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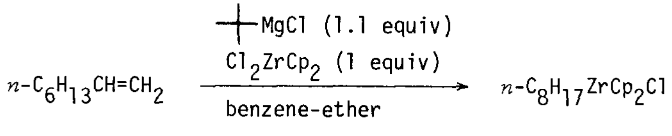
REACTION OF ALKENES AND DIENES WITH *t*-BUTYLMAGNESIUM HALIDES AND ZIRCONOCENE DIHALIDES. A CONVENIENT PROCEDURE FOR HYDROZIRCONATION AND A NOVEL *t*-BUTYLZIRCONATION OF CONJUGATED ALKENES[1]

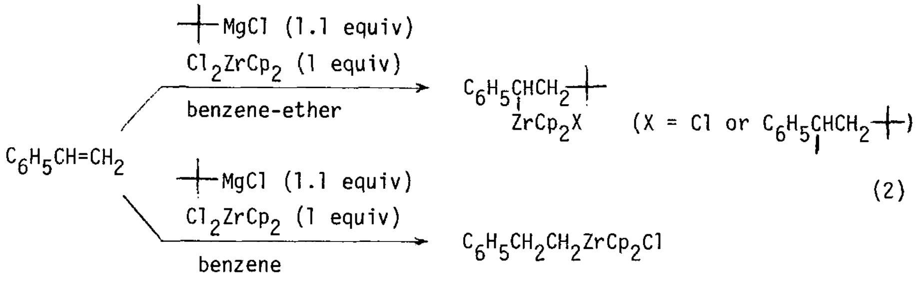
Ei-ichi Negishi,* Joseph A. Miller and Tadao Yoshida
Department of Chemistry, Purdue University, W. Lafayette, Indiana 47907 U.S.A.

SUMMARY: The reaction of nonconjugated monosubstituted alkenes with *t*-BuMgCl and Cl_2ZrCp_2 at room temperature produces the corresponding monoalkylzirconium derivatives in high yields, while conjugated alkenes undergo either a novel *t*-butylzirconation or hydrozirconation depending on the reaction conditions.

Hydrozirconation[2] is one of a relatively few reactions permitting the conversion of alkenes into terminally metalated alkylmetal derivatives under mild conditions. However, the preparation of the commonly used reagent, $HZrCp_2Cl$ (Cp = η^5-C_5H_5), by the reduction of Cl_2ZrCp_2 with an aluminum hydride, such as $LiAlH_4$[3] or $NaAlH_2(OCH_2CH_2OCH_3)_2$,[2b] requiring filtration under an inert atmosphere is inconvenient. We have found that the reaction of nonconjugated monosubstituted alkenes with 1.1 equiv of *t*-BuMgCl and 1 equiv of Cl_2ZrCp_2 in benzene-ether (5:1) at room temperature cleanly produces the corresponding monoalkylzirconium derivatives in high yields, as in eq 1. On the other hand, conjugated alkenes, such as styrene, 1,3-butadiene, and isoprene, undergo a novel *t*-butylzirconation, as in eq 2, under the same conditions. Interestingly, if Cl_2ZrCp_2 is treated first with *t*-BuMgCl in benzene in the absence of free ether and then with styrene, hydrozirconation of styrene is the major course of the reaction (eq 2). All of these reactions are indeed Zr-promoted, since none proceeds in the absence of Cl_2ZrCp_2 under otherwise comparable conditions.



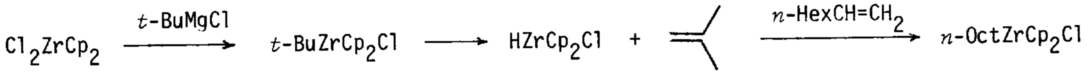
(1)



(2)

