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# HYDROMETALLATION OF ALKENES AND ALKYNES BY BIS-DIISOPROPYLAMINOALANE CATALYZED BY $Cp_2TiCl_2$

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Recently, the reduction of alkenes and alkynes by the reagent, $LiAlH_4$-transition metal halide has been reported.[1,2] Although one might assume that this reaction proceeds via hydrometallation, deuterolysis shows that only titanium compounds of the first row transition metals are effective in the formation of the hydrometallation intermediate, although other first row transition metal compounds (e.g. $NiCl_2$ and $CoCl_2$) are effective in catalyzing the formation of reduction products. Schwartz[3] has reported that hydrozirconation of alkenes and alkynes also involves a hydrometallation intermediate, although the zirconium compound must be used in stoichiometric amounts with respect to the substrate. Our research[2] has centered around the investigation of less expensive and more readily available catalyst systems (metal hydride + transition metal compound) to prepare the intermediate hydrometallated product. The importance of forming the hydrometallated intermediate rather than the reduction product (alkane or alkene) lies in the formation of an organometallic compound that can be easily functionalized. Although hydroboration proceeds readily between an olefin and diborane in THF in the absence of a catalyst, the C-B bond is relatively stable and not as susceptible to functionalization as C-Mg or C-Al compounds. Unfortunately $MgH_2$ and $AlH_3$ do not hydrometallate alkenes or alkynes at all readily compared to $B_2H_6$; however, reaction does take place when certain transition metal catalysts are present. The present study reports an excellent hydrometallation system that consists of $HAl(NR_2)_2$ compounds in the presence of a catalytic amount of $Cp_2TiCl_2$. Since $HAl(NR_2)_2$ compounds can be prepared by the reactions of Al, $H_2$ and $HNR_2$[4] in a one step reaction in quantitative yield and the resulting compounds are soluble in hydrocarbons as well as ethers, these hydrometallating agents should be both versatile and economically attractive.

We would like to report that the reaction of alkenes and alkynes with bis-diisopropylaminoalane, $HAl(NPr_2^i)_2$, in the presence of bis-(cyclopentadienyl)titanium dichloride, $Cp_2TiCl_2$, takes place in THF in high yield producing the hydrometallated intermediate as determined by deuterolysis of the reaction product. Table I contains the results of several representative alkenes and alkynes with the reagent system.

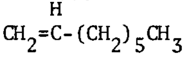
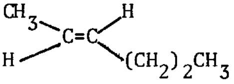
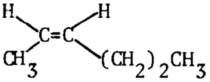
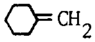
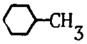
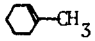
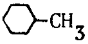
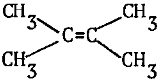
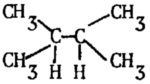
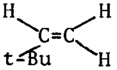
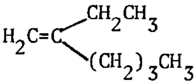
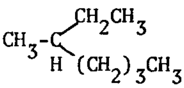
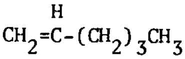
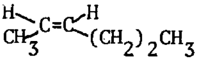
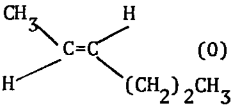
It is clear that both terminal olefins (1-octene, 2-ethyl-1-hexene and methylene cyclohexene) and internal olefins (cis- and trans-2-hexene) react in quantitative or high yield to form the corresponding alkane on hydrolysis or 72-86% yield representing the intermediate organometallic compound. The terminal alkyne, 1-hexyne, is reduced by $HAl(NPr_2^i)_2$-$Cp_2TiCl_2$ (Table I) to 1-hexene with high deuterium incorporation (79%) indicating formation of the intermediate hexenylaluminum compound; however, a substantial amount of hexane is also formed. The internal alkyne, 2-hexyne, (Tables I and II) is reduced to the corresponding cis olefin in high yield (90%) with no trace of trans olefin. When the reaction was carried out at room temperature only 52% deuterium incorporation was observed; however when the reaction was carried out at 0°, 85% deuterium incorporation was observed once again indicating formation of the intermediate hexenylaluminum compound in high yield. The amount of alkane was reasonably constant throughout the reaction at 0° indicating that the alkane is formed in the initial stages of the reaction by hydrogenation since $H_2$ is released when the $HAl(NPr_2^i)_2$ is added to $Cp_2TiCl_2$. Also considerable trans olefin is formed when the temperature is increased from 0 to 25° indicating the advantage of lower reaction temperatures.

For the olefins the following order of reactivity was observed: 1-octene > 3,3,dimethyl-1-butene $\geq$ methylenecyclohexane > cis-2-hexene > trans-2-hexene >> 2-ethylhexene >>> cyclohexene >> methylcyclohexene,2,3-dimethyl-2-butene. As the amount of catalyst was increased (Table III) the rate also increased with no loss in deuterium incorporation. The optimum catalyst concentration is considered to be 5 mole %. More recent data obtained using an all argon atmosphere (rigorous exclusion of $N_2$) shows that the reaction proceeds to completion in 30 minutes at room temperature.

