

## Single Electron Transfer in the Reaction of an Alkyl Iodide with $\text{LiAlH}_4$ and $\text{LiAlD}_4$ in the Absence of a Halogen Atom Radical Chain Process

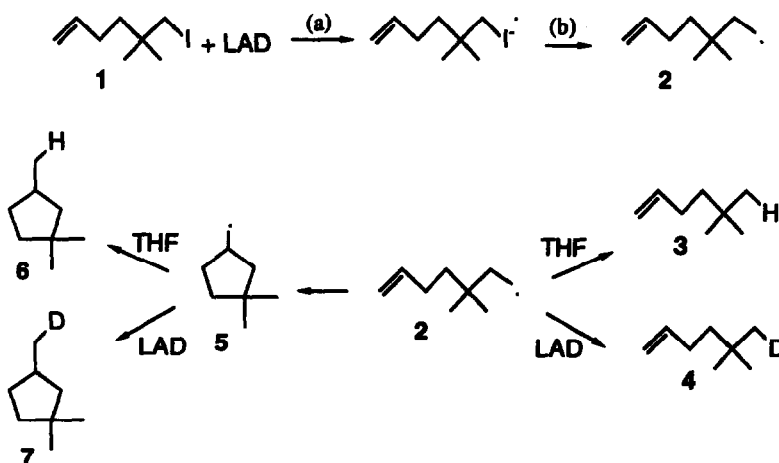
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**Summary:** Reactions of the noncyclizable alkyl iodide, 1-iodo-2,2-dimethylhexane (**9**), with  $\text{LiAlH}_4$  and  $\text{LiAlD}_4$  have been carried out under a variety of conditions. Although the structure of **9** prohibits a halogen atom radical chain process, deuterium incorporation studies provide convincing evidence for single electron transfer (SET) as the major reaction pathway.

In 1984 we reported that the reduction of a sterically hindered primary alkyl iodide by  $\text{LiAlH}_4$  (LAH) to the corresponding hydrocarbon proceeds predominantly through a SET process involving a radical intermediate.<sup>1</sup> As reported earlier<sup>1,2</sup> (Scheme 1), 6-iodo-5,5-dimethyl-1-hexene (**1**) accepts an electron from  $\text{LiAlD}_4$

Scheme 1. Mechanism of Reduction of 6-iodo-5,5-dimethylhexene (**1**) with LAD.



(LAD) to form the corresponding radical anion (step a) which rapidly dissociates to form the corresponding free radical (step b). The resulting radical **2** can then abstract a hydrogen atom from THF to form **3** or from LAD to form **4**, or radical **2** can



deuterium content due to a higher LAD to solvent ratio, as is reported (Table 1).

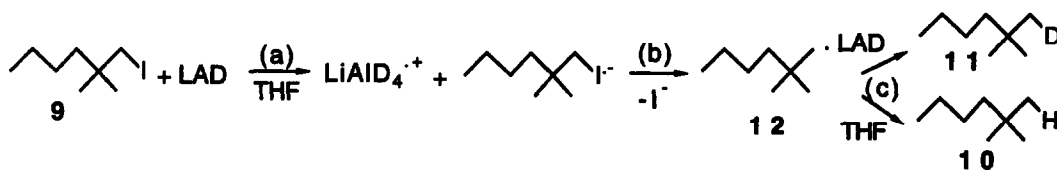
A variation of the stoichiometry should also affect the deuterium incorporation of the hydrocarbon if a radical intermediate is involved, but not if a  $S_N2$  mechanism is involved. A comparison of expts. 2 and 4 shows that a change in the ratio of 9 to LAD from 1:5 to 1:1 results in a decrease in the deuterium incorporation from 28% to 6% as expected since the solvent would compete more favorably as the concentration of LAD decreases.

**Table 1.** Reactions of 1-iodo-2,2-dimethylhexane (9) with LAH and LAD.<sup>a</sup>

Exp.	SH	Nuc	9:Nuc	[9] <sub>i</sub>	% yield	
					9	10 (%d)
1	THF	LAD	1:5	0.035M	2	86 (21)
2	THF	LAD	1:5	0.070M	<0.5	100 (28)
3	THF	LAD	1:5	0.27M	<0.5	100 (67)
4	THF	LAD	1:1	0.070M	28	67 (6)
5	Et <sub>2</sub> O	LAD	1:5	0.070M	8	84 (33)
6	Et <sub>2</sub> O	LAD	1:1	0.070M	26	63 (8)
7	THF-d <sub>8</sub>	LAH	1:5	0.070M	<0.5	96 (1)
8	THF-d <sub>8</sub>	LAH	1:1	0.070M	<0.5	88 (15) <sup>b</sup>
9	THF-d <sub>8</sub>	LAD	1:5	0.070M	<0.5	91 (89)

a) All reactions were carried out in a glove box under Ar atmosphere at room temperature in the absence of light. b) Also obtained 3% 3 and ~9% dimers.

**Scheme 2.** Mechanism of Reduction of 1-iodo-2,2-dimethylhexane (9) with LAD.



Reactions of 9 with LAD were also carried out in diethyl ether (exps. 5 and 6). A comparison of expts. 2 with 5 and 4 with 6 provides evidence that similar results are obtained in THF and diethyl ether and that radical formation is not an anomaly of the solvent.

Experiment 7 shows a very low deuterium incorporation when the solvent is THF-d<sub>8</sub> and the nucleophile is LAH; however exp. 8 demonstrates that deuterium

atoms are unarguably abstracted from the solvent under the more favorable conditions of a higher 9:LAH ratio. The competition between solvent and nucleophile for deuterium/hydrogen atoms lies heavily in favor of hydrogen atom abstraction from the nucleophile over deuterium atom abstraction from the solvent due to the primary deuterium kinetic isotope effect. Exp. 9 shows that high deuterium incorporation results only when THF- $d_8$  is employed as the solvent and LAD as the nucleophile.<sup>4</sup> It should be noted that deuterium incorporation did not vary when samples were quenched with  $D_2O$  instead of  $H_2O$  which supports the formation of radical intermediates over anionic intermediates.

In conclusion, it is evident from the above data that the major reaction pathway in the reduction of the hindered primary alkyl iodide **9** by LAH involves predominantly a SET process even though the nature of the probe prohibits the halogen atom radical chain process shown in eq. 1<sup>5</sup>. It seems reasonable to expect that the removal of a carbon-carbon double bond four carbon atoms removed from the carbon-iodine bond would not affect the initial step of the reaction which is an electron transfer from the nucleophile to the alkyl iodide. Thus we maintain that 6-iodo-5,5-dimethyl-1-hexene (**1**) is also reduced primarily by an electron transfer process,<sup>1</sup> and that it is a valid probe for establishing SET in reactions of alkyl halides with LAH.

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#### References and Notes

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2. a) Ashby, E.C. *Acc. Chem. Res.* **1988**, *21*, 414-421. b) Ashby, E.C.; Pham, T.N.; Amrollah-Madjdabadi, A. *J. Org. Chem.* **1991**, *56*, 1596-1603.
3. a) Newcomb, M.; Curran, D.P. *Acc. Chem. Res.* **1988**, *21*, 206-214. b) Park, S.U.; Chung, S.K.; Newcomb, M. *J. Org. Chem.* **1987**, *52*, 3275-3278.
4. 100% $d$  incorporation is not possible since the LAD contains only 98 atom % $D$ . The LAD in exp. 7 is used in 5-fold excess.
5. We are presently exploring other possible radical chain processes in this system involving the THF radical and will report on the findings at a later date.

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