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Addition/Elimination in the Rhodium(II) Perfluorobutyrate Catalyzed Hydrosilylation of 1-Alkenes. Rhodium Hydride Promoted Isomerization and Hydrogenation

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Rhodium(II) perfluorobutyrate catalyzes the hydrosilylation of 1-alkenes under mild conditions, and the mode of addition determines the products that are formed. When the alkene is added to triethylsilane, "normal" hydrosilylation occurs; reversed addition causes the formation of allyl- or vinylsilanes. Moderate yields of isolated hydrosilylation products are obtained from reactions performed in dichloromethane. Olefin isomerization, which requires only catalytic amounts of rhodium(II) perfluorobutyrate and triethylsilane, competes with hydrosilylation, and an intermediate rhodium hydride species is responsible for this transformation. Catalytic hydrogenation of 1-alkenes occurs in dichloromethane with the use of triethylsilane and alcohol. Deuterium labeling studies establish that rhodium hydride is the reagent which undergoes addition to alkenes and that the rhodium hydride is subject to rapid proton exchange. Hydrosilylation of styrene and ethyl acrylate, catalyzed by rhodium(II) perfluorobutyrate or octanoate, forms either the normal addition product or trans-disubstituted vinylsilane, depending on the mode of addition and the reaction temperature.

Although the combination of organosilane and alkenes in the presence of a variety of transition-metal catalysts normally yields the corresponding addition products,[2–9] there have been several recent reports of vinylsilane and allylsilane formation when these reactions are performed in the presence of ruthenium catalysts.[10–12] These "abnormal" hydrosilylation reactions formally occur by silyl group addition to the alkene and elimination of molecular hydrogen (Scheme I).

Scheme I

$$RCH_2CH{=}CH_2 + R'_3SiH \xrightarrow{ML_n} \underset{\mathbf{1}}{RCH{=}CHCH_2SiR'_3} + H_2 \quad (1)$$

$$RCH_2CH{=}CH_2 + R'_3SiH \xrightarrow{ML_n} \underset{\mathbf{2}}{RCH_2CH{=}CHSiR'_3} + H_2 \quad (2)$$

Allylsilanes are reported to be formed by catalytic isomerization of vinylsilanes,[10] but such an interpretation is, by no means, universally accepted.[12] With $Ru_3(CO)_{12}$ as the catalyst, vinylsilanes are the major products from reactions, performed at 50 °C, between triethylsilane and alkenes ranging from 1-hexene to 3-phenoxypropene; allylsilanes are minor products, but they become the major products when the same reactions are performed at 140 °C.[10b] In contrast ((1,2-η:5,6-η)-cyclooctadiene)((1–6-η)-cyclooctatriene)ruthenium, Ru(cod)(cot), effectively promotes allylsilane formation at temperatures ranging from 60 to 140 °C with no apparent temperature dependence on the allylsilane/vinylsilane product ratio.[12] Allylsilanes and vinylsilanes are of relatively minor importance in reactions catalyzed by $(Ph_3P)_3RhCl$,[13] and they are not observed in chloroplatinic acid catalyzed reactions.[1,14,15] However, with $Rh_2(Me_5C_5)_2Cl_4$ as the catalyst, addition of triethylsilane to 1-alkenes gives a temperature-dependent product distribution which favors vinylsilane and allylsilane products over the "normal" addition product as the reaction temperature increases.[15] However, only a few of these "abnormal" hydrosilylation processes have been examined systematically and most often by analogy with catalytic hydrogenation.

Table I. Hydrosilylation of 1-Alkenes by Triethylsilane Catalyzed by $Rh_2(pfb)_4$[a]

alkene	R in eq 3	amt of $Rh_2(pfb)_4$, mol %	isolated yield, %[b]	rel yield, % 1	2	3
1-hexene	$CH_3(CH_2)_2$	1.0	53	1	4	95
1-octene	$CH_3(CH_2)_4$	1.0	40	2	1	97
1-decene	$CH_3(CH_2)_6$	1.1	30	2		98
3-phenyl-1-propene	C_6H_5	1.0	52	4		96
3-(*p*-anisyl)-1-propene	*p*-$CH_3OC_6H_4$	1.1	48	3		97
3-(*n*-butoxy)-1-propene	*n*-BuO	1.0	54		2	98

[a] Reactions were performed under N_2 at 25 °C with a 60-min addition of 2.0 mmol of alkene in 3.0 mL of CH_2Cl_2 to 4.0 mmol of triethylsilane in 7.0 mL of CH_2Cl_2. [b] Product yield after distillation.

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Table II. Allylsilane/Vinylsilane Formation from $Rh_2(pfb)_4$-Catalyzed Reactions of 1-Alkenes with Triethylsilane[a]

alkene	R in eq 1–3	amt of $Rh_2(pfb)_4$, mol %	isolated yield, %[b]	rel yield, % 1[c]	2[d]	3
1-hexene	$CH_3(CH_2)_2$	1.0	60	34 (3.3)	6	61
1-octene	$CH_3(CH_2)_4$	1.1	66	32 (3.0)	5	63
1-decene	$CH_3(CH_2)_6$	1.0	62	31 (2.8)	3	66
3-phenyl-1-propene	C_6H_5	1.0	49	91 (>50)	1	8
3-(*p*-anisyl)-1-propene	*p*-$CH_3OC_6H_4$	1.1	58	86 (>50)	1	13
3-(*n*-butoxy)-1-propene	*n*-BuO	1.0	43	12 (0.35)	61	27

[a] Reactions were performed under N_2 at 25 °C with a 60-min addition of 2.0 mmol of triethylsilane in 3.0 mL of CH_2Cl_2 to 4.0 mmol of alkene in 7.0 mL of CH_2Cl_2. [b] Product yield after distillation. [c] *E*/*Z* isomer ratio in parentheses. [d] Only the *E* isomer was observed.

We wish to report the unusual reactivity/selectivity of rhodium(II) perfluorobutyrate, $Rh_2(pfb)_4$, for the hydrosilylation of 1-alkenes which occurs with accompanying olefin isomerization and hydrogenation. Normal hydrosilylation occurs when the alkene is added to triethylsilane, but upon reverse addition of the reagents, the major products are allylsilanes or vinylsilanes, and significant amounts of isomeric 2-alkenes are formed. These transformations implicate a reactive rhodium hydride intermediate in addition/elimination reactions that produce alkyl- and/or vinylsilanes as well as in isomerization and hydrogenation processes.

