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HYDROSILYLATION OF α,β-UNSATURATED NITRILES AND ESTERS CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM

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Summary

The hydrosilylation of α,β-unsaturated nitriles and esters such as acrylonitrile, crotononitrile, cinnamonitrile, ethyl and methyl acrylate, ethyl and methyl crotonate and ethyl and methyl methacrylate using tris(triphenylphosphine)chlororhodium as a catalyst is described. The hydrosilylation of α,β-unsaturated nitriles provided α-adduct exclusively in high yield except in the case of trichlorosilane which afforded β-adduct with acrylonitrile. On the other hand, the hydrosilylation of α,β-unsaturated esters gave rather complex results. The selectivity of the reactions was dramatically affected by the substituent of the ester group and that on the β-carbon. Thus, the hydrosilylation of ethyl acrylate with triethylsilane afforded a β-adduct, but, that of ethyl crotonate using the same hydrosilane gave a 1,4-adduct exclusively. Possible mechanisms for these reactions are discussed.

Introduction

The hydrosilylation of olefins and acetylenes has been studied extensively, and many effective catalyst systems have been found, e.g., UV light, benzoyl peroxide, Pt—C, $H_2PtCl_6 \cdot 6H_2O$, $(Ph_3P)_3RhCl$, etc. Chloroplatinic acid is by far the most effective and commonly used catalyst [1]. Rhodium—phosphine complexes seem comparable in efficiency to the platinum systems [2]. Dicobalt octacarbonyl [3] and iron pentacarbonyl [4] also are effective. Recently, phosphine complexes of platinum [5], palladium [6] and nickel [7] proved to be active hydrosilylation catalysts. However, the hydrosilylation of α,β-unsaturated nitriles and esters using such transition metal complex catalysts (except chloroplatinic acid and platinum metal catalyst) has received little attention.

In the hydrosilylation of acrylonitrile $NiCl_2$—pyridine or stainless steel foil—

pyridine catalyst afforded α-cyanoethyltrichlorosilane in 22—31% yield [8], and a nickel—phosphine catalyst also gave α-adduct in 51% yield [7b]. β-Cyanoethyltrichlorosilane was produced in 35—70% yield when chloroplatinic acid [9], platinized asbestos, benzoyl peroxide, amine bases or tertiary phosphines in a stainless steel vessel were employed [10]. α-Cyanoethylchlorosilanes also were obtained in 26—43% yield by using 5% Pt—C catalyst [11]. Recently, Chalk reported [2c] the effective hydrosilylation of acrylonitrile with dimethylphenylsilane catalyzed by tris(triphenylphosphine)carbonylhydridorhodium, which afforded the α-adduct in 80% yield, and mentioned that the addition of dimethylchlorosilane was more difficult.

On the other hand, the hydrosilylation of acrylates and methacrylates catalyzed by chloroplatinic acid or platinum metal catalyst has been extensively studied and it has been shown that the course of the addition depends upon the structure of the esters and the nature of hydrosilanes [2c,12]. For instance, chlorosilanes give mixtures of α- and β-addition (1,2-addition to the C=C bond) and 1,4-addition products, while triethylsilane shows regiospecific addition although ambiguity exists concerning the structure of the adduct. Petrov et al. claimed to have obtained a ketene acetal (1,4-addition product) but did not provide spectroscopic evidence [12a]. Later, Rijkens et al. isolated only β-triethylsilylpropionate ester (β-addition product) [12b]. Recently, a nickel—phosphine complex was proved to be an excellent catalyst for the hydrosilylation of methyl acrylate with dichloromethylsilane [7b], which afforded the α-adduct in 97% yield.

We have found that tris(triphenylphosphine)chlororhodium is a quite effective catalyst for the synthesis of α-cyanoalkylsilanes employing various hydrosilanes and α,β-unsaturated nitriles [13], and also found that this rhodium complex catalyzes the hydrosilylation of α,β-unsaturated esters to afford 1,2-adducts or 1,4-adducts selectively in high yields, depending upon the esters and hydrosilanes used. The selectivity observed was much different from that realized when other known catalysts were used. While our investigation was in progress, Yoshii et al. [14] reported similar results on the hydrosilylation of α,β-unsaturated esters with trialkylsilanes catalyzed by tris(triphenylphosphine)chlororhodium. We describe here full details of our research on the scope and limitations of the hydrosilylation of α,β-unsaturated nitriles and esters catalyzed by tris(triphenylphosphine)chlororhodium, and discuss plausible mechanisms of the reactions.

Results and discussion

Hydrosilylation of α,β-unsaturated nitriles

The hydrosilylation of α,β-unsaturated nitriles was performed in sealed tubes using dimethylphenylsilane, dimethylethylsilane, chlorodimethylsilane, dichloromethylsilane and triethoxysilane in the presence of 0.05—0.1 mol% of tris(triphenylphosphine)chlororhodium. 1,2-Addition of the silicon hydrides afforded only an α-adduct, except the case of trichlorosilane. In the case of chlorodimethylsilane and dichloromethylsilane, the reaction proceeded under mild conditions, while triethoxysilane required rather drastic conditions. The α,β-unsaturated nitriles employed were acrylonitrile, crotononitrile and cinnamonitrile. Results are summarized in Table 1. α-Cyanoalkylsilanes thus obtained were

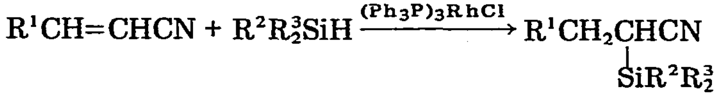
TABLE 1

HYDROSILYLATION OF ACRYLONITRILE, CROTONONITRILE AND CINNAMONITRILE CATALYZED BY $(Ph_3P)_3RhCl$

Nitrile	Hydrosilane	Conditions[a]	Product	Yield (%) (GLC)
$CH_2{=}CHCN$	$PhMe_2SiH$	100°C, 3 h	$CH_3\underset{\mathrm{SiPhMe_2}}{\underset{\vert}{C}}HCN$	87
	$EtMe_2SiH$	100°C, 24 h	$CH_3\underset{\mathrm{SiEtMe_2}}{\underset{\vert}{C}}HCN$	72
	Me_2ClSiH	50°C, 2 h	$CH_3\underset{\mathrm{SiClMe_2}}{\underset{\vert}{C}}HCN$	93
	$MeCl_2SiH$	60°C, 24 h	$CH_3\underset{\mathrm{SiCl_2Me}}{\underset{\vert}{C}}HCN$	80
	$(EtO)_3SiH$	120°C, 96 h	$CH_3\underset{\mathrm{Si(OEt)_3}}{\underset{\vert}{C}}HCN$	66
	Cl_3SiH	140°C, 24 h	$Cl_3SiCH_2CH_2CN$	80
$CH_3CH{=}CHCN$	$PhMe_2SiH$	60°C, 4 h	$CH_3CH_2\underset{\mathrm{SiPhMe_2}}{\underset{\vert}{C}}HCN$	87
	Me_2ClSiH	80°C, 60 h	$CH_3CH_2\underset{\mathrm{SiClMe_2}}{\underset{\vert}{C}}HCN$	90
$PhCH{=}CHCN$	$PhMe_2SiH$	100°C, 12 h	$PhCH_2\underset{\mathrm{SiPhMe_2}}{\underset{\vert}{C}}HCN$	72

[a] Temperature of the oil bath used.

shown to be very good reagents for the syntheses of α,β-unsaturated nitriles [13] through Peterson-type reactions [15] with carbonyl compounds.



$$R^1CH{=}CHCN + R^2R^3_2SiH \xrightarrow{(Ph_3P)_3RhCl} R^1CH_2\underset{\mathrm{SiR^2R^3_2}}{\underset{|}{C}}HCN$$

$(R^1 = H, CH_3, Ph$; a: $R^2 = Ph, R^3 = Me$, b: $R^2 = Et, R^3 = Me$, c: $R^2 = Cl, R^3 = Me$, d: $R^2 = Me, R^3 = Cl$, e: $R^2 = R^3 = EtO)$

