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REGIOSELECTIVE HYDROSILYLATION OF 1,3-DIENES CATALYZED BY PHOSPHINE COMPLEXES OF PALLADIUM AND RHODIUM *

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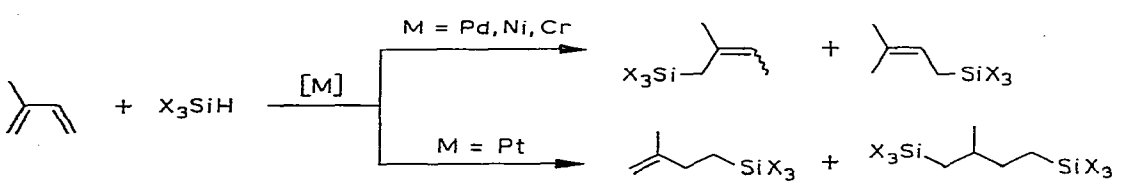
Summary

The hydrosilylation of isoprene catalyzed by a palladium complex using chlorohydrosilanes proceeded via 1,4-addition to give *Z*-2-methylbuten-2-yl-silanes exclusively, the stereochemistry of which was determined on the basis of NMR spectroscopy observing the nuclear Overhauser effect (NOE). The result clearly demonstrates that the reaction is highly regioselective and stereoselective. On the other hand, the reaction catalyzed by a rhodium complex afforded 3-methyl-buten-2-ylsilane as major product accompanied by *Z*-2-methylbuten-2-ylsilane, i.e., the regioselectivity of the reaction is opposite to that of other catalyst systems. Similar regioselectivities were observed in the hydrosilylation of myrcene and ocimene, although a considerable substituent effect was apparent, especially in the case of ocimene. Possible mechanisms of these reactions are proposed.

Introduction

Recently, several reports have been published on the hydrosilylation of isoprene catalyzed by transition metal complexes [1]. The reaction has been shown to proceed in a manner of 1,4-addition to give 2-methylbuten-2-ylsilane as major product except for the case of the platinum complex-catalyzed reaction, which affords 1,2-adduct predominantly [2,3].



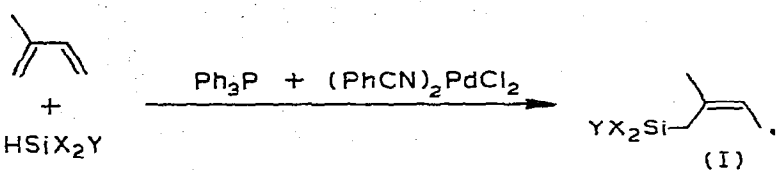
* This work was presented on the 8th International Conference on Organometallic Chemistry, Kyoto, September, 1977, Abstract No. 4B21.

Although the regiospecificity of the 1,4-addition was demonstrated in these reports, less attention has been drawn to the stereochemistry of the reaction. We have found that the hydrosilylation of isoprene, catalyzed by phosphine complexes of palladium and rhodium, proceeds regioselectively and stereoselectively to afford *Z*-2-methylbuten-2-ylsilane and/or 3-methylbuten-2-ylsilane, and have reported briefly and preliminary results [4]. We bring here a full account of our research on the regioselective hydrosilylation of isoprene, myrcene and ocimene, catalyzed by a palladium complex which was prepared in situ from triphenylphosphine and bis(benzonitrile)palladium dichloride, and by tris-(triphenylphosphine)rhodium chloride.

Results and discussion

Hydrosilylation of isoprene catalyzed by the phosphinepalladium complex

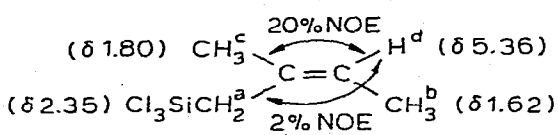
The hydrosilylation of isoprene catalyzed by a phosphinepalladium complex prepared in situ from triphenylphosphine and bis(benzonitrile)palladium dichloride was found to be regioselective and stereoselective, giving *Z*-2-methylbuten-2-ylsilane (I) exclusively: Chlorohydrosilanes were shown to be highly reactive to afford I in 90—100% yield while other hydrosilanes such as triethoxysilane, phenyldimethylsilane and triethylsilane did not add to isoprene at all under similar conditions.



(a) X = Y = Cl; (b) X = Cl, Y = Me; (c) X = Me, Y = Cl

GLC analysis and NMR spectra of these adducts clearly indicated that the reaction is extremely stereoselective, i.e., the adduct is not a mixture of *Z* and *E* isomers, but consists of either the *Z* or the *E* isomer. The NMR spectral data for 2-methyl-buten-2-ylsilanes are listed in Table 1.

In order to elucidate the stereochemistry of 2-methylbuten-2-ylsilanes thus obtained, we measured the nuclear Overhauser effect (NOE) [5] observed in the integration of the olefin proton H^d (δ 5.36 ppm, quartet *, *J* 7 Hz) by irradiating the methyl protons H^c (δ 1.80 ppm singlet *) or the methylene protons H^a (δ 2.35 ppm, singlet) of 2-methylbuten-2-yltrichlorosilane (Ia).



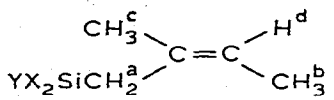
(Ia)

A relatively large NOE, 20% increase, was observed by irradiation of H^c pro-

* Small splittings arised from long range couplings are observed.

