Reduction of Carbonyl Compounds via Hydrosilylation. 4. Highly Regioselective Reductions of α,β-Unsaturated Carbonyl Compounds

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Highly regioselective reduction of α,β-unsaturated carbonyl compounds giving the corresponding α,β-saturated carbonyls or allylic alcohols as predominant product was effected by hydrosilylation catalyzed by tris(triphenylphosphine)chlororhodium followed by the methanolysis of the resulting adducts. Regiospecific deuteration was also achieved by using deuteriosilanes. The regioselectivity in the hydrosilylation was found to depend markedly on the nature of hydrosilanes used. In general, monohydrosilanes afforded silyl enol ethers (1,4 adduct) while dihydrosilanes gave silyl ethers (1,2 adduct). Other factors controlling the regioselectivity, e.g., the structure of α,β-unsaturated carbonyl compounds, the hydrosilane/substrate ratio, solvent, and the reaction temperature, also were investigated. A spin trapping experiment on the hydrosilylation of β-ionone with diphenylsilane was carried out, and the observed EPR signals were interpreted. Possible mechanisms that can accommodate the observed high regioselectivity are discussed.

Introduction

Selective reduction of α,β-unsaturated carbonyl compounds to the corresponding saturated ketones or aldehydes or to allylic alcohols by means of a variety of reducing agents has been attracting much interest for some time.[1] Among the procedures used, homogeneous hydrosilylation catalyzed by transition metals or metal complexes has served as a unique and effective method. For instance, Sadykh-Zade and Petrov reported in 1959[2] that the chloroplatinic acid catalyzed hydrosilylation of α,β-unsaturated ketones and aldehydes proceeded via 1,4 addition to give the corresponding saturated ketones and aldehydes after hydrolysis. Yoshii et al. applied this reduction system to the selective reduction of α,β-unsaturated esters in steroid systems.[3] In 1972, we reported briefly that the tris(triphenylphosphine)chlororhodium-catalyzed hydrosilylation of α,β-unsaturated ketones and aldehydes with monohydrosilanes gave 1,4 adducts while that with dihydrosilanes gave 1,2 adducts with high selectivity, and the 1,4 adducts and the 1,2 adducts were readily hydrolyzed to afford the corresponding saturated products and allylic alcohols, respectively.[4] Our reduction system was further applied to the asymmetric synthesis of chiral ketones and chiral allylic alcohols,[5-7] and recently Ogura et al. succeeded in obtaining 3(*S*),4(*R*)-faranal, a trail pheromone of the pharaoh ant, by using this method.[8] We will describe here a full account of our research on the highly selective reduction of α,β-unsaturated ketones and aldehydes via regioselective hydrosilylation catalyzed by tris(triphenylphosphine) chlororhodium.

Results and Discussion

Selective Reduction of Various α,β-Unsaturated Ketones and Aldehydes. We carried out the hydrosilylation of a variety of α,β-unsaturated ketones and aldehydes catalyzed by tris(triphenylphosphine)chlororhodium followed by the methanolysis of the adducts. Results are summarized in Table I.

As Table I clearly shows, monohydrosilanes bring about the selective hydrogenation of carbon–carbon double bond conjugated to carbonyl group via silyl enol ether I, whereas dihydrosilanes and trihydrosilanes effect the selective reduction of carbonyl group via allylic silyl ether II.

For instance, the reduction of geranial using triethylsilane afforded citronellal exclusively in 97% yield while that using diphenylsilane gave geraniol as sole product in 97% yield. In each reaction, no isomerization, hydrogenation, or hydrosilylation of the isolated double bond in the substrate and the product was observed. This is a synthetically valuable characteristic of the present reduction system: it should also be noted that catalytic hydrogenation with tris(triphenylphosphine)chlororhodium cannot be used for the preparation of citronellal from citral because of the occurrence of exclusive decarbonylation.[9]

It was also found that the dihydrosilane–$(Ph_3P)_3RhCl$ combination in the selective carbonyl reduction of α,β-unsaturated ketones and aldehydes displayed an exceedingly higher selectivity than usual metal hydrides. The comparison of the selectivities obtained by the present system with those attained by commonly used metal hydrides are shown in Table II.

As Table II shows, the reduction with lithium tri-*tert*-butoxyaluminum hydride or sodium borohydride suffers from the formation of side products in the case of both ketones.[10] Although lithium borohydride reduction of pulegone gave pulegol in excellent yield, that of piperitone afforded a large amount of the conjugated reduction product in addition to the desired menthenol.[10] Lithium aluminum hydride reduced both ketones exclusively to the corresponding allylic alcohols, but the conversion should remain low to achieve the excellent selectivity for pulegone.[10] On the other hand, either Et_2SiH_2–$(Ph_3P)_3RhCl$ or Ph_2SiH_2–$(Ph_3P)_3RhCl$ combination turned out to be

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(6) Ojima, I.; Kogure, T.; Nagai Y. *Chem. Lett.* **1975**, 985.
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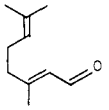
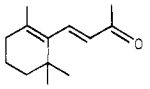
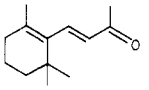
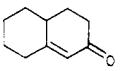
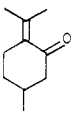
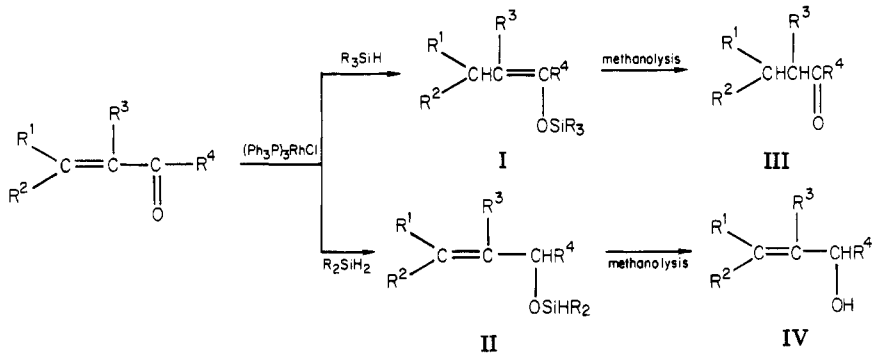
Table I. Regioselective Reductions of α,β-Unsaturated Ketones and Aldehydes via Hydrosilylation[a]

entry	substrate	hydrosilane	conditns	II/IV[e]	yield,[b] %
1	 1	Et_3SiH	50 °C, 1 h	99/1	95
		$PhSiH_3$	rt,[f] 1 h	1/99	95
2	 2	Et_3SiH	rt, 1 h	100/0	97
		Ph_2SiH_2	cooled with ice-water bath, 1 h	0/100	97
3	 3	$EtMe_2SiH$	benzene (10 mL), 25 °C, 15 h	98/2[c]	94
		Ph_2SiH_2	rt, 30 min	0/100[c]	98
4	 4	Et_3SiH	50 °C, 2 h	100/0[c]	96
		Ph_2SiH_2	rt, 30 min	0/100[c]	97
5	 5	$EtMe_2SiH$	45 °C, 4 h	98/2	90
		Ph_2SiH_2	cooled with ice-water bath, 30 min	1/99	97
6	 6	Et_3SiH	50 °C, 30 h	100/0	97
		Ph_2SiH_2	cooled with ice-water bath, 40 min	0/100	97
7	 7	Et_3SiH	80 °C, 25 h	94/6	96
		Et_2SiH_2	cooled with ice-water bath, 30 min	3/97	98
8	 8	$EtMe_2SiH$	benzene (10 mL), rt, 2 h	78/22[c]	97
		Ph_2SiH_2	rt, 20 min	0/100[c]	98
9	 9	Et_3SiH	benzene (10 mL), 50 °C, 5 h[d]	87/13	95
		Ph_2SiH_2	rt, 1 h	3/97	96

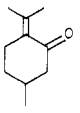
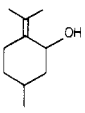
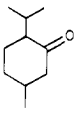
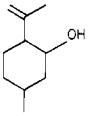
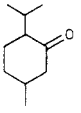
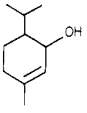
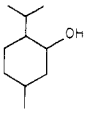
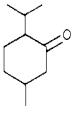
[a] Reactions were run with 10 mmol of substrate, 11 mmol of hydrosilane, and 1.0×10^{-2} mmol of $(Ph_3P)_3RhCl$ followed by methanolysis with K_2CO_3 (10 mg)-MeOH (10 mL) at room temperature unless otherwise noted. [b] GLC analysis unless otherwise noted. [c] NMR analysis. [d] 5.0×10^{-2} mmol of $(Ph_3P)_3RhCl$ was used. [e] α,β-Unsaturated ketone (aldehyde)/allylic alcohol. [f] Room temperature.



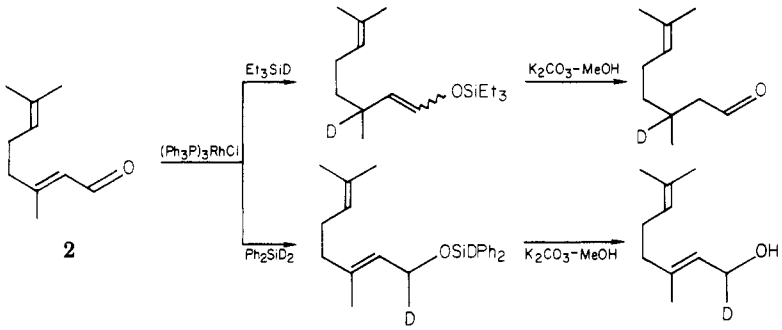
able to convert both ketones to the desired alcohols exclusively.