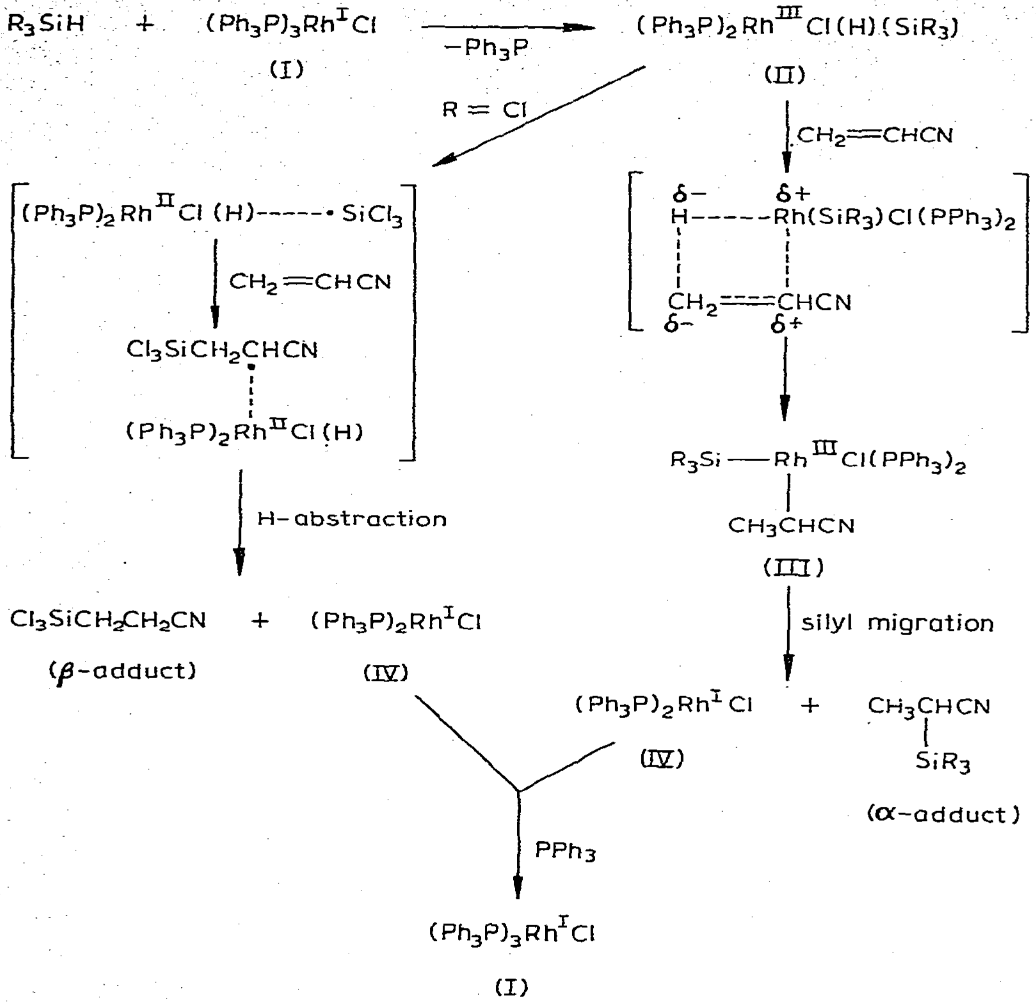
In the case of trichlorosilane, β-cyanoethyltrichlorosilane was obtained in 80% yield and formation of the α-adduct was not observed.

$$Cl_3SiH + CH_2{=}CHCN \xrightarrow{(Ph_3P)_3RhCl} Cl_3SiCH_2CH_2CN$$

It is noteworthy that chlorohydrosilanes have a high reactivity for the hydrosilylation of acrylonitrile in the present reactions in view of the fact that the rhodium complex is not an effective catalyst for the hydrosilylation of carbon—carbon multiple bonds when chlorohydrosilanes, especially trichlorosilane, are used. Such chlorohydrosilanes form a stable oxidative adduct with the rhodium complex [2b].

A possible mechanism which can explain the selectivity of the reaction is proposed as follows: α-Addition may result from nucleophilic attack of the silyl—rhodium(III) hydride (II) intermediate at the electron deficient β-carbon of acrylonitrile. The intermediate organorhodium(III) complex (III) thus formed gives the α-adduct and the rhodium(I) complex (IV) through silyl group migra-

SCHEME 1

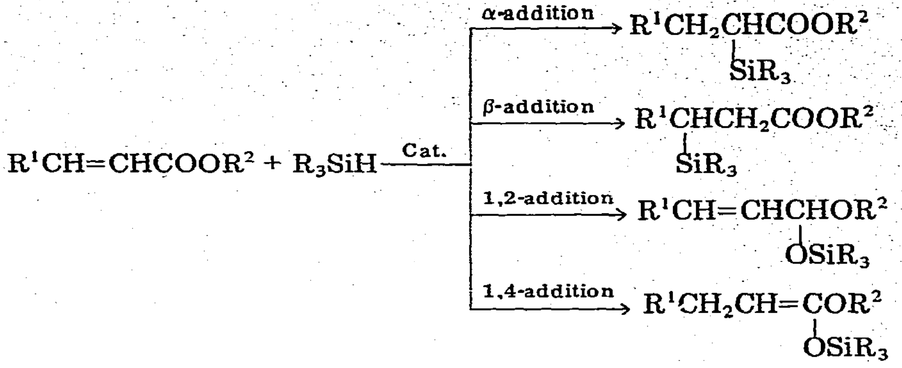


tion as shown in Scheme 1. In the case of trichlorosilane, a higher temperature (140° C) was required to initiate the reaction. Thus a radical process (with expected different regioselectivity) may be operative (cf. Scheme 1).

Hydrosilylation of α,β-unsaturated esters

In concept, there are four possible products in the hydrosilylation of α,β-unsaturated esters: The α- and β-adducts from 1,2-addition to the C=C bond, the 1,2-adduct produced by 1,2-addition to the carbonyl group, and the 1,4-adduct.

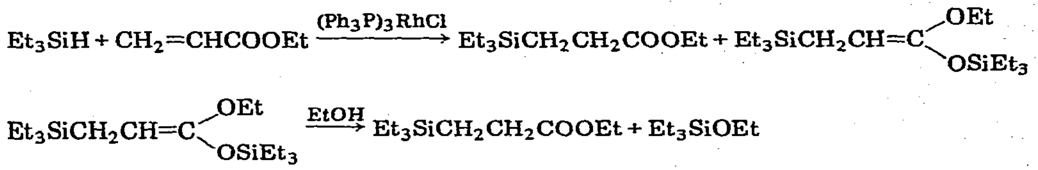
Selective α-addition has special synthetic value since the α-adduct has been shown to be a good reagent for the syntheses of α,β-unsaturated esters via Peterson-type reactions with carbonyl compounds [16]. Selective 1,4-addition may also provide a valuable method not only for the preparation of synthetically useful ketene silyl acetals, but also for the selective hydrogenation of the olefinic bond since ketene silyl acetals are readily hydrolyzed to saturated esters.



$$R^1CH{=}CHCOOR^2 + R_3SiH \xrightarrow{Cat.} \begin{cases} \xrightarrow{\alpha\text{-addition}} R^1CH_2CH(SiR_3)COOR^2 \\ \xrightarrow{\beta\text{-addition}} R^1CH(SiR_3)CH_2COOR^2 \\ \xrightarrow{1,2\text{-addition}} R^1CH{=}CHCH(OSiR_3)OR^2 \\ \xrightarrow{1,4\text{-addition}} R^1CH_2CH{=}C(OSiR_3)OR^2 \end{cases}$$

Hydrosilylation of ethyl acrylate and ethyl crotonate

The hydrosilylation of ethyl acrylate using dimethylphenylsilane and dimethylethylsilane was found to afford the β-adduct exclusively. β-Addition also was observed in the case of triethylsilane, but a disilylated product was obtained as a side product. The disilylated product was easily converted in quantitative yield to the β-adduct by the action of ethanol. Accordingly, the hydrosilylation of ethyl acrylate using triethylsilane afforded only the β-adduct after ethanolysis.

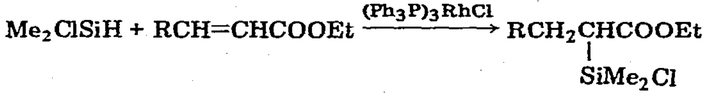


$$Et_3SiH + CH_2{=}CHCOOEt \xrightarrow{(Ph_3P)_3RhCl} Et_3SiCH_2CH_2COOEt + Et_3SiCH_2CH{=}C\begin{matrix}OEt\\OSiEt_3\end{matrix}$$

$$Et_3SiCH_2CH{=}C\begin{matrix}OEt\\OSiEt_3\end{matrix} \xrightarrow{EtOH} Et_3SiCH_2CH_2COOEt + Et_3SiOEt$$

In sharp contrast to the case of ethyl acrylate, the hydrosilylation of ethyl crotonate using trialkylsilanes proceeded via 1,4-addition without any side reactions to afford ketene silyl acetals in excellent yields.