TABLE 1

NMR DATA (δ (PPM) TMS) FOR *Z*-2-METHYLBUTEN-2-YLSILANES (I)



Silyl group		H^a	H^b	H^c	H^d	Solvent
a	Cl_3Si	2.35	1.62	1.80	5.36	CCl_4
b	Cl_2MeSi	2.12	1.59	1.80	5.30	CCl_4
c	$ClMe_2Si$	1.82	1.53	1.72	5.18	CCl_4
g	Me_3Si [a]	1.51	1.47	1.65	5.08	$CDCl_3$

[a] Ig was prepared from Ib by treatment with MeMgBr in ether, for comparison.

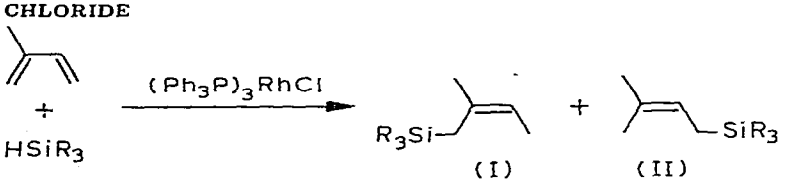
tons, while only +2% NOE was observed in the case of H^a protons. Therefore, it is concluded without ambiguity that the adduct is the *Z*-isomer. As Table 1 shows, the methyl (H^b) appears as doublet at higher field than the methyl (H^c) does. This fact implies a certain shielding effect of the silylmethyl group on the *cis*-methyl protons H^b.

Hydrosilylation of isoprene catalyzed by tris(triphenylphosphine)rhodium chloride

The hydrosilylation of isoprene catalyzed by tris(triphenylphosphine)rhodium chloride showed an unusual regioselectivity, in most cases affording 3-methylbuten-2-ylsilane (II) as major product in addition to lesser amounts of *Z*-2-methylbuten-2-ylsilane (I). Thus, the regioselectivity of the reaction is opposite to that observed in isoprene hydrosilylation catalyzed by other transition metal complexes [1]. Results obtained with several hydrosilanes are summarized in Table 2, and NMR spectral data for 3-methylbuten-2-ylsilane (II) are listed in Table 3. For the assignment of the two methyl resonances of II, a NOE measure-

TABLE 2

HYDROSILYLATION OF ISOPRENE CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE

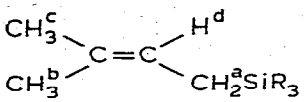


Hydrosilane		Conditions	Product ratio [a]		Yield (%) [a]
			I	II	
c	$ClMe_2SiH$	130°C/15 h	31	69	60
d	$(EtO)_3SiH$	110°C/2 h	29	71	82
e	$PhMe_2SiH$	80°C/2 h	28	72	98
f	$EtMe_2SiH$	80°C/2 h	44	56	90

[a] Estimated by GLC analysis.

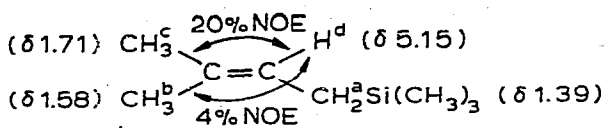
TABLE 3

NMR DATA (δ (PPM) TMS) FOR 3-METHYLBUTEN-2-YLSILANES (II)



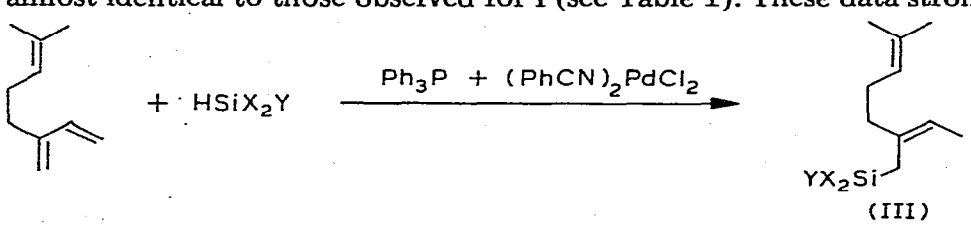
Silyl group		H^a	H^b	H^c	H^d	Solvent
c	$ClMe_2Si$	1.69	1.59	1.73	5.16	$CCl_4/CDCl_3$
d	$(EtO)_3Si$	1.38	1.54	1.65	5.02	CCl_4
e	$PhMe_2Si$	1.62	1.49	1.67	5.15	$CDCl_3$
f	$EtMe_2Si$	1.39	1.57	1.70	5.14	$CDCl_3$
g	Me_3Si	1.39	1.58	1.71	5.15	$CDCl_3$
		1.38	1.56	1.70	5.10	CCl_4

ment was performed on 3-methylbuten-2-yltrimethylsilane (IIg) by irradiating the two methyls. This compound was prepared by the reaction of 3-methylbuten-2-yl magnesium chloride with trimethylchlorosilane in tetrahydrofuran. A relatively large NOE (+23%) was observed in the integration of H^d proton on irradiating the methyl protons in the lower field (δ 1.71 ppm), whereas only 4% NOE (+) was observed by the irradiation of the other methyl protons (δ 1.58 ppm). Accordingly, it was elucidated that the methyl signal at lower field (δ 1.71 ppm) is due to the methyl (H^c) which is *cis* to the olefinic proton (H^d). This result confirms the aforementioned shielding effect of the silylmethyl group on the *cis*-methyl protons.