Results and Discussion

Hydrosilylation of 1-Alkenes. Addition of 1-hexene to a 2-fold molar excess of triethylsilane at room temperature in dichloromethane containing a catalytic amount of $Rh_2(pfb)_4$[16] produced 1-triethylhexane in moderate yield following distillation (eq 3, R = $CH_3CH_2CH_2$). Allylsilane

$$\mathrm{RCH_2CH{=}CH_2 + R'_3SiH \xrightarrow{ML_n} \underset{\mathbf{3}}{RCH_2CH_2CH_2SiR'_3}} \qquad (3)$$

and vinylsilane products were virtually absent from the reaction mixture, and the isomeric 2-(triethylsilyl)hexane was not formed under these conditions. Similar results were obtained with a series of representative 1-alkenes with essentially the same outcome (Table I). Cyclohexane was unreactive toward Et_3SiH under the same conditions.

Only moderate yields of **3** were obtained through this procedure, which was designed to optimize selectivity rather than isolated yield. However, under the same conditions, use of the well-established hydrosilylation catalysts H_2PtCl_6[2] and $(Ph_3P)_3RhCl$,[17] in place of $Rh_2(pfb)_4$, resulted in lower product yields and, in some cases, lower selectivities. For example, 1-decene underwent hydrosilylation catalyzed by H_2PtCl_6 to produce **3** in 15% isolated yield (99% selectivity), but with $(Ph_3P)_3RhCl$ the reaction products were formed in 30% yield and 81% selectivity for **3** (15% **1**, 4% **2**). Similar results were obtained with 1-hexene: H_2PtCl_6 (8% yield, 98% **3**); $(Ph_3P)_3RhCl$ (32% yield, 94% **3**). Unlike $Rh_2(pfb)_4$, which slowly decomposed to as yet unknown product(s) during these reactions, rhodium(II) octanoate did not observably change its constitution and was as effective as $Rh_2(pfb)_4$ for the hydrosilylation of 1-hexene (56% yield, 98% **3**).

In contrast, when triethylsilane was added to a 2-fold molar excess of 1-hexene under the same reaction conditions, a multiplicity of products resulted. Alkylsilane **3** (R = $CH_3CH_2CH_2$) was the major product, but allylsilane **1** was also formed in modest yield. Product yields from $Rh_2(pfb)_4$-catalyzed reactions in which triethylsilane was added to a series of 1-alkenes are presented in Table II. Results nearly identical to those obtained with 1-hexene were observed with 1-octene and 1-decene. With 3-aryl-1-propene, however, allylsilane **1** was the major product followed, in order of importance, by alkylsilane **3** and vinylsilane **2**. Allyl *n*-butyl ether yielded the corresponding vinylsilane as the major product. Allylsilanes were generally formed as the *E* stereoisomer with a high degree of stereocontrol, and when obtained in sufficient yield to monitor isomer compositions, vinylsilanes were produced exclusively in the *E* configuration. Cyclohexene did not react with triethylsilane under these conditions.

Hydrogenation of Alkenes. In view of the moderate yields of organosilane products formed in $Rh_2(pfb)_4$-catalyzed reactions leading to allyl- and vinylsilanes (eqs 1 and 2) and the anticipated formal production of molecular hydrogen, these reactions were subjected to more detailed examination. Competitive hydrogenation appears to be a common feature of hydrosilylation reactions with 1-alkenes catalyzed by ruthenium or rhodium compounds,[10–12] but comparable data for hydrogenation/hydrosilylation have rarely been provided. In the few reports that have described quantitative results for the hydrogenation process,[10,13] alkane product yields were nearly identical to those of vinylsilane and/or allylsilane, and accountability for the hydrogen formally released in these processes was obtained. A different accountability appears to be in place for results obtained from $Rh_2(pfb)_4$-catalyzed reactions of triethylsilane with 1-alkenes. For example, the addition of 1-decene to triethylsilane in the presence of $Rh_2(pfb)_4$ gave decane in 2–4% yield, and the reverse addition provided 1–2% of this hydrogenation product. Similar results were obtained with 1-octene. 3-Phenyl-1-propene yielded *n*-propylbenzene in 3–4% yield when the alkene was added to the organosilane and in 1–2% yield when triethylsilane was added to 3-phenyl-2-propene. In these cases hydrogenation probably results from $Rh_2(pfb)_4$-catalyzed hydrolysis of triethylsilane, as explained below.

As established through control experiments, consistent with reactivity considerations recently reported from investigations of silane alcoholysis,[18] water present in the reaction medium reacts with triethylsilane to form triethylsilanol and, subsequently, hexaethyldisiloxane (eq 4).

$$\mathrm{R'_3SiH + H_2O \xrightarrow[-H_2]{+Rh_2(pfb)_4} R'_3SiOH \xrightarrow[-H_2]{+R'_3SiH,\ Rh_2(pfb)_4} R'_3SiOSiR'_3} \qquad (4)$$

Since these transformations are at least 5–10 times faster than olefin hydrosilylation, organosilane product yields are necessarily limited by the content of water or other hydroxylic substances in the reaction medium. Treatment of 1-decene with a 2-fold molar excess of triethylsilane and

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Table III. Ionic Hydrogenation of Styrene by Et_3SiD/Et_3SiH and EtOH/EtOD in the Presence of $Rh_2(pfb)_4$[a]

Z in Et_3SiZ	amt of Et_3SiZ, equiv[b]	Z in EtOZ	amt of EtOZ, equiv[b]	no. of D atoms[c] benzylic position	terminal position	% $C_6H_5C_2H_{5-n}D_n$[d] d_0	d_1	d_2	d_3
H	2.02	D	1.02	0.41	0.62	13	65	22	
H	1.96	D	1.94	0.47	0.65	15	58	27	
D	1.90	H	1.14	0.70	0.83	3	55	35	7
D	1.95	D	1.03	1.00	1.18	<1	25	70	25

[a] Reactions were performed at 25 °C with 2.0 mol % of $Rh_2(pfb)_4$. [b] Based on styrene (0.20 M) in dichloromethane. [c] Values are ±5%. [d] Values are ±10% of recorded numbers.