With the hope of developing a convenient "one-pot" procedure for hydrozirconation, we treated a 1:1 mixture of 1-octene and Cl_2ZrCp_2 with various metal hydrides and alkylmetals. As indicated by the results summarized in Table 1, the course of reaction heavily depends on both the hydride source and solvents. Thus, $NaAlH_2(OCH_2CH_2OCH_3)_2$[2b] is a satisfactory reagent in benzene-ether, but $LiAlH_4$[3] is not, as judged by the yield of 1-iodooctane obtained after iodinolysis. However, $LiAlH_4$ is satisfactory in tetrahydrofuran (THF). Of the alkylmetals tested in this study only *t*-BuMgCl provided, after iodinolysis, 1-iodooctane in satisfactory yield. The competitive formation of *n*-octane in cases where $LiBH(Bu\text{-}s)_3$, *t*-BuLi, or *i*-BuMgCl is used may readily be accounted for in terms of the formation of *n*-$OctZrCp_2H$ followed by its reductive elimination.[4] Unlike $LiBH(Bu\text{-}s)_3$, *t*-BuLi, or *i*-BuMgCl, *t*-BuMgCl presumably is sufficiently unreactive toward *n*-$OctZrCp_2Cl$ so that its conversion into *n*-$OctZrCp_2H$ is much slower than the desired hydrozirconation. On the other hand, $HSn(Bu\text{-}s)_3$ and *t*-BuZnCl failed to induce even the desired hydrozirconation.

That the reaction of 1-octene with *t*-BuMgCl and Cl_2ZrCp_2 produces *n*-$OctZrCp_2Cl$ is indicated by a ^1H NMR singlet at 6.15 ppm[5] superimposable with that observed in the reaction of 1-octene with $HZrCp_2Cl$. The yield of *n*-$OctZrCp_2Cl$ determined by ^1H NMR using toluene as an internal standard is 86%. Hydrozirconation using *t*-BuMgCl and Cl_2ZrCp_2 may proceed by the transmetallation-elimination-hydrozirconation mechanism shown in eq 3. Alternatively, 1-octene may react directly with *t*-$BuZrCp_2Cl$ via a six-centered transition state, as shown in eq 4.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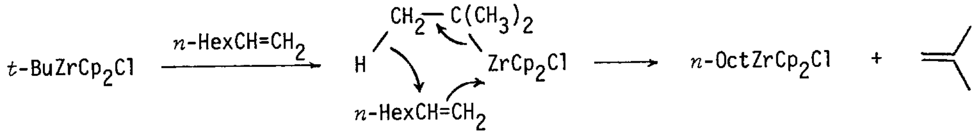
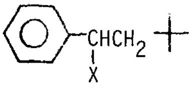
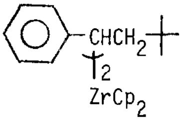

(4)

The *t*-BuMgCl-Cl_2ZrCp_2 procedure has also been applied to the conversion of 4-penten-1-ol and 4-vinyl-1-cyclohexene into 5-iodo-1-pentanol (56%) and 4-(2'-iodoethyl)-1-cyclohexene (81%), respectively, in isolated yields indicated in parentheses. The following procedure for the preparation of 4-(2'-iodoethyl)-1-cyclohexene is representative. 4-Vinyl-1-cyclohexene (0.22 g, 2.0 mmol) and Cl_2ZrCp_2 (0.58 g, 2.0 mmol) in 5 mL of benzene were treated with 2.18 *M* *t*-BuMgCl (1.0 mL, 2.2 mmol) in ether at room temperature. After stirring overnight at room temperature, the reaction mixture was treated with 0.65 g (2.5 mmol) of iodine dissolved in benzene. The mixture was treated with aqueous sodium sulfite and pentane. The organic layer was washed with aqueous NaCl, dried over $MgSO_4$, and distilled to give 0.38 g (81%) of 4-(2'-iodoethyl)-1-cyclohexene.[6] Since *t*-BuMgCl is obtainable from Mg and *t*-BuCl, which in turn is obtainable from isobutylene and HCl, a combination of HCl and Mg acts as an economical hydride source. In the conversion of an alkene into the corresponding alkenyl iodide, not only isobutylene but also X_2ZrCp_2 (X = Cl and/or I) are recyclable.