Hydrosilylation of myrcene and ocimene catalyzed by the palladium complex

Next, we performed the regioselective hydrosilylation of isoprene dimers using the palladium complex as catalyst. The hydrosilylation of myrcene (7-methyl-3-methyleneocta-1,6-diene), one of the isoprene dimers, catalyzed by the palladium complex using chlorohydrosilanes was found to proceed in a manner similar to that of isoprene to give 2-methyl-6-silylmethylocta-2,6-diene (III) as sole product in 81—90% yield. Triethoxysilane was less reactive, but could also add to myrcene under similar conditions to afford IIId in relatively low yield (29%). The stereochemistry of the buten-2-ylsilane moiety of III was established on the basis of NMR spectra. NMR spectral data for III are listed in Table 4. As Table 4 shows, the chemical shift of H^a, H^b and H^d protons are almost identical to those observed for I (see Table 1). These data strongly indi-

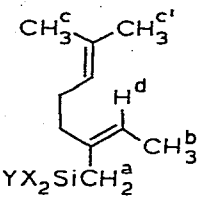


(III)

(a) X = Y = Cl; (b) X = Cl, Y = Me; (c) X = Me, Y = Cl; (d) X = Y = EtO

TABLE 4

NMR DATA (δ (PPM) TMS) FOR THE ADDUCT III OBTAINED IN THE HYDROSILYLATION OF MYRCENE CATALYZED BY THE PALLADIUM COMPLEX



Silyl group		H^a	H^b	H^c	$H^{c'}$	H^d	Solvent
a	Cl_3Si	2.35	1.61	1.57	1.65	5.37	$CDCl_3$
b	Cl_2MeSi	2.10	1.59	1.58	1.66	5.28	CCl_4
c	$ClMe_2Si$	1.81	1.53	1.58	1.65	5.22	CCl_4
d	$(EtO)_3Si$	1.56	1.56	1.58	1.65	5.11	$CDCl_3$
f	$EtMe_2Si$ [b]	1.51	1.50	1.59	1.67	5.10	$CDCl_3$
g	Me_3Si [b]	1.50	1.49	1.58	1.66	5.09	$CDCl_3$

[a] H^b appears as doublet (J 7 Hz) and H^d does as quartet (J 7 Hz). [b] IIIf and IIIg were prepared from IIIc and IIIb by treatment with EtMgBr and MeMgBr, respectively, in ether for comparison.

cate that the aforementioned shielding effect of the silyl-methyl group on *cis*-methyl protons is operative also in this case, and thus, it is concluded that the stereochemistry of these 2-homoprenylbuten-2-ylsilanes (III) is *Z*.

The corresponding reaction of ocimene (3,7-dimethylocta-1,3,6-triene), another isoprene dimer, under similar conditions proceeded in somewhat different fashion from that of isoprene and myrcene. For example, the reaction of ocimene with trichlorosilane catalyzed by the palladium complex afforded a mixture of 2,6-dimethyl-5-trichlorosilylocta-2,6-diene (IVa) and 2,6-dimethyl-7-trichlorosilylocta-2,5-diene (Va). The latter is an unusual 1,2-adduct since the usual 1,2-addition affords the product having the silyl group at the terminal position [3,6]. These adducts, IV and V, may be produced via a common π-allylic intermediate. The mechanism will be discussed later.

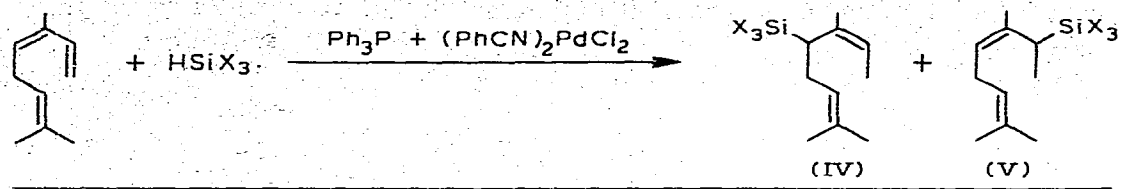
As Table 5 shows, the yield of the reaction is markedly dependent upon the structure of the hydrosilane employed, and the reactivity of hydrosilane seems to be affected by the number of chlorine atoms on silicon. Such a trend is not observed in the case of isoprene and myrcene. As for methyldichlorosilane and dimethylchlorosilane, the reaction proceeded in a manner of 1,4-addition to afford the adduct IV exclusively. The sterochemistry of the buten-2-ylsilane moiety of IV has not been elucidated as yet, but we believe that it is *Z* on account of the results obtained in the reaction of isoprene and myrcene. According to GLC analysis, the adducts IVa and Va contain little amounts of geometrical isomers.

Hydrosilylation of myrcene and ocimene catalyzed by tris(triphenylphosphine)-rhodium chloride

The hydrosilylation of myrcene catalyzed by the rhodium complex showed an unusual regioselectivity in a manner similar to that of isoprene, affording 2,6-dimethyl-8-silylocta-2,6-diene (VIA) (major) and III (minor). Results ob-

TABLE 5

HYDROSILYLATION OF OCIMENE CATALYZED BY THE PHOSPHINEPALLADIUM COMPLEX



(IV) (V)

Hydrosilane		Conditions	Product ratio [a]		Yield (%) [a]
			IV	V	
a	Cl_3SiH	100°C/24 h	42	58	100
b	$MeCl_2SiH$	100°C/42 h	100		76.5 [b]
c	Me_2ClSiH	100°C/42 h	100		18 [b]

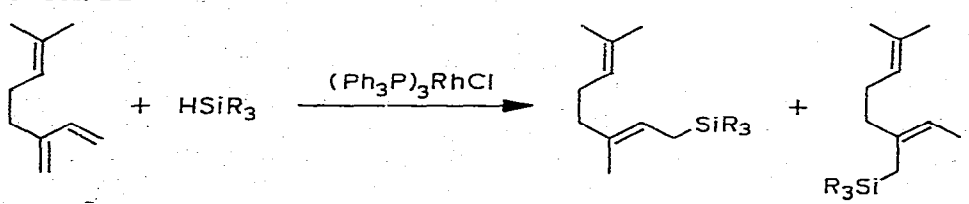
[a] Estimated by GLC analysis. [b] Yields are not optimized.

tained using several hydrosilanes are summarized in Table 6. It should be noted that the regioselectivity of the reaction is clearly dependent upon the structure of the hydrosilane employed. However, the extent of regioselectivity observed in this reaction is largely the same as that of isoprene. Accordingly, a substituent on the C(2) position of isoprene skeleton has only a slight effect on the regioselectivity of the reaction.

