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Preliminary Communication

REGIOSELECTIVE HYDROSILYLATION OF ISOPRENE CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM

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Summary

Hydrosilylation of isoprene catalyzed by tris(triphenylphosphine)chlororhodium was found to proceed smoothly at 80-130°C to give 3-methylbuten-2-ylsilane (major) and 2-methylbuten-2-ylsilane (minor). A possible mechanism of the reaction is proposed.

In the preceding paper, we have reported that the hydrosilylation of isoprene catalyzed by the phosphine-palladium complex was highly regioselective and stereoselective, giving (Z)-2-methylbuten-2-ylsilane (II) exclusively. We have found that hydrosilylation of isoprene catalyzed by tris(triphenylphosphine)chlororhodium shows an unusual regioselectivity, in most cases affording 3-methylbuten-2-ylsilane (I) as major product in addition to lesser amounts of (Z)-2-methylbuten-2-ylsilane (II). Thus, the regioselectivity of the reaction is opposite to that observed in isoprene hydrosilylation catalyzed by other transition metal complexes [1].

Typically, a mixture of dimethylphenylsilane (33 mmol), isoprene (30 mmol) and tris(triphenylphosphine)chlororhodium (20 mg, (0.022 mmol) was degassed and sealed in a glass tube, and was heated at 80°C for 6 hr. GLC analysis (3% OV-17) of the reaction mixture revealed that 3-methylbuten-2-yldimethylphenylsilane and 2-methylbuten-2-yldimethylphenylsilane were produced in 71% and 27% yield,

respectively. Distillation of the reaction mixture afforded the combined methylbutenylsilanes (bp. 135°C/30 mmHg) in 85% yield.

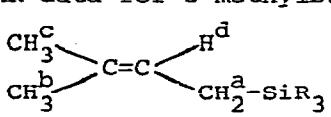
Results obtained with several hydrosilanes are summarized in Table 1, and NMR spectral data for 3-methylbuten-2-ylsilanes (I) are listed in Table 2. For the assignment of the two methyl resonances of 3-methylbuten-2-ylsilane (I), a nuclear Overhauser effect (NOE) measurement was performed on 3-methylbuten-2-yltrimethylsilane‡

Table 1. Hydrosilylation of isoprene catalyzed by tris(triphenylphosphine)chlororhodium

Hydrosilane	Conditions	Product Ratio[a]		B.P.	Yield[a]
		I	II	(°C/mmHg)	(%)
$EtMe_2SiH$	80°, 2 hr	56	44	150/760	90
$(EtO)_3SiH$	110°, 2 hr	71	29	115/42	82
$ClMe_2SiH$	130°, 15 hr	69	31	127/760	60
$PhMe_2SiH$	80°, 2 hr	72	28	135/30	98

[a] Estimated by GLC analysis

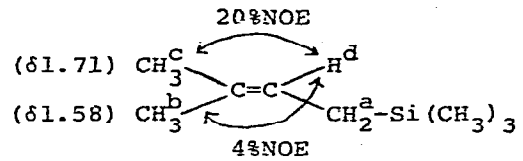
Table 2. NMR data for 3-methylbuten-2-ylsilanes



Silyl Group	H^a	H^b	H^c	H^d	Solvent
Me_3Si	1.39	1.58	1.71	5.15	$CDCl_3$
$EtMe_2Si$	1.39	1.57	1.70	5.14	$CDCl_3$
$(EtO)_3Si$	1.38	1.54	1.65	5.02	CCl_4
$ClMe_2Si$	1.69	1.59	1.73	5.16	CCl_4-$CDCl_3$
$PhMe_2Si$	1.62	1.49	1.67	5.15	$CDCl_3$

‡ 3-Methylbuten-2-yltrimethylsilane was prepared by the reaction of 3-methylbuten-2-yl magnesium chloride with trimethylchlorosilane in THF.

by irradiating the two methyls. Relatively large NOE (+23%) was observed in the integration of H^d proton on irradiating the methyl protons in the lower field (δ1.71), whereas only 4% NOE (+) was observed by the irradiation of the other methyl protons (δ1.58). Accordingly, it was confirmed that the methyl signal at lower field (δ1.71) is due to the methyl (H^c) which is cis to the olefinic proton (H^d).



