Short Communication

Reactions with Three Hydrozirconiation Reagents

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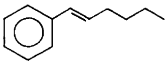
Annby, U., Gronowitz, S. and Hallberg, A., 1990. Reactions with Three Hydrozirconiation Reagents. – Acta Chem. Scand. 44: 862–863.

We have, for some years, been studying the process of hydrozirconiation.[1,2] Unlike internal alkenes which, with $Cp_2Zr(H)Cl$, give terminal σ-alkylzirconium compounds, the internally unsaturated substrates studied by us, e.g. amines,[3] ethers,[4] oxazolines,[5,6] oleyl alcohol[7] and aromatic olefins[8,9] produce mixtures of zirconium intermediates or products derived from them. Furthermore, some of these olefins react very sluggishly. We are therefore interested in improving the usefulness of the reaction.

To enhance the reactivity and improve the regioselectivity with respect to terminal alkylzirconiums, we decided to prepare modified zirconocene dihalides.[10] These were treated with 0.5 equiv. of $NaAlH_2(OCH_2CH_2OCH_3)_2$ (Red-Al) for the *in situ* generation of the corresponding monohydrides. Among those tested, only the $Cp^*CpZrCl_2$/Red-Al system ($Cp^* = \eta^5\text{-}C_5Me_5$) proved to be useful. It gave a clear solution with toluene and reacted much faster than $Cp_2Zr(H)Cl$ with (*Z*)- or (*E*)-5-decene to give 1-deuteriodecane after deuteriolysis.[10] The rate enhancement is probably due to the formation of very soluble zirconium hydride(s).

In a recent publication by Erker *et al.*, the preparation of $(MeCp)_2Zr(H)Cl$ is described.[11] It was found that this hydride reacts 6–7 times faster with 1-hexene or acetophenone, as compared with $Cp_2Zr(H)Cl$. The greater solubility of the bis(methylcyclopentadienyl)zirconium hydridochloride probably caused the rate enhancement.[11] These results prompted us to compare the reactivity of $Cp_2Zr(H)Cl$, $(MeCp)_2Zr(H)Cl$ and '$Cp^*CpZr(H)Cl$' towards some of the substrates previously used by us as model compounds. 1-Phenyl-1-hexene (**1**) and 4,4-dimethyl-2-[(*Z*)-3-heptenyl]-4,5-dihydro-oxazole (**2**) were chosen. This comparison was also made with the hope of improving the yields of terminal alkylzirconium compounds.



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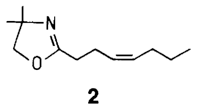

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Compound **1** reacts slowly with $Cp_2Zr(H)Cl$ at room temperature and gives α-deuteriated phenylhexane almost exclusively after quenching with deuterium oxide. The ω-selectivity may be improved simply by raising the temperature, but this results in a lower yield of alkylzirconium intermediates owing to competitive hydrogenation. Consequently, the degree of deuteriation also decreases.[8] When the oxazoline **2** is treated in the same way, a mixture of α-, β- and ω-deuterium isomers of the heptanyloxazoline is formed.[5,6]

The hydrozirconiations of 1-phenyl-1-hexene were performed under argon in anhydrous 1,4-dioxane. The conditions and results are given in Table 1. The $(MeCp)_2Zr(H)Cl$ reagent indeed reacted much faster than $Cp_2Zr(H)Cl$ at room temperature. Phenylhexane was formed in 80–85 % yield after only 2 h, as compared with 10–15 % when $Cp_2Zr(H)Cl$ was used. The ω-selectivity using $MeCp_2Zr(H)Cl$ was not improved. The $Cp^*CpZrCl_2$/Red-Al system, however, showed excellent terminal selectivity at 45 °C, with a satisfactory degree of deuteriation (71 %). On the other hand, the yield of deuteriated phenylhexane decreased ($\leq$ 50 %) with $Cp_2Zr(H)Cl$ under the conditions needed to achieve comparable ω-selectivity.[8]

We then turned to the oxazoline **2**. The substrate was treated with $Cp_2Zr(H)Cl$, $(MeCp)_2Zr(H)Cl$ (both isolated) and with the $Cp^*CpZrCl_2$/Red-Al system at 40 °C for 20–24 h in 1,4-dioxane. Previously, these conditions led to complete reaction when **2** was treated with Cp_2ZrCl_2/Red-Al.[6] Higher temperatures were not used since side reactions occur.[8,12–14] Although **2** was converted into the saturated analogue, we have so far only observed low to moderate terminal selectivity, irrespective of which zirconium hydride is used; various amounts of α- and β-deuterium isomers were also present in the deuteriated fractions upon deuteriolysis. We have previously suggested that the formation of α- and β-isomers is due to stabilisation of the corresponding alkylzirconium intermediates by metal–heteroatom interactions.[5,12,15] Such interactions may also be the reason why 1- and 2-deuterio amines and 3-deuteriostearyl alcohol are observed, in contrast with internally deute-

Table 1. Hydrozirconiation of 1-phenyl-1-hexene (**1**) with subsequent deuteriolysis.[a]

Hydrozirconiation reagent	[Zr]-H/ equiv.	Temperature/°C (time/h)	Yield (%)[b] of deuteriated phenylhexane	Deuterium distribution (%)[c]	
				α-D	ω-D
$Cp_2Zr(H)Cl$	2.0	20–25 (2)	– (10–15)	–	–
$(MeCp)_2Zr(H)Cl$[d]	1.2	20–25 (2)	– (80–85)	–	–
$Cp_2Zr(H)Cl$[e]	1.1–1.2	20–25 (20–24)	65 (68)	90–100	0–10[f]
$(MeCp)_2Zr(H)Cl$[d]	1.2	20–25 (21)	– (85–90)	89	11
$Cp^*CpZr(H)Cl$[g]	1.3	20–25 (20)	22 (28)	50	50
$Cp_2Zr(H)Cl$[e]	2.0	45 (24)	75 (85)	50	50[f]
$(MeCp)_2Zr(H)Cl$[d]	2.0	45 (21)	77 (96)	42	58
$Cp^*CpZr(H)Cl$[g]	2.0	45 (20)	68 (96)	5	95
$Cp_2Zr(H)Cl$[e]	2.0	60 (22)	$\leq$50 ($\leq$80)	10	90

[a] Anhydrous 1,4-dioxane was used as the solvent. For further experimental details, see Ref. 8. [b] Determined by combination of GLC and MS analyses as previously described.[8] Figures in parentheses are total yields (GLC) of phenylhexane. [c] Determined by ^2H NMR ($CHCl_3$) analysis as previously described.[8] [d] Prepared and isolated according to the literature.[11] [e] Results taken from Ref. 8. The hydride was generated *in situ*. [f] Less than 5 % incorporated deuterium was found at positions other than α or ω. [g] Generated *in situ*.

riated decane, after hydrozirconiation/deuteriolysis of unsaturated amines, oleyl alcohol and 5-decenes.[3,7,22] The C–O bond is cleaved when unsaturated ethers are treated with $Cp_2Zr(H)Cl$[4] and $(MeCp)_2Zr(H)Cl$.[11]

Acknowledgements. Grants from the Board of Technical Development and from the Swedish Natural Research Council to S.G. and A.H. are gratefully acknowledged. We also thank *Karlshamns AB* for financial support.

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Received March 30, 1990.