive S_N2 process. It also means that one electron transfer observed in the case of the iodide is not due to the influence of DCPH.

During the reduction of an alkyl halide by $LiEt_3BH$, the reduction product BEt_3 is formed which can react with lithium triethylborohydride to form the less reactive complex lithium hexaethyldiborohydride (eq 4).[4] In order to

$$RX + LiEt_3BH \xrightarrow[-LiX]{-RH} BEt_3 \xrightarrow{LiEt_3BH} Li[Et_3B\cdots H\cdots BEt_3] \quad (4)$$

determine the possible involvement of these byproducts in the electron-transfer process, 6-iodo-1-heptene (1) was treated with $Li(Et_3B)_2H$ (prepared in situ from *n*-BuI and $LiEt_3BH$) (eq 5) and LiI/BEt_3 (eq 6). The reduction of the iodide with $Li(Et_3B)_2H$ (eq 5) is slower than that with $LiEt_3BH$ (Table I); however, it is interesting that more cyclized products were formed (9% cyclized iodide and 6% cyclized hydrocarbon). No cyclization could be detected when the iodide 1 was treated with LiI and BEt_3 (eq 6). This shows that only the reaction byproduct $Li(Et_3B)_2H$ and not triethylborane alone is at least partially involved in the electron-transfer process occuring during the reduction of 6-iodo-1-heptene (1) by $LiEt_3BH$.





Scheme I

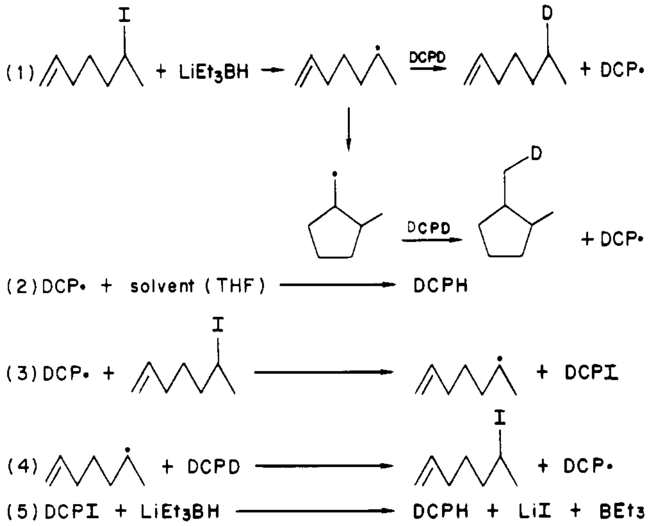
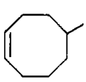
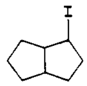
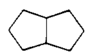
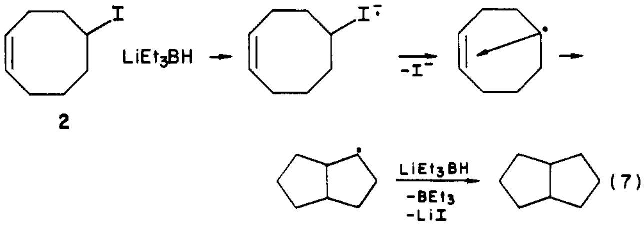


Table III. Rate-Profile Study of 0.1 M 5-Iodo-1-cyclooctene (2) with 0.2 M $LiEt_3BH$ in THF at Room Temperature

	% yield			
time, h				
0.5	60	8.0	35	1.0
1.0	40	9.0	51	1.0
2.0	14	13.0	70	1.5
5.5	0	15.0	79	5.0
20	0	8.0	80	16.0
72	0	0	78	25.0

To complete our mechanistic studies, we also examined the reduction of 5-iodo-1-cyclooctene (2), 5-bromo-1-cyclooctene (3), and 5-chloro-1-cyclooctene (4) by $LiEt_3BH$ in THF. We have already found that the cyclooctenyl system is a good cyclizable probe for reactions involving $LiAlH_4$.[10] Earlier Posner had observed that 5-bromo-1-cyclooctene cyclizes when allowed to react with $LiCuMe_2$.[11]

