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CHEMISTRY OF ORGANOSILICON COMPOUNDS

LXXI. RING CLOSURE OF (4-PENTENYL)HYDROSILANES BY INTRAMOLECULAR HYDROSILYLATION WITH TRANSITION METAL SALTS*

HIDEKI SAKURAI, TOSHIFUMI HIROSE and AKIRA HOSOMI

Department of Chemistry, Faculty of Science, Tohoku University, Aza Aoba Aramaki, Sendai 980 (Japan)

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Summary

The intramolecular hydrosilylation of (4-pentenyl)hydrosilanes with transition metal salt catalysts afforded five- and six-membered ring-closure products in high yields, with the former predominating. This has been rationalized in terms of a reaction scheme based on the Harrod—Chalk mechanism in which both Si—metal and C—metal bonds were involved. The seven-membered intermediate leading to the six-membered ring products is apparently less favorable than the six-membered intermediate. However, with dicobalt octacarbonyl, no ring closure occurred, and only izomerization was observed.

Introduction

During the course of our studies on Group IVB radicals, the behavior of silyl radicals having a double bond at the δ position was examined [1]. The ring-closure reaction of such silyl radicals led mostly to six-membered ring compounds. However, we have also found that intramolecular hydrosilylation of (4-pentenyl)hydrosilanes with chloroplatinic acid resulted in silacyclopentanes rather than silacyclohexanes [1,2]. Other investigators recently have reported similar results with different compounds [3-5]. Since such reactions are synthetically and mechanistically interesting, we have studied further such intramolecular hydrosilation with various catalysts and describe our results in this paper. When we had finished the manuscript, we received a report by Swisher and Chen [6] who described the ring-size effect in intramolecular hydrosilylation with chloroplatinic acid as a catalyst. Their results partly correspond to our findings.

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* Preliminary accounts of this paper can be found in refs. 1 and 2.

Results and discussion

(4-Pentenyl)hydrosilanes were prepared by the reaction of the Grignard reagent from 5-chloro-1-pentene with variously substituted chlorohydrosilanes (Table 1).

$$CH_2{=}CH(CH_2)_3MgCl \xrightarrow{R^1R^2SiClH} CH_2{=}CH(CH_2)_3SiR^1R^2H$$

Ia, $R^1 = R^2 = Ph$
Ib, $R^1 = R^2 = Me$
Ic, $R^1 = R^2 = Cl$
Id, $R^1 = Ph$; $R^2 = Me$
Ie, $R^1 = Me$; $R^2 = Cl$
If, $R^1 = Et$; $R^2 = Cl$
Ig, $R^1 = i\text{-}Pr$; $R^2 = Cl$

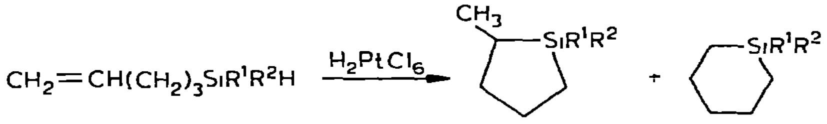
The purity of these compounds, especially with respect to the position of the double bonds, was checked by 100 MHz NMR. No isomerization was observed after the hydrosilylation reaction which was carried out with a catalytic amount of chloroplatinic acid in isopropyl alcohol. When the catalyst was added to these olefinic hydrosilanes without solvent, a smooth reaction took place at room temperature. 2-Methyl-1-silacyclopentanes (II) and silacyclohexanes (III) were obtained in good yields with the former as the predominant products.