In sharp contrast to this, the regioselectivity achieved in the hydrosilylation of ocimene catalyzed by the rhodium complex is much higher than that attained in the reactions of isoprene and myrcene. Especially, the reaction of ocimene with triethoxysilane afforded 2,6-dimethyl-8-triethoxysilylocta-2,6-diene (VIdB) in 98% regioselectivity. Results are listed in Table 7. These results clearly indi-

TABLE 6

HYDROSILYLATION OF MYRCENE CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE



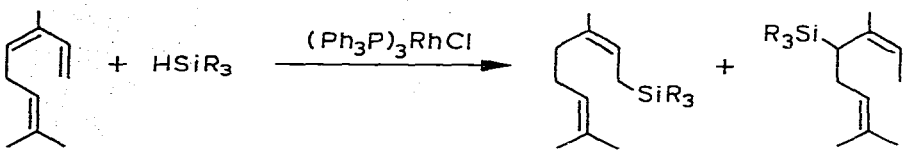
(VIA) (III)

Hydrosilane		Conditions	Product ratio [a]		Yield (%) [a]
			VIA	III	
c	$ClMe_2SiH$	100°C/15 h	64	36	91
d	$(EtO)_3SiH$	100°C/24 h	56	44	86
e	$PhMe_2SiH$	100°C/36 h	75	25	65
f	$EtMe_2SiH$	100°C/24 h	58	42	77

[a] Estimated by GLC analysis.

TABLE 7

HYDROSILYLATION OF OCIMENE CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE



(VIB) (IV)

	Hydrosilane	Conditions	Product ratio [a]		Yield (%) [a]
			VIB	IV	
d	$(EtO)_3SiH$	100°C/24 h	98	2	98
e	$PhMe_2SiH$	100°C/24 h	75	25	67
f	$EtMe_2SiH$	100°C/24 h	89	11	82
h	$(MeO)_3SiH$	110°C/22 h	94	6	92

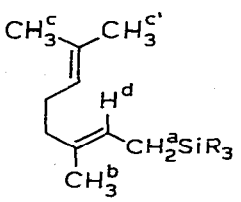
[a] Estimated by GLC analysis.

cate that a substituent on the C(1) position of the isoprene skeleton exerts a remarkable influence on the regioselectivity of the hydrosilylation catalyzed by the rhodium complex.

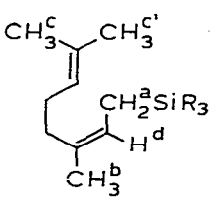
The stereochemistry of these adducts VIA and VIB was elucidated on the basis of NMR spectra. As Table 8 shows, (i) the chemical shifts of H^a, H^b and

TABLE 8

NMR DATA (δ (PPM) TMS) FOR THE ADDUCTS VIA AND VIB OBTAINED IN THE HYDROSILYLATION OF MYRCENE AND OCIMENE CATALYZED BY THE RHODIUM COMPLEX [a]



(VIA)



(VIB)

(myrcene origin adduct) (ocimene origin adduct)

	Silyl group	Diene	H^a	H^b	H^c	$H^{c'}$	H^d	Solvent
c	$ClMe_2Si$	myrcene	1.81	1.58	1.58	1.67	5.16	$CDCl_3$
d	$(EtO)_3Si$	myrcene	1.40	1.55	1.55	1.62	5.07	$CDCl_3$
	$(EtO)_3Si$	ocimene	1.40	1.64	1.58	1.67	5.16	$CDCl_3$
e	$PhMe_2Si$	myrcene	1.60	1.46	1.56	1.64	5.17	$CDCl_3$
	$PhMe_2Si$	ocimene	1.63	1.68	1.59	1.68	5.16	$CDCl_3$
f	$EtMe_2Si$	myrcene	1.38	1.54	1.59	1.67	5.10	$CDCl_3$
	$EtMe_2Si$	ocimene	1.37	1.66	1.59	1.66	5.10	$CDCl_3$
h	$(MeO)_3Si$	ocimene	1.40	1.64	1.58	1.64	5.04	CCl_4

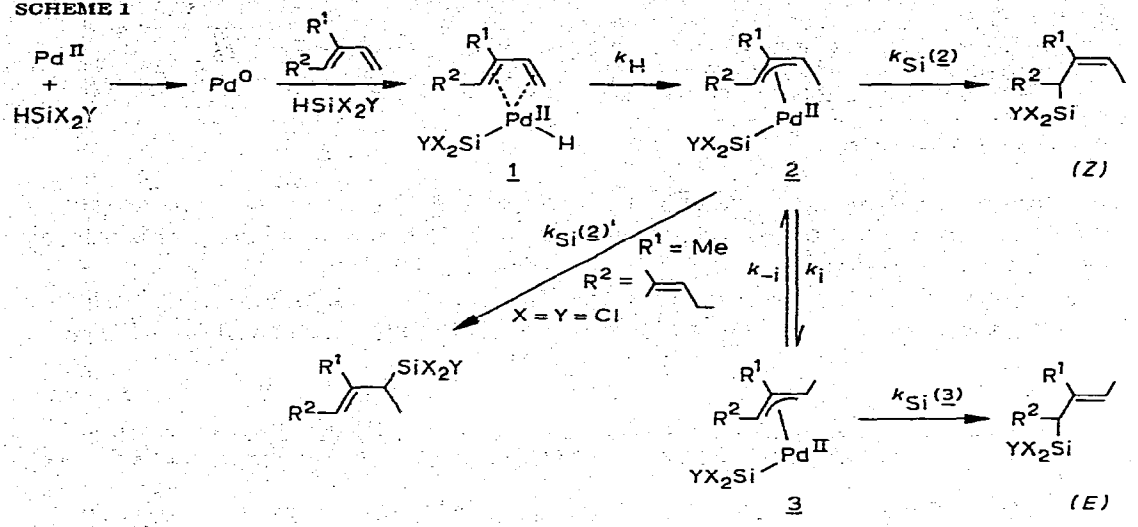
[a] H^a appears as doublet (J 8 Hz) and H^d as quartet (J 8 Hz).