Regioselective Deuteration with Diphenyldideuteriosilane and Triethyldeuteriosilane. We applied the present reduction method to the regioselective deuteration by using deuteriosilanes. Geranial was chosen as a typical substrate, and triethyldeuteriosilane and diphenyldideuteriosilane as the deuteriosilane. The deuteriosilylation of geranial using triethyldeuteriosilane followed by methanolysis was carried out in a usual conditions to give citronellal-*3-d* exclusively. Similarly, the reaction using diphenyldideuteriosilane afforded geraniol-*1-*d_1 exclusively. No scrambling of deuterium took place in both cases. Consequently the deuteriosilane–$(Ph_3P)_3RhCl$ combination can serve as a convenient reagent for regiospecific deuteration which leads either to the 1-d_1 allylic alcohol or to the 3-d_1 ketone or aldehyde (eq 1).

Table II. Selectivities in the 1,2-Reduction of Pulegone (8) and Piperitone (10) with Metal Hydrides

reducing agent	8[b]				10[b]			
								
Et_2SiH_2-$(Ph_3P)RhCl$		100				100		
Ph_2SiH_2-$(Ph_3P)_3RhCl$		100				100		
$LiAlH_4$[a]	49	51				100		
$LiAl(O\text{-}t\text{-}Bu)_3H$[a]	39	43	18		29	24		47
$LiBH_4$[a]	7	93			23	48.5	28.5	
$NaBH_4$[a]	18	36		46	60	22	18	

[a] See ref 10. [b] Substrate.



(1)

On the Factors Controlling the Regioselectivity of the Reaction. As Tables I and II demonstrate, the regioselectivity of the hydrosilylation of α,β-unsaturated ketones and aldehydes is governed by the type of hydrosilane employed, and Table I (entries 8 and 9) also indicates that the selectivity of the 1,4 addition of monohydrosilane is more or less dependent upon the structure of the substrate. Steric hindrance at C^α and C^β position seems to cause a decrease of regioselectivity. Accordingly, we examined the effects of the structures of substrate and hydrosilane on the regioselectivity. In the first place, mesityl oxide (1), geranial (2), and β-ionone (3) were chosen as the substrates, and ethyldimethylsilane, phenyldimethylsilane, triethylsilane, diisopropylsilane, diethylsilane, phenylmethylsilane, diphenylsilane, and phenylsilane were employed as the hydrosilanes. The results are summarized in Table III.

As Table III shows, the selectivity of 1,4 addition of a monohydrosilane as well as that of 1,2 addition of a dihydrosilane is considerably influenced by the substituent(s) on silicon and also by the structure of the substrate. Namely, it turns out that (i) mesityl oxide is a substrate which tends to favor the formation of 1,4 adduct, whereas β-ionone prefers the 1,2 addition, (ii) phenyl(s) and hydrogen(s) on silicon accelerate the 1,2 addition while alkyl(s) on silicon increases the ratio of the 1,4 addition, and (iii) as a rather special case, diisopropylsilane, which has bulky alkyl substituents, affords the 1,4 adduct predominantly in the reaction of mesityl oxide.

At any rate, a proper choice of hydrosilanes can achieve good to excellent regioselectivities as far as aliphatic α,β-unsaturated ketones and aldehydes are concerned. However, the introduction of phenyl group(s) to the conjugate enone system is found to bring about a dramatic change in the regioselectivity in some cases. For instance, the reduction of chalcone (11) or crotonophenone (12) with the hydrosilane-$(Ph_3P)_3RhCl$ system always afforded dihydrochalcone or butyrophenone via exclusive 1,4 addition regardless of the kind of hydrosilane employed. Dihydrochalcone was the sole product even when diphenylsilane or phenylsilane was used. The hydrosilylation of benzalacetone (13) with triethylsilane or diphenylsilane gave a mixture of the 1,4 adduct and 1,2 adduct. In con-

Table III. Effects of the Structure of Hydrosilane on the Regioselectivity of Hydrosilylation[a]

hydrosilane	mesityl oxide (1)[d] 1,4/1,2[b]	mesityl oxide (1)[d] yield, %	geranial (2)[d] 1,4/1,2[b]	geranial (2)[d] yield, %	β-ionone (3)[d] 1,4/1,2[c]	β-ionone (3)[d] yield, %
$EtMe_2SiH$	100/0	99	100/0	92	98/2	94
$PhMe_2SiH$	99/1	98			85/15	95
Et_3SiH	99/1	95	100/0	97	78/22	95
$i\text{-}Pr_2SiH_2$	87/13	93	49/51	94		
Et_2SiH_2	43/57	90	3/97	95	0/100	98
$PhMeSiH_2$	39/61	98				
Ph_2SiH_2	7/93	99	0/100	97	0/100	98
$PhSiH_3$	1/99	95				

[a] All reactions were run with 5.0 mmol of substrate, 5.5 mmol of hydrosilane and 5.0×10^{-3} mmol of $(Ph_3P)_3RhCl$. [b] Determined by GLC analysis of methanolyzed products. [c] Determined by NMR analysis of hydrosilylation products. [d] Substrate.

Table IV. Regioselectivities in the Hydrosilylation of Chalcone (11), Crotonophenone (12), Benzalacetone (13), and Cinnamaldehyde (14)[a]

substrate	hydrosilane	conditns	1,4/1,2[b]
PhCH=CHCOPh (11)	Et_3SiH	25 °C, 15 h[c]	100/0
	Ph_2SiH_2	0-25 °C, 6 h	100/0
	$PhSiH_3$	0-25 °C, 6 h	100/0
MeCH=CHCOPh (12)	Et_3SiH	45 °C, 15 h	100/0
	Ph_2SiH_2	0-25 °C, 6 h	100/0
PhCH=CHCOMe (13)	Et_3SiH	45 °C, 15 h	63/37
	Ph_2SiH_2	0-25 °C, 6 h	40/60
PhCH=CHCHO (14)	Et_3SiH	45 °C, 1 h[c]	100/0
	Ph_2SiH_2	0-25 °C, 2 h	0/100

[a] All reactions were run with 5.0 mmol of substrate, 6.0 mmol of hydrosilane, and 5.0×10^{-3} mmol of $(Ph_3P)_3RhCl$. [b] Determined by NMR analysis of the methanolyzed products. [c] Benzene (1 mL) was used as solvent.

Table V. Dependency of Regioselectivity on the Concentration of Reactants[a]

entry	substrate	hydrosilane	[substrate]/[hydrosilane]	solvent	temp, °C	time, h	method[b]	1,4/1,2[c]
1	mesityl oxide (1)	Ph_2SiH_2	1/1.5	none	0	1	A	7/93
2	1	Ph_2SiH_2	1/1.5	benzene (40 mL)	25	20	A	54/43
3	1	Ph_2SiH_2	1/1.5	benzene (100 mL)	25	20	A	63/37
4	1	Ph_2SiH_2	1/1.5	benzene (200 mL)	25	20	A	79/21
5	1	Ph_2SiH_2	1/1.5	none	25	2	B	2/98
6	1	Ph_2SiH_2	1/1.5	none	25	2	C	43/57
7	1	Et_3SiH	1/1.5	none	50	2	B	94/6
8	1	Et_3SiH	1/1.5	none	50	2	C	99/1
9	β-ionone (3)	Et_3SiH	1/10	none	50	3	A	64/36[d]
10	3	Et_3SiH	1/1.5	none	50	3	A	78/22[d]
11	3	Et_3SiH	1/1.5	benzene (10 mL)	50	12	A	86/14[d]

[a] Reactions were run with 2.0 mmol of substrate, 3.0–20 mmol of hydrosilane, and 4.0×10^{-3}–2.0×10^{-2} mmol of $(Ph_3P)_3RhCl$. [b] Method A: a mixture of substrate and hydrosilane was added to the catalyst. Method B: substrate was added dropwise to the mixture of hydrosilane and the catalyst. Method C: hydrosilane was added dropwise to the mixture of substrate and the catalyst (see Experimental Section). [c] Determined by GLC analysis of the methanolyzed products unless otherwise noted. [d] Determined by NMR analysis of the hydrosilylation products.

trast with these, the hydrosilylation of cinnamaldehyde (14) proceeded following the normal regioselectivity; i.e., the reaction with triethylsilane gave 1,4 adduct exclusively while that with diphenylsilane gave 1,2 adduct as sole product. Results are listed in Table IV.

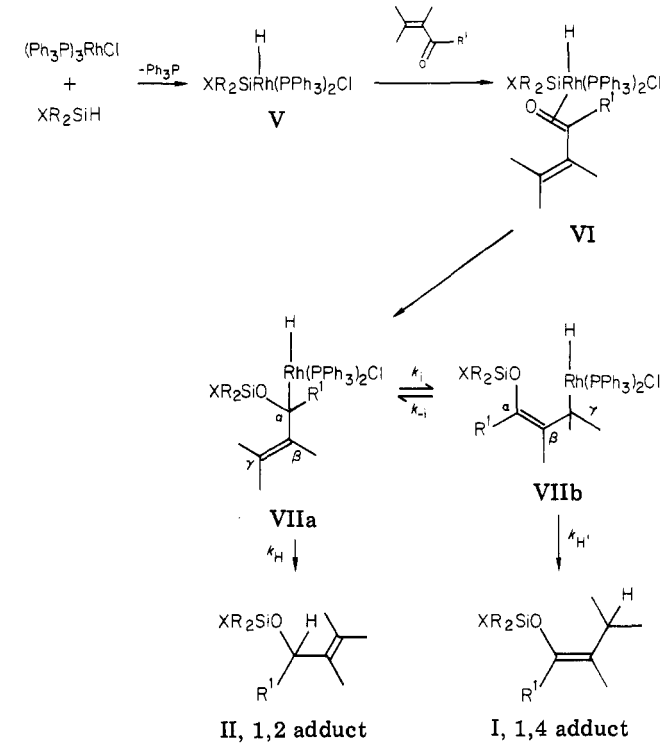
Next, we studied the effects of reaction variables on the regioselectivities. Table V illustrates the marked dependency of regioselectivity on the concentration of reactants using the reaction of mesityl oxide and diphenylsilane as a typical example. As is immediately seen from Table V, the 1,2 addition takes place with excellent selectivity at a high concentration of diphenylsilane (entries 1 and 5), whereas the 1,4 addition becomes predominant as the concentration of the hydrosilane decreases: The 1,4 addition/1,2 addition ratio is reversed to 79/21 at a high dilution of diphenylsilane. A similar dependency of regioselectivity on the concentration of hydrosilane was observed when triethylsilane and β-ionone were used. The results strongly imply that the reaction involves a bimolecular reductive elimination process.

