

REDUCTION OF ALKENES, ALKYNES AND HALIDES BY LITHIUM ALUMINUM
HYDRIDE - TRANSITION METAL CHLORIDE

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(Received in USA 27 June 1977; received in UK for publication 31 October 1977)

Recently, applications of transition metal hydrides in organic synthesis have received considerable attention. For example, hydrozirconation of alkenes and alkynes to form alkyl and alkenyl intermediates has been shown to have considerable potential for the functionalization of fundamental building blocks in organic chemistry. The reagents NaH-FeCl_2 ² and $\text{NaH-RONa-Ni(OAc)}_2$ ³ have also been found to be effective for the reduction of ketones, alkenes and alkynes. Admixtures of $\text{LiAlH}_4\text{-ZrCl}_4$ ⁴ and $\text{LiAlH}_4\text{-TiCl}_4$ ⁵ also have been used for reduction of alkenes and alkynes. These recent reports encourage us to report extensive studies carried out earlier concerning alkene and alkyne reduction by LiAlH_4 and first row transition metal halides. Our results are summarized in Tables I - IV. In Table I, the representative alkene, 1-octene, was reduced by $\text{LiAlH}_4\text{-TiCl}_3$, VCl_3 , CrCl_3 , MnCl_2 , FeCl_2 , FeCl_3 , CoCl_3 , NiCl_2 , CuI and ZnBr_2 respectively. The reduction is assumed to take place by hydrometallation which involves d-orbital overlap of the transition metal. MnCl_2 , CuI and ZnBr_2 have comparably lower activating abilities since their d-orbitals are filled (d^{10}) or half filled (d^5). Those reactions using stoichiometric amounts of transition metal halide show that Ti, Cr, Fe, Co and Ni chlorides give nearly quantitative reduction whereas in the catalytic reactions, TiCl_3 , CoCl_2 and NiCl_2 are the most effective catalysts studied giving > 94% reduction in each case.

The reagents, $\text{LiAlH}_4\text{-CoCl}_2$ and $\text{LiAlH}_4\text{-NiCl}_2$, were studied in greater scope by allowing these reagents to react with other alkenes (Table II). The data show that terminal alkenes are reduced catalytically by NiCl_2 or CoCl_2 in excellent yield, however internal alkenes are effectively reduced only by stoichiometric amounts of transition metal halide.

Terminal alkynes are reduced by $\text{LiAlH}_4\text{-NiCl}_2$ (Table III) to alkenes in 94-96% yield with high selectivity. 100% stereoselectivity was observed in the reduction of both of the internal alkynes to the corresponding cis olefin. $\text{LiAlH}_4\text{-NiCl}_2$ appears to be superior to $\text{LiAlH}_4\text{-CoCl}_2$ in forming specifically the kinetic product.

$\text{LiAlH}_4\text{-CoCl}_2$ and $\text{LiAlH}_4\text{-NiCl}_2$ have been found to be excellent reagents for reduction of organic halides.⁶ Primary halides (X = I, Br, Cl and F) can be converted to alkanes in quantitative yield (except in the case of fluorides) by the reaction of the halide with

Table I. Reduction of 1-octene with LiAlH_4 -Stoichiometric or Catalytic Transition Metal Halides^a

| <u>Metal Halides</u> | <u>1-Octene Recovery (%)</u> | | <u>Octane Yield (%)</u> | |
|----------------------|------------------------------|-------|-------------------------|------|
| TiCl_3 | 0 | (0) | 98 | (95) |
| VCl_3 | 100 | (64) | 0 | (42) |
| CrCl_3 | 0 | (80) | 100 | (19) |
| MnCl_2 | 71 | (100) | 25 | (0) |
| FeCl_2 | 0 | (95) | 98 | (5) |
| FeCl_3 | 0 | (95) | 98 | (5) |
| CoCl_2 | 0 | (0) | 100 | (98) |
| NiCl_2 | 0 | (5) | 100 | (94) |
| CuI | > 95 | (-) | < 5 | (-) |
| ZnBr_2 | 100 | (-) | 0 | (-) |

a. In stoichiometric reactions, the molar ratio of LiAlH_4 : metal halide: 1-octene is 1.0:1.0:0.5, and the reaction time 1 h. In catalytic reactions, the molar ratio is 1.0:0.1:1.0 and the reaction time 18 h. The catalytic results are given in parentheses.

Table II. Reduction of Alkenes with LiAlH_4 - CoCl_2 and LiAlH_4 - NiCl_2 ^a

| <u>Alkene</u> | <u>Metal Halide</u> | <u>Alkene Yield (%)</u> | |
|---------------------|---------------------|-------------------------|------|
| 1-hexene | CoCl_2 | (-) | (97) |
| 1-hexene | NiCl_2 | (-) | (97) |
| styrene | CoCl_2 | (-) | (92) |
| styrene | NiCl_2 | (-) | (92) |
| cis-2-hexene | CoCl_2 | 98 | (32) |
| cis-2-hexene | NiCl_2 | 95 | (28) |
| trans-2-hexene | CoCl_2 | 96 | (-) |
| trans-2-hexene | NiCl_2 | 95 | (-) |
| 2-ethyl-hexene | CoCl_2 | 98 | (35) |
| 2-ethyl-hexene | NiCl_2 | 82 | (15) |
| cyclohexene | CoCl_2 | 96 | (55) |
| cyclohexene | NiCl_2 | 94 | (40) |
| 1-methylcyclohexene | CoCl_2 | 91 | (0) |
| 1-methylcyclohexene | NiCl_2 | 94 | (0) |

a. Reaction time was 24 h. and the mole ratio of reactants: LiAlH_4 :metal halides: olefins is 1.0:1.0:2.0. The numbers in parenthesis indicate a ratio of 1.0:0.1:2.0.