TABLE 1

YIELDS AND PHYSICAL PROPERTIES OF (4-PENTENYL)HYDROSILANES [a]

Compound	Yield (%)	B.p. (°C/torr)	n_D^{20}	d_4^{20}	MR_D	
					obs.	calc.
Ia	73	157-158/4	1.5638	0.9922	82.72	83.66
Ib	51	120-121 (120-121) [b]	1.4211 (1.4219) [b]	0.7391 (0.7436) [b]	44.03	43.7
Ic	40	54/29 (65-66/28) [c]	1.4434	1.0540	42.57	44.08
Id	41	118-119/22	1.5042	0.8807	64.01	63.72
Ie	23	67/71	1.4394	0.9247	42.18	43.61
If	[d]	74-76/30	[d]	[d]		
Ig	55	83-84/26	1.4449	0.8915	52.76	52.91

[a] Satisfactory elemental analyses were obtained for all of the compounds except If which was not analyzed. [b] Ref. 3. [c] Ref. 5. [d] Not determined.



(I) (II) (III)

a, $R^1 = R^2 = Ph$

b, $R^1 = R^2 = Me$

c, $R^1 = R^2 = Cl$

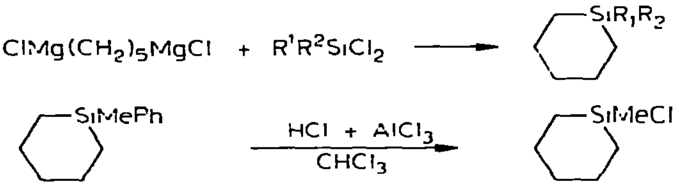
d, $R^1 = Ph$; $R^2 = Me$

e, $R^1 = Me$; $R^2 = Cl$

f, $R^1 = Et$; $R^2 = Cl$

g, $R^1 = i\text{-}Pr$; $R^1 = Cl$

Authentic samples of the six-membered products were prepared by the reaction of a di-Grignard reagent with a dichlorosilane followed by appropriate secondary transformations, e.g.,



(IIId) (IIIe)

Since the five-membered ring compounds with the 2-methyl group are tedious to prepare by other unequivocal routes, some of the authentic samples were prepared by known derivatizations applied to 1,1-diphenyl-2-methyl-1-silacyclopentane (IIa) whose structure was verified by spectroscopic studies.

