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Evidence for Single-Electron Transfer in the Reactions of Unhindered Saturated Primary Alkyl Iodides with Lithium Aluminum Hydride. Reactions of 1-Halooctanes with Lithium Aluminum Deuteride

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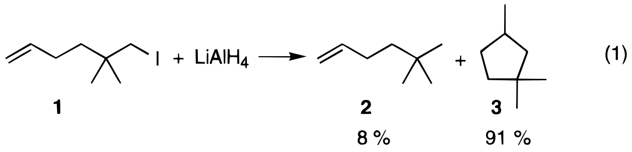
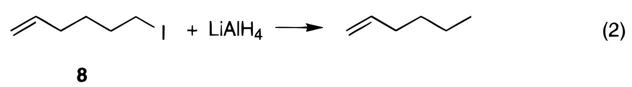
Evidence for single-electron transfer (SET) in the reactions of lithium aluminum hydride (LAH) with unhindered, saturated primary alkyl halides has not been available. In this study, experiments have been carried out that provide convincing evidence that the unhindered, saturated primary alkyl iodide 1-iodooctane reacts with lithium aluminum deuteride (LAD) in a 1:0.2 ratio to form 1-deuteriooctane with up to 38% incorporation of protium. Since the protium incorporation increased as the reaction proceeded, studies involving the reaction of 1-iodooctane with AlD_3 (one of the byproducts in the reaction of LAD with alkyl halides) were carried out in order to determine the effect of AlD_3. With AlD_3, protium incorporations as high as 84% were observed, indicating that the reaction of AlD_3 with 1-iodooctane proceeds via a pathway that involves at least 84% radical formation. The study also included the effect of reaction vessel surface, concentration, and leaving group on the course of the reaction. Factors previously suggested by Newcomb to explain the results of the reactions of $LiAlH_4$ with cyclizable radical probes, e.g., a halogen atom radical-chain process, can be excluded as a valid argument in the present study.

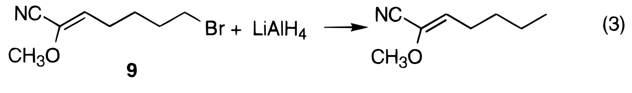
Introduction

In the past, we have found evidence for extensive cyclization in the reaction of the hindered alkyl iodide radical probe, 6-iodo-5,5-dimethyl-1-hexene (**1**), with $LiAlH_4$ (eq 1) and have proposed that this reaction proceeds by a single-electron transfer (SET) process involving radical intermediates (Scheme 1).[1] Newcomb has reported in several papers his objections to this proposed mechanism and instead has contended that the reactions we have reported as SET are actually S_N2 in nature.[2]