of ethanol in the presence of 1.0 mol % $Rh_2(pfb)_4$ resulted in a 94% yield of decane (eq 5, 27%) and 2-decene (73%)

$$Et_3SiH + RCH{=}CH_2 + EtOH \xrightarrow[CH_2Cl_2]{Rh_2(pfb)_4} RCH_2CH_3 + Et_3SiOEt \quad (5)$$

with less than 3% hydrosilylation products. *trans*-Cinnamyl alcohol, which possesses its own internal hydroxyl group, formed (3-phenyl-1-propoxy)triethylsilane quantitatively when treated with 2.0 equiv of Et_3SiH in the presence of a catalytic amount of $Rh_2(pfb)_4$.[18] Under the same conditions as employed with 1-decene, styrene was converted to ethylbenzene in 89% yield; however, when styrene was maintained with 1.0 mol % $Rh_2(pfb)_4$ under an atmosphere of molecular hydrogen in anhydrous dichloromethane for the same amount of time, no reduction to ethylbenzene occurred. This latter observation calls into question an earlier report that $Rh_2(OAc)_4$ can serve as an effective hydrogenation catalyst[19] and suggests that the formation of alkanes from alkenes in the presence of organosilanes occurs through the process of ionic hydrogenation.[20,21]

Two mechanisms may be advanced to account for ionic hydrogenation of alkenes. In both $Rh_2(pfb)_4$ initiates the transformation by activation of triethylsilane toward alcoholysis (hydrolysis), and these steps (eqs 6 and 7) have

$$Rh_2(pfb)_4 + Et_3SiH \rightleftharpoons Rh_2(pfb)_4(Et_3SiH) \quad (6)$$

$$Rh_2(pfb)_4(Et_3SiH) + 2R'OH \rightarrow [(pfb)_4Rh_2H]^- + R'OSiEt_3 + R'OH_2^+ \quad (7)$$

been verified in our earlier investigations of silane alcoholysis.[18] In the first hydrogenation mechanism (Scheme II), protonation of the alkene forms an intermediate carbocation that is subsequently reduced by either $[(pfb)_4Rh_2H]^-$ or Et_3SiH. However, ether formation, which should be competitive with hydride transfer to the intermediate carbocation, is not observed, and control experiments establish that no reaction occurs in the absence of Et_3SiH. In an alternate mechanism (Scheme III) the intermediate rhodium hydride undergoes Markovnikov addition to the alkene, and alkane formation occurs by protonolysis of the organorhodium intermediate. These two mechanisms differ by the order in which the elements of hydrogen, from triethylsilane and alcohol, are introduced into the alkene. Consequentily, when styrene is treated with triethylsilane in the presence of EtOD and $Rh_2(pfb)_4$, or with triethyldeuteriosilane in the presence of EtOH and $Rh_2(pfb)_4$, the placement of deuterium in the ethylbenzene product should distinguish between these two mechanisms. In Scheme II deuterium should reside exclusively in the methyl group when the deuterium source is EtOD, whereas in Scheme III deuterium should be in the methylene group. Alternatively, with Et_3SiD as the source of deuterium, the opposite placements should occur.

Scheme II

$$R'OH_2^+ + RCH{=}CH_2 \rightleftharpoons R'OH + RC^+HCH_3 \quad (8)$$

$$RC^+HCH_3 + [(pfb)_4Rh_2H]^- \rightarrow RCH_2CH_3 + Rh_2(pfb)_4 \quad (9)$$

Scheme III

$$[(pfb)_4Rh_2H]^- + RCH{=}CH_2 \rightarrow [RCH(CH_3)\text{-}Rh_2(pfb)_4]^- \quad (10)$$

$$[RCH(CH_3)\text{-}Rh_2(pfb)_4]^- + R'OH_2^+ \rightarrow RCH_2CH_3 + Rh_2(pfb)_4 + R'OH \quad (11)$$

Treatment of styrene with Et_3SiH and EtOD in the presence of $Rh_2(pfb)_4$ resulted in the production of ethylbenzene possessing mainly one deuterium, which by mass spectral and ^1H NMR analyses was shown to reside on both positions, but mainly on the terminal carbon (Table III). Similar results were obtained when EtOD was replaced by deuterium oxide, and when the amount of EtOD was doubled, no significant increase in deuterium incorporation was observed. However, treatment of styrene with Et_3SiD and EtOH in the presence of $Rh_2(pfb)_4$ gave essentially the same result—deuterium incorporation occurred at both positions, but mainly at the terminal carbon. In addition, a larger fraction of ethylbenzene molecules contained two deuterium atoms (35%), and residual styrene, when the reaction was terminated prior to complete hydrogenation, contained a fractional amount of deuterium at the terminal vinylidene carbon (7–9% at 30% conversion). When styrene was treated with Et_3SiD and EtOD in the presence of $Rh_2(pfb)_4$, mainly two deuterium atoms were incorporated, one each at the benzylic and terminal positions of ethylbenzene, but a significant amount of trideuterioethylbenzene was obtained in which two deuterium atoms resided at the terminal position. Also, at 80% conversion deuterium incorporation into styrene was at 60%, all at the terminal carbon, with nearly 20% more deuterium trans to the phenyl group than cis.

Scheme II can be eliminated from further consideration since, although reactions performed with EtOD approach the expected result, these performed with Et_3SiD do not. By itself, Scheme III does not account for the observed results, but if the intermediate rhodium hydride is subject to proton (or deuteron) exchange (eq 12) with the hydroxylic solvent, EtOD or EtOH, the similarity in results for deuterium incorporation with the use of either Et_3SiD or EtOD can be explained. Furthermore, the incorporation of more than one deuterium into ethylbenzene from either

$$[(pfb)_4Rh_2H]^- + EtOD \rightleftharpoons [(pfb)_4Rh_2D]^- + EtOH \quad (12)$$