As for the effects of reaction temperature on the regioselectivity, it turned out that higher temperatures favored the production of the 1,4 adduct. For example, in the hydrosilylation of mesityl oxide (5.0 mmol) with diphenylsilane (6.0 mmol) in benzene (10 mL) the ratio of 1,4 addition/1,2 addition changed from 15/85 at ice-water cooled temperature to 64/36 in refluxing benzene: 30/70 at 25 °C and 45/55 at 50 °C.

During the course of our investigation, Sharf et al. reported similar preliminary results by using 2-cyclohexenone as substrate and diphenylsilane and phenylsilane as the hydrosilanes.[11]

On the Mechanism of Regioselective Hydrosilylation. As to the mechanism of the hydrosilylation of simple carbonyl compounds catalyzed by Wilkinson-type rhodium complexes, we and others proposed the one which involves an initial silicon migration from the oxidative adduct to the carbonyl oxygen of the coordinated substrate giving (α-siloxyalkyl)rhodium hydride as the key intermediate.[7,12] Recent spin-trapping experiments done by Kagan et al. also support the proposed mechanism.[13] Thus, it is quite reasonable to assume that the hydrosilylation of α,β-unsaturated ketones and aldehydes also follows the proposed mechanism. In addition, the possible isomerization of the produced 1,2 adduct to 1,4 adduct was excluded since no change in I/II ratio was observed at all by NMR analysis even when the reaction mixture was heated at 80–100 °C for a prolonged period of time.

Scheme I



The most plausible mechanism which can accommodate the observed regioselectivity is illustrated in Scheme I. The mechanism involves an (α-siloxyallyl)rhodium hydride (VIIa) as the key intermediate and a hydrogen shift from VIIa gives the 1,2 adduct II, whereas an isomerization of VIIa gives the other intermediate, (γ-siloxyallyl)rhodium hydride (VIIb), and a hydrogen shift from VIIb then affords the 1,4 adduct (I).

In connection with the proposed mechanism shown in Scheme I, we carried out the spin-trapping experiment in the hope of obtaining supporting evidence of the intermediacy of VIIa,b. The EPR spectra, obtained by adding nitrosodurene to the hydrosilylation system which consists of β-ionone, diphenylsilane, and $(Ph_3P)_3RhCl$, are shown in Figures 1 and 2. Figure 1 shows the EPR spectrum measured 15 min after mixing of the reagents. The

(11) Sharf, V. Z.; Treidlin, L. Kh.; Shekoyan, I. S.; Krutii, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 1087.

(12) (a) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. (b) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. (c) Ojima, I.; Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3722; (d) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 124. (e) Yamamoto, K.; Hayashi, T.; Kumada, M. *Ibid.* **1973**, *54*, C45.

(13) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211.

Table VI. Spectral Data for Hydrosilylation Products (I and II)

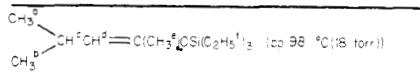
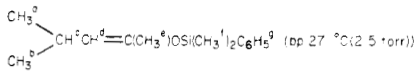
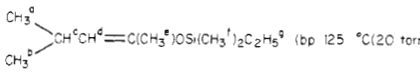
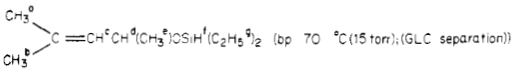
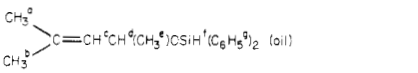
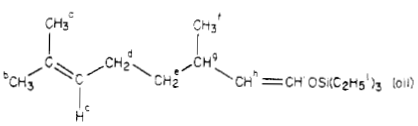
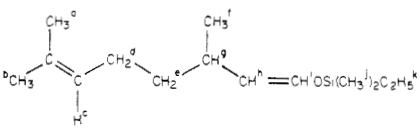
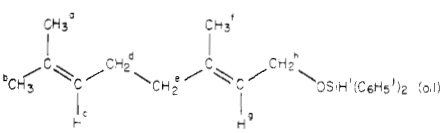
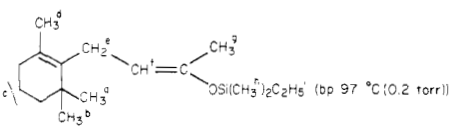
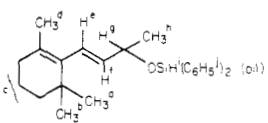
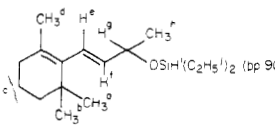
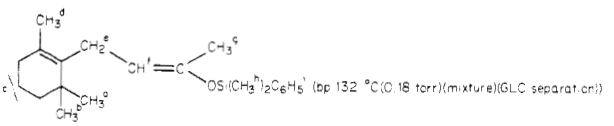
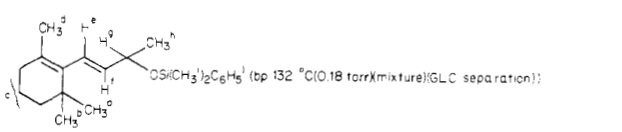
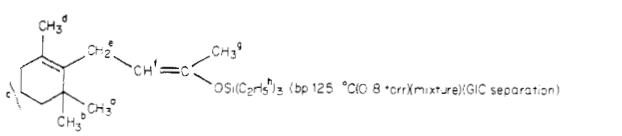
hydrosilylation product	^{1}H NMR (δ (ppm); solvent CCl_4 unless otherwise noted)
 (bp 98 °C(18 torr))	0.30–1.25 (m, 15 H) (H^f), [0.90 (d, J = 7 Hz) (E), 0.95 (d, J = 7 Hz) (Z)] (6 H) (H^a, H^b), 1.72 (m, 3 H) (H^e), 2.20–2.90 (m, 1 H) (H^c), [4.15 (d, J = 9 Hz) (Z), 4.39 (d, J = 9 Hz (E)] (1 H) (H^d)
 (bp 27 °C(2.5 torr))	0.15 (s, 6 H) (H^f), 0.40–1.30 (m, 11 H) (H^a, H^b, H^g), 1.70 (m, 3 H) (H^e), 2.30–3.00 (m, 1 H) (H^c), [4.16 (d, J = 9 Hz) (Z) 4.37 (d, J = 9 Hz) (E)] (1 H) (H^d)
 (bp 125 °C(20 torr))	0.42 (s, 6 H) (H^f), 0.89 (d, J = 7 Hz, 6 H) (H^a, H^b), 1.65 (m, 3 H) (H^e), 2.30–3.00 (m, 1 H) (H^c), [4.23 (d, J = 9 Hz) (Z), 4.40 (d, J = 9 Hz) (E)] (1 H) (H^d), 7.10–7.70 (m, 5 H) (H^g)
 (bp 70 °C(15 torr); (GLC separation))	0.30–1.30 (m, 13 H) (H^g, H^e), 1.70 (m, 6 H) (H^a, H^b), 4.25–4.75 (m, 1 H) (H^d), 4.35 (quintet, J = 2 Hz, 1 H) (H^f), 5.13 (m, J_{c-d} = 9 Hz, 1 H) (H^c)
 (oil)	1.23 (d, J = 6.5 Hz, 3 H) (H^e), 1.40 (d, J_{a-c} = 1.5 Hz, 3 H) (H^a), 1.60 (d, J_{b-c} = 1.2 Hz, 3 H) (H^b), 4.57 (d of quartet, J_{c-d} = 8.5 Hz, J_{d-e} = 6.5 Hz, 1 H) (H^d), 5.15 (m, J_{c-d} = 8.5 Hz, 1 H) (H^c), 7.00–7.70 (m, 10 H) (H^g)
 (oil)	0.40–1.40 (m, 20 H) (H^j, H^f, H^e), 1.55 (s, 3 H) (H^a), 1.63 (s, 3 H) (H^b), 1.90 (m, 2 H) (H^d), 2.62 (m, 1 H) (H^g), [4.11 (d of d, J_{g-h} = 9 Hz, J_{h-i} = 6 Hz) (Z), 4.68 (d of d, J_{g-h} = 9 Hz, J_{h-i} = 12 Hz) (E)] (1 H) (H^h), 5.00 (m, 1 H) (H^c), [6.04 (d, J_{h-i} = 6 Hz) (Z), 6.07 (d, J_{h-i} = 12 Hz) (E) (1 H) (H^i)
 (oil)	0.13 (s, 6 H) (H^j), 0.40–1.40 (m, 10 H) (H^k, H^f, H^e), 1.58 (s, 3 H) (H^a), 1.66 (s, 3 H) (H^b), 1.90 (m, 2 H) (H^d), 2.59 (m, 1 H) (H^g), [4.17 (d of d, J_{g-h} = 9 Hz, J_{h-i} = 6 Hz) (Z), 4.69 (d of d, J_{g-h} = 9 Hz, J_{h-i} = 6.5 Hz) (E)] (1 H) (H^h), 5.02 (m, 1 H) (H^c), [6.04 (d, J_{h-i} = 6.5 Hz) (Z), 6.09 (d, J_{h-i} = 12 Hz) (E)] (1 H) (H^i)
 (oil)	1.52 (s, 3 H) (H^f), 1.60 (s, 3 H) (H^a), 1.69 (s, 3 H) (H^b), 1.80–2.26 (m, 4 H) (H^d, H^e), 4.31 (d, J = 7 Hz, 2 H) (H^h), 5.10 (m, 1 H) (H^c), 5.38 (t, J = 7 Hz, 1 H) (H^g), 5.39 (s, 1 H) (H^i), 7.20–7.85 (m, 10 H) (H^j)
 (bp 97 °C(0.2 torr))	0.19 (s, 6 H) (H^h), 0.40–1.20 (m, 5 H) (H^i), 0.98 (s, 6 H) (H^a, H^b), 1.25–2.16 (m, 6 H) (H^c), 1.54 (s, 3 H) (H^d), 1.73 (d, J_{f-g} = 1.5 Hz, 3 H) (H^g), 2.60 (d, J_{e-f} = 6.5 Hz, 2 H) (H^e), [4.34 (t, J_{e-f} = 6.5 Hz) (E), 4.50 (t, J_{f-g} = 6.5 Hz) (E)] (1 H) (H^f)
 (oil)	0.94 (s, 6 H) (H^a, H^b), 1.33 (d, J_{g-h} = 7 Hz, 3 H) (H^h), 1.61 (s, 3 H) (H^d), 1.20–2.20 (m, 6 H) (H^c), 4.48 (quintet, J_{f-g} = J_{g-h} = 7 Hz, 1 H) (H^g), 5.45 (d of d, J_{f-g} = 7 Hz, J_{e-f} = 16 Hz, 1 H) (H^f), 5.50 (s, 1 H) (H^i), 6.00 (d, J_{e-f} = 16 Hz, 1 H) (H^e), 7.20–7.80 (m, 10 H) (H^j) (in $CDCl_3$)
 (bp 90 °C(0.23 torr))	0.40–1.20 (m, 16 H) (H^a, H^b, H^j), 1.28 (d, J_{g-h} = 7 Hz, 3 H) (H^h), 1.64 (s, 3 H) (H^d), 1.40–2.30 (m, 6 H) (H^c), 4.35 (quintet, J_{e-f} = J_{f-g} = 7 Hz, 1 H) (H^g), 4.49 (quintet, J = 2 Hz, 1 H) (H^i), 5.41 (d of d, J_{e-f} = 16 Hz, J_{f-g} = 7 Hz, 1 H) (H^f), 6.05 (d, J_{e-f} = 16 Hz, 1 H) (H^e) (in $CDCl_3$)
 (bp 132 °C(0.18 torr)(mixture)(GLC separation))	0.46 (s, 6 H) (H^h), 0.95 (s, 6 H) (H^a, H^b), 1.54 (s, 3 H) (H^d), 1.69 (d, J_{f-g} = 1.5 Hz, 3 H) (H^g), 1.40–2.20 (m, 6 H) (H^c), 2.67 (d, J_{e-f} = 7 Hz, 2 H) (H^e), 4.28 (t, J_{e-f} = 7 Hz, 1 H) (H^f), 7.20–7.70 (m, 5 H) (H^i) (in $CDCl_3$)
 (bp 132 °C(0.18 torr)(mixture)(GLC separation))	0.38 (s, 6 H) (H^i), 0.95 (s, 6 H) (H^a, H^b), 1.33 (d, J_{g-h} = 7 Hz, 3 H) (H^h), 1.54 (s, 3 H) (H^d), 1.40–2.20 (m, 6 H) (H^c), 4.37 (quintet, J_{f-g} = J_{g-h} = 7 Hz, 1 H) (H^g), 5.39 (d of d, J_{e-f} = 16 Hz, J_{f-g} = 7 Hz, 1 H) (H^f), 5.95 (d, J_{e-f} = 16 Hz, 1 H) (H^e), 7.20–7.70 (m, 5 H) (H^j) (in $CDCl_3$)
 (bp 125 °C(0.8 torr)(mixture)(GLC separation))	0.40–2.20 (m, 21 H) (H^h, H^a, H^b), 1.54 (s, 3 H) (H^d), 1.75 (d, J_{f-g} = 1.5 Hz, 3 H) (H^g), 1.40–2.20 (m, 6 H) (H^c), 2.67 (d, J_{e-f} = 7 Hz, 2 H) (H^e), 4.17 (t, J_{e-f} = 7 Hz, 1 H) (H^f) (in $CDCl_3$)