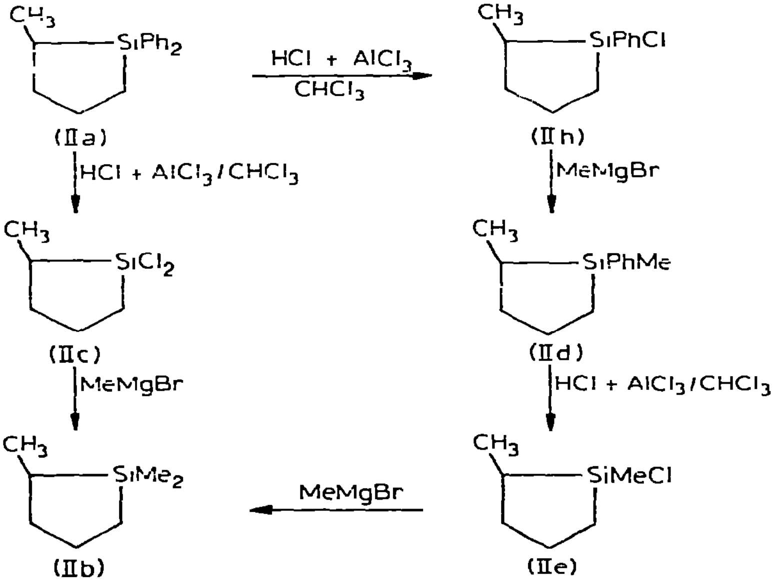


TABLE 2

HYDROSILYLATION OF (4-PENTENYL)HYDROSILANES (CH_2=$CHCH_2CH_2CH_2SiR^1R^2H$) WITH CHLOROPLATINIC ACID

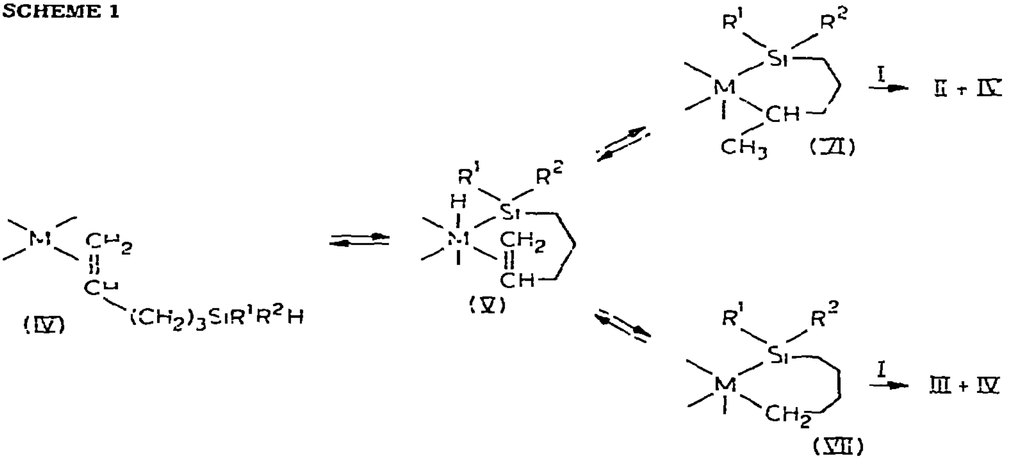
Compound	R^1	R^2	Product (%)		
			II	III	II/III
Ia	Ph	Ph	85.2	3.8	22
			88.8	4.5	20
Ib	Me	Me	49.0	4.7	10
			[a]	[a]	13
Ic	Cl	Cl	47.7	11.8	4.0
			40.9	9.4	4.4
Id	Ph	Me	76.3	5.5	14
			64.0	4.0	16
Ie	Me	Cl	57.8	10.0	5.8
			44.3	7.8	5.7
If	Et	Cl	45.0	7.4	6.1
			42.2	6.2	6.8
Ig	i-Pr	Cl	53.6	10.4	5.2
			54.2	9.1	6.0

[a] Only relative yield was determined.

All of the products were identified by comparing retention times on GLC and IR and NMR spectra with those of the authentic samples, except for If and Ig. In latter cases, identification of the products and relative yields were assumed by analogous behavior of the products on GLC.

Table 2 lists yields and distribution of the products. Scheme 1, based on the Harrod—Chalk mechanism of hydrosilylation [7, 8], in which both Si—Pt and Pt—C bonds are involved [1,5,6], can rationalize satisfactorily the results. Thus, the seven-membered intermediate VII, leading to the six-membered ring product, is apparently less favorable than the six-membered intermediate VI which obviously leads to the five-membered ring product.

SCHEME 1



With other homogeneous catalysts, similar results were obtained, as indicated in Table 3. It is interesting to note that in the reaction of Ia with di-

TABLE 3

HYDROSILYLATION OF (4-PENTENYL)HYDROSILANES WITH TRANSITION METAL SALTS AS CATALYSTS

Catalyst [a]	T (°C)	R¹	R²	Product (%) II	III	II/III
π-$C_5H_5Co(CO)_2$	135 [b]	Ph	Me	29.8	7.1	4.2
$[(C_2H_4)_2RhCl]_2$	80 [c]	Ph	Me	21.2	2.7	7.9
$(Ph_3P)_3RhCl$	80 [b]	Ph	Me	35.4	16.8	2.1
	80 [c]	Ph	Me	35.4	12.3	2.9
	80 [b]	Ph	Ph	77.3	11.7	6.6
	80 [c]	Ph	Ph	92.3	5.8	16
$LPt(C_2H_4)Cl_2$	80 [d]	Ph	Me	89.3	trace	
L'Pt(*trans*-butene)Cl	80 [d]	Ph	Me	89.3	trace	
L'Pt(*cis*-butene)Cl	80 [d]	Ph	Me	78.2	trace	

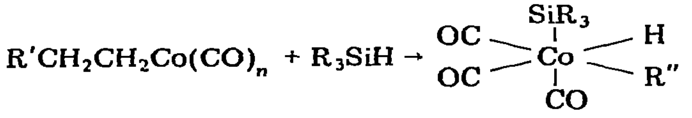
[a] L = phenylalanine; L' = L-proline. [b] Neat. [c] In n-hexane. [d] In toluene.

cobalt octacarbonyl neither IIa nor IIIa was obtained although the carbonyl is known to be an effective catalyst of hydrosilylation [9].