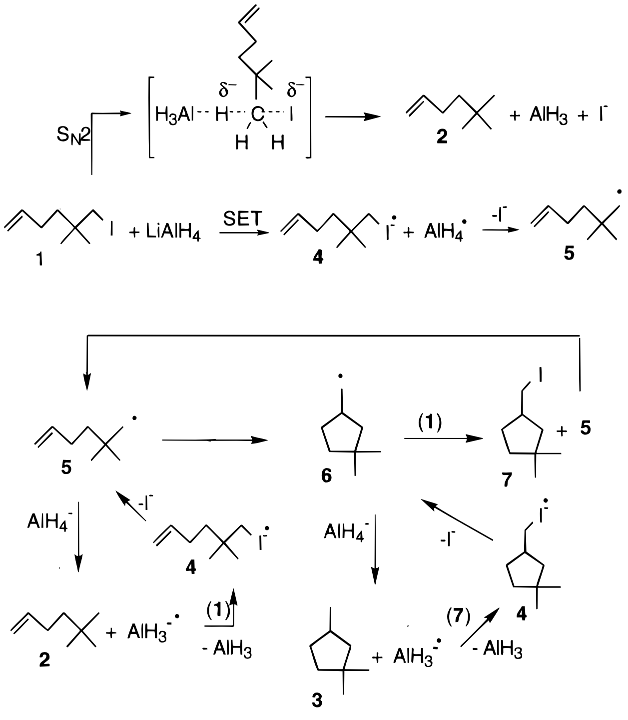


We have also previously reported the results of experiments involving the unhindered, unsubstituted cyclizable radical probe, 6-iodo-1-hexene (**8**), with LAH (eq 2).[1c] In that study, no evidence of a radical intermediate was found. Therefore, in 1987 when Newcomb reported that he also had found no evidence of a radical intermediate in the reaction of an unhindered primary alkyl halide with LAH,[2d] we were not surprised (eq 3).





Scheme 1



We modified Newcomb's probe **9** to probe **10** in order to remove the undesirable α,*β*-unsaturated nitrile moiety, which is reactive toward LAH, but incorporated Newcomb's idea[3] that a substituted radical probe should

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[1] (a) Ashby, E. C.; Pham, T. N.; Amrollah-Madjdabadi, A. *J. Org. Chem.* **1991**, *56*, 1596. (b) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414. (c) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545. (d) Tolbert, L. M.; Sun, X. J.; Ashby, E. C. *J. Am. Chem. Soc.* **1995**, *117*, 2681.

[2] (a) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (b) Newcomb, M.; Kaplan, J.; Curran, D. P. *Tetrahedron Lett.* **1988**, *29*, 3451. (c) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195. (d) Park, S. U.; Chung, S. K.; Newcomb, M. *J. Org. Chem.* **1987**, *52*, 3275.

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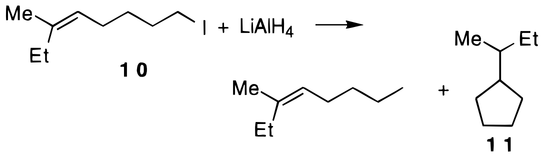
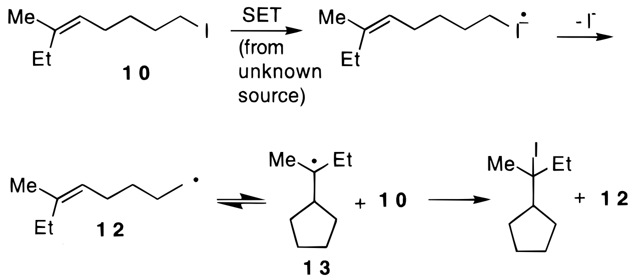
cyclize faster than the corresponding unsubstituted compound. We also modified the halide from bromide to iodide because we have always observed more evidence of radical intermediates using alkyl iodide probes.[1] Upon reaction with LAH, alkyl iodide **10** was found to yield cyclized product **11** in up to 18% yield (eq 4),[4] but



(4)

Newcomb argues[5] that the cyclized product may arise from an equilibrium of tertiary radical **13** with primary radical **12**, which he suggested was initially formed from an unknown impurity, through an iodine atom exchange (Scheme 2).

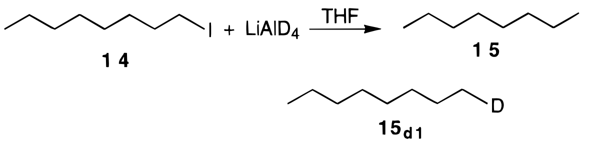
Scheme 2



In the present study, we have eliminated the pathway involving radical formation via a halogen atom radical-chain process (Scheme 2) by removing the double bond in the radical probe and carrying out studies with the unhindered, saturated, unsubstituted primary alkyl iodide, 1-iodooctane (**14**). We have dealt in detail with Newcomb's arguments in our previous paper[6] in regard to hindered primary alkyl halides and herein extend the scope of the SET interpretation from hindered to unhindered primary alkyl iodides. We have studied the following effects in the reaction of 1-halooctanes with LAD: (1) stoichiometry, (2) involvement of byproduct AlD_3, (3) influence of the reaction vessel, (4) concentration, and (5) leaving group.