H^a protons in a myrcene origin adduct are nicely superimposed on those observed in the corresponding *Z*-3-methylbuten-2-ylsilane (II) (see Table 3), and (ii) the H^b methyl of the myrcene origin adduct appears at higher field than that of the corresponding ocimene adduct: The fact implies the existence of the aforementioned shielding effect of the silyl-methyl group on the *cis*-methyl H^b only in the case of the myrcene-derived adduct. Therefore, the stereochemistry of the latter is determined to be *E*, and that of the ocimene-derived adduct is *Z*.

Possible mechanisms of these reactions

A proposed mechanism of the palladium complex-catalyzed reaction is depicted in Scheme 1, which accounts for the observed stereoselectivity. It is

SCHEME 1

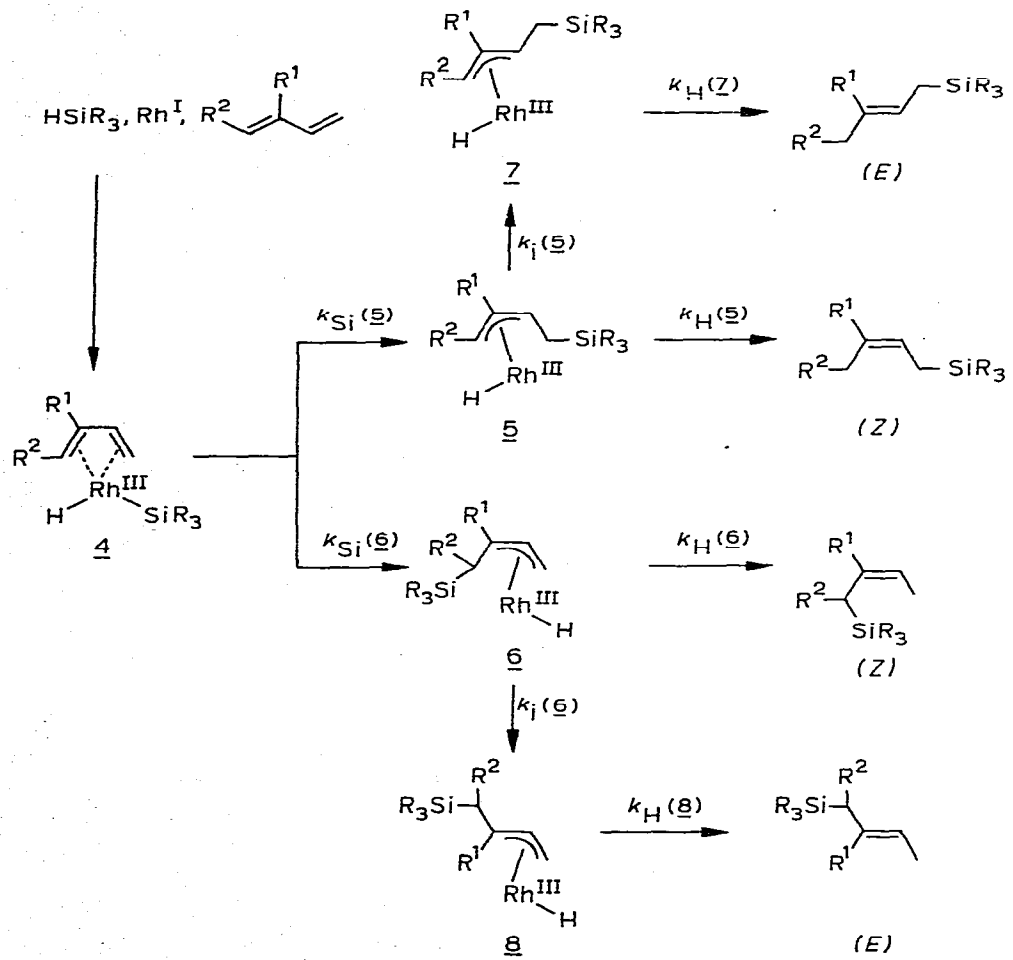


reasonable to assume that the reaction proceeds through a π-allylic intermediate of the type proposed for many catalytic reactions of dienes [1,7]. In fact, the formation of the unusual 1,2-adduct, Va, in addition to the normal 1,4-adduct, IV, in the case of ocimene strongly suggests the existence of such a π-allylic silylpalladium complex (2, R^1 = Me, R^2 = 3-methylbuten-2-yl) as a common intermediate. Our results imply that the reaction involves an extremely regioselective hydride shift from an oxidative adduct (1) to the coordinated 1,3-diene to produce the π-allylic silylpalladium complex (2). Subsequent silicon–carbon bond formation then gives *Z*-2-alkylbuten-2-ylsilane as shown in Scheme 1. If an isomerization of the intermediate 2 to the *exo*-methyl intermediate 3 is faster than the silicon migration, i.e., $k_i > k_{Si}$ (2), the adduct is a mixture of the *Z* and *E* isomers, e.g., the occurrence of the interconversion of *syn*- and *anti*-forms of π-allylic silylnickel complexes was suggested by Čapka and Hetflejš [8]. However, our results clearly demonstrate that the silicon migration is much faster than the isomerization, i.e., k_{Si} (2) >> k_i, and thus the *Z*-isomer is formed exclusively.