Table III. Reduction of Alkynes with $\text{LiAlH}_4\text{-CoCl}_2$ and $\text{LiAlH}_4\text{-NiCl}_2$

| Alkyne | Metal Halide | Reaction Condition | Products(%) | | |
|--------------------------------|-----------------|-----------------------------|-------------|----|--------|
| | | | Alkene | | Alkane |
| 1-octyne ^a | CoCl_2 | -40°C 1h | 70 | | 17 |
| 1-octyne ^a | NiCl_2 | -40°C 1h | 96 | | 1 |
| phenylacetylene ^a | CoCl_2 | -40°C 10 min. | 35 | | 8 |
| phenylacetylene ^a | NiCl_2 | -40°C 1h | 94 | | 0 |
| | | | cis trans | | |
| 2-hexyne ^a | CoCl_2 | RT, 2h | 40 | 5 | 4 |
| 2-hexyne ^a | NiCl_2 | RT, 24h | 91 | 0 | 4 |
| diphenylacetylene ^b | CoCl_2 | RT, 24h | 18 | 10 | 0 |
| diphenylacetylene ^b | NiCl_2 | RT, 24h | 75 | 0 | 15 |

^a The molar ratio of LiAlH_4 : metal chloride: substrate = 1.0:0.1:2.0.

^b The molar ratio of LiAlH_4 : metal chloride: substrate = 1.0:0.1:1.0.

Table IV. Reduction of Alkyl Halides with LiAlH_4 -Stoichiometric and Catalytic Transition Metal Halides^a

| Halide Substrate | Metal Halide | Alkane Yield (%) |
|--------------------------------|-----------------|------------------|
| 1-iododecane ^b | CoCl_2 | dodecane (100) |
| 1-iododecane ^b | NiCl_2 | dodecane (100) |
| 1-bromodecane ^b | CoCl_2 | dodecane (98) |
| 1-bromodecane ^b | NiCl_2 | dodecane (100) |
| 1-chlorodecane ^b | CoCl_2 | dodecane (98) |
| 1-chlorodecane ^b | NiCl_2 | dodecane (98) |
| 1-fluorodecane ^b | CoCl_2 | dodecane (10) |
| 1-fluorodecane ^b | NiCl_2 | dodecane (7) |
| 3-bromodecane ^c | CoCl_2 | decane (98) |
| 3-bromodecane ^c | NiCl_2 | decane (92) |
| bromocyclohexane ^c | CoCl_2 | cyclohexane (99) |
| bromocyclohexane ^c | NiCl_2 | cyclohexane (99) |
| 1-bromoadamantane ^c | CoCl_2 | adamantane (100) |
| 1-bromoadamantane ^c | NiCl_2 | adamantane (100) |
| bromobenzene ^c | CoCl_2 | benzene (25) |
| bromobenzene ^c | NiCl_2 | benzene (100) |

^a Reaction time, 24h.

^b Mole ratio LiAlH_4 : Metal Chloride: Substrate = 1.0:0.1:1.0.

^c Molar ratio of LiAlH_4 : Metal Chloride: Substrate = 1.0:1.0:1.0.

LiAlH_4 and either CoCl_2 or NiCl_2 in 10 mole %. Secondary, tertiary, alicyclic and aryl bromides which are normally more difficult to reduce, can be nearly quantitatively reduced to the corresponding alkane in each case reported by reactions of LiAlH_4 with stoichiometric amounts of NiCl_2 or CoCl_2 .

The experiments were carried out by the following procedure. The transition metal halide was transferred into a 10 ml Erlenmeyer flask which had been oven dried, equipped with a magnetic stirrer and sealed with a rubber septum. About 1 ml of THF was syringed into the flask and the temperature then adjusted by dry ice (ca - 40°C). 0.1205 mmole of organic substrate in THF was then added followed by the addition of LiAlH_4 . During LiAlH_4 addition, gas evolution and a black solid were observed. After 10 minutes, the reaction was warmed to room temperature and the reaction mixture quenched with a minimum amount of distilled water (~0.5 mls). After a few minutes the reaction mixture was worked up by extraction with THF and the resulting solution dried over MgSO_4 (~2g). The product and yield were determined by GC and NMR using the authentic compounds and internal standards.

The use of the new reagents, LiAlH_4 -transition metal halide, to reduce alkenes, alkynes and organic halides is highly recommended for the rapid and nearly quantitative reduction of these classes of compounds.

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