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A NOVEL ZIRCONIUM-CATALYZED HYDROALUMINATION OF OLEFINS

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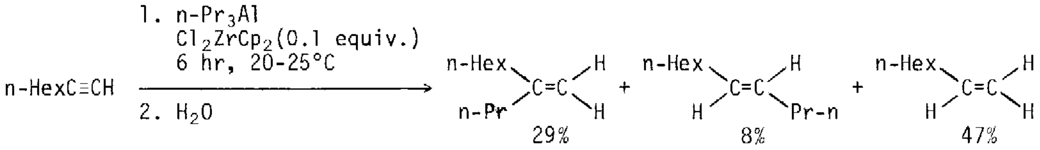
Abstract: Sterically hindered trialkylalanes, such as triisobutylalane, react with olefins at or below room temperature under the influence of a catalytic amount of Cl_2ZrCp_2 to effect hydroalumination of the olefins. The reaction can tolerate certain hetero-functional groups, such as OH, SPh and Br, which tend to interfere with previously reported hydroalumination procedures.

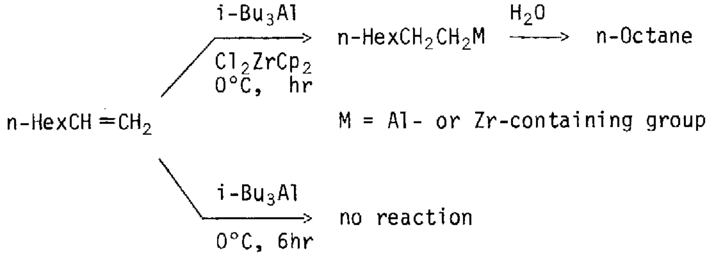
We wish to report a novel and chemoselective Zr-catalyzed hydroalumination of olefins which does not involve the use of a preformed metal hydride reagent. Although hydroalumination[1] is a synthetically useful reaction, its applicability has been severely limited by (a) the relatively low reactivity of aluminum hydride reagents toward olefins and (b) the general difficulty in accommodating various functional groups that are sensitive to aluminum hydride reagents. During the course of our study of the Zr-catalyzed carboalumination[2] with homogeneous reagents obtained by mixing trialkylalanes (R_3Al) with Cl_2ZrCp_2 (Cp = η^5-cyclopentadienyl) we noted that, when the R group contains sp^3 carbon-bound β-hydrogens, the desired carbometallation was seriously competed by hydrometallation, as exemplified by the results summarized in eq 1.



(1)

Since only 10 mole % of Cl_2ZrCp_2 for each mole of 1-octyne was used, the reaction must be catalytic in Cl_2ZrCp_2. These results prompted us to develop a Zr-catalyzed hydroalumination reaction which might permit us to alleviate the above-mentioned difficulties.

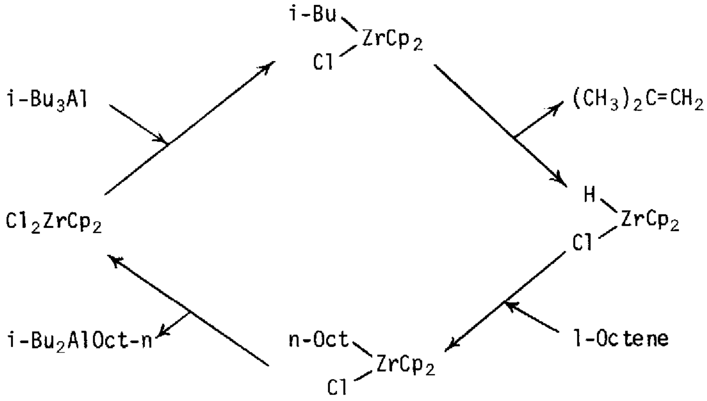
We have indeed found that the reaction of 1-octene with triisobutylalane (TIBA) in $(CH_2Cl)_2$ in the presence of Cl_2ZrCp_2 proceeds exclusively via hydrometallation to form, after protonolysis, n-octane in quantitative yield. The reaction was essentially complete within 6 hr at 0°C, when the 1-octene:TIBA:Cl_2ZrCp_2 ration was 1:2:0.1. In the absence of Cl_2ZrCp_2 no more than a trace of 1-octene was hydrometallated in 6 hr under otherwise comparable conditions. Even after 120 hr at room temperature was 1-octene hydrometallated only to the extent of 25%. Therefore, the 1-octene-TIBA-Cl_2ZrCp_2 reaction is catalytic in Cl_2ZrCp_2.