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Table IV. **Rhodium(II) Alkanoate Catalyzed Reactions of Styrene with Triethylsilane**[a]

compd added (amt, mmol)	other reactant (amt, mmol)	solvent	reacn temp, °C	catalyst	isolated yield, %[b]	rel yield, %		
						4	5	6
Et_3SiH (1.0)	styrene (2.0)	CH_2Cl_2	25	$Rh_2(pfb)_4$	59	21	4	75
Et_3SiH (2.0)	styrene (2.2)	CH_2Cl_2	40	$Rh_2(pfb)_4$	72	16	<1	84
Et_3SiH (1.1)	styrene (2.1)	$CHCl_3$	65	$Rh_2(pfb)_4$	71	5	<1	95
styrene (1.0)	Et_3SiH (2.0)	CH_2Cl_2	25	$Rh_2(pfb)_4$	50	65	11	24
styrene (2.1)	Et_3SiH (2.0)	CH_2Cl_2	40	$Rh_2(pfb)_4$	68	60	4	36
styrene (2.2)	Et_3SiH (2.2)	PhH	80	$Rh_2(pfb)_4$	55	54	3	43
Et_3SiH (2.1)	styrene (2.1)	PhH	80	$Rh_2(oct)_4$	53	68	7	25
styrene (2.1)	Et_3SiH (2.1)	PhH	80	$Rh_2(oct)_4$	75	84	5	11

[a] Reactions were performed under N_2 with 1.0 mol % of catalyst, relative to the limiting reagent, with an addition time of 1 h. [b] Product yield after distillation.

or each of the deuterated reactants is consistent with reversible addition/elimination of the rhodium hydride to styrene (e.g., eqs 13 and 14), and this process is confirmed

$$[(pfb)_4Rh_2D]^- + PhCH{=}CH_2 \rightleftharpoons [PhCH(CH_2D)\text{–}Rh_2(pfb)_4]^- \quad (13)$$

$$[PhCH(CH_2D)\text{–}Rh_2(pfb)_4] \rightleftharpoons [(pfb)_4Rh_{\infty}H] + PhCH{=}CHD \quad (14)$$

by the observation of β-deuteriostyrene. Although $[(pfb)_4RhH]^-$ is postulated here to be the catalytically active reactant, our attempts to detect this species spectroscopically have not yet been successful, and the possibility exists that some other rhodium hydride species can account for the observed results.

Alkene Isomerization. Rhodium hydride addition to alkenes has yet another consequence in hydrosilylation reactions catalyzed by $Rh_2(pfb)_4$. The principal competing process in reactions reported in Tables I and II is alkene isomerization (eq 15), and the yield of these products varies

$$RCH_2CH{=}CH_2 \xrightarrow[Et_3SiH]{Rh_2(pfb)_4} RCH{=}CHCH_3 \quad (15)$$

with reaction time, concentration of reactants, and mode of addition. Thus, for example, 1-decene yielded 20–30% 2-decene (E/Z = 1.2) when triethylsilane was the limiting reagent and 8–10% 2-decene when 1-decene was the limiting reagent. 3-Phenyl-1-propene gave 35–40% 1-phenyl-1-propene (E/Z = 3.5–4.0) when triethylsilane was added to the reaction mixture and 20–30% 1-phenyl-1-propene when the reverse mode of addition was performed. Catalytic isomerization was also observed in $(Ph_3P)RhCl$- and H_2PtCl_6-catalyzed reactions.

When 1-decene was treated with a catalytic amount of Et_3SiH in the presence of 1.0 mol % $Rh_2(pfb)_4$ and this dichloromethane solution was allowed to remain at room temperature, slow conversion of 1-decene to 2-decene and 3-decene was observed (Figure 1) and, after 24 h, isomerization was >90% complete. The initial (<5 h) E/Z ratio of the isomeric 2-decenes was 0.92, but subsequent conversion of (Z)-2-decene to 3-decene increased the ratio to >3 at 72 h; (E)-2-decene did not undergo isomerization during this time. As suggested by the time course of this reaction (Figure 1), there is no obvious induction period for isomerization. Similar isomerizations were observed with 1-octene and 3-phenyl-1-propene, but not with 3-(n-butoxy)-1-propene (<2% in 48 h).

The mechanism for alkene isomerization is consistent with addition of a rhodium hydride to the carbon–carbon double bond and subsequent elimination of this reactive intermediate (Scheme IV). Olefin isomerization occurs preferentially with 1-alkenes and cis-disubstituted alkenes, but not with those that are trans-disubstituted, where steric influences probably inhibit rhodium hydride addition. The virtual absence of isomerization with 3-(n-butoxy)-1-propene, and its preferential formation of vinylsilane products upon triethylsilane addition (Table II), suggests that electronic factors play a role in reductive elimination of rhodium hydride from the intermediate alkylrhodium. Furthermore, olefin isomerization must have taken place by Markovnikov addition of the rhodium hydride followed by reductive elimination in order to have produced the observed results. However, although this orientation for addition could be only a minor pathway, as it is for several monohydride catalysts of rhodium(I),[22] relative to one in which the rhodium hydride adds the elements of rhodium and hydrogen in an anti-Markovnikov fashion, results obtained from the hydrogenation of styrene with Et_3SiD or EtOD suggest that Markovnikov addition is the major, if not the sole, orientation.

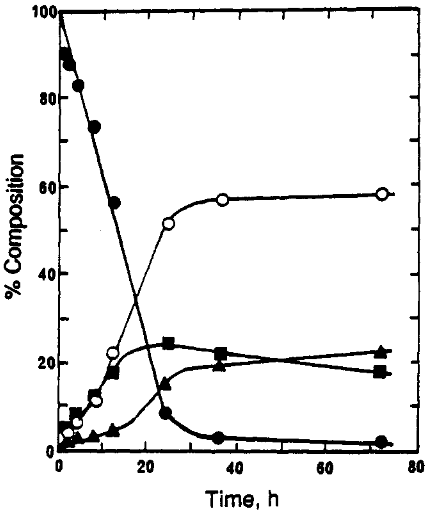

Figure 1. Percent composition versus time for the isomerization of 1-decene (0.280 g, 2.00 mmol) catalyzed by $Rh_2(pfb)_4$ (0.020 g, 0.020 mmol) and Et_3SiH (0.035 g, 0.30 mmol) at room temperature in 5.0 mL of dichloromethane: (●) 1-decene; (○) (E)-2-decene; (■) (Z)-2-decene; (▲) 3-decene.