It has been generally accepted that a hydride shift from oxidative addition product, i.e., silyl-transition metal hydride, to coordinated olefin is the first step in the hydrosilylation of olefins and that subsequent silicon migration gives the hydrosilylated product [2]. In fact, the results of the hydrosilylation of isoprene catalyzed by the palladium complex which was reported in the preceding paper can be explained in accordance with this mechanism. However, the results of the rhodium complex-catalyzed reaction cannot be accomodated by this mechanism since the regioselectivity is opposite to that observed with other catalytic systems. Thus, we propose a possible mechanism for the present reaction as shown in Scheme 1. The proposed mechanism involves a regioselective silicon migration from the oxidative addition product (III) to the coordinated isoprene to produce the π-allylic rhodium hydride complexes (IV) and (V).[$] The regioselectivity of this step may be markedly dependent upon the steric and electronic nature of the

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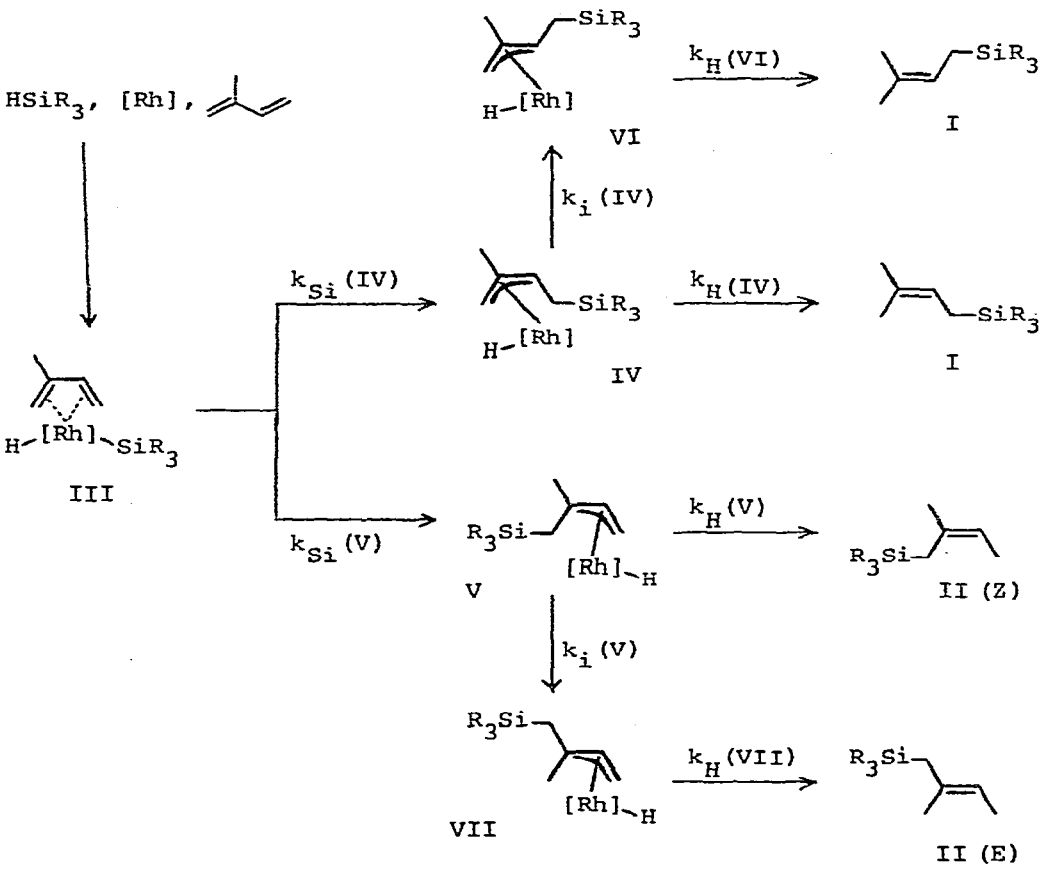
[$] A similar mechanism was also proposed by Rejhon and Hetflejš in the hydrosilylation of butadiene catalyzed by rhodium complexes [3]. As for the hydrosilylation of alkyne and α,β-unsaturated ester, we proposed an initial silyl migration mechanism [4].

silicon-rhodium bond. Succeeding hydride shifts from the intermediates (V) and (IV) afford 3-methylbuten-2-ylsilane (I) and (Z)-2-methylbuten-2-ylsilane (II), respectively. Since the isomerization of intermediate (V) [5] was found to be negligible, i.e., $k_H(V) >> k_i(V)$, the isomerization of intermediate (IV) also may not have occurred. The stereochemistry of 2-methylbuten-2-ylsilanes, thus obtained, was determined on the basis of NMR spectra in a manner similar to that described in the preceding paper.



Scheme 1.

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