It has been generally accepted that a hydride shift from the oxidative addition product, i.e., silyl-transition-metal hydride, to the coordinated olefin is the first step in the hydrosilylation of olefins and that subsequent silicon migration

gives the hydrosilylated product [9]. In fact, the results of the hydrosilylation of isoprene, myrcene and ocimene catalyzed by the palladium complex just mentioned above can be explained in accordance with this mechanism. However, the results of the rhodium complex-catalyzed reaction cannot be interpreted in terms of this mechanism since the regioselectivity is opposite to that observed with the other catalytic systems. Thus, we would like to propose a possible mechanism for the present reaction which can accomodate the unusual regioselectivity as shown in Scheme 2. The proposed mechanism involves a

SCHEME 2



regioselective silicon migration from the oxidative addition product, 4, to the coordinated 1,3-diene to produce the π-allylic rhodium hydride complexes 5 and 6 *. Succeeding hydride shifts from the intermediates 5 and 6 afford 3-

* We already proposed an initial silyl migration mechanism for the hydrosilylation of alkyne and α,β-unsaturated ester catalyzed by tris(triphenylphosphine)rhodium chloride [10]. A similar mechanism was also proposed by Rejhon and Hetflejš in the hydrosilylation of butadiene catalyzed by rhodium complexes [11].

alkylbuten-2-ylsilane and *Z*-2-methylbuten-2-ylsilane, respectively.

The regioselectivity of the silicon migration in the first step may be markedly dependent upon the nature of the silicon—rhodium bond and the structure of the diene. Thus, a bulky substituent on the C(1) position, as in the case of ocimene, may strongly favor the production of the intermediate 5, which then leads to the formation of the prenyl, geranyl or nerylsilane.

The isomerization of the intermediates 5 and 6 was found to be negligible also in this case, i.e., $k_H(5) >> k_i(5)$; $k_H(6) >> k_i(6)$. Thus, the reaction proceeds in an extremely stereoselective manner to afford *Z*-isomers exclusively.

Experimental

Measurement

The boiling points were uncorrected. The nuclear magnetic resonance spectra were recorded on a Varian HA-100 or a Varian T-60 spectrometer, using TMS as the internal standard. Analytical gas chromatography (GLC) was carried out on a Shimadzu GC-5A or GC-3BF using a column packed with 3% OV-17. Preparative GLC was performed on a Shimadzu GC-3BT using a column packed with 20% SE-30 or 20% PEG-20M.

Materials

Chlorohydrosilanes were commercially available and other hydrosilanes were prepared by known methods. Bis(benzonitrile)palladium dichloride was prepared from palladium dichloride and benzonitrile [12]. Tris(triphenylphosphine) rhodium chloride was prepared from rhodium trichloride trihydrate and triphenylphosphine [13]. Isoprene and myrcene were obtained from commercial sources and were purified by distillation before use. Ocimene was obtained commercially from T. Hasegawa Co. Ltd., and was used without further purification.

Hydrosilylation of isoprene catalyzed by the phosphinepalladium complex

In a typical experiment, dichloromethylsilane (3.80 g, 33 mmol) was allowed to react with freshly distilled isoprene (2.04 g, 30 mmol) in the presence of triphenylphosphine (40 mg, 0.15 mmol) and bis(benzonitrile)palladium dichloride (25 mg, 0.065 mmol) in a degassed sealed tube at 70°C for 6 h. GLC analysis of the reaction mixture showed that the adduct was produced in quantitative yield. A direct distillation of the reaction mixture afforded *Z*-2-methylbuten-2-yldichloromethylsilane (Ib) in 95% yield.

Similarly, 2-methylbuten-2-yltrichlorosilane (Ia) and 2-methylbuten-2-yldimethylchlorosilane (Ic) were obtained by the reaction of isoprene with trichlorosilane and dimethylchlorosilane in 100 and 90% yield, respectively.

Ia: B.p. 99°C/100 Torr (lit. [2e], 164.5—165.5°C/760 Torr).

Ib: B.p. 157.5°C/760 Torr (lit. [2d], 62°C/19 Torr).

Ic: B.p. 87°C/77 Torr (Found: C, 51.91; H, 9.48; Cl, 21.50. $C_7H_{15}ClSi$ calcd.: C, 51.66; H, 9.29; Cl, 21.79%).

Preparation of 2-methylbuten-2-yltrimethylsilane (Ig)

To an ether solution (1000 ml) of 2-methylbuten-2-yldichloromethylsilane

(Ib) (36.6 g, 0.2 mol) was added an ether solution (1000 ml) of methylmagnesium bromide prepared from methyl bromide (gas) and magnesium turnings (16 g, 0.667 g atom) at ambient temperature with stirring for 2 h. The reaction mixture was hydrolyzed with saturated aqueous solution of ammonium chloride at 0°C. The organic layer was separated, dried over anhydrous magnesium sulfate, concentrated and distilled to afford 2-methylbuten-2-yltrimethylsilane (Ig) (18.5 g, 65%).

Ig: B.p. 88°C/150 Torr (lit. [14], 133—135°C/760 Torr).