The mechanism proposed for hydrosilylation catalyzed by the carbonyl involves six-coordinate species such as X formed via alkylcobalt carbonyls [9].

$$R_3SiH + Co_2(CO)_8 \rightarrow R_3SiCo(CO)_4 + HCo(CO)_n$$

$$HCo(CO)_n + R'CH{=}CH_2 \rightleftharpoons R'CH_2CH_2Co(CO)_n$$

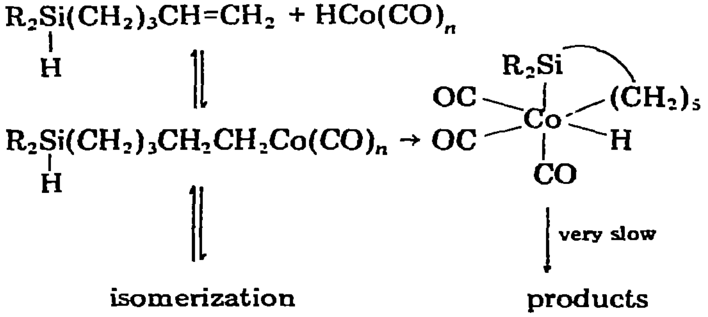


$$R'CH_2CH_2Co(CO)_n + R_3SiH \rightarrow$$

(X)

$$X \rightarrow R_3SiCH_2CH_2R' + HCo(CO)_n$$

Formation of alkylcobalt carbonyls precedes the reaction with the silicon hydride; therefore, the alkyl group in X must be primary. In the case of 4-pentenylsilanes, the step to an intermediate similar to X must be very slow for the reason discussed before.



As a result, extensive isomerization occurred at the olefinic position, being substantiated by GLC analysis of the recovered starting materials. Therefore, as described by Chalk and Harrod, the rate of olefin isomerization exceeded that of olefin hydrosilylation.

Experimental

Preparation of 4-pentenylsilanes

All 4-pentenylsilanes except Ib were prepared by the reaction of 4-pentenylmagnesium chloride with appropriate chlorohydrosilanes (R^1R^2SiClH) in ether. For Ib, (4-pentenyl)dimethylchlorosilane, b.p. 51°/16 torr, was prepared first and was reduced to the corresponding hydrosilane with $LiAlH_4$.

Preparation of 1-silacyclohexane derivatives

Reaction of di-Grignard reagent prepared from 1,5-dichloropentane in THF with $R^1R^2SiCl_2$ afforded the following 1-silacyclohexane derivatives: 1,1-diphenyl-(IIIa), b.p. 187-189°/5 torr; n_D^{20} 1.5710 [lit. [10] b.p. 159-162°/5 torr; n_D^{20} 1.5779], 1,1-dimethyl-(IIIb), b.p. 132-135° (lit. [11] 131.2-131.3°), 1,1-dichloro-(IIIc), b.p. 54-58°/18 torr (lit. [12] 170°), 1-phenyl-1-methyl-(IIId), b.p. 76.5°/3 torr. 1-Methyl-1-chloro-1-silacyclohexane (IIe) was prepared by chlorodephenylation of IIId with HCl—$AlCl_3$ in chloroform, b.p. 67°/77 torr, (lit. [11] 167°).

Preparation of 1,1-diphenyl-2-methyl-1-silacyclopentane (IIa)

Hydrosilylation of Ia catalyzed by chloroplatinic acid gave a mixture composed of mainly 1,1-diphenyl-2-methyl-1-silacyclopentane (IIa) which was subsequently purified by preparative GLC, n_D^{20} 1.5788; NMR (δ, CCl_4) 1.0-2.4 (m, 10H), 7.40 (m, 10H); IR (neat, cm^{-1}) 1110, 1430; Masspec M^+ m/e 252, m/e 174 (M—78, 100%). Analysis found: C, 80.93; H, 8.17. $C_{17}H_{20}Si$ calcd.: C, 80.89; H, 7.99%.