On the other hand, the hydrosilylation of these α,β-unsaturated esters using chlorodimethylsilane proceeded differently.



$$Me_2ClSiH + RCH{=}CHCOOEt \xrightarrow{(Ph_3P)_3RhCl} RCH_2CH(SiMe_2Cl)COOEt$$

(R = H, CH_3)

Thus, the hydrosilylation of ethyl acrylate or ethyl crotonate using chlorodimethylsilane gave only the α-adduct.

Our results are listed in Table 2. It should be noted that the course of the reaction was dramatically affected by only changing the substituent on β-carbon of the α,β-unsaturated esters, and that on the silicon atom.

Hydrosilylation of methyl acrylate and methyl crotonate

Methyl acrylate and methyl crotonate also were chosen as substrates for the reaction since it has been shown that the mode of addition depends upon the structure of the ester group in hydrosilylations catalyzed by platinum metal or

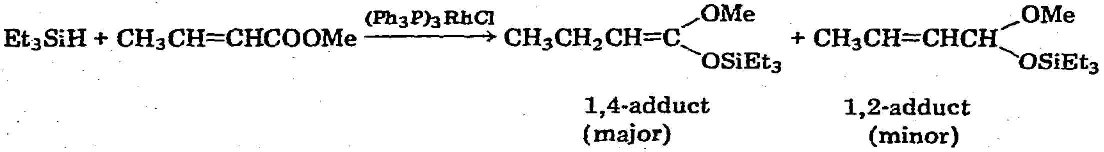
TABLE 2

HYDROSILYLATION OF ACRYLATES, CROTONATES AND METHACRYLATES CATALYZED BY $(Ph_3P)_3RhCl$

Ester	Hydrosilane	Conditions [a]	Yield [b] (%)	Product ratio (%) [c]				
				α	β	di	1,4	1,2
$CH_2{=}CHCOOEt$	Et_3SiH	70°C, 3 h [d]	80		65	35		
	$PhMe_2SiH$	80°C, 2 h	85		100			
	$EtMe_2SiH$	reflux, 12 h	83		100			
	Me_2ClSiH	70°C, 12 h	65	100				
$CH_2{=}CHCOOMe$	Et_3SiH	60°C, 1 h [d]	77		70	30		
	$PhMe_2SiH$	60°C, 12 h	80		100			
	$EtMe_2SiH$	80°C, 12 h	78		100			
$CH_3CH{=}CHCOOEt$	Et_3SiH	50°C, 1 h	95				100	
	$PhMe_2SiH$	50°C, 1 h	95				100	
	$EtMe_2SiH$	reflux, 1 h	82				100	
	Me_2ClSiH	110°C, 6 h	65	100				
$CH_3CH{=}CHCOOMe$	Et_3SiH	60°C, 1 h	95				77	23
	$PhMe_2SiH$	70°C, 2 h [d]	70				100	
	$EtMe_2SiH$	70°C, 12 h [d]	73				100	
$CH_2{=}C(Me)COOEt$	Et_3SiH	80°C, 2 h [d]	80				92	8
	$PhMe_2SiH$	65°C, 1 h	87				80	20
	$EtMe_2SiH$	40°C, 16 h	90				95	5
$CH_2{=}C(Me)COOMe$	Et_3SiH	70°C, 2 h [d]	80				92	8
	$PhMe_2SiH$	60°C, 2 h	95				75	25
	$EtMe_2SiH$	70°C, 12 h [d]	92				93	7

[a] Reaction was carried out without solvent unless otherwise noted. [b] GLC yield based on the ester. [c] Products ratio was determined by GLC using a column packed with 3%, 10%, and 20% SE-30 on Chromosorb W or/and NMR spectra. [d] Benzene was used as solvent.

chloroplatinic acid [12]. Results are summarized in Table 2; these show that the selectivities of the reactions are almost the same as those realized in the case of the corresponding ethyl ester. The reaction with methyl acrylate afforded β-adducts exclusively, except for the reaction of triethylsilane with the methyl ester, which provided also the disilylated product as a side product. The reactions with methyl crotonate afforded 1,4-adduct exclusively, although the reaction using triethylsilane produced a 1,2-adduct as a side product, which was not observed in the case of the ethyl ester.



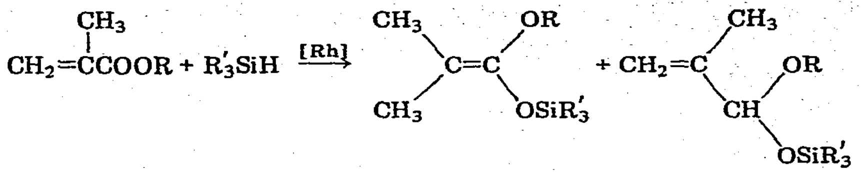
$$Et_3SiH + CH_3CH{=}CHCOOMe \xrightarrow{(Ph_3P)_3RhCl} CH_3CH_2CH{=}C\begin{matrix}OMe\\OSiEt_3\end{matrix} + CH_3CH{=}CHCH\begin{matrix}OMe\\OSiEt_3\end{matrix}$$

1,4-adduct (major)

1,2-adduct (minor)

Hydrosilylation of methacrylates

As the substituent of the ester group and that on the β-carbon changed the nature of the reaction observed quite dramatically, as described above, the hydrosilylation of methacrylates was carried out in order to estimate the effect of a methyl substituent on the α-carbon. As seen in Table 2, the reaction afforded a mixture of a ketene silyl acetal (predominant) and the 1,2-addition product (minor), exactly as in the case of methyl crotonate. Accordingly, the effect of a methyl on the α-carbon is similar to that on the β-carbon in enhancing the occurrence of 1,4-addition.



1,4-adduct (major) 1,2-adduct (minor)

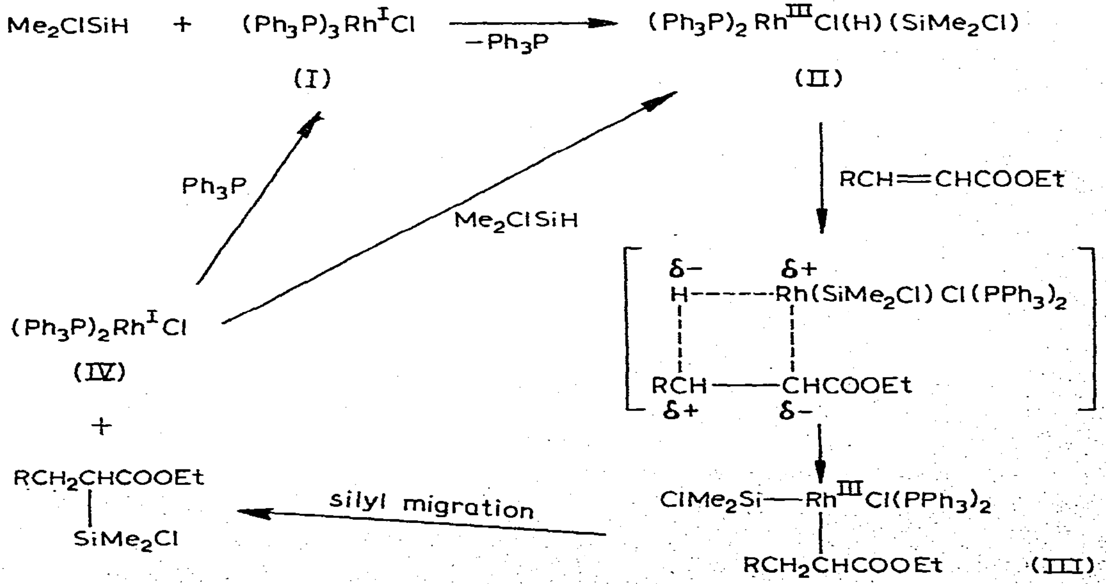
Although Yoshii et al. reported the exclusive formation of 1,4-adducts in the hydrosilylation of methyl crotonate and methyl methacrylate by triethylsilane [14], we observed the formation of the 1,2-adduct as a side product. Moreover, we found that the reaction of methyl acrylate using triethylsilane afforded the β-adduct and the disilylated product, whereas Yoshii et al. reported the formation of β-adduct and 1,4-adduct.