The experiments were carried out by the following procedure. A 0.02 M solution of $Cp_2TiCl_2$ in benzene was prepared.[5] The desired amount of catalyst was transferred to a 13 x 18 mm test tube which had been flame dried, cooled under argon, equipped with a magnetic stirrer and sealed with a rubber septum cap. About 2 ml of benzene was syringed into the test tube. The desired amount of substrate and internal standard was then added. After adjusting to the desired temperature, the $HAl(NPr_2^i)_2$ in benzene was added under argon. Quenching was accomplished with a saturated solution of $NH_4Cl$. The product and yield were determined by glc.

The $HAl(NPr_2^i)_2$ was prepared by allowing $AlH_3$ in THF to react with the appropriate amount of diisopropylamine for 5 hrs. at room temperature. The THF was removed under vacuum and replaced by benzene.

Table I. Reactions of Alkenes and Alkynes with Bis-diisopropylaminoalane and 5 Mole % Bis(cyclopentadienyl)titanium Dichloride [a]

| Substrate | Recovered Substrate (%) | Hydrolysis Products | (% yield) | Mass Balance(%) | % D Incorporation |
|---|---|---|---|---|---|
|  $CH_2=\overset{H}{C}-(CH_2)_5CH_3$ | 0 | $CH_3(CH_2)_6CH_3$ | (100) | 98.2 | 86 |
|  | 0 | $CH_3(CH_2)_4CH_3$ | (100) | 86.8 | 83 |
|  | 0 | $CH_3(CH_2)_4CH_3$ | (100) | 89.5 | 81 |
|  | 56.3 |  | (47.3) | 96.0 | 29 |
|  | |  | (100) | 89.7 | 72 |
|  | 100 |  | (trace) | 96.5 | --- |
|  | 100 |  | (0) | 89.8 | --- |
|  | 0 | t-Bu-$CH_2CH_3$ | (100) | 87.5 | 0 |
|  | 10.2 |  | (89.8) | 96.9 | 75 |
| $HC\equiv C-(CH_2)_3CH_3$ | 0 | $CH_3(CH_2)_4CH_3$ | (53.2) | 87.8 | --- |
| | |  $CH_2=\overset{H}{C}-(CH_2)_3CH_3$ | (46.2) | | 79 |
| $CH_3-C\equiv C-(CH_2)_2CH_3$[b] | 0 | $CH_3(CH_2)_4CH_3$ | (9.7) | 89.3 | |
| | |  | (90.3) | | 52(85)[c] |
| | |  | (0) | | --- |

a) The reactions were carried out at 58° for 10 hours. b) The reaction was carried out at R.T. for 1 hour. c) 52% at RT, 85% at 0°C.

Table II. Reactions of 2-Hexyne with $HAl(NPr_2^i)_2$ and $Cp_2TiCl_2$ in 1.0:2.0:0.1 Mole Ratio[a].

| Exp. | Time (hr) | 2-Hexyne Recovered % | Hydrolysis Products | | Trans-2-Hexene (%) | % D in Product |
|---|---|---|---|---|---|---|
| | | | Hexane (%) | Cis-2-Hexene (%) | | |
| 1 | 0.7 | 80.1 | 6.5 | 16.9 | — | — |
| 2 | 1 | 74.5 | 7.6 | 20.4 | — | 85.3 |
| 3 | 2 | 64.9 | 7.9 | 29.9 | trace | 86.0 |
| 4 | 4 | 52.5 | 8.0 | 39.1 | trace | 85.0 |
| 5 | 8 | 29.5 | 8.0 | 65.3 | trace | 85.0 |
| 6 | 16[c] | 0 | 22.8 | 47.3 | 26.2 | 50.7 |

a) Reactions were carried out in benzene at 0°. b) Yield was determined by glc using octane as the internal standard. c) The temperature was allowed to increase to room temperature.

Table III. Reactions of 1-Octene with $HAl(NPr_2^i)_2$-$Cp_2TiCl_2$. Effect of Temperature and Catalyst Concentration.

| Mole % $Cp_2TiCl_2$ | Temp. (°C) | Time | Octane (%) | % D Incorporation |
|---|---|---|---|---|
| 5 | 58 | 2 hr. | 100 | 88 |
| 10 | 58 | 1 hr. | 100 | 83 |
| 20 | 58 | 15 min. | 100 | 86 |
| 5 | 25 | 12 hr. | 100 | 86 |
| 5 | 25 | 1.5 hr. | 10 | — |

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## Literature Cited

1. F. Sato, S. Sato and M. Sato, J. Organometal. Chem., 122 (1976), C-25.
2. E. C. Ashby, J. J. Lin and A. B. Goel, J. Org. Chem., (in press).
3. J. Schwartz, Angew. Chem. Int. Ed. Engl., 15 (1976), 333.
4. R. A. Kovar and E. C. Ashby, Inorg. Chem., 10, 893 (1971).
5. Obtained from Alpha Division, Ventron Corporation.