Results and Discussion

Reduction of 1-iodooctane (**14**) with LAD to form substantial amounts of protio product **15** cannot be explained by a S_N2 process or the presence of impurities followed by a halogen atom radical-chain process (eq 5).



(5)

In the present study, we do indeed find the formation of protio *n*-octane in up to 38% yield in the reaction of **14** with $LiAlD_4$. The extent to which protium incorporation was observed in the reaction of 1-iodooctane (**14**) with LAD in THF was very surprising to us.

Table 1. Effect of Stoichiometry in the Reaction of 1-Iodooctane (14) with LAD in THF[a]

expt	RI:LAD	time, h	products % **14**	 % **15** (% D)	MB
1	1:5	0.5	0	100 (99)	100
2	1:1	0.25	0	100 (99)	100
3	1:0.2	0.25	77	20 (96)	97
		1	72	21 (93)	93
		2.5	66	25 (87)	91
		8	64	27 (86)	91
		24	63	29 (85)	92

[a] All reactions were carried out at a concentration of 0.070 M with respect to **14** in an Ar atmosphere glovebox in the absence of light at room temperature in used Pyrex flasks. Teflon-coated stir bars were employed.

The Effect of Stoichiometry on the Reaction of 1-Iodooctane (14) with LAD. The data in Table 1 show the effect of variation of stoichiometry on the reaction of 1-iodooctane (**14**), an unhindered primary alkyl iodide, with LAD. As in the case of the hindered primary probes discussed previously,[6] lower stoichiometries of LAD should lead to lower deuterium incorporation, if the resulting hydrocarbon were formed via a radical intermediate.

In both the 1:5 RI:LAD reaction (experiment 1) and the 1:1 reaction (experiment 2), complete deuterium incorporation was observed in the product *n*-octane (99% D), which was formed in 100% yield, in both experiments. When the stoichiometry was further reduced to 1:0.2, so that less than 1 equiv of LAD was employed in the reaction, siginificant hydrogen atom abstraction was observed only after 20% reaction (i.e., after reaction of one deuteride from the 0.2 equiv of $LiAlD_4$).

In experiment 3, after 0.25 h, 20% *n*-octane (**15**) containing 96% D was formed. After 24 h, 29% *n*-octane was formed containing 85% D. Using eq 6, the percent deuterium in the 9% octane formed from the 0.25 h aliquot to the 24 h aliquot can be calculated. As shown,

$$(29\ \%\mathbf{15})(85\ \%d) = (20\ \%\mathbf{15})(96\ \%d) + (9\ \%\mathbf{15})(X\ \%d)$$
$$X = 61\ \%d \qquad (6)$$

the average deuterium content in the 9% octane formed after 0.25 h was 61% D. It seems reasonable to conclude that no evidence of SET was observed with LAD; however, the byproduct (AlD_3) reacted with 1-iodooctane (**14**) in a fashion to produce a radical intermediate.

Removal of the hindrance of the dimethyl groups present in the 1-halo-2,2-dimethylhexanes studied earlier[6] resulted in an unhindered system (1-halooctanes) that was no longer S_N2 impeded. Thus, the balance between SET and S_N2 that was present in the neopentyl type probes should be shifted to favor S_N2 in the unhindered probes. When 0.2 equiv of LAD was employed, after 20% reaction, AlD_3 is the major hydride species in solution. It is apparently the AlD_3 that is responsible for the decrease in the deuterium content of the product as the reaction proceeds beyond 20% reaction.

Effect of Aluminum Deuteride on the Reaction of 1-Iodooctane (14) with LAD. Since evidence for a radical intermediate in the reaction of **14** with LAD was observed only when less than 1 equiv of LAD was present, a study of the reaction of AlD_3 (the expected

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

(4) Ashby, E. C.; Pham, T.; Madjdabadi, A. A. *J. Org. Chem.* **1988**, *53*, 6156.

(5) Newcomb, M.; Varick, T. R.; Choi, S. Y. *J. Org. Chem.* **1992**, *57*, 373 and references cited therein.