Table VI (*Continued*)

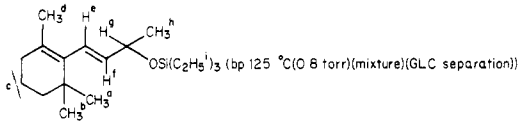
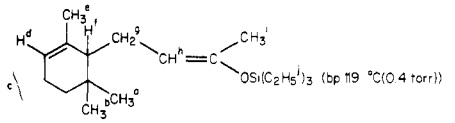
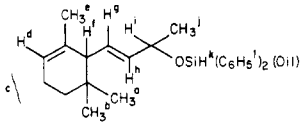
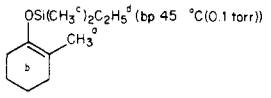
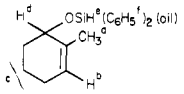
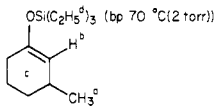
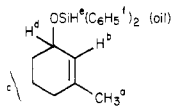
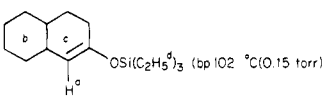
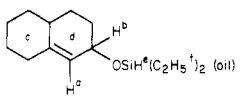
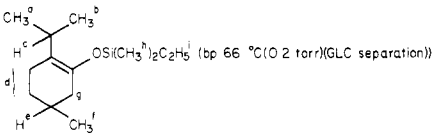
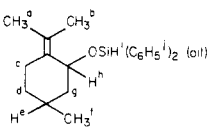
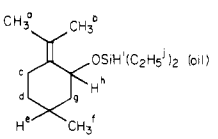
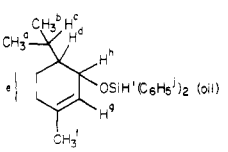
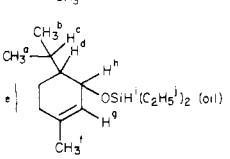
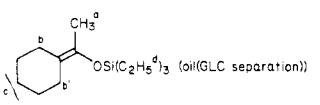
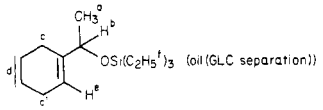
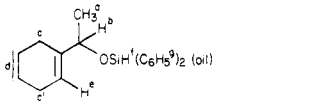
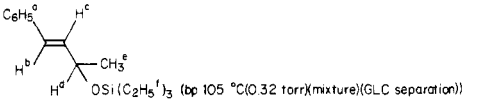
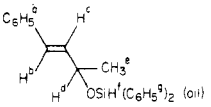
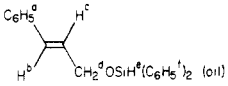
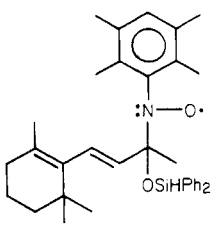
hydrosilylation product	^{1}H NMR (δ (ppm); solvent CCl_4 unless otherwise noted)
	0.40–2.20 (m, 21 H) (H^i, H^a, H^b), 1.22 (d, J_{g-h} = 7 Hz, 3 H) (H^h), 1.54 (s, 3 H) (H^d), 1.40–2.20 (m, 6 H) (H^c), 4.27 (quintet, $J_{f-g} = J_{g-h}$ = 7 Hz, 1 H) (H^g), 5.33 (d of d, J_{e-f} = 16 Hz, J_{f-g} = 7 Hz, 1 H) (H^f), 5.94 (d, J_{e-f} = 16 Hz, 1 H) (H^e) (in $CDCl_3$)
	0.40–1.30 (m, 21 H) (H^j, H^a, H^b), 1.30–2.30 (m, 13 H) (H^c, H^e, H^f, H^g, H^i), 4.32 (t, J = 7 Hz, 1 H) (H^h), 5.27 (b s, 1 H) (H^d)
	0.77 (s, 3 H) (H^a), 0.86 (s, 3 H) (H^b), 1.27 (d, J_{i-j} = 6 Hz, 3 H) (H^j), 1.53 (m, 3 H) (H^e), 1.00–2.30 (m, 5 H) (H^c, H^f), 4.39 (m, 1 H) (H^i), 5.18–5.55 (m, 3 H) (H^d, H^g, H^h), 5.40 (s, 1 H) (H^k), 7.10–7.80 (m, 10 H) (H^l)
	0.11 (s, 6 H) (H^c), 0.30–1.30 (m, 5 H) (H^d), 1.68 (s, 3 H) (H^a), 1.35–2.40 (m, 8 H) (H^b)
	1.10–2.30 (m, 6 H) (H^c), 1.70 (b s, 3 H) (H^a), 4.17 (m, 1 H) (H^d), 5.44 (m, 1 H) (H^b), 5.49 (s, 1 H) (H^e), 7.10–7.80 (m, 10 H) (H^f)
	0.30–1.20 (m, 18 H) (H^a, H^d), 1.35–2.50 (m, 7 H) (H^c), 4.62 (m, 1 H) (H^b)
	1.20–2.40 (m, 6 H) (H^c), 1.64 (m, 3 H) (H^a), 4.33 (m, 1 H) (H^d), 5.42 (m, 1 H) (H^b), 5.45 (s, 1 H) (H^e), 7.10–7.70 (m, 10 H) (H^f)
	0.28–1.35 (m, 15 H) (H^d), 1.35–2.41 (m, 14 H) (H^b, H^c), 4.44 (b s, 1 H) (H^a)
	0.25–1.35 (m, 10 H) (H^f), 1.35–2.30 (m, 13 H) (H^c, H^d), 4.17 (m, 1 H) (H^b), 4.43 (quintet, J = 2 Hz, 1 H) (H^e), 5.28 (b s, 1 H) (H^a)
	0.14 (s, 6 H) (H^h), 0.30–1.35 (m, 14 H) (H^a, H^b, H^f, H^i), 1.35–2.30 (m, 7 H) (H^d, H^e, H^g), 2.94 (septet, J = 7 Hz, 1 H) (H^c)
	0.60–1.90 (m, 8 H) (H^d, H^e, H^f, H^g), 1.46 (s, 3 H) (H^b), 1.56 (s, 3 H) (H^a), 2.24 (m, 2 H) (H^c), 4.89 (t, J = 4 Hz, 1 H) (H^h), 5.40 (s, 1 H) (H^i), 7.20–7.90 (m, 10 H) (H^j)
	0.30–1.35 (m, 13 H) (H^f, H^j), 1.35–2.00 (m, 6 H) (H^d, H^e, H^g), 1.69 (s, 3 H) (H^b), 1.76 (s, 3 H) (H^a), 2.22 (m, 2 H) (H^c), 4.35 (quintet, J = 2 Hz, 1 H) (H^i), 4.67 (t, J = 4 Hz, 1 H) (H^h)
	0.93 (d, J = 7 Hz, 6 H) (H^a, H^b), 1.35–2.10 (m, 6 H) (H^c, H^d, H^e), 1.60 (b s, 3 H) (H^f), 4.30 (m, 1 H) (H^h), 5.43 (m, 1 H) (H^g), 5.45 (s, 1 H) (H^i), 7.10–7.90 (m, 10 H) (H^j)
	0.30–1.35 (m, 10 H) (H^j), 0.92 (d, J = 7 Hz, 6 H) (H^a, H^b), 1.35–2.20 (m, 6 H) (H^c, H^d, H^e), 1.67 (b s, 3 H) (H^f), 4.12 (m, 1 H) (H^h), 4.43 (quintet, J = 2 Hz, 1 H) (H^i), 5.50 (m, J_{g-h} = 5 Hz, 1 H) (H^g)
	0.30–1.05 (m, 15 H) (H^d), 1.32–1.55 (m, 6 H) (H^c), 1.75 (s, 3 H) (H^a), 1.80–2.30 (m, 4 H) (H^b, $H^{b'}$) (in $CDCl_3$)