The reaction of conjugated alkenes with *t*-BuMgCl-Cl_2ZrCp_2 under the same conditions took an entirely different course. Thus, for example, styrene gave, after protonolysis, 1-phenyl-3,3-dimethylbutane (**1a**) in 86% yield along with only 9% of ethylbenzene. Deuterolysis of the mixture with D_2O led to an essentially 100% incorporation of deuterium in the benzylic position giving **1b**. The product before quenching must therefore be an organometal represented by **1c**. ^{1}H NMR examination of the reaction mixture before quenching reveals the presence of three sharp singlets at δ 5.95, 6.20, and 6.41 ppm. We tentatively conclude on the basis of the above observations that the three signals correspond to **2**, **1d**, and Cl_2ZrCp_2, respectively. The integrations of the Cp signals relative to that for the methyl group of toluene added as an internal standard indicate that the yields of these species are 25, 46,and 10%,respectively. Treatment of the reaction mixture with iodine produced, after a standard workup, an 88% yield of (*E*)-β-*t*-butylstyrene (**3**) along with a small amount (7%) of 2-iodoethylbenzene. It is likely that **1e** was the initial product, even though no attempts have been made to isolate and/or identify **1e**. The corresponding reaction of *s*-BuMgCl under otherwise the same conditions produced, after iodinolysis, 2-iodoethylbenzene in 66% yield, with 25% of styrene still remaining unreacted. Thus, the scope of the novel carbometallation reaction appears to be limited to tertiary alkylmagnesium derivatives. The *t*-BuMgCl-Cl_2ZrCp_2 reagent system also reacts with 1,3-butadiene and isoprene to produce, after protonolysis, 5,5-dimethyl-1-hexene (88%) and a 3:2 mixture of 2,5,5-trimethyl-1-hexene and 3,5,5-trimethyl-1-hexene (55% combined), respectively, in yields indicated in parentheses. The apparent requirements for conjugated alkenes and tertiary alkylmagnesium derivatives as well as the observed regiochemistry suggest that the carbometallation reaction may be a free radical process. Although this point remains to be clarified, it is certain that the reaction does not proceed in the absence of Cl_2ZrCp_2 under otherwise comparable conditions. When Cl_2ZrCp_2 was treated first with *t*-BuMgCl in benzene in the absence of free ether (15 min, room temp) and then with styrene (18 h, room temp), ethylbenzene was obtained in ca. 60% yield after protonolysis along with only a trace of **1a**. Iodinolysis of the reaction mixture produced a 9:1 mixture of 2- and 1-iodoethylbenzenes in 55% yield. This regiochemistry is in sharp contrast with that producing benzylmetal species observed in the Cl_2TiCp_2-catalyzed hydromagnesation of styrene with PrMgBr.[7d]



1 **a**: X = H, **b**: X = D, **c**: X = M
d: X = $ZrCp_2Cl$, **e**: X = I



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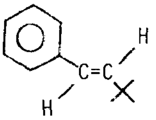

3

Unlike the Ti-catalyzed hydromagnesation[7] or the Zr-catalyzed hydroalumination,[8] the reaction of alkenes with Grignard reagents and Cl_2ZrCp_2 is not catalytic in Zr. We believe that the transition metal-catalyzed hydrometallation requires two transmetallation steps proceeding in the mutually opposite directions and that such a catalytic system requires a pair of metals whose electronegativities are close to each other. The Mg-Ti and Al-Zr combinations evidently satisfy the above requirement, whereas the experimental data presented herein indicate that the Mg-Zr system is incapable of transferring an alkyl group from Zr to Mg.

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Table I. Treatment of a 1:1 Mixture of 1-Octene and Zirconocene Dichloride with a Metal Hydride or an Alkylmetal[a]

Metal hydride or alkylmetal	Time, h	1-Octene, %	Product yield,[b] %	
			n-Octane	*n*-OctI
$LiAlH_4$[c]	1	20	24	29
$LiAlH_4$[c,d]	1	8	5	84
$NaAlH_2(OCH_2CH_2OCH_3)_2$[e]	1	trace	trace	93
LiBH(Bu-*s*)$_3$	1	9	18	69
HSn(Bu-*n*)$_3$	3	95	trace	trace
t-BuLi	1	15	29	49
t-BuMgCl	18[f]	trace	trace	93
i-BuMgCl	1	45	43	6
t-BuZnCl	3	80	trace	trace

[a] Unless otherwise mentioned, the reaction was carried out at 25°C in benzene-ether using 1 mol equiv of the reagent. [b] The reaction mixture was treated with iodine and analyzed by GLC (SE-30). [c] One quarter molar equiv was used. [d] The reaction was carried out in THF. [e] One half molar equiv was used. [f] The minimum required time was not established.

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