



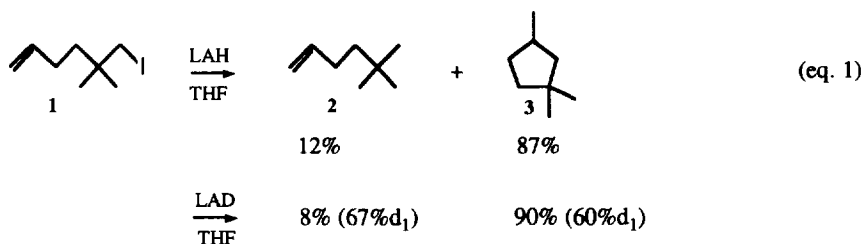
## The Effect of Reactor Surfaces on Single Electron Transfer Reactions. The Reaction of 1-Iodo-2,2-dimethylhexane with Lithium Aluminum Deuteride.

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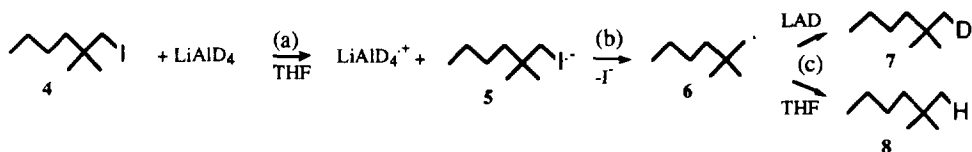
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**Abstract:** Reactions of 1-iodo-2,2-dimethylhexane (**4**) with  $\text{LiAlD}_4$  have been carried out in a variety of reaction vessels. In vessels of used pyrex, teflon, and stainless steel, the surface of the reactor plays a role in the product distribution. However, treated pyrex, new pyrex and quartz vessels yield consistent data that support single electron transfer as the major reaction pathway in the reduction of **4** with  $\text{LiAlD}_4$ .

As early as 1984 we reported on the reaction of the cyclizable radical probe, 6-iodo-5,5-dimethyl-1-hexene (**1**), with lithium aluminum hydride (LAH).<sup>1</sup> We found significant evidence for single electron transfer (SET) as determined by the formation of the cyclized alkane (**3**), significant protium incorporation in both products **2** and **3** in reactions involving lithium aluminum deuteride (LAD) (eq. 1), and radical trapping experiments.



In 1993 we studied the reaction of 1-iodo-2,2-dimethylhexane (**4**), the corresponding saturated alkyl iodide of **1**, with LAD.<sup>2</sup> Since alkyl iodide **4** cannot cyclize, the products, 1-deuterio-2,2-dimethylhexane (**7**) and 2,2-dimethylhexane (**8**), were analyzed by mass spectrometry for evidence of protium incorporation

**Scheme 1.** Mechanism of Reduction of 1-Iodo-2,2-dimethylhexane (**4**) with LAD.

(product **8**). Any protium incorporation product must have resulted from a radical intermediate that abstracted a hydrogen atom from a suitable donor, such as the solvent (Scheme 1). As reported earlier<sup>2</sup>, alkyl iodide **4** accepts an electron from LAD to form the corresponding radical anion **5** (Scheme 1, step a) which rapidly dissociates to form the corresponding free radical **6** (step b). The resulting radical **6** can then abstract a deuterium atom from LAD to form the deuterio alkane **7** or abstract a hydrogen atom from THF to form the protio alkane **8** (step c). As in the case of the unsaturated alkyl iodide **1**, we found that the major reaction pathway in the reduction of the saturated alkyl iodide **4** by LAD is also the SET pathway, as evidenced by significant protium incorporation (72%) in the 2,2-dimethylhexane.<sup>2</sup>

In recent studies we have explored irregularities observed in multiple experiments carried out under apparently identical conditions. After study of a number of reaction variables (concentration, stoichiometry, etc.), it became evident that the surface of the reaction flask might play a role in the product ratios. Evidence that supports surface influence includes a small variation in reaction rate as well as a variation in deuterium content in 2,2-dimethylhexane (**7** & **8**). Therefore, we initiated a study involving the effect of different reactor surfaces on the above reaction (Scheme 1) in order to find a vessel that does not influence the mechanistic course of the reaction (Table 1).

Teflon has been used as a reactor surface in reactions in which glass is suspected of catalyzing the reaction. To test the integrity of teflon as a reaction vessel in the presence of LAH, a homogeneous solution of LAH in THF (0.32 M) was allowed to stir in a teflon flask for two days. Ion chromatographic analysis of the quenched basic solution revealed the presence of fluoride ions. Therefore, LAH does react with teflon, and even though data are included on teflon (Exp. 2, Table 1), it is not a suitable vessel for reactions involving LAH. Likewise, the use of teflon coated stirring bars should be avoided in studying the mechanisms involved in reactions concerning LAH.

