Hydrosilylation Catalysed by Organoneodymium Complexes

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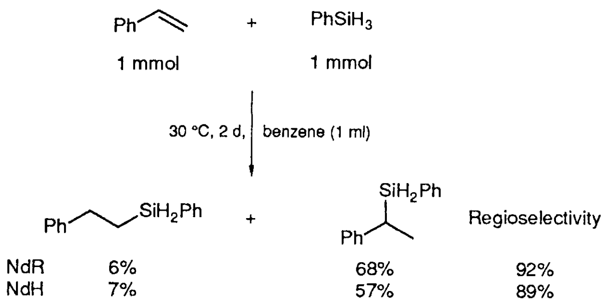
$[(C_5Me_5)_2NdH]_2$ and $(C_5Me_5)_2NdCH(SiMe_3)_2$ effectively catalyse the hydrosilylation of alkenes with di- or tri-hydrosilanes at 30 to 80 °C; the regioselectivity in the reaction of styrene depends to a considerable extent on the substituents of the silanes.

The application of organolanthanide complexes to catalysis is an interesting and challenging subject in view of their unique reactivities, which have been extensively reported in the last decade.[1] The abundance and the low price of lanthanide elements as compared with noble metals are also attractive. However, examples of organolanthanide-catalysed reactions are still limited.[2] We now report the first successful utilization of organoneodymium complexes as a catalyst in hydrosilylation of alkenes.

The reaction was carried out in the presence of $[(C_5Me_5)_2NdH]_2$,[2a] $(C_5Me_5)_2NdCH(SiMe_3)_2$[2a] or $[(C_5Me_5)_2NdCl_2]Li(ether)_2$[3] (abbreviated as NdH, NdR and NdCl, respectively). In a typical experiment, benzene solutions of $PhSiH_3$ (0.25 mmol in 2 cm^3) and of styrene (0.25 mmol in 2 cm^3) were added to the catalyst (0.01 mmol). The mixture was heated at 80 °C for 48 h, and the yields were evaluated by GC using an internal standard. The results are summarized in Table 1. In the reactions of styrene with phenysilane, the hydro and alkyl complexes exhibited high catalytic activities to give the branched product as the major isomer while the chloro complex was inactive. The reaction can be carried out even at a lower temperature to give high regioselectivity (Scheme 1). Interestingly, when a slight excess of $PhSiH_3$ was used, the completion of the hydrosilylation was easily visualized by the colour change of the reaction mixture from brown-orange to bright green. Considerable amounts of ethylbenzene and Ph_2SiH_2 were formed as byproducts. The existence of a small amount of a trisilane, $PhSiH_2SiPhHSiH_2Ph$, and a double silylated product, $PhCH(SiH_2Ph)CH_2SiH_2Ph$, was also revealed by high resolution GC–MS.[4] Although it may be premature to discuss the reaction mechanism, possible active species in the hydrosilylation are $(C_5Me_5)_2NdH$ and $(C_5Me_5)_2NdSiH_2Ph$. The insertion of styrene to these complexes followed by the reaction with $PhSiH_3$ may yield hydrosilylation products.[2c]

In contrast with the reactions with phenylsilane, styrene, when treated with hexylsilane, gave the linear isomer as the major product. Even higher linear selectivity was observed in the reactions with methylphenylsilane. However, styrene did not react with dimethylphenylsilane.

Hydrosilylation of styrene usually gives a linear silylation product irrespective of the silane structure.[5] To the best of our knowledge, the only exceptions in which high selectivity for branched products is observed are the reactions with trichlorosilane.[6] With regard to hydrosilylation with organotrihydrosilanes or diorganodihydrosilanes,[7] examples are still rare so that we cannot find any general trend. Nevertheless, in the only known reaction of styrene with phenylsilane effected in the presence of H_2PtCl_6, a linear product was exclusively formed.[8] In view of these precedents, the following conclusions can be drawn from the foregoing results of the neodymium-catalysed reactions of styrene; (*i*) the branched selectivity observed with phenylsilane is quite unusual, and (*ii*) the regioselectivity is exceptionally sensitive to the nature of substituents bound to silicon.



Scheme 1

Table 1 Neodymium-catalysed hydrosilylation of alkenes[a]

Alkene	Silane	Cat.[b]	Hydrosilylation products (%)[c] Linear	Branched	Regioselectivity[d] (%)
Styrene	$PhSiH_3$	NdH	27	60	69
Styrene	$PhSiH_3$	NdR	16	72	82
Styrene	$PhSiH_3$	NdCl	<1	<1	—
Styrene	n-C_6H_{13}-SiH_3	NdH	49	15	77
Styrene	n-C_6H_{13}-SiH_3	NdR	56	11	84
Styrene	$PhMeSiH_2$	NdH	75	7	91
Styrene	$PhMeSiH_2$	NdR	33	5	87
Styrene	$PhMe_2SiH$	NdH	n.o.	n.o.	—
Dec-1-ene	$PhSiH_3$	NdH	73	n.o.	~100
Dec-1-ene	$PhSiH_3$	NdR	53	n.o.	~100
Dec-1-ene	n-C_6H_{13}-SiH_3	NdH	87	n.o.	~100
Dec-1-ene	n-C_6H_{13}-SiH_3	NdR	89	n.o.	~100
Dec-1-ene	$PhMeSiH_2$	NdH	45	n.o.	~100
Dec-1-ene	$PhMeSiH_2$	NdR	43	n.o.	~100
Hept-2-ene	$PhSiH_3$	NdH	19	n.o.	~100

[a] *Reaction conditions*: Alkene (0.25 mmol), silane (0.25 mmol), catalyst (0.01 mmol) benzene (4 cm^3), 80 °C, 2 days. [b] NdH: $[(C_5Me_5)_2NdH]_2$. NdR: $(C_5Me_5)_2NdCH(SiMe_3)_2$. NdCl: $[(C_5Me_5)_2NdCl_2]Li(ether)_2$. [c] Yields were determined by GLC using an internal standard. n.o. = not observed. [d] (Major isomer/total of hydrosilylation products) × 100.

The hydrosilylation of dec-1-ene took place in moderate to excellent yields and the linear isomers were obtained with nearly 100% regioselectivities irrespective of the nature of silanes. A linear product was also formed in the reaction of hept-2-ene. This suggests that alkylneodymium intermediates isomerize rapidly. The formation of the linear product is not so surprising since it is also a common feature of hydrosilylation of internal alkenes in the presence of transition metal complex catalysts.[5]

In summary, hydrosilylation of alkenes with polyhydrosilanes is catalysed by organoneodymium complexes in good yields and with high regioselectivity. Since the silylated products still have Si–H bonds, they can be easily transformed further: *e.g.* oxidation to alcohols with H_2O_2.[9]

Received, 30th August 1990; Com. 0/03953E

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