(6) Ashby, E. C.; Welder, C. O. *J. Org. Chem.* **1997**, *62*, 3542.

Table 2. Effect of Aluminum Deuteride in the Reaction of 1-Iodooctane (14) with LAD in THF[a]

			products		
expt	nuc	time, h	% **14**	% **15** (% D)	MB
1	LAD	0.25	77	20 (96)	97
		1	72	21 (93)	93
		2.5	66	25 (87)	91
		8	64	27 (86)	91
		24	63	29 (85)	92
2	AlD_3	0.08	93	1.6 (93)	95
		0.17	90	2.1 (83)	92
		0.25	93	2.5 (72)	96
		0.5	89	3.1 (56)	92
		1	94	4.9 (37)	99
		20	82	18 (16)	100
3[b]	AlD_3	0.25	95	1.3 (83)	96
		1	94	2.2 (76)	96
		2.5	96	2.8 (51)	99
		5	83	8 (35)	91
		24	81	12 (27)	93

[a] All reactions were carried out at a concentration of 0.070 M with respect to **14** with a RI:Nuc ratio of 1:0.2. Also, all reactions were carried out in an Ar atmosphere glovebox in the absence of light at room temperature in used Pyrex flasks, and Teflon-coated stir bars were employed. [b] The AlD_3 used in experiment 3 was made with excess sulfuric acid, ensuring that no LAD was present in the reaction of **14** with AlD_3.

byproduct of the reaction of LAD with **14**) with **14** at a 1:0.2 **14**:AlD_3 ratio was carried out. As shown in experiment 2, Table 2, even the earliest aliquot, in which only 1.6% octane (containing 93% D) was formed, showed evidence of protium incorporation and hence a radical intermediate. The amount of hydrogen atom abstraction increased rapidly as the reaction proceeded. After 20 h, 18% *n*-octane was formed that contained only 16% D. Therefore, the average deuterium content in the octane formed between 0.08 and 20 h was 8.5% D as calculated from eq 7. It appears that the reaction is proceeding

$$(18\ \%\mathbf{15})(16\ \%d) = (1.6\ \%\mathbf{15})(93\ \%d) + (16.4\ \%\mathbf{15})(X\ \%d)$$
$$X = 8.5\ \%d \qquad (7)$$

exclusively by a radical intermediate that can only be explained by a SET process. The initiation of the reaction by impurities followed by a halogen atom radical-chain process cannot explain these results.

AlD_3 solutions were prepared by the addition of 100% H_2SO_4 to a homogeneous solution of LAD.[7] If any LAD remained in the AlD_3 solution, it would be expected to react quickly to yield *n*-octane (**15**) with a very high deuterium content on the basis of earlier results (Table 1). For this reason, a reaction was carried out to ensure that the initially high deuterium incorporation noted in the AlD_3 experiment (Table 2, experiment 2) was not due to a small amount of LAD that remained in the AlD_3 solution. Any remaining LAD could have reacted with 1-iodooctane (**14**) to give completely deuterated product followed by SET reduction of **14** by AlD_3 with significant hydrogen atom abstraction. Therefore, an AlD_3 solution was prepared by adding a 10% excess of 100% sulfuric acid to a LAD solution, thus ensuring that no LAD was present in the resulting AlD_3 solution. It was this solution of AlD_3 that was used in experiment 3 (Table 2).

Table 3. Effect of Reaction Vessel Surface in the Reaction of 1-Iodooctane (14) with LAD in THF[a]

			products		
expt	reaction vessel	time, h	% **14**	% **15** (% D)	MB
1	used Pyrex	0.25	77	20 (96)	97
		1	72	21 (93)	93
		2.5	66	25 (87)	91
		8	64	27 (86)	91
		24	63	29 (85)	92
2	Teflon	0.25	70	21 (94)	91
		1	74	24 (92)	98
		5	67	28 (80)	95
		8	60	31 (74)	91
		24	64	30 (75)	94
3	quartz	0.25	78	18 (93)	96
		1	75	20 (87)	95
		5	68	27 (67)	95
		8	65	29 (63)	94
		24	63	31 (62)	94

[a] All reactions were carried out at a concentration of 0.070 M with respect to **14** with a RI:LAD ratio of 1:0.2. Also, all reactions were carried out in an Ar atmosphere glovebox in the absence of light at room temperature in the absence of Teflon-coated stir bars.