Possible mechanisms for these reactions

As is seen from Table 2, the mode of the hydrosilylation of α,β-unsaturated esters seems to be divided into three cases. They are (*i*) α-addition, (*ii*) β-addition and di-silylation, and (*iii*) 1,4-addition and 1,2-addition, and these reactions were not mixed with each other.

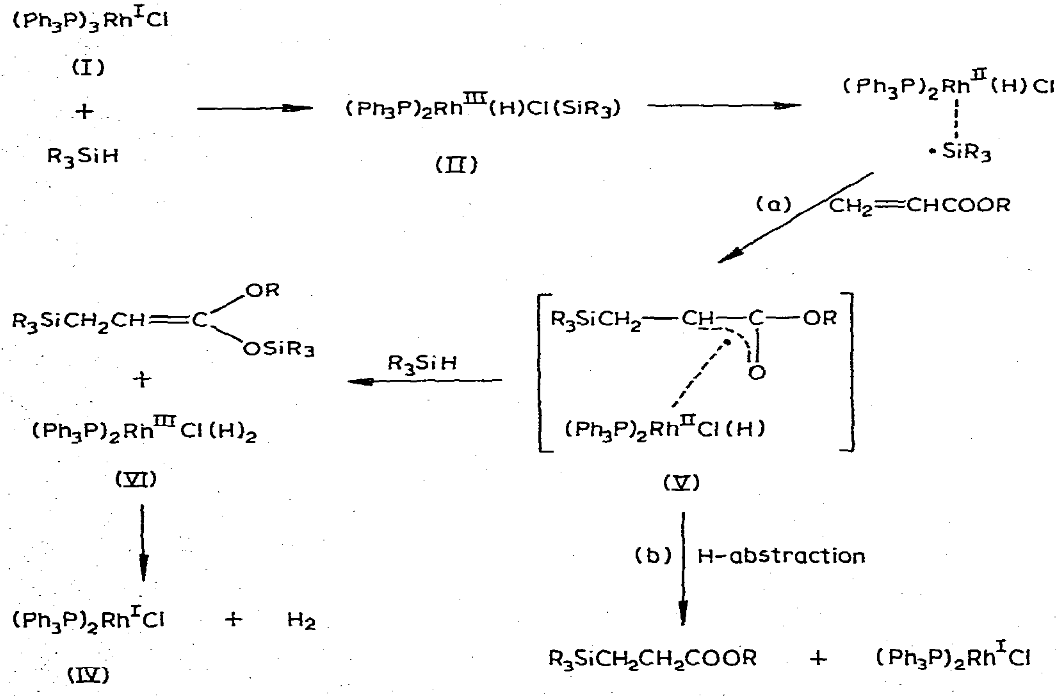
(i) α-Addition. α-Addition was observed only in the case of the reaction of chlorodimethylsilane. In a manner similar to the case of acrylonitrile, α-addition may be a result of hydride attack involving the silyl—rhodium(III) hydride (II) at the electron deficient β-carbon of ethyl acrylate and ethyl crotonate as shown in Scheme 2.

SCHEME 2



(ii) β-Addition and di-silylation. β-Addition was observed only when an acrylate was employed as substrate, and di-silylation as well as the β-addition occurred when triethylsilane was used. The possibility of a dehydrogenative condensation of the initially formed β-adduct and triethylsilane, which would give the disilylated product was excluded in a control experiment in which the β-adduct was allowed to react with triethylsilane in the presence of the rhodium catalyst under the conditions employed for the hydrosilylation: the formation of the disilylated product could not be observed at all. Consequently, disilylated products may be formed through the intermediate (or transition state) closely related to that of the β-addition. The β-addition may occur via initial addition of the coordinated silyl radical (similar to that postulated in the case of the addition of trichlorosilane to acrylonitrile catalyzed by the rhodium catalyst to form the complex V) and subsequent hydrogen abstraction as shown in Scheme 3. Thus, the disilylation would proceed through a silyl abstraction of the coordinated radical V from triethylsilane, which would form a dihydrorhodium complex VI.

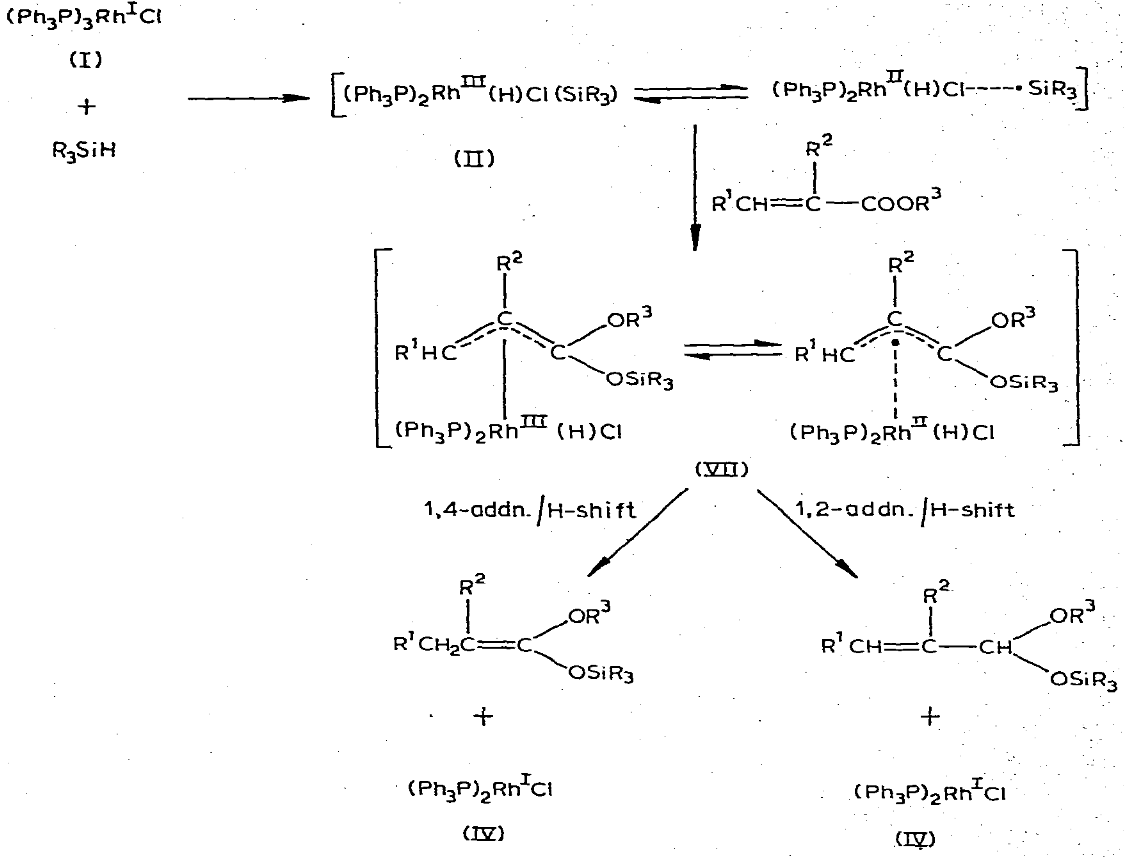
SCHEME 3



(iii) 1,4- and 1,2-Addition. Predominant 1,4-addition was observed when a crotonate or a methacrylate was employed as substrate. Although 1,2-addition also occurred to some extent in these cases, other modes of addition were not observed. Thus, 1,4- and 1,2-additions are expected to proceed via a common intermediate or transition state. The fact that a methyl group on one of the olefinic carbons is essential for the selective 1,4- and 1,2-addition indicates the intermediacy of a π-allylrhodium complex. In fact, silyl migration to the car-

bonyl oxygen of the crotonate or methacrylate may take place initially to form complex VII, and subsequent hydrogen migration would give the 1,4-adduct or 1,2-adduct as shown in Scheme 4. A methyl group on an olefinic carbon atom may effectively stabilize the resulting π-allyl radical (or π-allyl carbonium ion) which would have strong interaction with the hydridorhodium complex. This stabilizing effect may be one of the driving forces of the initial silyl migration to the carbonyl carbon.