Scheme IV

$$[(pfb)_4Rh_2H]^- + RCH_2CH{=}CH_2 \rightleftharpoons [RCH_2CH(CH_3)\text{–}Rh_2(pfb)_4]^- \quad (16)$$

$$[RCH_2CH(CH_3)\text{–}Rh_2(pfb)_4]^- \rightarrow RCH{=}CHCH_3 + [(pfb)_4Rh_2H]^- \quad (17)$$

Vinylsilane Formation. In the presence of catalytic amounts of $Rh_2(pfb)_4$, addition of triethylsilane to styrene produced the corresponding vinylsilane (**6**) in competition with hydrosilylation (eq 18). Increasing the reaction temperature brought about an increase in the relative yield

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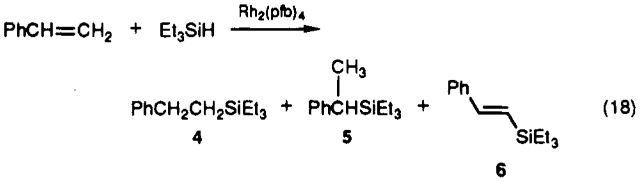
[22] Mixing these reagents together at 70 °C produced the β-triethylsilyl addition product without vinylsilane: Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1976**, *111*, 43.

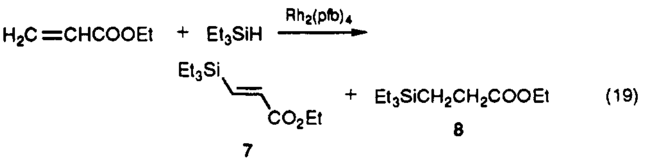


(18)

of the vinylsilane product (Table IV), which was formed solely as the *E* isomer. Reversing the mode of addition caused predominant formation of hydrosilylation products whose composition also changed with increasing reaction temperature. Rhodium(II) octanoate, $Rh_2(oct)_4$, in refluxing benzene also catalyzed the addition of Et_3SiH to styrene, but the product distributions showed 6 to be a minor constituent, and the product ratios were only minimally dependent on the mode of addition. Ethylbenzene was also formed in these reactions, but its yield relative to hydrosilylation products was not determined; however, in no case was this hydrogenation product formed in greater than 10% yield. In contrast to results with $Rh_2(pfb)_4$, $(Ph_3P)_3RhCl$ catalysis of this same transformation gave, at best, a 54% relative yield of 6, and even $(Ph_3P)_3Rh(CO)H$ catalysis under optimized conditions produced 6 in only 85% relative yield.[13b] Use of $Ru_3(CO)_{12}$, however, produced 6 without concomitant formation of 4 or 5, but hydrogenation of styrene reduced the yield of 6, based on styrene, to 50%.[10b]

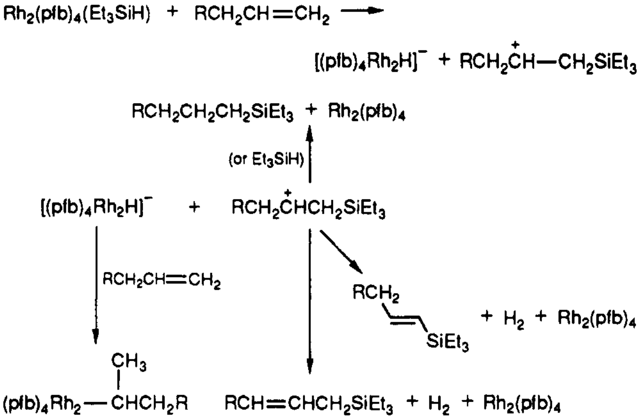
A mechanism for hydrosilylation that is consistent with other chemical events that occur in $Rh_2(pfb)_4$-catalyzed reactions of trialkylsilanes with alkenes is outlined in Scheme V. $Rh_2(pfb)_4$ coordination with triethylsilane (eq 6) activates silyl group transfer to the 1-alkene. Written here as an ionic process, the cationic intermediate reacts with the rhodium hydride to undergo either addition or elimination. Alternatively, in the presence of excess Et_3SiH, hydride transfer may take place from the silane in addition to or instead of the rhodium hydride, either because of a lower reactivity for the rhodium hydride or because addition of rhodium hydride to the alkene siphons off this hydride donor from direct hydrogen transfer to the carbocation. This mechanism also explains the dominant trans addition of organosilanes to 1-alkynes, catalyzed by $Rh_2(pfb)_4$,[23] since hydride addition to an intermediate vinyl cation would provide the observed selectivity, and hydride migration could also account for the observed formation of allylsilane products. A mechanism alternate to that of Scheme V, similar to those proposed previously for ruthenium-catalyzed hydrosilylation reactions,[10-12] in which a triethylsilyl-rhodium species is the product-determining intermediate cannot account for olefin isomerization or hydrogenation. However, the existence of such a species that would undergo triethylsilyl-rhodium addition in hydrosilylation reactions cannot be completely excluded.

The combination of ethyl acrylate and triethylsilane in the presence of $Rh_2(pfb)_4$ also resulted in competitive hydrosilylation/vinylsilane formation (eq 19). Addition of triethylsilane to ethyl acrylate at room temperature in dichloromethane afforded 7 and 8 in 74% and 26% relative yield, respectively (60% distilled yield). However, increasing the reaction temperature to 40 and to 65 °C had no measurable influence on the product distribution (±1%), although product yields were 70–80%. The reverse mode of addition at room temperature resulted in the nearly exclusive formation of 8 (>98%), but at 65 °C even this addition mode provided 7 as the major product (70%). With $Ru_3(CO)_{12}$ as the catalyst, ethyl acrylate formed these same products in a 76:24 ratio (7:8) and in an overall yield of 51%.[10b] $(Ph_3P)_3RhCl$ catalyzed the formation of these products in a 67:33 ratio (72% yield),[22] and with H_2PtCl_6 they were produced in a 32:68 ratio (27% yield). Neither acrylonitrile nor acrylamide underwent $Rh_2(pfb)_4$-catalyzed hydrosilylation or vinylsilane formation.



(19)

Scheme V



That a "free" carbocation is formed in catalytic reactions with ethyl acrylate is unlikely in view of the products obtained. In this case $Rh_2(pfb)_4$-catalyzed oxidative hydrosilylation may be occurring by triethylsilyl-rhodium addition/rhodium hydride elimination, rather than by the pathway described in Scheme V.