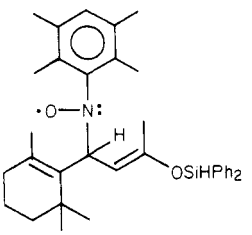
Table VI (*Continued*)

hydrosilylation product	^{1}H NMR (δ (ppm); solvent CCl_4 unless otherwise noted)
	0.30-1.05 (m, 15 H) (H^f), 1.16 (d, J_{a-b} = 6.5 Hz, 3 H) (H^a), 1.55 (m, 4 H) (H^d), 1.96 (m, 4 H) (H^c, $H^{c'}$), 4.10 (quartet, J_{a-b} = 6.5 Hz, 1 H) (H^b), 5.56 (m, 1 H) (H^e) (in $CDCl_3$)
	1.27 (d, J_{a-b} = 6.5 Hz, 3 H) (H^a), 1.50 (m, 4 H) (H^d), 1.92 (m, 4 H) (H^c, $H^{c'}$), 4.30 (quartet, J_{a-b} = 6.5 Hz, 1 H) (H^b), 5.41 (s, 1 H) (H^f), 5.56 (m, 1 H) (H^e), 7.20-7.80 (m, 10 H) (H^g) (in $CDCl_3$)
$C_6H_5{}^aCH_2{}^bCH^c{=}C(C_6H_5{}^d)OSi(C_2H_5{}^e)_3$ (oil)	0.30-1.13 (m, 15 H) (H^e), 3.42 [(d, J = 8 Hz) (E), 3.56 (d, J = 7 Hz) (Z)] (2 H) (H^b), [5.21 (t, J = 8 Hz) (E), 5.30 (t, J = 7 Hz) (Z)] (1 H) (H^c), 7.00-8.20 (m, 10 H) (H^a, H^d) (in $CDCl_3$)
$C_6H_5{}^aCH_2{}^bCH^c{=}C(C_6H_5{}^d)OSiH^e(C_6H_5{}^f)_2$ (oil)	[3.52 (d, J = 7.5 Hz) (E), 3.59 (d, J = 7 Hz) (Z)] (2 H) (H^b), 5.30 (t, J = 7 Hz, 1 H) (H^c, E + Z), [5.67 (s) (E), 5.69 (s) (Z)] (1 H) (H^e), 6.95-7.75 (m, 20 H) (H^a, H^d, H^f)
$CH_3{}^aCH_2{}^bCH^c{=}C(C_6H_5{}^d)OSi(C_2H_5{}^e)_3$ (bp 89 °C (0.2 torr))	0.30-1.50 (m, 18 H) (H^a, H^e), [2.09 (quintet, J = 7 Hz) (E), 2.21 (quintet, J = 7 Hz) (Z)] (2 H) (H^b), [5.00 (t, J = 7 Hz) (E), 5.07 (t, J = 7 Hz) (Z)] (1 H) (H^c), 7.10-8.00 (m, 5 H) (H^d) (in $CDCl_3$)
$CH_3{}^aCH_2{}^bCH^c{=}C(C_6H_5{}^d)OSiH^e(C_6H_5{}^f)_2$ (oil)	[0.85 (t, J = 7 Hz) (Z), 0.87 (t, J = 7 Hz) (E)] (3 H) (H^a), [2.18 (quintet, J = 7 Hz) (Z), 2.18 (quintet, J = 7 Hz) (E)] (2 H) (H^b), [5.12 (t, J = 7 Hz) (Z), 5.20 (t, J = 7 Hz) (E)] (1 H) (H^c), [5.60 (s) (E), 5.62 (s) (Z)] (1 H) (H^e), 7.00-7.80 (m, 15 H) (H^d, H^f) (in $CDCl_3$)
$C_6H_5{}^aCH_2{}^bCH^c{=}C(CH_3{}^d)OSi(C_2H_5{}^e)_3$ (bp 105 °C (0.32 torr) (mixture) (GLC separation))	0.30-1.15 (m, 15 H) (H^e), 1.82 (s, 3 H) (H^d), [3.29 (d, J = 7 Hz) (Z), 3.36 (d, J = 7 Hz) (E)] (2 H) (H^b), [4.59 (t, J = 7 Hz) (E), 4.86 (t, J = Hz) (Z)] (1 H) (H^c), 7.00-7.40 (m, 5 H) (H^a)
	0.30-1.15 (m, 15 H) (H^e), 1.31 (d, J = 6 Hz, 3 H) (H^e), 4.45 (quintet, J = 6 Hz, 1 H) (H^d), 6.18 (d of d, J_{b-c} = 15 Hz, J_{c-d} = 6 Hz, 1 H) (H^c), 6.53 (d, J_{b-c} = 15 Hz, 1 H) (H^b), 7.00-7.40 (m, 5 H) (H^a)
$C_6H_5{}^aCH_2{}^bCH^c{=}C(CH_3{}^d)OSiH^e(C_6H_5{}^f)_2$ (oil)	1.83 (s, 3 H) (H^d), 3.18 (d, J = 7 Hz, 2 H) (H^b), 5.10 (t, J = 7 Hz, 1 H) (H^c), 5.60 (s, 1 H) (H^e), 6.90-7.80 (m, 15 H) (H^a, H^f)
	1.37 (d, J = 6 Hz, 3 H) (H^e), 4.60 (quintet, J = 6 Hz, 1 H) (H^d), 5.50 (s, 1 H) (H^f), 6.17 (d of d, J_{b-c} = 15 Hz, J_{c-d} = 6 Hz, 1 H) (H^c), 6.48 (d, J_{b-c} = 15 Hz, 1 H) (H^b), 6.90-7.80 (m, 15 H) (H^a, H^g)
$C_6H_5{}^aCH_2{}^bCH^c{=}CH^dOSi(C_2H_5{}^e)_3$ (bp 155 °C (20 torr))	0.40-1.15 (m, 15 H) (H^e), [3.15 (d of d, J_{b-c} = 7.5 Hz, J_{b-d} = 1.5 Hz) (E), 3.34 (d of d, J_{b-c} = 7.5 Hz, J_{b-d} = 1.5 Hz) (Z)] (2 H) (H^b), [4.53 (d of t, J_{b-c} = 7.5 Hz, J_{c-d} = 5.5 Hz) (Z), 5.01 (d of t, J_{b-c} = 7.5 Hz, J_{c-d} = 12.5 Hz) (E)] (1 H) (H^c), [3.12 (d of t, J_{c-d} = 5.5 Hz, J_{b-d} = 1.5 Hz) (Z), 6.20 (d of t, J_{c-d} = 12.5 Hz, J_{b-d} = 1.5 Hz) (E)] (1 H) (H^d), 6.95-7.35 (m, 5 H) (H^a)
	4.43 (d, J_{c-d} = 6 Hz, 2 H) (H^d), 5.50 (s, 1 H) (H^e), 6.22 (d of d, J_{b-c} = 15 Hz, J_{c-d} = 6 Hz, 1 H) (H^c), 6.60 (d, J_{b-c} = 15 Hz, 1 H) (H^b), 6.95-7.90 (m, 15 H) (H^a, H^f) (in $CDCl_3$)

spectrum indicates that there are two sets of signals, i.e., one triplet (g = 2.0069, a_N = 12.6 G) and one doublet of triplet (g = 2.0069, a_N = 12.9 G, a_H = 8.4 G). Figure 2 shows the spectrum measured after 30 min, in which the triplet diminishes and the doublet of triplet becomes predominant. It is suggested that the triplet is due to α-siloxyallyl nitroxide (**15**) and the doublet of triplet, to γ-siloxyallyl nitroxide (**16**).