SCHEME 4



Effect of the addition of a radical scavenger to the reaction system

Since the rate of the hydrosilylation of α,β-unsaturated esters is sensitive to oxygen and a radical process is supposed to be involved in these reactions, a reaction was carried out in the presence of 10 mol% of the galvinoxyl radical * in

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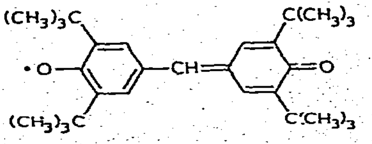
* 2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy:



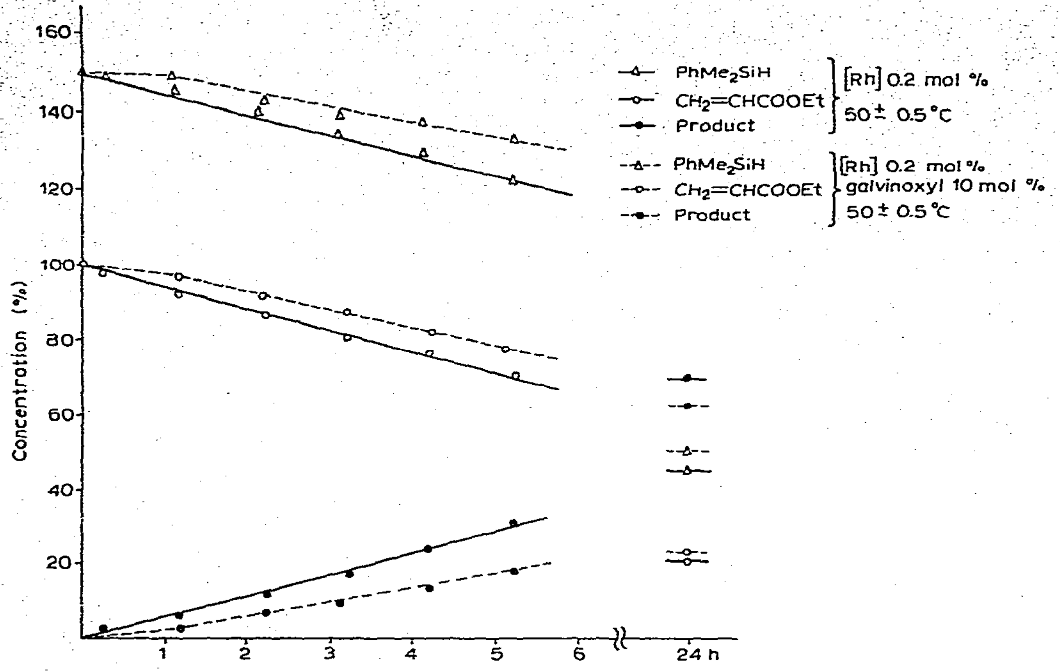


Fig. 1. Plots of [Silane], [Ester], and [Product] against time.

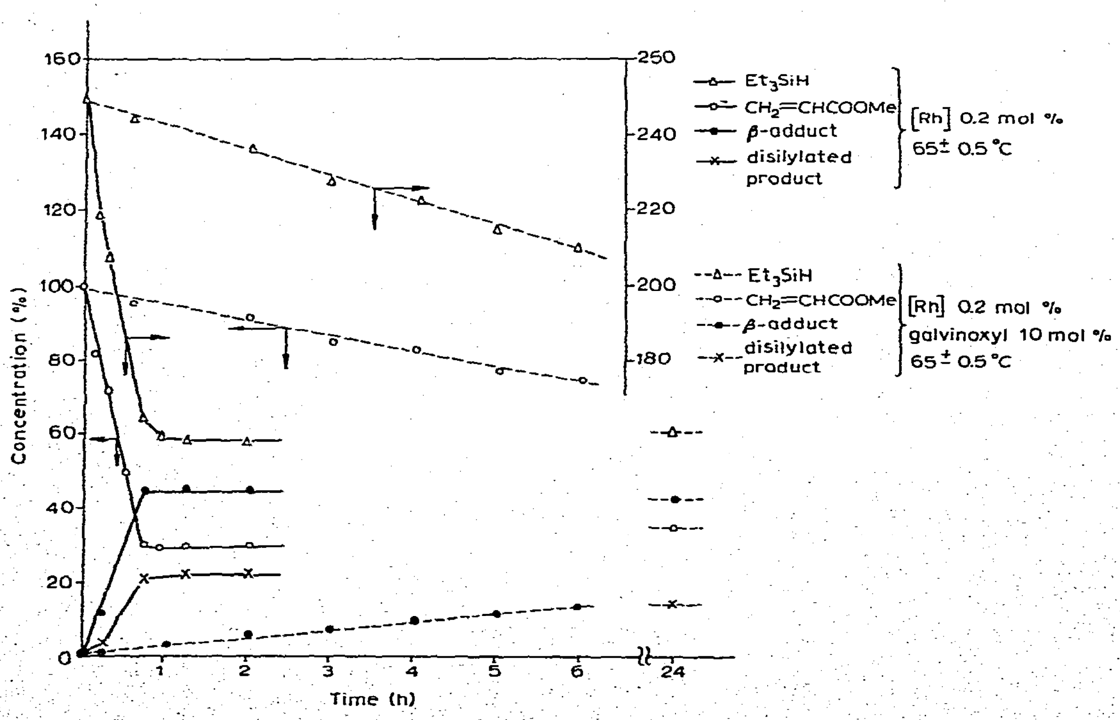


Fig. 2. Plots of [Silane], [Ester], and [Products] against time.

the expectation of inhibiting radical processes. Results are shown in Figs. 1—3.

As is seen from Fig. 1, the rate of reaction of dimethylphenylsilane with ethyl acrylate, which proceeds via β-addition, was retarded and an induction period was observed when 10 mol% of galvinoxyl was added to the system. Moreover, the yield of the adduct decreased about 10% compared with that attained without scavenger, although the conversions of these reactions were nearly the same. This strongly suggests that the reaction involves a radical process and that the scavenger traps the organic radicals.

In the case of the reaction of triethylsilane with methyl acrylate, which gave the β-adduct and the disilylated product, the reaction was effectively suppressed by the radical scavenger as shown in Fig. 2. If the scavenger traps only the resulting silyl radical or organic radicals, the suppression should be limited within 10%. However, the observed results cannot be accomodated by this assumption at all. Namely, the results clearly indicate that a certain catalytic species also may be trapped by the scavenger. Since galvinoxyl is quite bulky and the rhorium(I) complex is a stable species, it is not appropriate to assume that $(Ph_3P)_3$-Rh^ICl or $(Ph_3P)_2Rh^ICl$ forms an inactive complex with the scavenger. Moreover, if the Rh^I complexes form an inactive complex, the extent of the suppression should be almost the same in every case. However, the mode of the observed suppression was quite different with each case as can be seen from Figs. 1—3. Thus, we suggest that the rhodium(II) hydride complexes, i.e., II or V in Scheme 3, form an inactive or less reactive charge transfer complex with galvinoxyl.

As shown in Fig. 3, a dramatic suppression of the reaction was observed when the reaction of triethylsilane with methyl crotonate, which proceeds predomi-