Hydrosilylation of isoprene catalyzed by tris(triphenylphosphine)rhodium chloride

Typically, a mixture of dimethylphenylsilane (4.08 g, 30 mmol) and freshly distilled isoprene (2.04 g, 30 mmol) and tris(triphenylphosphine)rhodium chloride (20 mg, 0.022 mmol) was degassed and sealed in a glass tube, and was heated at 80°C for 6 h. GLC analysis of the reaction mixture revealed that 3-methylbuten-2-yldimethylphenylsilane (IId) and 2-methylbuten-2-yldimethylphenylsilane (Id) were produced in 71 and 27% yield, respectively. Distillation of the reaction mixture afforded the combined methylbutenylsilanes in 85% yield.

IIc + Ic: B.p. 127°C/760 Torr, (Found: C, 51.95; H, 9.45; Cl, 21.60. $C_7H_{15}ClSi$ calcd.: C, 51.66; H, 9.29; Cl, 21.79%).

IId + Id: B.p. 115°C/42 Torr, (Found: C, 56.76; H, 10.51. $C_{11}H_{24}O_3Si$ calcd.: C, 56.85; H, 10.41%).

IIe + Ie: B.p. 135°C/30 Torr, (Found: C, 76.62; H, 10.02. $C_{13}H_{20}Si$ calcd.: C, 76.40; h, 9.86%).

IIf + If: B.p. 150°C/760 Torr, (Found: C, 69.07; H, 13.09. $C_9H_{20}Si$ calcd.: C, 69.14; H, 12.89%).

3-Methylbuten-2-yltrimethylsilane (IIg) was prepared by the reaction of 3-methylbuten-2-ylmagnesium chloride with trimethylchlorosilane in accordance with the procedure reported by Calas and coworkers [15].

Hydrosilylation of myrcene and ocimene catalyzed by the phosphinepalladium complex

A typical procedure is described for the hydrosilylation of ocimene by trichlorosilane: A mixture of ocimene (2.72 g, 20 mmol), trichlorosilane (2.94 g, 22 mmol), triphenylphosphine (40 mg, 0.15 mmol) and bis(benzonitrile)palladium dichloride (25 mg, 0.065 mmol) was sealed in a pyrex ampoule and was heated at 100°C for 24 h with stirring. GLC analysis of the reaction mixture revealed that 2,6-dimethyl-5-trichlorosilylocta-2,6-diene (IVa) and 2,6-dimethyl-7-trichlorosilylocta-2,5-diene (Va) were produced in 42 and 58% yield, respectively. Distillation of the reaction mixture under reduced pressure gave the adducts IVa and Va in 95% yield. IVa and Va were separated and isolated by means of a preparative GLC using a column packed with 20% SE-30, and their structures were elucidated on the basis of their NMR spectra.

In similar manner, myrcene was employed as substrate. However, the purity of the commercially available myrcene, after simple distillation, was found to be 83.8% on the basis of GLC analysis. As myrcene was found to be consumed selectively in the present reaction, the yield of the adduct was calibrated by the purity of myrcene.

IIIa: 90% yield, B.p. 139.5°C/26 Torr, (Found: C, 44.34; H, 6.20; Cl, 39.15. $C_{10}H_{17}Cl_3Si$ calcd.: C, 44.21; H, 6.31; Cl, 39.15%).

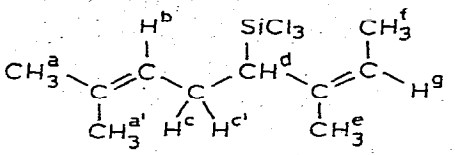
IIIb: 90% yield, B.p. 134°C/25 Torr, (Found: C, 52.62; H, 7.96; Cl, 28.36. $C_{11}H_{20}Cl_2Si$ calcd.: C, 52.58; H, 8.02; Cl, 28.22%).

IIIc: 81% yield, B.p. 130°C/23 Torr, (Found: C, 62.35; H, 10.10; Cl, 15.30. $C_{12}H_{23}ClSi$ calcd.: C, 62.43; H, 10.04; Cl, 15.36%).

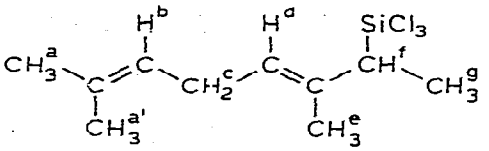
IIId: 29% yield, B.p. 150°C/21 Torr, (Found: C, 63.78; H, 10.54. $C_{16}H_{32}O_3Si$ calcd.: C, 63.95; H, 10.73%).

IVa + Va: B.p. 122°C/16 Torr, (Found: C, 43.95; H, 6.23; Cl, 38.91. $C_{10}H_{17}Cl_3Si$ calcd.: C, 44.21; H, 6.31; Cl, 39.15%).

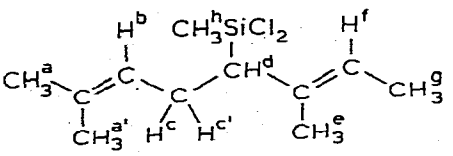
IVa (NMR, $CDCl_3$, δ (ppm)): 1.57 (d, J 7 Hz, 3H) (H^f), 1.61 (s, 3H) (H^a), 1.65 (s, 3H) (H^e), 1.70 (s, 3H) ($H^{a'}$), 2.38 (octet, J^{cd} 11 Hz, $J^{c'd}$ 4 Hz, 2H) (H^c, $H^{c'}$), 2.63 (quartet, J^{cd} 11 Hz, $J^{c'd}$ 4 Hz, 1H) (H^d), 4.96 (t, J 7 Hz, 1H) (H^b) and 5.44 (quartet, J 7 Hz, 1H) (H^g).