15



16

When diphenylsilane was mixed with nitrosodurene in toluene, the EPR spectrum of the solution only showed the signals due to $PhCH_2N(O)C_6H(Me)_4$ (g = 2.007, a_N = 13.6 G, a_M = 8.0 G). The EPR spectrum of a mixture of β-ionone, $(Ph_3P)_3RhCl$, and nitrosodurene in toluene displayed very complicated signals which were completely different from those shown in Figures 1 and 2.

The results strongly suggest the intermediacy of (α-siloxyallyl)- and (γ-siloxyallyl)rhodium hydride complexes (VIIa and VIIb) as well as the possible isomerization of VIIa to VIIb.

Accordingly, the selectivity is possibly governed by the following: (A) The relative ease of the hydride shift from VIIa compared with the isomerization of VIIa: 1,4 addition takes place exclusively when the isomerization is by far faster than the hydride shift, i.e., $k_i \gg k_H$, and exclusive 1,2 addition occurs when the hydride shift is by far faster than the isomerization, i.e., $k_i \ll k_H$. (B) The relative

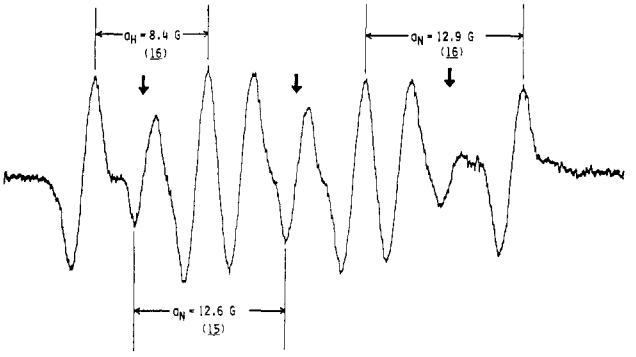


Figure 1. EPR spectrum of the reaction mixture of β-ionone (**3**), diphenylsilane, $(Ph_3P)_3RhCl$, and nitrosodurene in toluene at 25 °C 15 min after the reagents were mixed. The arrows indicate the signals ascribed to the spin adduct **15**.

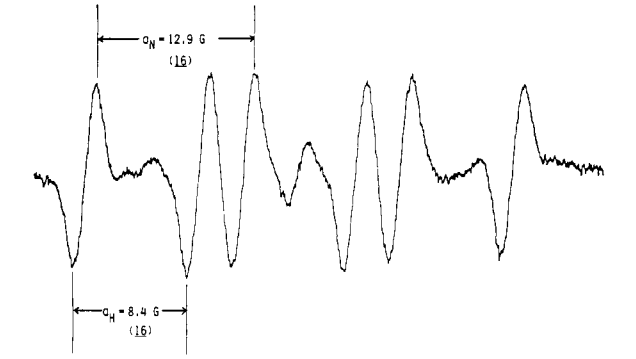
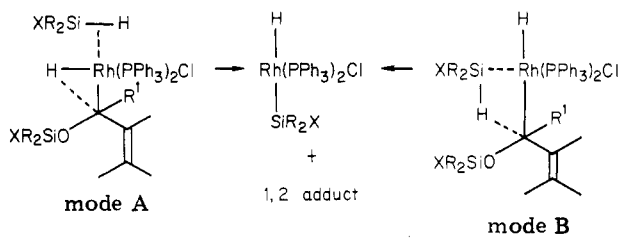


Figure 2. EPR spectrum (25 °C) of the spin adducts 30 min after the reagents were mixed.

stability of the intermediate VIIa vs. VIIb provided that the rate of the hydride shift is slower than that of the isomerization, i.e., k_i, $k_{-i} > k_H$, $k_{H'}$.

It is reasonable to assume that VIIb is thermodynamically much more favorable than VIIa, i.e., $k_i \gg k_{-i}$, because of the steric hindrance between the α-siloxy group and the rhodium moiety in VIIa and also because of the stabilization of the carbon–carbon double bond by the vinyl ether linkage in VIIb. Thus, possibility B mentioned above is unlikely, and possibility A is most likely to accommodate the results. Namely, the 1,4 addition/1,2 addition ratio should reflect the k_i/k_H ratio. The factors that have strong influence on the k_i/k_H ratio are the following: (a) the bulkiness of α-siloxy group with regard to the steric repulsion with the rhodium moiety and (b) a through-bond electronic effect of silyl group on the nature of the allylic system with regard to the relative ease of isomerization. In addition to these factors, we should take into account the participation of another molecule of hydrosilane in the acceleration of hydride migration, factor c, which is shown in Table V. Although the mechanism of this acceleration is unclear at this stage, we can illustrate the plausible modes A and B.



In conclusion the following are suggested: (i) *in the case of di- and trihydrosilanes*, factor a is less favorable for the isomerization since the bulkiness of the α-siloxy group is much smaller than that generated from monohydrosilanes, whereas factor c is much more advantageous for the hydride shift since the participation of the polyhydrosilanes in the hydride migration step is much easier than that of monohydrosilanes either by steric reasons or by reactivity for oxidative addition: as a result, 1,2 addition takes place exclusively especially when the polyhydrosilanes are used in high concentration. (ii) *In the case of monohydrosilanes*, factors a, b, and c are all favorable for the isomerization, thus 1,4 addition is exclusive especially when monohydrosilanes are used in low concentration.

Experimental Section

Measurements. The boiling points and melting points were uncorrected. The infrared spectra (IR) were recorded on a Hitachi EPI-G3 spectrophotometer, using samples as neat liquid or KBr disks. The nuclear magnetic resonance spectra (NMR) were obtained by the use of a Varian HA-100 or a Varian T-60 spectrometer, using Me_4Si as the internal standard. The electron paramagnetic resonance spectra (EPR) were measured with a JEOL JES-ME-1X spectrometer by using a manganese(II) marker. Analytical gas chromatography (GLC) was carried out on a Shimadzu GC-3BT or GC-3BF using columns (1.2 or 2.1 m × 3.5 mm) packed with 3% and 20% SE-30, 3% OV-17, and 15% PEG-1000.

Materials. Hydrosilanes were prepared from chlorosilanes by known methods. Deuteriosilanes were prepared by reducing corresponding chlorosilanes with lithium aluminum deuteride.[14] Tris(triphenylphosphine)chlororhodium was prepared from rhodium trichloride trihydrate and triphenylphosphine.[15] α-Ionone, β-ionone, geranial, mesityl oxide, pulegone, 3-methyl-2-cyclohexenone, 1-acetyl-1-cyclohexene, chalcone, benzalacetone, crotonophenone, and cinnamaldehyde were commercially available and purified by distillation or recrystallization prior to use. 2-Methyl-2-cyclohexenone, $\Delta^{1,9}$-2-octalone, and piperitone were prepared by known methods. Authentic samples of the reduction products were either obtained commercially or prepared by standard methods.

Reduction of α,β-Unsaturated Aldehydes and Ketones via Hydrosilylation Catalyzed by Tris(triphenylphosphine)-chlororhodium. The present reduction method consists of hydrosilylation and solvolysis. The ^1H NMR spectral data used for the identification of the hydrosilylation products, I and II, are summarized in Table VI.

Typical procedure is described for the reductions of α-ionone.

(A) A mixture of α-ionone (1.91 g, 10 mmol), triethylsilane (1.27 g, 11 mmol), and tris(triphenylphosphine)chlororhodium (9 mg, 1×10^{-2} mmol) was stirred at 50 °C for 2 h under nitrogen; then α-ionone was completely consumed. The NMR spectrum of the reaction mixture showed the exclusive formation of 1,4 adduct: NMR (CCl_4) δ 0.4–1.20 (m, 21 H), 1.20–1.75 (m, 3 H), 1.63 (br s, 3 H), 1.72 (br s, 3 H), 1.75–2.25 (m, 4 H), 4.28 (t, J = 7 Hz, 1 H), 5.23 (m, 1 H). The silyl enol ether was smoothly desilylated by the action of K_2CO_3 (10 mg)–MeOH (10 mL) with stirring for 1 h at room temperature (96% yield based on the GLC analysis). The ratio of the products, dihydro-α-ionone/*trans*-ionol, was found to be 100/0 on the basis of GLC and NMR analyses. After the solvent was evaporated, the residue was distilled under reduced pressure to afford dihydro-α-ionone (1.70 g, 88.1%), bp 88 °C (2.5 torr).

(B) A mixture of α-ionone (1.93 g, 10 mmol), diphenylsilane (2.02 g, 11 mmol), and tris(triphenylphosphine)chlororhodium (9 mg, 1×10^{-2} mmol, 0.1 mol %) was stirred at room temperature under nitrogen. An exothermic reaction took place and the hydrosilylation was completed within 30 min. The NMR spectrum of the reaction mixture indicated that 1,2 adduct was formed exclusively: NMR (CCl_4) δ 0.77 (s, 3 H), 0.86 (s, 3 H), 1.0–1.72 (m, 5 H), 1.27 (d, J = 6 Hz, 3 H), 1.72–2.20 (m, 3 H), 4.39 (m, 1 H), 5.18–5.55 (m, 3 H), 5.40 (s, 1 H), 7.10–7.80 (m, 10 H). To the reaction mixture was added 50 mL of *n*-hexane, and the

(14) Kniseley, R. N.; Fassel, V. A.; Conrad, E. E. *Spectrochim. Acta* **1959**, 651.

(15) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 68.

precipitated catalyst was filtered off. Then, MeOH (10 mL) and K_2CO_3 (10 mg) were added to the filtrate. Methanolysis completed within 1 h at room temperature. The ratio of dihydro-α-ionone/*trans*-ionol was found to be 0/100 on the basis of GLC and NMR analyses. After the solvent was evaporated, the residue was distilled under reduced pressure to give *trans*-ionol (1.74 g, 89%), bp 99 °C (2 torr).