To observe the effect of a metal surface, we employed a stainless steel vessel (Exp. 3, Table 1). In this experiment, the formation of several dimers was observed very early in the reaction and dimer formation was found to be more extensive than deuterium or hydrogen atom abstraction of intermediate **6** to form either **7** or **8**; however, a high yield of dimer was not observed in a duplicate experiment. The stainless steel surface appears to catalyze the reduction of alkyl iodide **4**, and thus, it is inappropriate as a reaction vessel.

Reactions in used pyrex flasks that had been treated with dichlorodimethylsilane to deactivate the surface were monitored as well (Exp. 4, Table 1). Encouragingly, consistent results were obtained with the deuterium

**Table 1.** The Reaction of 1-Iodo-2,2-dimethylhexane (**4**) with LAD in Various Reaction Vessels.<sup>a</sup>

Exp.	rxn. vessel	time, h	% <b>4</b>	2,2-dimethyl- hexane (%d <sub>1</sub> )	%dimers	material balance
1	used pyrex	1	88	4 (48)	-	92
		5	60	33 (42)	trace	93
		8	33	58 (39)	trace	91
		24	5	84 (34)	3	92
2	teflon	1	90	3 (61)	-	93
		5	74	18 (54)	-	92
		8	61	33 (52)	trace	94
		24	9	77 (42)	1	87
3	stainless steel	1	61	17 (26)	21	99
		2	37	24 (26)	31	92
		5	16	34 (27)	45	95
		8	8	41 (27)	48	97
		24	0	47 (27)	50	97
4	treated pyrex	1	93	4 (37)	-	97
		5	51	32 (34)	2	85
		8	29	44 (32)	4	77
		24	1	83 (29)	7	91
5	new pyrex	1	94	5 (40)	-	99
		5	64	26 (39)	trace	90
		8	45	39 (39)	1	85
		24	7	71 (32)	2	80
		48	0	78 (35)	5	83
6	quartz	1	96	4 (40)	-	100
		5	62	31 (35)	trace	93
		8	33	53 (34)	trace	86
		24	0	88 (30)	2	90

<sup>a</sup>All experiments were carried out under identical conditions. Initial concentration of **4** was 0.070 M in THF and a 5-fold excess of LAD as a homogeneous solution in THF was employed. Reactions were carried out in the absence of light in an Ar filled glovebox and were complete in 48 h. All deuterium incorporation information was determined from the molecular ion. The deuterium incorporation values have been estimated to have 5% error.

content of alkane **7** & **8** found to be 37% d<sub>1</sub> in the initial aliquot (4% reaction) and 29% d<sub>1</sub> at completion. (Decreasing deuterium content over the course of the reaction was also observed in used pyrex and teflon flasks. However, in used pyrex and teflon flasks, the amount of deuterium in the product (**7** & **8**) was not consistent between duplicate experiments.) Reactions carried out in treated pyrex flasks, as well as new pyrex flasks (Exp. 5) and quartz (Exp. 6), were found to be reproducible. Protium incorporation in 2,2-dimethylhexane appears to be consistent between reaction vessels (Exps. 4-6) as well.

The surface of the reaction vessel is not the only factor that plays a significant role in this reaction. When unfiltered, heterogeneous solutions of LAH or LAD were employed, inconsistent results were noted as well. Formation of dimers originating from the alkyl radical **6** ranged from <0.5-25% when undissolved solids were present in the flask. However, when filtered, homogeneous solutions were employed in the reaction, dimers were consistently formed in low yield (Table 1).

As can be seen, surfaces play an important role in the reaction of LAD with the sterically hindered primary alkyl iodide **4**. Used pyrex flasks gave inconsistent rates and deuterium incorporation in 2,2-dimethylhexane. Teflon was found to react with LAH and thus is an inappropriate reaction vessel. Stainless steel appeared to catalyze the reduction of **4** and the rate of formation of dimers originating from radical **6**. Consistent results were obtained in used pyrex flasks treated with dichlorodimethylsilane, new pyrex flasks, and quartz flasks; therefore, these flasks are appropriate as reaction vessels. Also, solids present in heterogeneous solutions of LAH and LAD catalyzed the formation of several dimers. In conclusion, future mechanistic reactions should be carried out in treated pyrex, new pyrex, or quartz flasks using homogeneous solutions of LAH or LAD in the absence of a teflon coated stirring bar. Importantly, we maintain that 1-iodo-2,2-dimethylhexane (**4**) is reduced by LAH or LAD primarily by an electron transfer process regardless of the variations in surfaces present since several reaction flasks (new pyrex, treated pyrex, and quartz) gave consistent and reproducible results with large amounts of protium incorporation in the product (**7** & **8**) in the reaction of **4** with LAD.<sup>3</sup>

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### References and Notes

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2. Ashby, E.C.; Welder, C.O.; and Doctorovich, F. *Tetrahedron Lett.* **1993**, *34*, 7235-7238.
3. We are continuing our studies involving the reaction of 6-iodo-5,5-dimethyl-1-hexene (**1**) with LAH or LAD in a quartz flask. Also, we are studying the reactions of **1** with sodium trimethyltin<sup>4</sup> and lithium diisopropylamide<sup>5</sup> by carrying out the reactions in a quartz vessel and comparing the results to those obtained in previous studies.
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