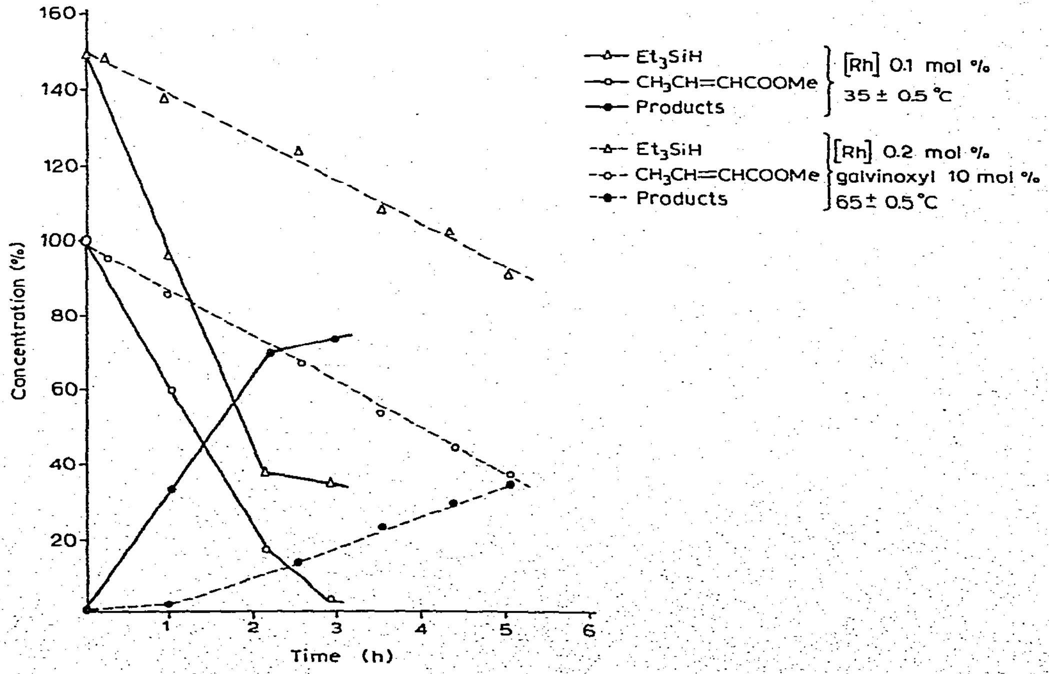


Fig. 3. Plots of [Silane], [Ester], and [Products] against time.
]

nantly via 1,4-addition, was carried out in the presence of galvinoxyl. The reaction without the radical scavenger was too fast to be measured at 65° C, but the reaction in the presence of galvinoxyl proceeded with rates suitable for a kinetic study at the same temperature. The results obtained for the reaction at 35° C are depicted in Fig. 3.

The separation of the rhodium—carbon bond in the complex II or VII in Scheme 4 may be large, i.e., both the π-allyl group and the rhodium complex may have a clear radical nature. Consequently, the scavenger may trap the rhodium(II) hydride species quite effectively.

Experimental

Measurement

The boiling points were uncorrected. The infrared spectra were recorded on Hitachi EPI-G3 and Hitachi 285 spectrophotometers, using neat liquid samples. The nuclear magnetic resonance spectra were obtained by the use of a Varian HA-100 or a Varian T-60 spectrometer, using TMS as the internal standard. Analytical gas chromatography (GLC) was carried out on a Shimazu GC-3BT, GC-3BF, or GC-5A using a column packed with 3%, 10% or 20% SE-30, and 3% OV-17.

Materials

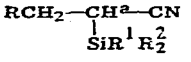
Hydrosilanes were prepared by known methods. Tris(triphenylphosphine)chlororhodium was prepared from rhodium trichloride trihydrate and triphenylphosphine. α,β-Unsaturated nitriles and esters are commercially available and purified by distillation.

Hydrosilylation of α,β-unsaturated nitriles in the presence of tris(triphenylphosphine)chlororhodium

A typical procedure is described for the hydrosilylation of acrylonitrile by

TABLE 3

SPECTRAL DATA FOR α-CYANOALKYLSILANES



$\underset{\textstyle SiR^1R^2_2}{RCH_2\text{—}CH^a\text{—}CN}$ (I)

	R	R^1	R^2	Bp. (°C/ Torr)	NMR (δ) Methine Proton (H^a)	IR (cm^{-1}) ν(C≡N)
a	H	Ph	Me	91/0.5	1.93 (quartet ^{a} J 7 Hz, 1H)	2220
b	H	Et	Me	85/20	1.83 (quartet ^{a}, J 7 Hz, 1H)	2220
c	H	Cl	Me	60/5	2.09 (quartet ^{a}, J 7 Hz, 1H)	2220
d	H	Me	Cl	60/4	2.41 (quartet ^{a}, J 7 Hz, 1H)	2220
e	H	EtO	EtO	68/1.5	1.85 (quartet ^{a}, J 7 Hz, 1H)	2220
f	Me	Ph	Me	113/2.5	1.80 (t ^{a}, J 7.5 Hz, 1H)	2220
g	Me	Cl	Me	95/20	1.95 (quartet, J 4.5, 10.5 Hz, 1H)	2220
h	Ph	Ph	Me	145/0.5	2.05 (t ^{a}, J 7.5 Hz, 1H)	2240

^{a} Small splittings were observed, which may be due to the long range coupling with methyls on the silicon atom.

dimethylphenylsilane: A mixture of 1.59 g (30 mmol) of acrylonitrile, 4.48 g (33 mmol) of dimethylphenylsilane and 30 mg (0.1 mol%) of $(Ph_3P)_3RhCl$ was stirred in a reaction flask which was flushed with argon under reflux for 3 h. The reaction mixture was distilled under reduced pressure to afford α-dimethylphenylsilylpropionitrile (Ia) (4.08 g) in 72% yield (GLC yield: 87%). Results are summarized in Table 1, and the spectral data used in the identification of the products are listed in Table 3.

The reaction of trichlorosilane with acrylonitrile required high temperatures. A mixture of acrylonitrile (1.59 g, 30 mmol), trichlorosilane (4.89 g, 36 mmol) and $(Ph_3P)_3RhCl$ (30 mg, 0.1 mol%) was sealed in a pyrex ampoule under argon and was heated at 140° C for 24 h with stirring. Distillation of the reaction mixture under reduced pressure afforded β-trichlorosilylpropionitrile (II) (2.8 g) in 50% yield as the only product (GLC yield 80%).

II: b.p. 78° C/7 Torr (lit. [8] 109° C/30 Torr). NMR ($CDCl_3$): δ 1.80 (m, 2H), and 2.65 (m, 2H). IR (neat): 2240 cm^{-1} (ν(C≡N)).

Hydrosilylation of ethyl acrylate and ethyl crotonate

Ethyl acrylate (3.0 g, 30 mmol) was allowed to react with dimethylphenylsilane (4.49 g, 33 mmol) in the presence of 30 mg (0.1 mol%) of $(Ph_3P)_3RhCl$ at 80° C for 2 h with stirring. Distillation of the reaction mixture under reduced pressure afforded ethyl β-dimethylphenylsilylpropionate (IVb) (4.9 g) in 70% yield (GLC yield 85%).

Dimethylethylsilane was allowed to react in a similar manner with ethyl acrylate to afford ethyl β-dimethylethylsilylpropionate (IVc) in 60% yield (GLC yield 83%).

When triethylsilane was used, the β-adduct and a disilylated product were obtained. Ethyl acrylate (3.0 g, 30 mmol) was allowed to react with triethylsilane (4.52 g, 39 mmol) in the presence of $(Ph_3P)_3RhCl$ (30 mg, 0.1 mol%) at 70°C for 3 h. GLC analysis revealed that two products had been produced in 65 : 35 ratio in 80% total yield. Distillation of the reaction mixture under reduced pressure gave ethyl β-triethylsilylpropionate (IVa) (b.p. 80°C/0.1 Torr) and 1-ethoxy-1-triethylsilyloxy-3-triethylsilylprop-1-ene (VIIa) (b.p. 124°C/1.5 Torr).

VIIa: NMR ($CDCl_3$): δ 0.40—1.50 (m, 32H), 1.23 (t, J 7 Hz, 3 H), 3.33 (t, J 8 Hz, 1H), and 3.59 (quartet, J 7 Hz, 2H). IR (neat): 1680 cm^{-1} (ν(C=C)). (Found: C, 61.88; H, 11.66. $C_{17}H_{38}O_2Si$ calcd.:C, 61.75; H, 11.58%.)

The ratio of IVa to VIIa did not change even when two equivalents of triethylsilane were used. Furthermore, the attempted reaction of ethyl β-triethylsilylpropionate with triethylsilane in the presence of $(Ph_3P)_3RhCl$ did not give the disilylated product at all.

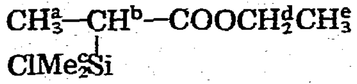
In a similar manner to that described above, ethyl crotonate (30 mmol) was allowed to react with other trialkylsilanes (33 mmol) in the presence of 0.1 mol% of $(Ph_3P)_3RhCl$ to afford 1-ethoxy-1-trialkylsilyloxybut-1-enes (VI). The obtained ketene silyl acetals (VI) were easily hydrolyzed to the corresponding saturated esters in quantitative yield by the action of aqueous or methanol solutions of *p*-toluenesulfonic acid at ambient temperature for 0.5 h.

Results are summarized in Table 2, and the spectral data of the β-adducts (IV) and the ketene silyl acetals (VI) are listed in Tables 4 and 5, respectively.