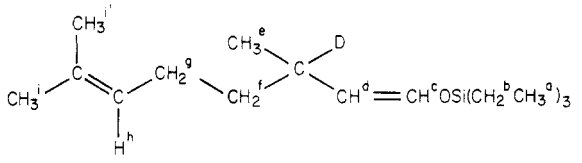
Reaction of Mesityl Oxide under Controlled Conditions. (A) Under Diluted Conditions. A mixture of mesityl oxide (200 mg, 2.0 mmol), diphenylsilane (650 mg, 3.5 mmol), and tris(triphenylphosphine)chlororhodium (40 mg, 4.3×10^{-2} mmol) in 40–200 mL of benzene was stirred at ambient temperature for 1–20 h under nitrogen. After mesityl oxide was completely consumed (GLC analysis), the reaction mixture was concentrated and the ratio of 1,4 addition/1,2 addition was determined by NMR analysis. The products ratio after methanolysis was also determined by GLC analysis.

The results are summarized in Table IV.

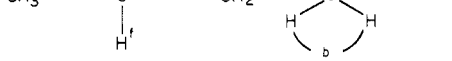
(B) By Dropwise Addition of Mesityl Oxide. To a mixture of diphenylsilane (1.1 g, 6.0 mmol) and tris(triphenylphosphine)chlororhodium (4.5 mg, 4.7×10^{-3} mmol) was added mesityl oxide (250 mg, 2.5 mmol) at aka rate of 2–3 drops/min with stirring at 25 °C. After methanolysis of the hydrosilylation products, the ratio of 1,4 addition/1,2 addition was determined to be 2/98 by GLC analysis.

(C) By Dropwise Addition of Diphenylsilane. To a mixture of mesityl oxide (250 mg, 2.5 mmol) and tris(triphenylphosphine)chlororhodium (4.5 mg, 4.7×10^{-3} mmol) was added diphenylsilane (470 mg, 2.5 mmol) at a rate of 2–3 drops/min with stirring at 25 °C. After methanolysis of the hydrosilylation product, the ratio of 1,4 addition/1,2 addition was determined to be 43/57 by GLC analysis.

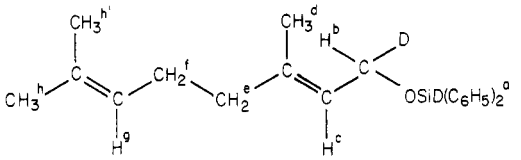
Deuteriosilylation of Geranial with Triethyldeuteriosilane and Diphenyldideuteriosilane Catalyzed by Tris(triphenylphosphine)chlororhodium. (A) A mixture of geranial (458 mg, 3.0 mmol), triethyldeuteriosilane (399 mg, 3.3 mmol), and tris(triphenylphosphine)chlororhodium (5.5 mg, 5.9×10^{-3} mmol) was stirred at 50 °C for 1 h. The NMR spectrum of the reaction mixture showed that 1-(triethylsiloxy)-3,7-dimethylocta-1,6-diene-*3-d* was produced exclusively; i.e., no scrambling of deuterium took place at all: NMR ($CDCl_3$) δ 0.40–1.12 (m, 18 H) (H^a, H^b, H^c), 1.22 (t, J = 7 Hz, 2 H) (H^f), 1.56 (s, 3 H) ($H^{i'}$), 1.65 (s, 3 H) (H^i), 1.93 (q, J = 7 Hz, 2 H) (H^g), [4.20 (d, J_{c-d} = 6 Hz) (H^c, Z), 4.82 (d, J_{c-d} = 12 Hz) (H_c, E) (1 H) (E/Z = 29/71)], 5.11 (m, 1 H), [6.13 (d, J_{c-d} = 6 Hz) (H^d, Z), 6.18 (d, J_{c-d} = 12 Hz) (H^d, E) (1 H) (E/Z = 29/71)].



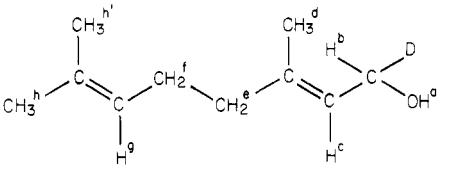
The silyl enol ether thus formed was desilylated by mixing with K_2CO_3 (5 mg)–MeOH (5 mL) at room temperature for 2 h (95% yield based on GLC analysis). Citronellal-*3-d* was obtained by distillation under reduced pressure: NMR ($CDCl_3$) δ 0.90 (s, 3 H) (H^c), 1.30 (m, 2 H) (H^d), 1.59 (s, 3 H) ($H^{g'}$), 1.67 (s, 3 H) (H^g), 2.27 (d of AB_q, J_{a-b} = 1.5 Hz, J_{b-b} = 15 Hz, 2 H) (H^b), 5.07 (m, 1 H) (H^f), 9.73 (t, J_{a-b} = 1.5 Hz, 1 H) (H^a).



(B) A mixture of geranial (153 mg, 1.0 mmol), diphenyldideuteriosilane (205 mg, 1.1 mmol), and tris(triphenylphosphine)chlororhodium (2.0 mg, 2.2×10^{-3} mmol) was stirred at ice-bath temperature for 1 h. The NMR spectrum of the reaction mixture showed the exclusive formation of 1-(diphenyldeuteriosiloxy)-3,7-dimethylocta-2,6-diene-*1-d*: NMR ($CDCl_3$) δ 1.50 (s, 3 H) (H^d), 1.59 (s, 3 H) ($H^{h'}$), 1.66 (s, 3 H) (H^h), 1.80–2.15 (m, 4 H) (H^e, H^f), 4.28 (d, J_{b-c} = 6 Hz, 1 H) (H^b), 5.04 (m, 1 H) (H^g), 5.38 (d, J_{b-c} = 6 Hz, 1 H) (H^c), 7.20–7.25 (m, 10 H) (H^a).



Methanolysis of the silyl ether by K_2CO_3 (5 mg)–MeOH (5 mL) at room temperature for 2 h (92% yield based on GLC analysis) and subsequent column chromatography on silica gel (benzene–$CHCl_3$) gave geraniol-*1-d*: NMR ($CDCl_3$) δ 1.58 (s, 3 H) ($H^{h'}$), 1.67 (s, 6 H) (H^d, H^h), 1.80–2.40 (m, 5 H) (H^a, H^e, H^f), 4.10 (d, J_{b-c} = 7 Hz, 1 Hz) (H^b), 5.07 (m, 1 H) (H^g), 5.38 (d, J = 7 Hz, 1 H) (H^c).



Spin Trapping with Nitrosodurene. Solutions (1 M) of β-ionone and diphenylsilane and 2.0×10^{-2} M solutions of nitrosodurene and tris(triphenylphosphine)chlororhodium in toluene were prepared and carefully degassed.

A mixture of 1 M silane (0.2 mL), 2.0×10^{-2} M spin trap (0.2 mL), and 2.0×10^{-2} M catalyst (0.2 mL) was prepared through syringe transfer under argon in an EPR measurement tube equipped with a septum cap and a glass pod for mixing, and then 1 M substrate (0.2 mL) was added by syringe through the septum, and four components were mixed just before the EPR measurement. The EPR spectra were measured at 25 °C (sweep time, 5 min).

Similarly, (i) a mixture of 1 M silane (0.2 mL) and 2.0×10^{-2} M spin trap (0.3 mL) in toluene, and (ii) a mixture of 1 M β-ionone (0.2 mL), 1 M silane (0.2 mL), and 2.0×10^{-2} M spin trap (0.2 mL) in toluene were prepared and submitted to EPR measurements.

Registry No. **1**, 141-79-7; **2**, 141-27-5; **3**, 79-77-6; **4**, 127-41-3; **5**, 1121-18-2; **6**, 1193-18-6; **7**, 1196-55-0; **8**, 89-82-7; **9**, 932-66-1; **10**, 89-81-6; **11**, 94-41-7; **12**, 495-41-0; **13**, 122-57-6; **14**, 104-55-2; **15**, 82798-35-4; **16**, 82798-36-5; (*E*)-I ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_3 = (C_2H_5)_3$), 57137-74-3; (*Z*)-I ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_3 = (C_2H_5)_3$), 57137-75-4; (*E*)-I ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_3 = (CH_3)_2C_2H_5$), 82798-03-6; (*Z*)-I ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_3 = (CH_3)_2C_2H_5$), 82798-40-1; (*E*)-I ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_3 = (CH_3)_2C_6H_5$), 57137-78-7; (*Z*)-I ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_3 = (CH_3)_2C_6H_5$), 57137-79-8; (*E*)-I ($R^1 = (CH_2)_2CH{=}C(CH_3)_2$, $R^2 = CH_3$, $R^3 = R^4 = H$, $R_3 = (C_2H_5)_3$), 82798-06-9; (*Z*)-I ($R^1 = (CH_2)_2CH{=}C(CH_3)_2$, $R^2 = CH_3$, $R^3 = R^4 = H$, $R_3 = (C_2H_5)_3$), 82798-41-2; (*E*)-I ($R^1 = (CH_2)_2CH{=}C(CH_3)_2$, $R^2 = CH_3$, $R^3 = R^4 = H$, $R_3 = (CH_3)_2C_2H_5$), 82798-07-0; (*Z*)-I ($R^1 = (CH_2)_2CH{=}C(CH_3)_2$, $R^2 = CH_3$, $R^3 = R^4 = H$, $R_3 = (CH_3)_2C_2H_5$), 82798-42-3; (*E*)-I (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_3 = (CH_3)_2C_2H_5$), 82798-09-2; I (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_3 = (CH_3)_2C_6H_5$), 52784-79-9; I (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_3 = (C_2H_5)_3$), 82798-13-8; I (R^1 = 2,6,6-trimethyl-2-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R^3 = (C_2H_5)_3$), 52784-78-8; (*E*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = (C_2H_5)_3$), 82798-28-5; (*Z*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = (C_2H_5)_3$), 82798-43-4; (*E*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = H(C_6H_5)_2$), 82798-29-6; (*Z*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = H$, $(C_6H_5)_2$), 82798-44-5; (*E*)-I ($R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = (C_2H_5)_3$), 57137-76-5; (*Z*)-I ($R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = (C_2H_5)_3$), 57137-77-6; (*E*)-I ($R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = H$, $(C_6H_5)_2$), 82798-30-9; (*Z*)-I ($R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = C_6H_5$, $R_3 = H$, $(C_6H_5)_2$), 82798-45-6; (*E*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_3 = (C_2H_5)_3$), 82798-31-0; (*Z*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_3 = (C_2H_5)_3$), 82798-46-7; I ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_3 = H$, $(C_6H_5)_2$), 82798-32-1; (*E*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$, $R_3 = (C_2H_5)_3$), 52341-09-0; (*Z*)-I ($R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$, $R_3 = (C_2H_5)_3$), 52341-10-3; II ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_2 = (C_2H_5)_2$), 82798-04-7; II ($R^1 = R^2 = R^4 = CH_3$, $R^3 = H$, $R_2 = (C_6H_5)_2$), 82798-05-8; (*E*)-II ($R^1 = (CH_2)_2CH{=}C(CH_3)_2$, $R^2 =$