(2)

Interestingly, the corresponding reaction of diisobutylaluminum hydride (DIBAH) with 1-octene in the presence of a catalytic amount (10 mole %) of Cl_2ZrCp_2 does not proceed to any detectable extent (< 1-2%) in 6 hr at 0°C.[3] It is therefore unlikely that DIBAH is an intermediate in the 1-octene-TIBA-Cl_2ZrCp_2 reaction.

As in the previously reported carbometallation reaction,[2] the final organometallic product in the present hydrometallation reaction is largely an organoalane. The intermediacy of a monoalkylzirconium species, however, was indicated by ^1H NMR examination. Thus, when the 1-octene: TIBA:Cl_2ZrCp_2 ratio was 1:1:1, the reaction mixture contained, after 2 hr, a 42% yield of n-Oct(Cl)$ZrCp_2$ along with Cl_2ZrCp_2 ($\sim$ 60% recovery) as judged by the areas of peaks at δ 6.22 and 6.46 ppm, respectively, relative to that of benzene added as an internal standard. The amount of Cl_2ZrCp_2 increased with time at the expense of n-Oct(Cl)$ZrCp_2$, and essentially complete regeneration of Cl_2ZrCp_2 was achieved within 24 hr at room temperature. All of the experimental observations described above are in accord with the following transmetallation-dehydrozirconation-hydrozirconation-transmetallation mechanism.



It is well documented that H(Cl)$ZrCp_2$ readily hydrozirconates olefins.[4] It is also known that monoalkylzirconium derivatives can be treated with appropriate aluminum compounds to form organoalanes via transmetallation.[5] The preparation of organoalanes by these reactions, however, requires the stoichiometric amount of H(Cl)$ZrCp_2$, the reported preparation of which, in turn, requires the stoichiometric amount of an appropriate aluminum hydride, e.g., $NaAlH_2(OCH_2CH_2OCH_3)_2$. Neither requirement exists in the i-Bu_3Al-Cl_2ZrCp_2 procedure. One distinct advantage of avoiding the use of a preformed metal hydride reagent is the possibility of developing a chemoselective hydroalumination procedure. We have indeed found that the i-Bu_3Al-Cl_2ZrCp_2 procedure can readily tolerate SPh, OH, Br and olefin groups (Table I). Thus, for example, allyl phenyl sulfide was converted to a 97:3 mixture of 3- and 2-deuterio-n-propyl phenyl sulfide in 77% combined yield via hydrometallation-deuterolysis, the amount of benzenethiol formed via C-S cleavage being only 12%. On the other hand, the $LiAlH_4$-$TiCl_4$ procedure reported recently[6] leads to extensive C-S cleavage (53%) and a low yield (17%) of n-propyl phenyl sulfide. Similarly, 5-bromo-1-pentene was readily converted to a 97:3 mixture of 5- and 4-deuterio-1-bromopentane in 92% combined yield by the i-Bu_3Al-Cl_2ZrCp_2 procedure, whereas the yield of 1-bromopentane obtained by the $LiAlH_4$-$TiCl_4$ procedure via protonolysis was only 26%, the major product being n-pentane formed in 41% yield.