Reaction of chlorodimethylsilane with ethyl acrylate and ethyl crotonate

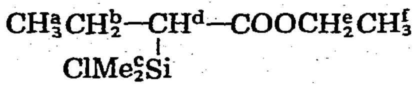
A mixture of chlorodimethylsilane (3.15 g, 33 mmol), ethyl acrylate (3.0 g, 30 mmol) and $(Ph_3P)_3RhCl$ (30 mg, 0.1 mol%) was sealed in a pyrex ampoule and heated at 70° C for 12 h with stirring. The reaction mixture was distilled under reduced pressure to afford ethyl α-chlorodimethylsilylpropionate (IIIa) in 55% yield (GLC yield 65%).

IIIa: b.p. 80° C/15 Torr. NMR (CCl_4): δ 0.46 (s, 3H) (H^c), 0.49 (s, 3H) (H^c), 1.06—1.43 (m, 6H) (H^a, H^e), 2.25 (quartet, J 7 Hz, 1H) (H^b), and 4.13 (octet, J_{dd} 7 Hz, J_{de} 7 Hz, 2H) (H^d). IR (neat): 1725 cm^{-1} (ν(C=O)). (Found: C, 43.01; H, 7.69. $C_7H_{15}O_2SiCl$ calcd.: C, 43.17; H, 7.76%.)



$CH^{a}_{3}—\underset{\mathrm{ClMe^{c}_{2}Si}}{\underset{|}{CH^{b}}}—COOCH^{d}_{2}CH^{e}_{3}$

(IIIa)



$CH^{a}_{3}CH^{b}_{2}—\underset{\mathrm{ClMe^{c}_{2}Si}}{\underset{|}{CH^{d}}}—COOCH^{e}_{2}CH^{f}_{3}$

(IIIb)

Similarly, the reaction of chlorodimethylsilane with ethyl crotonate gave ethyl α-chlorodimethylsilylbutyrate (IIIb) in 45% yield (GLC yield 65%).

IIIb: b.p. 85° C/15 Torr. NMR (CCl_4): δ 0.44 (s, 6H) (H^c), 0.96 (t, J 7 Hz, 3H) (H^a), 1.23 (t, J 7 Hz, 3H) (H^f), 1.42—2.25 (m, 3H) (H^b, H^d), and 4.08 (quartet, J 7 Hz, 2H) (H^e). IR (neat): 1720 cm^{-1} (ν(C=O)). (Found: C, 46.27; H, 7.97. $C_8H_{17}O_2SiCl$ calcd.: C, 46.03; H, 8.21%.)

In both cases, the IR spectra of the crude products showed a very weak absorption at 2120 cm^{-1} due to Si—H stretching band. This may mean that a disproportionation of chlorodimethylsilane occurred during the reaction to some extent [2c].

Hydrosilylation of methyl acrylate and methyl crotonate

To a mixture of methyl acrylate (0.86 g, 10 mmol) and triethylsilane (1.75 g, 15 mmol) in 10 ml benzene was added 10 mg (0.1 mol%) of $(Ph_3P)_3RhCl$ under argon, and the mixture was stirred at 60° C for 1 h. GLC analysis revealed the production of methyl β-triethylsilylpropionate (IVd) (54%) and 1-methoxy-1-triethylsilyloxy-3-triethylsilylprop-1-ene (VIIb) (23%). These products could be readily separated by distillation.

VIIb: b.p. 122° C/2.5 Torr. NMR ($CDCl_3$): δ 0.38—1.55 (m, 32H), 3.30 (t, J 8 Hz, 1H), and 3.42 (s, 3H). IR (neat): 1680 cm^{-1} (ν(C=C)). (Found: C, 60.55; H, 11.40. $C_{16}H_{36}O_2Si$ calcd.: C, 60.69; H, 11.46%.)

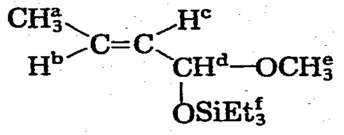
When the reaction was carried out without solvent, 1-methoxy-1-triethylsilyloxyprop-1-ene (VIg) was obtained in 7% yield in addition to these 2 products.

In a similar manner, the reaction of dimethylphenylsilane with methyl acrylate afforded methyl β-dimethylphenylsilylpropionate (IVe) in 80% yield when benzene was used as solvent, while the reaction without solvent gave a mixture of the silyl propionate IVe and 1-methoxy-1-dimethylphenylsilyloxyprop-1-ene (VIh) in 65 : 35 ratio. In the case of dimethylethylsilane, methyl β-dimethylethylsilylpropionate (IVf) was obtained as a sole product in 78% yield.

In a similar manner to that described above, methyl crotonate (30 mmol) was allowed to react with dimethylphenylsilane or dimethylethylsilane (33 mmol) in the presence of $(Ph_3P)_3RhCl$ (0.1 mol%) to afford 1-methoxy-1-dimethylphenylsilyloxybut-1-ene (VIe) (70%) or 1-methoxy-1-dimethylethylsilyloxybut-1-ene (VIf) (73%).

In contrast with these two cases, the formation of 1,2-adduct as well as 1,4-adduct was observed when triethylsilane was used. The reaction of methyl crotonate (30 mmol) with triethylsilane (33 mmol) in the presence of $(Ph_3P)_3RhCl$ (0.1 mol%) at 50°C for 0.5 h with stirring afforded a mixture of 1-methoxy-1-triethylsilyloxybut-1-ene (VId) (71%) and 1-methoxy-1-triethylsilyloxybut-2-ene (V) (24%) which was identified on the basis of its NMR spectrum.

V: b.p. 77°C/5 Torr. NMR (CCl_4): δ 0.50—1.08 (m, 15H) (H^f), 1.69 (d, J 6 Hz, 3H) (H^a), 3.16 (s, 3H) (H^e), 4.97 (d, J_{cd} 5 Hz, 1H) (H^d), 5.39 (quartet, J_{cd} 5 Hz, J_{bc} 15.5 Hz, 1H) (H^c), and 5.71 (octet, J_{ab} 6 Hz, J_{bc} 15.5 Hz, 1H) (H^b). IR (neat): 1640 cm^{-1} (ν(C=C)). (Found: C, 61.09; H, 11.13. $C_{11}H_{24}O_2Si$ calcd.: C, 61.05; H, 11.18%.)



(V)

Results are summarized in Table 2. The spectral data of the β-adducts (IV) and 1,4-adducts, i.e., ketene silyl acetals (VI), are listed in Tables 4 and 5, respectively.

Hydrosilylation of ethyl and methyl methacrylate

In a similar manner described above, ethyl methacrylate (30 mmol) was allowed to react with triethylsilane (33 mmol) in the presence of $(Ph_3P)_3RhCl$ (0.1 mol%) at 80°C for 2 h with stirring to afford a mixture of 1-ethoxy-1-triethylsilyloxy-2-methylprop-1-ene (VIIIa) and 1-ethoxy-1-triethylsilyloxy-2-methylprop-2-ene (IXa) in 80% yield. The ratio of VIIIa/IXa was determined to be 92 : 8 on the basis of 100 MHz NMR spectrum.

The results of the hydrosilylation of ethyl and methyl methacrylate using several hydrosilanes are summarized in Table 2 and the spectral data of the products are listed in Table 6.