The reaction profile of 2 with $LiEt_3BH$ is given in Table III; 0.1 M 2 was reduced with 0.2 M lithium triethylborohydride. The reactivity of 5-iodo-1-cyclooctene (2) is comparable to that of 6-iodo-1-heptene (1), and the reduction was complete after 72 h at room temperature. It is remarkable that 25% of bicyclo[3.3.0]octane was formed in addition to 78% cyclooctene. The formation of cyclized hydrocarbon can be explained by an involvement of alkyl radicals in the reduction process (eq 7). Table III shows that after a reaction time of only 30 min already 8% bicyclic iodide is formed and its amount increased to 15% after 5.5 h. At this time no more 5-iodo-1-cyclooctene (2) was present and so the amount of cyclooctene did not increase any more at the latter stage of the reaction, and only the reduction of the bicyclic iodide continued.



Looking once again for the possible involvement of a radical mechanism during the formation of the monocyclic hydrocarbon, again some trapping reactions were carried out. The results are given in Table IV. In experiments 1 and 2, the reduction of 5-iodo-1-cyclooctene (2) was

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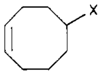
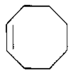
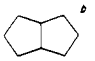
[9] Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613.

[10] Ashby, E. C.; Pham, T. N. (unpublished results).

[11] Posner, G. H.; Ting, J. S. *Tetrahedron Lett.* **1974**, 683.

Table IV. Effect of DCPH and DCPD on the Reduction of 5-Halo-1-cyclooctene by $LiEt_3BH$ and $LiEt_3BD$ in THF at Room Temperature[a]

					% yield	
expt		reagent	additive	time, h		[b]
1	I	$LiEt_3BD$		72	91 (92% d_1)	2.5 (76% d_1)
2	I	$LiEt_3BD$	DCPH	48	97 (49% d_1)	2.0 (0% d_1)
3	I	$LiEt_3BH$		72	78	25
4	I	$LiEt_3BH$	DCPD	48	84 (13% d_1)	13.5 (1% d_1)
5	Br	$LiEt_3BH$		23	55	15
6	Br	$LiEt_3BD$		75	40 (88% d_1)	4.0 (66% d_1)
7	Br	$LiEt_3BD$	DCPH	75	48 (74% d_1)	3.5 (60% d_1)
8	Cl	$LiEt_3BH$		120	0.0	0.0

[a] 0.1 M halide and 0.2 M reducing agent and radical trap were used. [b] Recovered alkyl halide accounts for the material balance in expts 5–8.

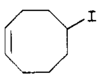
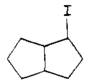
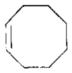
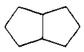
conducted with $LiEt_3BD$ in the absence and presence of DCPH. The amount of deuterium incorporation for the monocyclic hydrocarbon decreased from 92% (experiment 1) to 49% when the radical trap DCPH was present (experiment 2), which shows clearly that at least 50% of this monocyclized product was produced via an electron-transfer pathway or radical chain process. The trapping of the bicyclic compound was complete by DCPH and solvent (0% d_1) because DCPH is such a good radical trap.

In experiments 3 and 4 (Table IV) $LiEt_3BH$ was used with and without added DCPD. The results show once again that DCPD is not as good a trapping agent as DCPH (deuterium isotope effect): only 13% deuterium incorporation in the monocyclic hydrocarbon and 1% in the bicyclic hydrocarbon could be detected by GC/MS (experiment 4).