The deuterium incorporation in the *n*-octane was similar for experiments 2 and 3 (Table 2). When an excess of H_2SO_4 was used to prepare the AlD_3 solution (experiment 3, Table 2), the resulting octane still had high deuterium incorporation in the first aliquot (experiment 3, Table 2, 0.25 h), although the deuterium content (83%) was more than in experiment 2 (Table 2, 0.25 h) (72%). However, the trend of decreasing deuterium incorporation over the course of the reaction resembled that of experiment 2 (Table 2). Therefore, the initially high deuterium incorporation in the octane observed in the early aliquots of the AlD_3 experiment was also observed when LAD was rigorously excluded from the reaction. The rapid decrease in deuterium incorporation as the reaction proceeds (experiments 2 and 3, Table 2) is due to the fact that the concentration of AlD_3 decreases as the reaction proceeds, and therefore, the generated radicals have a better chance of abstracting a hydrogen atom from THF than abstracting a deuterium atom from AlD_3.

The Effect of Reactor Surfaces on the Reaction of 1-Iodooctane (14) with LAD. Once an appropriate stoichiometry for observing SET in the unhindered primary alkyl iodide system had been determined (RI:LAD = 1:0.2), reactions were carried out in used Pyrex, Teflon, and quartz, in order to study the effect of the surface of the vessel on the reaction (Table 3). A comparison of the reactions carried out in used Pyrex (experiment 1, Table 3), Teflon[8] (experiment 2, Table 3), and quartz (experiment 3, Table 3) reveals that the rates of the reaction in these three vessels were similar, although more hydrogen atom abstraction occurred in the reaction carried out in quartz.

The deuterium incorporation in the second aliquot of the reaction carried out in quartz (experiment 3, Table 3, 1 h) contained 87% D in the 20% *n*-octane formed. This deuterium incorporation (87%) is too low for a direct displacement of iodide by deuteride, as in a S_N2 reaction. Therefore, it appears as if some radicals were formed in solution during the first 20% of product formation.

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(7) (a) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464. (b) Brown, H. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 849.

(8) We have previously shown that Teflon is not a suitable reaction vessel for reactions involving $LiAlH_4$. Ashby, E. C.; Welder, C. O. *Tetrahedron Lett.* **1995**, *36*, 7171.

Table 4. Effect of Concentration in the Reaction of 1-Iodooctane (14) with LAD in THF[a]

				products		
expt	[**14**], M	**14**:LAD	time, h	% **14**	% **15** (% D)	MB
1	0.14	1:0.2	0.08	75	21 (98)	96
			0.25	77	22 (96)	99
			1	76	21 (94)	97
			20	67	33 (81)	100
2	0.070	1:0.2	0.08	84	13 (98)	97
			0.25	82	16 (96)	98
			1	82	18 (90)	100
			20	72	28 (68)	100
3	0.035	1:0.2	0.08	84	15 (97)	99
			0.25	79	20 (96)	99
			1	74	22 (90)	96
			20	71	28 (74)	99
4	0.035	1:0.1	1	80	11 (81)	91
			20	76	14 (66)	90
			41	74	15 (66)	89

[a] All reactions were carried out in an Ar atmosphere glovebox in the absence of light at room temperature in used Pyrex flasks, and Teflon-coated stir bars were employed.

Quartz gave somewhat stronger evidence supporting SET during the first 20% reaction when 0.2 equiv of LAD was allowed to react with 1-iodooctane.