CH_3, $R^3 = R^4 = H$, $R_2 = (C_6H_5)_2$), 82798-08-1; (*E*)-II (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_6H_5)_2$), 82798-10-5; (*E*)-II (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_2H_5)_2$), 82798-11-6; II (R^1 = 2,6,6-trimethyl-2-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_6H_5)_2$), 82798-15-0; II ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_6H_5)_2$), 82798-33-2; II ($R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$, $R_2 = (C_6H_5)_2$), 82798-34-3; $(Ph_3P)_3RhCl$, 14694-95-2; $EtMe_2SiH$, 758-21-4; $PhMe_2SiH$, 766-77-8; $PhMeSiH_2$, 766-08-5; Ph_2SiH_2, 775-12-2; $PhSiH_3$, 694-53-1; Et_3SiH, 617-86-7; *i*-Pr_2SiH_2, 18209-66-0; Et_2SiH_2, 542-91-6; piperitol, 491-04-3; 4-methyl-2-pentanone, 108-10-1; 4-methyl-3-penten-2-ol, 4325-82-0; citronellal, 106-23-0; geraniol, 106-24-1; dihydro-β-ionol, 3293-47-8; *trans*-β-ionol, 472-80-0; dihydro-α-ionol, 13720-37-1; α-ionol, 25312-34-9; 2-methylcyclohexanone, 583-60-8; 2-methyl-2-cyclohexen-1-ol, 20461-30-7; 3-methylcyclohexanone, 591-24-2; 3-methyl-2-cyclohexen-1-ol, 21378-21-2; 2-octalone, 4832-17-1; $\Delta^{1,9}$-2-octalol, 39879-90-8; 2-isopropyl-5-methylcyclohexanone, 10458-14-7; 2-isopropylidene-5-methylcyclohexanol, 529-02-2; cyclohexyl methyl ketone, 823-76-7; 1-(1-cyclohexen-1-yl)-ethanol, 18325-75-2; dihydrochalcone, 1083-30-3; butyrophenone, 495-40-9; 4-phenyl-2-butanone, 2550-26-7; hydrocinnamaldehyde, 104-53-0; 4-phenyl-3-buten-2-ol, 17488-65-2; cinnamyl alcohol, 104-54-1; (*E*)-1-[3-(dimethylphenylsiloxy)but-1-ene]-2,6,6-trimethyl-1-cyclohexene, 82798-12-7; (*E*)-1-[3-(triethylsiloxy)but-1-ene]-2,6,6-trimethyl-1-cyclohexene, 82798-14-9; 1-(dimethylethylsiloxy)-2-methyl-1-cyclohexene, 82798-16-1; 1-(diphenylsiloxy)-2-methyl-2-cyclohexene, 82798-17-2; 1-(triethylsiloxy)-3-methyl-1-cyclohexene, 18407-91-5; 1-(diphenylsiloxy)-3-methyl-2-cyclohexene, 82798-18-3; 2-(triethylsiloxy)-$\Delta^{1,2}$-octalin, 57137-82-3; 2-(diethylsiloxy)-$\Delta^{1,9}$-octalin, 82798-19-4; 1-(dimethylethylsiloxy)-2-isopropyl-5-methyl-1-cyclohexene, 82798-20-7; 1-(diphenylsiloxy)-2-isopropylidene-5-methylcyclohexane, 82798-21-8; 1-(diethylsiloxy)-2-isopropylidene-5-methylcyclohexane, 82798-22-9; 3-(diphenylsiloxy)-4-isopropyl-1-methyl-1-cyclohexene, 82798-23-0; 3-(diethylsiloxy)-4-isopropyl-1-methyl-1-cyclohexene, 82798-24-1; 1-cyclohexylidene-1-(triethylsiloxy)ethane, 82798-25-2; 1-(cyclohex-1-en-1-yl)-1-(triethylsiloxy)-ethane, 82798-26-3; 1-(cyclohex-1-en-1-yl)-1-(diphenylsiloxy)ethane, 82798-27-4; nitrosodurene, 38899-21-7; triethyldeuteriosilane, 1631-33-0; (*E*)-1-(triethylsiloxy)-3,7-dimethylocta-1,6-diene-*3-d*, 82798-37-6; citronellal-*3-d*, 82798-38-7; diphenyldideuteriosilane, 17950-94-6; (*E*)-1-(diphenyldeuteriosiloxy)-3,7-dimethylocta-2,6-diene-*1-d*, 82798-39-8; geraniol-*1-d*, 82863-21-6; (*Z*)-1-(triethylsiloxy)-3,7-dimethylocta-1,6-diene-*3-d*, 82798-47-8; 4-phenyl-2-(triethylsiloxy)-3-butene, 82798-48-9.

Communications

Thermally Induced Reductive Ligand Coupling in Chromium π Complexes of Aromatic Ketones[1]

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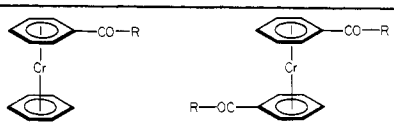
Summary: Thermolysis below or at the melting point of crystalline samples of bis(η^6-acylbenzene)chromium(0) complexes yields ethene derivatives as main products. An intramolecular mechanism of ligand coupling is ruled out as the result of cross thermolysis experiments. Evidence for the intermediacy of arylcarbenes, formed via deoxygenation of the π-bonded aromatic ketones by Cr(0), is provided by the minor products of the thermolysis.

Deoxygenative coupling of carbonyl compounds to symmetrical alkenes can be effected in a variety of ways,[2] employing low-valent transition-metal compounds[3,4] or even metal(0) slurries.[5]

In this communication we present a reductive coupling reaction which is autogenic in that the carbonyl components are present as ligands in a bis(η^6-arene)chromium(0) complex and the role of the coupling agent is played by the central metal atom. This work was triggered by the observation that the mass spectra of a series of new acyl derivatives **6**–**10** of bis(η^6-benzene)chromium (Table I), which we had prepared to study spin delocalization in the corresponding ketyl radical complexes,[6] displayed high intensity peaks from tetraarylethene molecular ions.[7]

Table I. Bis(η^6-benzene)chromium Complexes Studied in Thermolysis Reactions



R		
H	1	6 (135)[a]
C_6H_5	2	7 (150)
4-$C_6H_4CH_3$	3	8 (150)
4-$C_6H_4CF_3$	4	9 (162)
4-C_5H_4N	5	10 (205)

[a] Temperature (°C) of decomposition of neat sample.

These signals were absent in the mass spectra of the monoacyl derivatives **1**–**5**. It was soon realized that deoxygenative ligand dimerization is a thermally induced reaction of the neutral complexes rather than a reaction of the parent ion generated in the mass spectrometer and we therefore studied more thoroughly the thermolysis of complexes **6**–**10** in the crystalline state as well as in solution.

When samples of **6**–**10** are heated in a nitrogen atmosphere, vigorous reaction occurs at temperatures characteristic for the respective complex. The product distribution from thermolysis reactions of complexes **6** and **7**

(1) Metal π Complexes of Benzene Derivatives. 18. Part 17: Ch. Elschenbroich and J. Koch, *J. Organomet. Chem.*, **229**, 139 (1982).
(2) Tse-Lok Ho, *Synthesis*, 1 (1979) for leading references.
(3) J. E. McMurry, *Acc. Chem. Res.*, **7**, 281 (1974).
(4) H. Leddon, I. Tkatchenko, and D. Young, *Tetrahedron Lett.*, 173 (1979).
(5) (a) J. E. McMurry and M. P. Fleming, *J. Org. Chem.*, **41**, 896 (1976); (b) J. E. McMurry and L. R. Krepski, *ibid.*, **41**, 3929 (1976); (c) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *ibid.*, **43**, 3255 (1978).
(6) Ch. Elschenbroich, J. Heck, and F. Stohler, *Chem. Ber.*, to be submitted for publication.
(7) In the mass spectra of 1,1′-diacylferrocenes there are no indications for interligand coupling.
(8) The residue of the toluene extraction process analyzes to a composition of 25.45% C, 2.35% H, 36.6% Cr, and 34.6% O (difference to 100%) which leads to a ratio of Cr/O ≈ 1:3, implying that, apart from Cr_2O_3 or CrO_2, some oxygen must be present in insoluble organic material.

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