Experimental Section

General Considerations. ^1H NMR spectra were obtained on a 300-MHz instrument, and mass spectra were taken on a quadrupole GC/MS system operated at 70 eV. Rhodium(II) perfluorobutyrate and rhodium(II) octanoate were prepared from rhodium(II) acetate according to the established procedures,[24] and rhodium(II) acetate was prepared from rhodium(III) chloride.[25] Triethyldeuteriosilane was prepared from triethylchlorosilane and $LiAlD_4$.[26] Dichloromethane was distilled from P_2O_5 prior to use, and all alkenes were purified by distillation. Microanalyses were performed at Texas Analytical Laboratories, Inc.

Hydrosilylation of Alkenes. General Procedure. To a solution of 4.00 mmol of triethylsilane and 0.021 g (0.020 mmol) of $Rh_2(pfb)_4$ in 7.0 mL of anhydrous CH_2Cl_2 was added by syringe pump 2.00 mmol of alkene in 3.0 mL of CH_2Cl_2 at a rate of 3 mL/h. The initially green solution that was stirred at room temperature turned brown within approximately 30 min but, although the rate of reaction was diminished, relative yields of products were not affected. After addition was complete, stirring was continued for an additional 3 h, after which time the solvent was removed under reduced pressure, and the reaction products were isolated by Kugelrohr distillation. Reported yields were determined by weight, and relative yields were obtained by capillary GC and ^1H NMR analyses. 1-(Triethylsilyl)decane,[27] -octane,[28] and -hexane,[12] 1-phenyl-2-(triethylsilyl)ethane,[29] 1-

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phenyl-3-(triethylsilyl)propane,[28] and 1-carboethoxy-2-(triethylsilyl)ethane[22] have previously been characterized. Elemental and spectral analyses were performed on previously unreported organosilanes.

1-(*p*-Anisyl)-3-(triethylsilyl)propane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (d, *J* = 8.7 Hz, 2 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 3.79 (s, 3 H), 2.57 (t, *J* = 7.6 Hz, 2 H), 1.65–1.52 (m, 4 H), 0.92 (t, *J* = 7.9 Hz, 9 H), 0.54 (q, *J* = 7.9 Hz, 6 H). Mass spectrum (*m/e* (relative abundance)): 264 (M, 2), 235 (77, M – Et), 221 (10), 147 (9), 121 (13), 115 (60), 88 (10), 87 (100), 77 (8), 59 (89). Anal. Calcd for $C_{16}H_{28}OSi$: C, 72.66; Si, 10.62. Found: C, 72.61; H, 10.78; Si, 10.51.

1-(*n*-Butoxy)-3-(triethylsilyl)propane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.42 (t, *J* = 6.6 Hz, 2 H), 3.36 (t, *J* = 7.2 Hz, 2 H), 1.63–1.52 (m, 4 H), 1.38 (sex, *J* = 7.7 Hz, 2 H), 0.92 (t, *J* = 7.9 Hz, 9 H), 0.91 (t, *J* = 7.4 Hz, 3 H), 0.51 (q, *J* = 7.9 Hz, 6 H). Mass spectrum (*m/e* (relative abundance)): 201 (M – Et, 32), 159 (23), 145 (13), 115 (15), 103 (100), 87 (21), 75 (30), 59 (15), 57 (15). Anal. Calcd for $C_{13}H_{30}OSi$: C, 67.76; H, 13.02; Si, 12.19. Found: C, 67.95; H, 13.11; Si, 12.20.

Allylsilane/Vinylsilanes from Hydrosilylation of Alkenes. General Procedure. To a solution of 4.00 mmol of alkene and 0.021 g (0.020 mmol) of $Rh_2(pfb)_4$ in 7.0 mL of anhydrous CH_2Cl_2 was added by syringe pump 2.00 mmol of triethylsilane in 3.0 mL of CH_2Cl_2 at a rate of 3 mL/h. The initially green solution turned brown within approximately 30 min, but although the rate of reaction was diminished, relative yields of products were unaffected. However, increasing the rate of addition increased the relative percentage of **3**. After addition was complete, stirring was continued for an additional 3 h, after which time the solvent was removed under reduced pressure, and the reaction products were isolated by Kugelrohr distillation. Reported yields were determined by weight, and relative yields were obtained by capillary GC and ^{1}H NMR analyses. 1-(Triethylsilyl)-2-decene,[27] 1-(triethylsilyl)-2-hexene,[10b] (*E*)-1-phenyl-2-(triethylsilyl)ethene,[30] 1-phenyl-3-(triethylsilyl)-1-propene,[27] and (*E*)-1-carboethoxy-2-(triethylsilyl)ethene[12,22] have previously been characterized. Elemental analyses were performed on previously unreported organosilanes.

1-(Triethylsilyl)-2-octene was obtained as a mixture of isomers, bp 105–120 °C (0.25 Torr). Anal. Calcd for $C_{14}H_{30}Si$: C, 74.22; H, 13.38. Found: C, 73.97; H, 13.45. *E* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.36 (dt, *J* = 21.6, 6.6 Hz, 1 H), 5.26 (dt, *J* = 21.6, 7.6 Hz, 1 H), 1.95 (q, *J* = 6.6 Hz, 2 H), 1.44 (d, *J* = 7.6 Hz, 2 H), 1.45–1.20 (m, 6 H), 0.93 (t, *J* = 7.9 Hz, 9 H), 0.88 (t, *J* = 7.0 Hz, 3 H), 0.52 (q, *J* = 7.9 Hz, 6 H); mass spectrum (*m/e* (relative abundance)) 226 (M, 1), 197 (M – Et, 2), 116 (8), 115 (66), 88 (10), 87 (100), 59 (50), 57 (10). *Z* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.40 (dt, *J* = 14.6, 6.6 Hz, 1 H), 5.25 (dt, *J* = 14.6, 7.6 Hz, 1 H), 1.98 (q, *J* = 6.6 Hz, 2 H), 1.49 (d, *J* = 7.6 Hz, 1 H), 1.45–1.20 (m, 6 H), 0.92 (t, *J* = 7.9 Hz, 9 H), 0.89 (t, *J* = 7.0 Hz, 3 H), 0.50 (q, *J* = 7.9 Hz, 6 H); mass spectrum (*m/e* (relative abundance)) 226 (M, 4), 199 (28), 197 (3), 171 (7), 116 (9), 115 (89), 87 (100), 59 (31).