Importantly, lower deuterium incorporation (62% after 24 h) in the product from the quartz experiment indicates that more radicals were trapped by a hydrogen atom donor in quartz than in any other vessel studied. Since more hydrogen atom abstraction is observed in quartz, reactions in used Pyrex vessels should represent a minimum amount of protium incorporation products, which are indicative of a radical intermediate. More importantly, the results in quartz, in particular, show clearly that the reaction of LAD with a simple unhindered primary alkyl iodide proceeds, to some extent, via a radical intermediate, and therefore, SET is involved in the reduction of unhindered primary alkyl iodides with LAD.

The Effect of Concentration on the Reaction of 1-Iodooctane (14) with LAD. As explained previously for the hindered primary alkyl iodide system,[6] a decrease in the concentration of the reactants should lead to more hydrogen atom abstraction product for a radical reaction as compared to more concentrated reactants under otherwise identical conditions. As reported for the reaction of LAD with iodide **1**, more hydrogen atom abstraction was also observed at lower reactant concentrations in the reaction of iodide **14** with LAD (Table 4).

In the most concentrated reaction studied (experiment 1, Table 4, 0.14 M), the deuterium content of the product ranged from 98% to 81% over a 20 h period. When the concentration was decreased from 0.14 to 0.070 M (experiment 2, Table 4), the deuterium content of the resulting *n*-octane ranged from 98% to 68%. A further decrease in the concentration to 0.035 M (experiment 3, Table 4) had very little effect on the reaction. In a further attempt to minimize the deuterium content of the *n*-octane, the stoichiometry of **14** to LAD was reduced from 1:0.2 to 1:0.1 (experiment 4, Table 4). The deuterium content of the product at the lower stoichiometry significantly decreased, in the 11−15% product range, more than the previous experiments, as expected.

The Effect of the Leaving Group on the Reaction of 1-Halooctanes with LAD. In order to observe the effect of the leaving group, 1-bromooctane (**16**) was allowed to react with LAD (Table 5). The data show that only 21% octane was formed after 20 h when the bromide was allowed to react with 0.2 equiv of LAD, indicating that the byproducts of LAD (e.g., AlD_3) do not easily reduce the alkyl bromide **16**, unlike the alkyl iodide **14** that was further reduced by the byproducts of LAD.

Table 5. Reactions of 1-Halooctanes with LAD in THF[a]

			products		
expt	X	time, h	% RX	% **15** (% D)	MB
1	I	0.25	77	20 (96)	97
		1	72	21 (93)	93
		2.5	66	25 (87)	91
		8	64	27 (86)	91
		24	63	29 (85)	92
2	Br	0.25	93	7 (98)	100
		1	83	17 (98)	100
		20	77	21 (97)	98

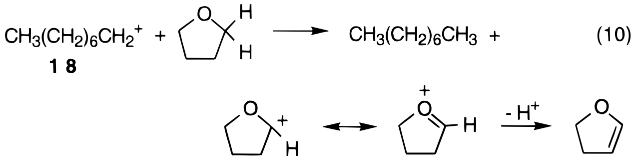
[a] All reactions were carried out at a concentration of 0.070 M with respect to RX at a RX:Nuc ratio of 1:0.2. Also, all reactions were carried out in an Ar atmosphere glovebox in the absence of light at room temperature in used Pyrex flasks, and Teflon-coated stir bars were employed.

The reaction of bromide **16** with LAD (Table 5, experiment 2) can be compared to the reaction of 1-bromo-2,2-dimethylhexane (**17**) with LAD.[6] Even though in the unhindered primary alkyl bromide reaction no evidence for SET was observed, evidence for SET was significant in the case of the hindered primary bromide **17** yet still much less than in the case of the corresponding iodide **1**.

