

Preliminary communication

**ADDITION OF LITHIUM ALUMINIUM HYDRIDE TO OLEFINS
CATALYZED BY ZIRCONIUM TETRACHLORIDE: A CONVENIENT ROUTE
TO ALKANES AND 1-HALOALKANES FROM 1-ALKENES**

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Summary

Lithium aluminium hydride adds to olefins in the presence of zirconium tetrachloride under mild conditions. This facile reaction offers a convenient laboratory method for the hydrogenation of olefins or for the preparation of 1-haloalkanes from olefins in high yield. Unstrained internal olefins appear to be unreactive.

In general, the carbon—carbon double bond is comparatively inert to lithium aluminium hydride or aluminium hydride unless the reaction is carried out at fairly high temperatures. Thus 1-hexene and lithium aluminium hydride react only at 110°C in the absence of ether [1] (in the presence of ether this reaction does not take place). Some substances (such as AlCl₃, ZnCl₂, FeCl₃, alkali halides, carbonates or phosphates), which had been claimed to catalyze the reaction [2], was found actually to have no effect at all [3]. Therefore, though it is evident that the addition of aluminium hydride to olefins to form organo-aluminium compounds is closely related to the reaction of boron hydrides with olefins, in cases where the synthetic route involves a choice between the organo-aluminium or the organoborane, the latter procedure has proved preferable for laboratory work [4].

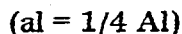
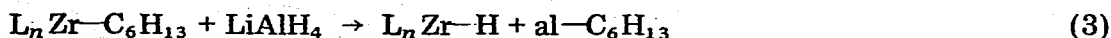
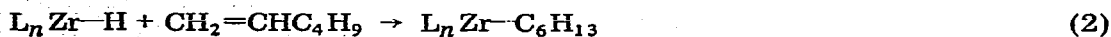
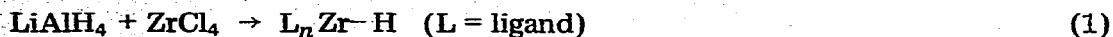
We report here that lithium aluminum hydride adds to carbon—carbon double bonds in the presence of zirconium tetrachloride, and that this facile reaction offers a convenient laboratory method for the hydrogenation of olefins or for the preparation of 1-haloalkanes from 1-alkenes.

The preparation of 1-bromohexane (or n-hexane) from 1-hexene via this route proceeded as follows. To a suspension of ZrCl₄ (150 mg, 0.64 mmol) in benzene was added dropwise a clear solution of LiAlH₄ in tetrahydrofuran (53 ml of 0.2 molar, 10.6 mmol) with stirring at 7°C. Then 1-hexene (3.20 g, 38.1 mmol) was added neat and the reaction mixture was stirred at 25°C under nitrogen. After 30 hours of stirring, the reaction mixture was hydrolyzed by adding ice to

TABLE 1
YIELDS AND PRODUCTS OF ADDITION REACTIONS OF OLEFINS

Olefin	Reaction conditions		Temp. (°C)	Time (h)	Hydrolysis or halogenolysis	Product, yield (%) ^a
	Molar ratio LiAlH ₄ /ZrCl ₄	Olefin/LiAlH ₄				
1-Hexene	without ZrCl ₄	3.6	25	30	H ₂ O	No reaction
	16.6	3.6	25	30	H ₂ O Cl ₂ ^b	n-Hexane, 99 1-Chlorohexane, 89 1-Bromohexane, 92 1-Iodohexane, 83
1-Octene	16.6	3.6	25	30	Bx ₂ ^c I ₂ ^c	n-Octane, 98
1-Decene	16.6	3.6	26	30	H ₂ O	n-Decane, 99
Styrene	16.6	3.6	60	7	H ₂ O	Ethylbenzene, 100
2-Methyl-1-pentene	4.0	3.0	25	40	H ₂ O	2-Methyl-1-pentane, 60
Cyclopentene	16.6	3.6	25	90	H ₂ O	Cyclopentane, 70

^aYields were determined by VPC and are based on olefin. ^bCl₂ added slowly at -20°C in pyridine/n-hexane solution. ^cI₂ added at 5°C in benzene solution.



the reaction mixture to give n-hexane in nearly quantitative yield (> 99%), together with small amounts of *cis*- and *trans*-2-hexene. In another experiment, the solvent was removed from the reaction mixture under vacuum and the residue was treated with bromine (6.4 g, 40 mmol) in benzene to afford 1-bromohexane (5.8 g, 92% yield based on 1-hexene). Similar reactions with chlorine and iodine were used to prepare 1-chloro- and 1-iodo-hexane*.

As shown in Table 1, olefins suitable for the reaction with lithium aluminium hydride include 1-alkenes, 2-methyl-1-pentene and cyclopentene. *cis*- or *trans*-2-hexene and cyclohexene are practically unreactive.

The function of the catalyst is presently under investigation. It can be assumed that a zirconium hydride, formed by reaction of zirconium tetrachloride with lithium aluminium hydride, plays an important role as evidenced by the following facts. (1) The reaction of an equimolar mixture of ZrCl_4 and LiAlH_4 in tetrahydrofuran in the absence of olefin at room temperature evolved hydrogen during about 3 hours and precipitation of metallic compounds (presumably, of zirconium and aluminium) was observed. (2) An equimolar mixture of zirconium tetrachloride and lithium aluminium hydride catalyzed the isomerization of 1-hexene to *cis*- and *trans*-2-hexene. Thus, a mixture of ZrCl_4 (100 mg, 0.43 mmol) and LiAlH_4 (16 mg, 0.42 mmol) in tetrahydrofuran changed 1-hexene (3.20 g, 38.1 mmol) completely into *cis*- and *trans*-2-hexene after 4 days at room temperature.

In view of the recently developed hydrozirconation reaction [6], it is most conceivable that the conversion of alkenes into LiAlR_4 by $\text{LiAlH}_4/\text{ZrCl}_4$ proceeds via hydrozirconation of the double bond followed by zirconium-aluminium exchange as shown in eqns. 1-3.

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*The reactions of trialkylaluminum compounds with halogens were reported to yield the corresponding alkyl halides [5].