(*E*)-1-(*p*-Anisyl)-3-(triethylsilyl)-1-propene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.24 (d, *J* = 8.8 Hz, 2 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.22 (d, *J* = 15.9 Hz, 1 H), 6.10 (dt, *J* = 15.9, 7.5 Hz, 1 H), 3.78 (s, 3 H), 1.66 (dd, *J* = 7.5, 1.3 Hz, 2 H), 0.96 (t, *J* = 7.9 Hz, 9 H), 0.56 (q, *J* = 7.9 Hz, 6 H). Mass spectrum (*m/e* (relative abundance)): 262 (M, 12), 247 (36), 233 (2), 147 (4), 115 (49), 88 (10), 87 (100), 77 (3), 59 (50). Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98; Si, 10.70. Found: C, 72.88; H, 10.21; Si, 10.63.

3-(*n*-Butoxy)-1-(triethylsilyl)-1-propene was obtained as a mixture of isomers. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.34; Si, 12.30. Found: C, 68.28; H, 12.36; Si, 12.20. *E* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.11 (dt, *J* = 18.9, 5.0 Hz, 1 H), 5.83 (dt, *J* = 18.9, 1.5 Hz, 1 H), 4.01 (dd, *J* = 5.0, 1.5 Hz, 2 H), 3.43 (t, *J* = 6.6 Hz, 2 H), 1.63–1.54 (m, 2 H), 1.43–1.34 (m, 2 H), 0.95 (t, *J* = 7.9 Hz, 9 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 0.57 (q, *J* = 7.9 Hz, 6 H); mass spectrum (*m/e* (relative abundance)) 199 (M – Et, 42), 171 (31), 143 (16), 131 (29), 115 (38), 113 (11), 103 (32), 99 (18), 97 (13), 89 (28), 87 (39), 75 (100), 59 (56), 57 (50). *Z* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.87 (dt, *J* = 6.1, 1.4 Hz, 1 H), 4.30 (dt, *J* = 8.5, 6.1 Hz, 1 H), 3.68 (t, *J* = 6.5 Hz, 2 H), 1.65–1.51 (m, 2 H), 1.46 (dd, *J* = 8.5, 1.4 Hz, 2 H), 1.46–1.32 (m, 2 H), 0.94 (t, *J* = 7.9 Hz, 9 H), 0.92 (t, *J* = 7.2 Hz, 3 H), 0.52 (q, *J* = 7.9 Hz, 6 H).

(*E*)-1-(*n*-Butoxy)-3-(triethylsilyl)-1-propene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.08 (dt, *J* = 12.3, 1.3 Hz, 1 H), 4.76 (dt, *J* = 12.3, 8.2 Hz, 1 H), 3.60 (t, *J* = 6.5 Hz, 2 H), 1.65–1.51 (m, 2 H), 1.46–1.32 (m, 2 H), 1.27 (dd, *J* = 8.2, 1.3 Hz, 2 H), 0.94 (t, *J* = 7.9 Hz, 9 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 0.51 (q, *J* = 7.9 Hz, 6 H). Spectral characteristics match those of previously prepared 1-alkoxy-3-(triethylsilyl)-1-propenes.[23]

Hydrogenation of Styrene by Triethylsilane–Ethanol Catalyzed by $Rh_2(pfb)_4$. To a solution of styrene (0.108 g, 1.04 mmol), ethanol (0.099 g, 2.14 mmol), and $Rh_2(pfb)_4$ (0.011 g, 0.010 mmol) in 5.0 mL of anhydrous CH_2Cl_2, contained in a 25-mL flask sealed by a septum, was added 0.238 g (2.05 mmol) of triethylsilane by syringe. Gas evolution was observed upon triethylsilane addition. The initially blue solution was stirred at room temperature for 28 h, at which time the color was green. After the reaction solution was filtered through a short plug of neutral alumina and the plug was eluted with additional CH_2Cl_2, the solvent was evaporated under reduced pressure and the residue was weighed (0.378 g) and analyzed by GC and NMR methods to reveal 25% ethylbenzene, 3% styrene, and 72% ethoxytriethylsilane for an isolated yield of 63% ethylbenzene.

Hydrogenation of Styrene with Deuterated Reagents. A solution of styrene (0.207 g, 1.99 mmol), ethanol (0.0956 g, 2.03 mmol), $Rh_2(pfb)_4$ (0.043 g, 0.040 mmol), and triethylsilane (0.469 g, 4.03 mmol) in 10 mL of dichloromethane was placed in a round-bottom flask, which was sealed tightly with a rubber septum. Stirring of the blue solution was continued at room temperature for 24 h, after which the solvent was distilled, and ethylbenzene, ethoxytriethylsilane, and unreacted triethylsilane were isolated by Kugelrohr distillation at atmospheric pressure and then analyzed by NMR and GC/MS methods. The molar amounts of the reagents were retained for each experiment involving EtOD and Et_3SiD. All reactions were complete within 4 h, and only trace amounts of hydrosilylation products were observed. Deuterium incorporation into ethylbenzene was determined by NMR integration and MS relative abundance determinations. Deuterium incorporation into styrene was determined by analyses performed on incomplete reactions.

Hydrogenation–Isomerization of 1-Decene by Triethylsilane–Ethanol Catalyzed by $Rh_2(pfb)_4$. Reaction was performed as previously described with styrene, and products were isolated by the same method. Products from 1-decene included 1-decane (27%), *trans*-2-decene (52%), and *cis*-2-decene (21%), and the isolated yield of these products was 94%.

Alkene Isomerization. To 3-phenyl-1-propene (0.236 g, 2.00 mmol) and $Rh_2(pfb)_4$ (0.020 g, 0.020 mmol, 1.0 mol %) in 5.0 mL of anhydrous CH_2Cl_2 was added Et_3SiH (0.035 g, 0.30 mmol), and the resulting blue solution was stirred at room temperature. Aliquots were removed at regular intervals, diluted with hexane, passed through a short plug of alumina to remove the catalyst, and then analyzed by GC. The amount of hydrosilylation products was less than 5%. Isomerization was half complete within 20 h, and the isomeric 1-phenylpropenes were formed with a *E*/*Z* ratio of 4.0 that did not change markedly over a 120-h period. The same procedure was performed with 1-decene, 1-octene, and 3-(*n*-butoxy)-1-propene. With 3-(*n*-butoxy)-1-propene isomerization was less than 5% at 120 h.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for their support of this research. We also wish to thank the Johnson Matthey Co. for their loan of rhodium(III) chloride and Sara Dastgheib-Hosseini for preliminary results on vinylsilane production.