The results with 1-bromooctane are very significant in that, if the results of the experiment with 1-iodooctane and $LiAlD_4$ (experiment 1, Table 5) can be described by an ionic process (eqs 8−10), then more protium incoporation should have been observed in experiment 2 than in experiment 1 (Table 5) since AlD_2Br is a stronger Lewis acid than AlD_2I and, therefore, should have produced more carbocation **18**.

$$CH_3(CH_2)_6CH_2Br + AlD_3 \xrightarrow{S_N2} CH_3(CH_2)_6CH_2D + AlD_2Br \quad (8)$$

$$CH_3(CH_2)_6CH_2Br + AlD_2Br \longrightarrow \underset{\mathbf{18}}{CH_3(CH_2)_6CH_2^+} + AlD_2Br_2^- \quad (9)$$



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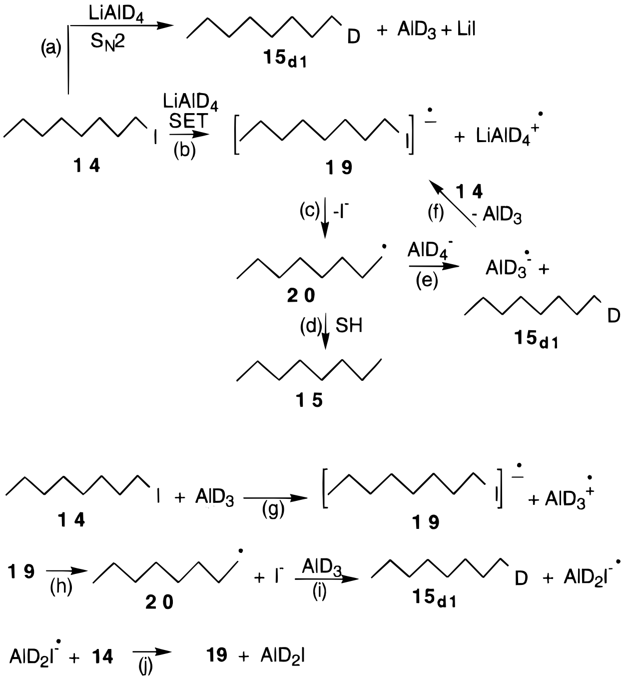
Effect of Transition Metal Impurities in Initiating the Reactions of $LiAlH_4$ with Alkyl Halides. In 1978, we reported a study entitled, “Transition Metal Catalyzed Reactions of Lithium Aluminum Hydride with Alkyl and Aryl Halides.”[9] The data show that in the reaction of $LiAlH_4$ with 1-iodododecane, the reaction proceeds at approximately the same rate and yield when 10 mol % $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ are added as when no additives are present. In the reaction of 1-bromodecane, the yield is 92% with pure $LiAlH_4$, considerably lower in the presence of 10 mol % VCl_3, $CrCl_3$, and $MnCl_2$, and only slightly higher in the presence of $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$. The data show that as much as 10 mol % of several transition metal impurities have little effect (except detrimental) in the reactions of $LiAlH_4$ with 1-iodo- and 1-bromoalkanes. Any transition-metal impurities in $LiAlH_4$ would have to be in the small ppm or ppb range, especially since these halides in most cases would be reduced to the metal (e.g., $TiCl_3$ is reduced to Ti^0 in the presence of $LiAlH_4$), which is insoluble in THF and would be removed in the filtration process. (Clear, colorless solutions of $LiAlH_4$ in THF were used in all of these studies.)

In all of the studies,[9] $FeCl_2$ showed similar activity to $CoCl_2$, $NiCl_2$, and $TiCl_3$. We reported in an earlier paper[1c] that recrystallized $LiAlH_4$, redissolved in THF, showed no difference in reactivity toward the alkyl iodide, 6-iodo-5,5-dimethyl-1-hexene, in the presence or absence of 10 mol % $FeCl_3$, indicating once again that transition metal impurities in the ppm and ppb range are not affecting the reaction.