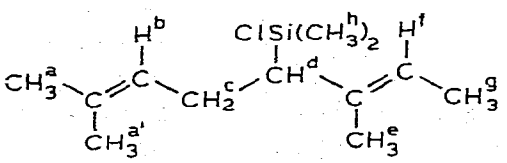
Va (NMR, $CDCl_3$, δ (ppm)): 1.31 (d, J 7 Hz, 3H) (H^g), 1.60 (s, 3H) (H^a), 1.67 (s, 3H) (H^e), 1.70 (s, 3H)(($H^{a'}$), 2.23 (quartet, J 7 Hz, 1H) (H^f), 2.69 (t, J 7 Hz, 2H) (H^c), 5.03 (t, J 7 Hz, 1H) (H^b) and 5.23 (t, J 7 Hz, 1H) (H^d).



IVb: B.p. 116°C/15 Torr, (Found: C, 52.59; H, 8.12; Cl, 28.14. $C_{11}H_{20}Cl_2Si$ calcd.: C, 52.58; H, 8.02; Cl, 28.22%). NMR ($CDCl_3$, δ (ppm)): 0.74 (s, 3H) (H^h), 1.57 (d, J 7 Hz, 3H) (H^g), 1.65 (s, 3H) (H^a), 1.69 (s, 6H) ($H^{a'}$, H^e), 2.44 (octet, J^{cd} 3 Hz, $J^{c'd}$ 6 Hz, $J^{cc'}$ 12 Hz, 2H) (H^c, $H^{c'}$) 2.44 (t, J^{cd} 3 Hz, $J^{c'd}$ 6 Hz, 1H) (H^d), 5.02 (t, J 7 Hz, 1H) (H^b) and 5.42 (quartet, J 7 Hz, 1H) (H^f).



IVc: B.p. 109°C/15 Torr, (Found: C, 62.15; H, 9.89; Cl, 15.31. $C_{12}H_{23}ClSi$ calcd.: C, 62.43; H, 10.04; Cl, 15.36%). NMR ($CDCl_3$, δ (ppm)): 0.41 (s, 6H) (H^h), 1.54 (d, J 7 Hz, 3H) (H^g), 1.63 (s, 6H) (H^a, H^e), 1.65 (s, 3H) ($H^{a'}$), 1.77 (m, 1H) (H^d), 2.28 (m, 2H) (H^c), 5.04 (m, 1H) (H^b) and 5.30 (quartet, J 7 Hz, 1H) (H^f).



Preparation of 2-methyl-6-ethyldimethylsilylmethylocta-2,6-diene (IIIf) and 2-methyl-6-trimethylsilylmethylocta-2,6-diene (IIIg)

2-Methyl-6-ethyldimethylsilylmethylocta-2,6-diene (IIIf) was prepared from 2-methyl-6-dimethylchlorosilylmethylocta-2,6-diene (IIIc) by the reaction with ethylmagnesium bromide in ether in a manner similar to that described for the preparation of 2-methylbuten-2-yltrimethylsilane (Ig). Similarly, 2-methyl-6-trimethylsilylmethylocta-2,6-diene (IIIg) was prepared from 2-methyl-6-dichloromethylsilylmethylocta-2,6-diene (IIIb) by treating the latter with methylmagnesium bromide in ether.

IIIg: B.p. 110°C/16 Torr, (Found: C, 73.95; H, 12.40. $C_{13}H_{26}Si$ calcd.: C, 74.20; H, 12.45%).

Hydrosilylation of myrcene and ocimene catalyzed by tris(triphenylphosphine) rhodium chloride

The hydrosilylation of myrcene by triethoxysilane is described: A mixture of myrcene (1.59 g, 83.8% purity), triethoxysilane (1.64 g, 10 mmol) and tris(triphenylphosphine)rhodium chloride (10 mg, 0.011 mmol) was sealed in a pyrex ampoule and was heated at 100°C for 24 h. 2,6-Dimethyl-8-triethoxysilylocta-2,6-diene (VIdA) and 2-methyl-6-triethoxysilylmethylocta-2,6-diene (IIId) were found to be found in 48 and 38% yield, respectively. Distillation of the reaction mixture afforded a mixture of VIdA and IIId in 75% yield.

VIcA + IIIc: B.p. 126°C/21.5 Torr, (Found: C, 62.33; H, 10.06; Cl, 15.29. $C_{12}H_{23}ClSi$ calcd.: C, 62.43; H, 10.04; Cl, 15.36%).

VIdA + IIId: 150°C/21 Torr (Found: C, 64.03; H, 10.74. $C_{16}H_{32}O_3Si$ calcd.: C, 63.95; H, 10.73%).

VIdB: B.p. 145°C/19 Torr, (Found: C, 63.88; H, 10.70. $C_{16}H_{32}O_3Si$ calcd.: C, 63.95; H, 10.73%).

VIeA + IIIe: B.p. 141.5°C/2.3 Torr, (Found: C, 79.21; H, 10.20. $C_{18}H_{28}Si$ calcd.: C, 79.34; H, 10.36%).

VIeB + IVe: B.p. 138°C/2.1 Torr, (Found: C, 79.50; H, 10.32. $C_{18}H_{28}Si$ calcd.: C, 79.34; H, 10.36%).

VIfA + IIIf: B.p. 125°C/17 Torr, (Found: C, 74.80; H, 12.57. $C_{14}H_{28}Si$ calcd.: C, 74.91; H, 12.57%).

VIfB: B.p. 127°C/21 Torr, (Found: C, 74.79; H, 12.59. $C_{14}H_{28}Si$ calcd.: C, 74.91; H, 12.57%).

VIhB: B.p. 145°C/25 Torr, (Found: C, 60.31; H, 10.20. $C_{13}H_{26}O_3Si$ calcd.: C, 60.42; H, 10.14%).

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