Registry No. (*E*)-1 (R = $CH_3(CH_2)_2$), 79643-98-4; (*E*)-1 (R = $CH_3(CH_2)_4$), 133969-35-4; (*E*)-1 (R = $CH_3(CH_2)$), 90605-21-3; (*E*)-1 (R = C_6H_5), 63522-98-5; (*E*)-1 (R = *p*-$CH_3OC_6H_4$), 138090-54-7; (*Z*)-1 (R = $CH_3(CH_2)_4$), 133969-36-5; (*E*)-1 (R = *n*-BuO), 138090-57-0; (*Z*)-1 (R = *n*-BuO), 138090-58-1; (*Z*)-1 (R = $CH_3(CH_2)_2$), 90584-20-6; (*Z*)-1 (R = $CH_3(CH_2)_6$), 90605-22-4;

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(*E*)-2 (R = $CH_3(CH_2)_2$), 42067-72-1; (*E*)-2 (R = $CH_3(CH_2)_4$), 31930-43-5; (*E*)-2 (R = *n*-BuO), 138090-55-8; (*Z*)-2 (R = *n*-BuO), 138090-56-9; (*E*)-2 (R = $CH_3(CH_2)_6$), 90584-19-3; (*E*)-2 (R = C_6H_5), 104014-92-8; (*E*)-2 (R = *p*-$CH_3OC_6H_4$), 138090-59-2; **3** (R = $CH_3(CH_2)_2$), 13810-04-3; **3** (R = $CH_3(CH_2)_4$), 10175-53-8; **3** (R = $CH_3(CH_2)_6$), 18408-00-9; **3** (R = C_6H_5), 13183-69-2; **3** (R = *p*-$CH_3OC_6H_4$), 138090-52-5; **3** (R = *n*-BuO), 138090-53-6; **4**, 14355-62-5; **5**, 87555-71-3; **6**, 21209-32-5; **7**, 104014-91-7; **8**, 10399-74-3; $Rh_2(pfb)_4$, 73755-28-9; $Rh_2(oct)_4$, 73482-96-9; Et_3SiH, 617-86-7; $CH_3(CH_2)_2CH_2CH{=}CH_2$, 592-41-6; $CH_3(CH_2)_4CH_2CH{=}CH_2$, 111-66-0; $CH_3(CH_2)_6CH_2CH{=}CH_2$, 872-05-9; $C_6H_5CH_2CH{=}CH_2$, 300-57-2; *p*-$CH_3OC_6H_4CH_2CH{=}CH_2$, 140-67-0; *n*-$BuOCH_2CH{=}CH_2$, 3739-64-8; $PhCH{=}CH_2$, 100-42-5; $H_2C{=}CHCOOEt$, 140-88-5.

[2 + 4] Cycloadditions between Germenes and α-Ethylenic Aldehydes and Ketones: A Route to Germaoxacyclohexenes

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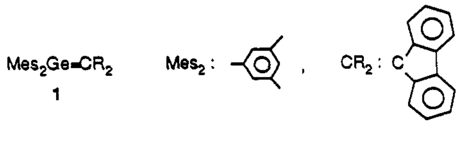
Received June 10, 1991

Dimesityl(fluorenylidene)germene (1) reacts with various α-ethylenic aldehydes and ketones to afford, by a [2 + 4] cycloaddition, the six-membered-ring heterocycles 2–7. Hydrolysis of these germaoxacyclohexenes leads to germylated aldehydes and ketones.

Introduction

Organometallic alkenes, such as silenes >Si=C<[1] and germenes >Ge=C<,[2] are now intensively studied. However, nothing is known about their reactivity toward α-ethylenic aldehydes and ketones, except the reaction between a silene and cyclopentadienones performed by Märkl.[3] Moreover, both [2 + 2] and [2 + 4] cycloadditions have been observed by Wiberg[4] in the reactions between transient silenes and germenes and benzophenone, which, in this case, behaves as a conjugated ketone.

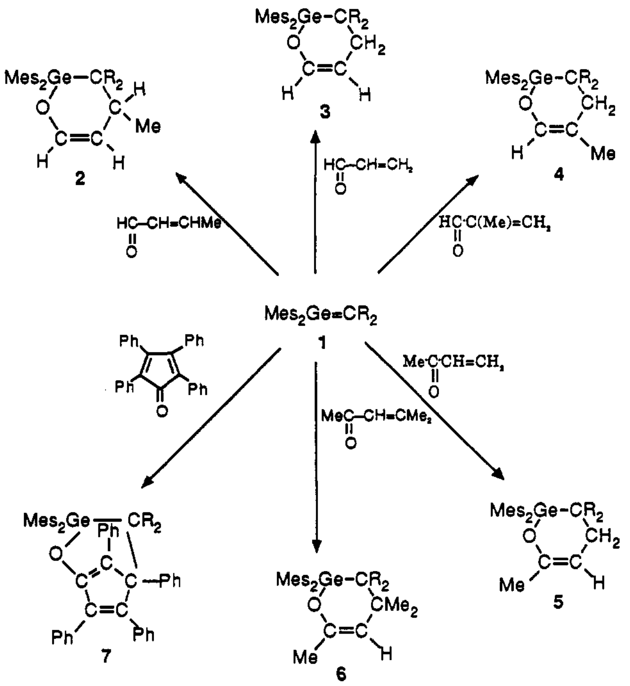
We describe in this paper the reactivity of dimesityl(fluorenylidene)germene (1)[5] toward some α-ethylenic aldehydes (acrolein, methacrolein, and crotonaldehyde) and α-ethylenic ketones (methyl vinyl ketone, mesityl oxide, and tetraphenylcyclopentadienone).



Results and Discussion

Two reactions could occur: [2 + 2] cycloaddition to the carbonyl group leading to germaoxetanes (I) or [2 + 4] cycloaddition with the formation of the corresponding six-membered rings (II).

Scheme I



Although these carbonyl derivatives have differing steric and electronic properties, particularly different electronic charges on carbons 2 and 4,[6] we have observed in all cases

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