Proposed Mechanism of Reduction of 1-Iodooctane (14) by LAD and Its Byproduct, AlD_3. The above data are consistent with the reaction mechanism shown in Scheme 3. It is proposed that LAD can react with alkyl iodide **14** by either an S_N2 pathway (step a) to give 1-deuteriooctane ($\mathbf{15_{d1}}$) or a SET pathway (step b) to give the radical anion **19**. Loss of iodide from **19** yields radical **20** (step c). Radical **20** either abstracts a hydrogen atom from the solvent (THF) to form the nondeuterated product **15** (step d) or it abstracts a deuterium atom from AlD_4^- to form deuterated octane $\mathbf{15_{d1}}$ (step e) and the AlD_3 radical anion. As shown in step f, the AlD_3 radical anion can act as an electron donor to alkyl iodide **14** in a radical-chain process to yield **19** and AlD_3. As shown in step g, AlD_3 can react with **14** to yield **19** and the AlD_3 radical cation. Radical anion **19** can lose iodide (step h) to form **20**, which then abstracts a deuterium atom from AlD_3 to yield $\mathbf{15_{d1}}$ and the AlD_2I radical anion. The AlD_2I radical anion can then react with **14** (step j) to form **19** and AlD_2I in yet another radical-chain process. It is clear from the results of these studies that the reaction of 1-iodooctane with $LiAlD_4$, and by comparison, $LiAlH_4$, proceeds to a significant extent by a SET pathway involving AlH_3.

Scheme 3



Summary and Conclusions

Evidence for the SET nature of the reaction of LAH with *hindered* primary alkyl iodides is overwhelming. The present report shows for the first time that SET is also involved in the reaction of LAH with *unhindered* and unsubstituted primary alkyl iodides. In the case of the latter reaction with unhindered and unsubstituted primary alkyl iodides, it appears that a true competition between the SET and S_N2 pathways is possible, although we have no evidence that the S_N2 pathway is involved at all.[1d] In the past, high deuterium incorporation (99%) in the product from the reaction of 1-iodooctane with LAD would have been interpreted as evidence for a S_N2 pathway; however, we know from the present work that when the ratio of alkyl halides:LAD is 1:0.2 and the reaction is carried out in a quartz vessel, that deuterium incorporation in the product is as low as 62%, which indicates that the reaction proceeds to a significant extent via a radical intermediate.

Experimental Section

Materials. Tetrahydrofuran (THF) was purchased from Fisher Scientific and distilled from $NaAlH_4$ prior to use. $LiAlD_4$ was purchased from Aldrich, allowed to stir in THF overnight, and then filtered in an argon atmosphere glovebox to obtain a homogeneous solution that was titrated before use. 1-Iodooctane (Aldrich) and 1-bromooctane (Fisher) were distilled prior to use. An authentic sample of *n*-octane (Eastman) was obtained in order to verify its formation in the mechanistic studies. Solutions of aluminum deuteride were prepared according to literature procedures.[7] Techniques for titration of LAD solutions and calculation of deuterium content were reported previously.[6]

Instrumentation. GLC analyses were performed on a Varian 3700 gas chromatograph with a J & W DB-5 fused silica column (30 m, 0.25 mm i.d., 25 μm film thickness) equipped with a flame ionization detector. Mass spectra were obtained from a VG 70-SE mass spectrometer equipped with a double sector magnetic analyzer.

Typical Reduction of 1-Halooctanes. To a flask in an Argon atmosphere glovebox at room temperature was added 1-iodooctane (0.034 g, 0.14 mmol), decane (15 μL, an internal standard for GC), and THF (1.93 mL). To this solution was added a homogeneous solution of $LiAlD_4$ in THF (91 μL, 0.31 M, 0.028 mmole). The reaction vessel was then covered in aluminum foil to shield the reaction from light. At the desired time, an aliquot (0.1−0.2 mL) was removed and quenched in an approximately equal volume of water. The organic compounds were extracted with diethyl ether (0.2 mL), and the organic layer was analyzed by GC and/or GC/MS. Unless otherwise noted in the tables, experiments were carried out in used Pyrex flasks employing a Teflon-coated stir bar.[8]

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[9] Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1978**, *43*, 1263.