A few other trialkylalanes, such as t-Bu_3Al, have been shown to be satisfactory reagents, but no advantage over TIBA has been noticed. Benzene is a reasonable solvent, but it is somewhat inferior to $(CH_2Cl)_2$ in terms of product yield. On the other hand, CH_2Cl_2 seems to be at least as satisfactory as $(CH_2Cl)_2$. As reported recently, TIBA does not react with olefins under the influence of Cl_2TiCp_2.[7] We have found that $TiCl_4$(14%) and $ZrCl_4$(48%) are not effective catalysts for the TIBA-olefin reaction either, the extents of hydrometallation observed with 1-octene after 5 hr at 0°C being as shown in parentheses. Finally, internal olefins, such as cis-5-decene and cyclohexene, also react with the TIBA-Cl_2ZrCp_2 reagent system to form, after protonolysis, the corresponding saturated hydrocarbons in 70-80% yields after 2-3 days at room temperature. The exact course of the reaction in these cases, however, appears to be more complicated than that which was proposed above, as judged by GLC examination of the reaction mixtures after iodinolysis. These reactions are under further investigation.

The following procedure is representative. To 0.73g(2.5 mmol) of Cl_2ZrCp_2 placed in a dry flask equipped with a magnetic stirring bar, a septum inlet, and an outlet leading to a mercury bubbler were added sequentially at 0°C 50 ml of 1,2-dichloroethane, TIBA(9.9g, 12.6 ml, 50 mmol), and allyl phenyl sulfide (3.75g, 3.67 ml, 25 mmol). After stirring the reaction mixture for 36 hr at 0°C, deuterium oxide (6.0g, 5.42 ml, 300 mmol) was added. The product thus formed was extracted with 100 ml of pentane, washed and dried. Distillation provided 2.68g (70%) of a 97:3 mixture of 3- and 2-deuterio-n-propyl phenyl sulfide: bp 65-66°C(1.7 mm Hg); $n^{22}D$ 1.4825; ^1H NMR($CDCl_3$, TMS) δ 0.75-1.20(m, 2.03 H), 1.20-1.95(m, 1.97 H), 2.87(t, J = 7.0Hz, 2.0 H), and 7.05-7.50(m, 5.0 H)ppm.

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Table I. Zirconium-Catalyzed Hydroalumination of Olefins[a]

Olefin	Reaction time, hr	Yield of protonolysis product, %	Derivatization		
			Reagent	Product yield,[b] %	Terminal[c]/Internal
1-Octene	5	97	I_2	94	$\geq$99/1
Allyl phenyl sulfide	36	85	D_2O	77(70)[d]	97/3
4-Penten-1-ol	9	95	O_2	-(82)[d]	$\geq$95/5
10-Undecen-1-ol	9	98	O_2	-(88)[d]	99/1
4-Vinyl-cyclohexene	24	94	O_2	71(61)[d]	$\geq$99/1
cis-5-Decene[e]	78	73	-	-	-
Cyclohexene[e]	72	73	-	-	-
5-Bromo-1-pentene	7	92	D_2O	92(78)	97/3

[a] Unless otherwise mentioned, the reaction was run in $(CH_2Cl)_2$ at 0°C, in the presence of 10 mole % of Cl_2ZrCp_2 using a 100 mole % excess of TIBA. [b] GLC yield. The products of iodinolysis, deuterolysis and oxidation are alkyl iodides, deuterioalkanes and alcohols, respectively. [c] Regioisomeric ratio of the terminally and internally functionalized isomers. The regioisomeric ratios were determined by either GLC or ^1H NMR (60 and 360 MHz). The diol products were converted to their diacetates. [d] The numbers in parentheses are isolated yields. All isolated products have been identified by IR, NMR and mass spectorscopy. [e] A 20 mole % of Cl_2ZrCp was used, and the reaction was run at 25°C.

References and Notes

1. For a review of hydroalumination, see T. Mole and E. A. Jeffery, "Organoaluminum Compounds," Elsevier, Amsterdam, 1972
2. D. E. Van Horn and E. Negishi, J. Am. Chem. Soc., 100, 2252 (1978).
3. A careful investigation of the 1-octene-DIBAH-Cl_2ZrCp_2 reaction has revealed that it proceeds rapidly if the Cl_2ZrCp_2:DIBAH ratio is ≥ 1, whereas it does not proceed to any detectable extent at 0°C if the Cl_2ZrCp_2:DIBAH ratio is substantially less than 1, e.g., 0.25, regardless of the absolute amounts of these reagents.
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