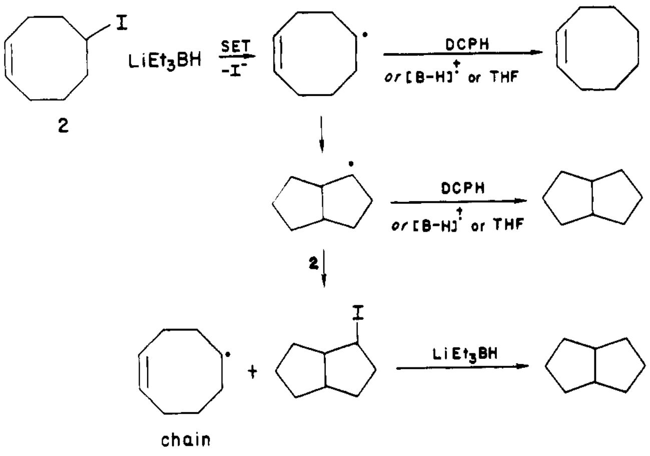
Experiment 1 in Table IV shows again that THF is also reacting as a radical trap because only 76% d_1 of the bicyclic hydrocarbon was observed when **2** was reduced with $LiEt_3BD$ which means 24% of the intermediate radical was trapped by THF. Experiments 5 and 6 indicate that the alkyl bromide **3** also reacts with $LiEt_3BH$ and $LiEt_3BD$ partially by an electron-transfer pathway; 15% and 4% bicyclic hydrocarbon were formed. The reduction of **3** was also carried out by using $LiEt_3BD$ in the presence of DCPH (experiment 7), and the deuterium incorporation study shows that 26% of the monocyclic and 40% of the bicyclic compound were trapped by a hydrogen atom which means that a least 26% of the 48% monocyclic compound was formed via an electron-transfer mechanism of a radical chain process. Finally $LiEt_3BH$ was added to 5-chloro-1-cyclooctene (**4**) but even after 120 h no hydrocarbon could be detected (experiment 8). Considering the data presented in Tables III and IV, it is clear that the reduction of the alkyl iodide **2** with lithium triethylborohydride is proceeding in major part by a radical pathway and the alkyl bromide **3** in proceeding at least to some extent by a SET process.

5-Iodo-1-cyclooctene (**2**) was allowed to react with only 0.2 equiv of lithium triethylborohydride in THF at room temperature in order to determine the possibility of a radical chain mechanism. The results are presented in Table V. After a reaction time of 1 h, already 6% cyclized products (iodide and hydrocarbon) were formed, and after 217 h, a total amount of 87% cyclization could be detected. These data indicated that $LiEt_3BH$ is cyclizing the alkyl iodide by a chain reaction involving iodine atom transfer (Scheme II). The bicyclic iodo compound can then be reduced by $LiEt_3BH$ by a radical or by a S_N2 process. The alkyl bromide **3**, to a lesser extent, is also reduced with $LiEt_3BH$ by a similar radical mechanism as suggested for the reduction of 6-iodo-1-heptene (**1**).

Table V. Reaction of 0.1 M 5-Iodo-1-cyclooctene with 0.02 M $LiEt_3BH$ in THF at Room Temperature

	% yield			
time, h				
1	85	3	5	3
217	0	74	7	13

Scheme II



In conclusion it is clear that lithium triethylborohydride does not reduce alkyl halides exclusively via an S_N2 pathway as recently reported,[4] but rather alkyl iodides are reduced in major part by an electron-transfer pathway and alkyl bromides are reduced to a lesser extent by a similar pathway.

Experimental Section

Materials. Reactions were performed under dry nitrogen at the bench by using Schlenk-tube techniques. Calibrated syringes equipped with stainless steel needles were used for transfer of reagents. Glassware and syringes were heated and cooled under a flow of nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from a deep purple solution of sodium benzophenone ketyl. Lithium triethylborohydride (Super-hydride) and lithium triethylborodeuteride (Super-deuteride) were purchased from Aldrich as 1 M solutions in THF and were reanalyzed for active hydride by hydrolysis of a sample and measuring the hydrogen evolved.

Dicyclohexylphosphine from Aldrich was distilled and stored under nitrogen. Deuterated dicyclohexylphosphine (DCPD) was prepared analogous to Issleib's method for DCPH.[12]

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[12] (a) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 704. (b) Ashby, E. C.; DePriest, R. N.; Su, W.-Y. (submitted for publication).

Trityl bromide was obtained from Aldrich and 6-iodo-1-heptene (1) was prepared from its tosylate and sodium iodide as reported earlier.[6]

5-Chloro-1-cyclooctene (4), 5-bromo-1-cyclooctene (3), and 5-iodo-1-cyclooctene (2) can be obtained in nearly quantitative yield by Pritzkow's method of adding dry HX to 1,5-cyclooctadiene in CH_2Cl_2.[13]

Gas chromatographic analyses were conducted on a Hewlett-Packard Model 700 instrument using a FID detector and packed columns. Quantitative GLC analyses were obtained with the use of response factor corrected peak areas using internal standards.

Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer.

Mass spectra were obtained on a Varian MAT 112S, and for EPR studies spectra were recorded on a Varian E 109 ES.