(continued on p. 60)

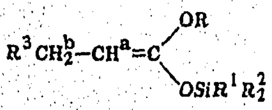
TABLE 4

SPECTRAL DATA FOR β-SILYLPROPIONATES $R^1R^2_2SiCH_2CH^a_2COOR$ (IV)

	R	R^1	R^2	Bp. (°C/Torr)	NMR (δ) Methylene protons (H^a)	IR (cm^{-1}) ν(C=O)
a	Et	Et	Et	80/1.0	2.26 (m, 2H)	1745
b	Et	Ph	Me	103/3	2.20 (m, 2H)	1740
c	Et	Et	Me	90/15	2.25 (m, 2H)	1745
d	Me	Et	Et	75/3	2.30 (m, 2H)	1745
e	Me	Ph	Me	115/4.5	2.21 (m, 2H)	1745
f	Me	Et	Me	86/20	2.21 (m, 2H)	1745

TABLE 5

SPECTRAL DATA FOR KETEN SILYL ACETALS FROM CROTONATES



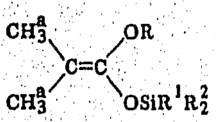
$$R^3CH_2^b{-}CH^a{=}C\begin{matrix}OR\\OSiR^1R_2^2\end{matrix}$$

(VI)

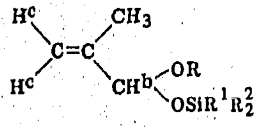
VI	R	R^1	R^2	R^3	B.p. (°C/Torr)	NMR (δ)		IR (cm^{-1}) ν(C=C)
						Methine proton (H^a)	Methylene (or Methyl) protons (H^b)	
a	Et	Et	Et	Me	80/3	3.26 (t, *J* 7 Hz, 1H)	1.93 (quintet, *J* 7 Hz, 2H)	1680
b	Et	Ph	Me	Me	115/4	3.30 (t, *J* 7 Hz, 1H)	2.01 (quintet, *J* 7 Hz, 2H)	1680
c	Et	Et	Me	Me	84/15	3.30 (t, *J* 7 Hz, 1H)	1.96 (quintet, *J* 7 Hz, 2H)	1680
d	Me	Et	Et	Me	77/5	3.31 (t, *J* 7 Hz, 1H)	1.95 (quintet, *J* 7 Hz, 2H)	1685
e	Me	Ph	Me	Me	95/2.5	3.32 (t, *J* 7 Hz, 1H)	1.96 (quintet, *J* 7 Hz, 2H)	1680
f	Me	Et	Me	Me	72/15	3.32 (t, *J* 7 Hz, 1H)	1.91 (quintet, *J* 7 Hz, 2H)	1680
g	Me	Et	Et	H	70/3	3.42 (quartet, *J* 6.5 Hz, 1H)	1.51 (d, *J* 6.5 Hz, 3H)	1690
h	Me	Ph	Me	H	105/4.5	3.36 (quartet, *J* 6.5 Hz, 1H)	1.48 (d, *J* 6.5 Hz, 3H)	1690

TABLE 6

SPECTRAL DATA FOR KETEN SILYL ACETALS AND SILYL ACETALS FROM METHACRYLATES



(VIII) 1,4-adduct



(IX) 1,2-adduct

	R	R^1	R^2	Adduct	B.p. (°C/Torr)	NMR (δ)			IR (cm^{-1})
						H^a	H^b	H^c	ν(C=C)
a	Et	Et	Et	1,4	65/1.7	1.48 (s, 3H)	4.92 (s, 1H)	4.80 (s, 1H)	1705
				1,2		1.51 (s, 3H)		4.92 (s, 1H)	
b	Et	Ph	Me	1,4	109/4	1.43 (s, 3H)	4.85 (s, 1H)	4.74 (s, 1H)	1705
				1,2		1.49 (s, 3H)		4.85 (s, 1H)	
c	Et	Et	Me	1,4	55/4	1.51 (s, 3H)	5.01 (s, 1H)	4.88 (s, 1H)	1710
				1,2		1.56 (s, 3H)		5.01 (s, 1H)	
d	Me	Et	Et	1,4	65/1.7	1.48 (s, 3H)	4.88 (s, 1H)	4.88 (s, 1H)	1705
				1,2		1.50 (s, 3H)		4.95 (s, 1H)	
e	Me	Ph	Me	1,4	90/1.5	1.44 (s, 3H)	4.84 (s, 1H)	4.84 (s, 1H)	1705
				1,2		1.50 (s, 3H)		4.93 (s, 1H)	
f	Me	Et	Me	1,4	80/15	1.49 (s, 3H)	4.86 (s, 1H)	4.86 (s, 1H)	1710
				1,2		1.54 (s, 3H)		4.95 (s, 1H)	

Reactions of acrylate and crotonate with hydrosilane in the presence of radical scavenger

Ethyl acrylate (0.50 g, 5 mmol), dimethylphenylsilane (1.02 g, 7.5 mmol), galvinoxyl (200 mg, 10 mol% based on the ester) and $(Ph_3P)_3RhCl$ (10 mg, 0.2 mol% based on the ester) were dissolved under argon in 5 ml of benzene, containing n-octane (0.285 g, 2.5 mmol) and n-pentadecane (0.53 g, 2.5 mmol) as internal standards. After the mixture was sufficiently degassed, the reaction flask was immersed in an oil bath at 50 ± 0.5°C and the contents were stirred.

The consumption of the ester and the hydrosilane, and the formation of the product, i.e., the β-adduct, was followed by means of gas chromatography on Shimazu GC-5A equipped with a temperature programing apparatus using a digital integrator. The results are shown in Fig. 1.

For comparison, the same reaction, on the same scale except for the absence of galvinoxyl, was also carried out. The results also are depicted in Fig. 1.

In a similar manner to that described above, the reactions of methyl acrylate or methyl crotonate with triethylsilane in the presence of and in the absence of the radical scavenger were carried out. Results are shown in Figs. 2 and 3.

References

1 J.W. Ryan and J.L. Speier, J. Org. Chem., 31 (1966) 2968, and their earlier papers cited therein; A.J. Chalk and J.P. Harrod, J. Amer. Chem. Soc., 87 (1965) 16.
2 (a) F. de Charentenay, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1968) 787; (b) R.N. Haszeldine, R.V. Parish and D. J. Parry, J. Chem. Soc. A, (1969) 683; (c) A.J. Chalk, J. Organometal. Chem., 21 (1970) 207; (d) A.J. Chalk, Trans. N.Y. Acad. Sci., Ser. II, 32 (1970) 481.
3 A.J. Chalk and J.F. Harrod, J. Amer. Chem. Soc., 89 (1967) 1640.
4 E.Ts. Chukovskaya, N.A. Kuz'mina and M.I. Rozhkova, Zh. Obshch. Khim., 36 (1966) 2170.
5 K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 28 (1971) C37; W. Fink, Helv. Chim. Acta, 54 (1971) 1304.
6 S. Takahashi, T. Shibano and N. Hagihara, Chem. Commun., (1969) 161; S. Takahashi, T. Shibano, H. Kojima and N. Hagihara, Organometal. Chem. Syn., 1 (1970/1971) 193; M. Hara, K. Ohno and J. Tsuji, Chem. Commun., (1971) 247.
7 (a) M. Kumada, Y. Kiso and M. Umeo, Chem. Commun., (1970) 611; (b) Y. Kiso, M. Kumada, K. Tamao and M. Umeo, J. Organometal. Chem., 50 (1973) 297.
8 S. Nozakura and S. Konotsune, Bull. Chem. Soc. Japan, 29 (1956) 326.
9 Z.V. Belyakova, S.A. Golubtsov and T.M. Yakusheva, Zh. Obshch. Khim., 32 (1962) 1997.
10 (a) S. Nozakura and S. Konotsune, Bull. Chem. Soc. Japan, 29 (1956) 322; (b) R.A. Pike, J.E. McMahon, V.B. Jex, W.T. Black and D.L. Bailey, J. Org. Chem., 24 (1959) 1939.
11 L. Goodman, R.M. Silverstein and A. Benitez, J. Amer. Chem. Soc., 79 (1957) 3073.
12 (a) A.D. Petrov, S.I. Sadykh-Zade and E.I. Filatova, Zh. Obshch. Khim., 29 (1959) 2936; (b) F. Rijkens, M.J. Janssen, W. Drenth and G.J.M. van der Kerk, J. Organometal. Chem., 2 (1964) 347; (c) L.H. Sommer, F.P. Mackay, O.W. Steward and P.G. Campbell, J. Amer. Chem. Soc., 79 (1957) 2764; (d) J.W. Curry and G.W. Harrison, J. Org. Chem., 23 (1958) 627; (e) L. Goodman, R.M. Silverstein and J.N. Shoolery, J. Amer. Chem. Soc., 78 (1956) 4493; (f) J.L. Speier, J.A. Webster and G.H. Barnes, J. Amer. Chem. Soc., 79 (1957) 974.
13 I. Ojima, M. Kumagai and Y. Nagai, Tetrahedron Lett., (1974) 4005.
14 E. Yoshii, Y. Kobayashi, T. Koizumi and T. Oribe, Chem. Pharm. Bull., 22 (1974) 2767.
15 D.J. Peterson, J. Org. Chem., 33 (1968) 780.
16 S.L. Hartzell, D.F. Sullivan and M.W. Rathke, Tetrahedron Lett., (1974) 1403; K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto and H. Nozaki, J. Amer. Chem. Soc., 96 (1974) 1620.