Mass spectra of silacyclopentanes and silacyclohexanes

Mass spectra of a number of cyclic silaalkanes have been examined. Although we will report the details in a forthcoming paper, data for VIIIa, IIIa, and IIa may be pertinent to list here. Values of m/e and relative intensities in % were: VIIIa (70eV): 238 (M^+, 64) 210 (24), 183 (47), 182 (100), 181 (77), 160 (42), 132 (34), 107 (24), 105 (89), 82 (25), 57 (25), 44 (24), 43 (24); IIIa (25 eV): 252 (M^+, 23), 209 (16), 183 (33), 182 (126), 181 (20) 175 (26), 174 (100), 147 (11), 146 (19), 132 (10), 121 (10), 105 (10), 98 (20), 97 (19), 96 (50), 43 (18); IIa (70eV): 252 (M^+, 69) 224 (19), 210 (14), 209 (12), 196 (33), 184 (19), 183 (100), 182 (78) 181 (70), 180 (18), 174 (26), 159 (18), 132 (15), 121 (12), 105 (90), 96 (18), 79 (15).

For VIIIa the existence of the peak at (M^+—C_2H_4) is characteristic and can be generally used as a diagnostic pattern of silacyclopentanes. Thus, IIa gave correspondingly peaks at m/e 224 (M^+—C_2H_4) and 210 (M^+—$CH_3CH{=}CH_2$). For the isomeric silacyclohexane IIIa there was no such peak.

Derivatization of IIIa to various 2-methylsilacyclopentanes

When dry hydrogen chloride gas was bubbled into a solution of IIIa in chloroform in the presence of a catalytic amount of aluminum chloride, two phenyl groups were replaced by chlorine in a stepwise manner. The course of the reaction can be monitored by GLC and monochloro (IIh) and dichloro (IIc) derivatives were obtained, respectively, as chloroform solutions. After the chloroform was evaporated under reduced pressure, a methylmagnesium bromide solution in ether was added to IIh. After work-up, IId was obtained, b.p. 61°/3 torr; IR (neat, cm^{-1}); 1431 (Si—Ph), 1253 (Si—Me), 1115 (Si—Ph); NMR (CCl_4, δ): 0.29 (s, 3H), 0.36 (s, 3H), 0.75-2.0 (m, 10H), 7.26 (m, 5H). Analysis found: C, 75.76; H, 9.67. $C_{12}H_{18}Si$ calcd.: C, 75.72; H, 9.53%.

Similar treatment of IIc with methylmagnesium bromide gave IIb, IR(neat) 1248 cm^{-1} (Si—Me); NMR (CCl_4, δ) -0.02 (s, 3H), 0.01 (s, 3H), 0.3-2.1 (m, 10H).

Chlorodephenylation of IId with hydrogen chloride—aluminum chloride in chloroform resulted in the formation of IIe, IR (neat) 1253 cm^{-1} (Si—Me); NMR (CCl_4, δ): 0.49 (s, 3H), 0.54 (s, 3H), 0.6-2.35 (m, 10H), which gave IIb on treatment with methylmagnesium bromide. Thus, the consistency of the derivatization of silacyclopentanes was established.

Hydrosilylation reactions

In a small Pyrex tube were placed the 4-pentenylhydrosilane (150-200 mg) and an internal standard. To this mixture 2-3 μl of a 0.02 M solution of chloroplatinic acid in isopropyl alcohol was added and the Pyrex tube was stoppered with a rubber cap or sealed. Usually a smooth reaction started without external heating.

With other catalysts listed in Table 3 reactions were carried out in a constant temperature bath kept at 135° or 80°.

Acknowledgement

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