General Procedure for Reduction of Alkyl Halides. The appropriate amounts of alkyl halide (0.1 M) and metal hydride (0.2 M) were combined in a reaction tube under N_2 in THF and shielded from light. For the EPR study, the reagents were combined in an EPR tube under N_2. In those cases where DCPH or DCPD were employed, the additive was added to the metal hydride, followed by the addition of the appropriate alkyl halide. Control experiments showed that no reaction occurred between $LiEt_3BD$ and DCPH, as determined by the constancy of the P–H stretching band at 2260 cm^{-1} in THF at room temperature. DCPH was also unreactive (as determined by GLC) toward alkyl halides in the absence of $LiEt_3BH$.

At the chosen time, reaction mixtures were carefully quenched with water, internal standard added, and GLC analyses performed. A 20-ft column of 8% Apiezon L was used at 70 °C to separate the products formed in the reactions with benzene as internal standard. The iodides were analyzed by using a 4-ft column of 8% Apiezon L at 70 °C with *n*-decane as internal standard. The products were identified by comparing their retention times with the retention times of authentic samples.

Deuterium incorporation was evaluated by GC–mass spectroscopy.

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Registry No. 1, 13389-36-1; 2, 32654-09-4; DCPD, 91523-73-8; DCPH, 829-84-5; $LiEt_3BH$, 22560-16-3; $LiEt_3BD$, 74540-86-6; $Ph_3C\cdot$, 2216-49-1; Ph_3CBr, 596-43-0; 5-bromo-1-cyclooctene, 4103-12-2; 5-chloro-1-cyclooctene, 1855-55-6; 2-iodo-1-methylcyclopentane, 92285-02-4; 1-heptene, 592-76-7; *cis*-1,2-dimethylcyclopentane, 1192-18-3; *trans*-1,2-dimethylcyclopentane, 822-50-4; 6-deuterio-1-heptene, 80963-54-8; 1-methyl-2-(deuteriomethyl)cyclopentane, 92285-03-5; 2-iodobicyclo[3.3.0]octane, 92285-04-6; cyclooctene, 931-88-4; bicyclo[3.3.0]octane, 694-72-4.

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Preparation and Properties of Quaternary Ammonium and Phosphonium Permanganates

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General methods for the preparation and purification of quaternary ammonium and phosphonium permanganates have been developed. Solubility studies indicate that these compounds exist in solution as either ion pairs or aggregates with aggregation being promoted by high concentrations, low temperatures, and solvents of low polarity. In general, the greatest solubilities in nonpolar solvents are observed for compounds such as methyltri-*n*-octylammonium permanganate which permit the anions to penetrate the organophilic cations. None of the compounds prepared exhibit high thermal stability; however, both benzyltriethylammonium permanganate and (*p*-fluorobenzyl)tri-*n*-butylammonium permanganate have good shelf lives under cool (room temperature or lower) conditions. The structures of methyltriphenylphosphonium permanganate and *n*-heptyltriphenylphosphonium permanganate have been determined by X-ray diffraction. The former compound is polymorphic with one form orthorhombic, $Pbc2_1$, $Z = 8$, $a = 12.626$ (3) Å, $b = 14.320$ (26) Å, $c = 19.806$ (7) Å, and the other, $P2_1/c$, $Z = 4$, $a = 10.637$ (6) Å, $b = 13.424$ (10) Å, $c = 15.036$ (8) Å, $\beta = 119.44$ (4)°. The latter compound is orthorhombic $P2_12_12_1$, $Z = 4$, $a = 13.122$ (10) Å, $b = 10.801$ (3) Å, $c = 17.154$ (6) Å.

The permanganate anion, when combined with an organophilic cation, becomes a very useful agent for the oxidation of organic compound in nonaqueous solvents.[1] In some procedures the soluble permanganate salts are formed in phase-transfer processes and utilized in situ without isolation.[2-5] In others, the salts are first isolated as semistable solids and then dissolved in the desired solvent.[6-11] *When used under the latter conditions care must be taken to avoid violent thermal decompositions.*[12-14]

The cations most commonly used to solvate permanganate in nonpolar solvents are quaternary ammonium[8,15] or phosphonium[8] ions and polyether complexes (cyclic[16-18] and linear[18,19]). All evidence indicates that these compounds exist as ion pairs when dissolved in organic solvents.[20]

[†] Observed and calculated structure amplitudes are available from this author.

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