

HOMOGENEOUS CATALYSIS

IX *. HYDROSILYLATION USING TRIS(PENTANEDIONATO)RHODIUM-(III)-TRIALKYLALUMINIUM AS CATALYST **

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Summary

The two component (Ziegler) catalyst $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ (or an analogue with an alternative cocatalyst) has been investigated for the hydrosilylation by SiHX_3 of alkynes, dienes, alkenes, styrene, or allylbenzene at 60°C . Terminal alkynes did not yield adducts, but internal alkynes $\text{RC}\equiv\text{CR}'$ gave products of *cis*-addition with SiHEt_3 or $\text{SiH}\text{Et}_2\text{Me}$ (but not $\text{SiH}(\text{OEt})_3$), without regiospecificity for the case of $\text{R} \neq \text{R}'$. Acyclic dienes gave 1/1 adducts with SiHX_3 ($\text{X} = \text{Me}, \text{Et}, \text{OEt}, \text{or OSiMe}_3$; but not $\text{X} = \text{Ph}$), predominantly (or, for penta-1,3-diene, exclusively) the products of 1,4-addition. Among cyclic dienes, only cyclohexa-1,3- (or -1,4)-diene was hydrosilylated with SiHEt_3 to yield cyclohex-2-enyltriethylsilane; cycloocta-1,3-diene was merely rearranged to the 1,5-isomer, norbornadiene was polymerised, and no reaction was observed with 2,5-dimethylhexa-2,4-diene. Internal straight-chain alkenes $\text{RR}'\text{C}=\text{CHR}''$, $\text{RR}'\text{C}=\text{CR}''\text{R}'''$, or cyclohexene proved unreactive; however disubstituted olefins $\text{RCH}=\text{CHR}'$ gave the terminal (isomerised) 1/1-adducts, e.g., $\text{n-C}_5\text{H}_{11}\text{SiEt}_3$ from $\text{MeCH}=\text{CH}\text{Et}$ and SiHEt_3 . Likewise terminal alkenes $\text{RCH}=\text{CH}_2$ gave $\text{RCH}_2\text{CH}_2\text{SiX}_3$ ($\text{X} = \text{Ph}$ or OEt) or ($\text{X} = \text{Et}$) a mixture of isomeric 1/1 adducts. With styrene and SiHEt_3 , or to a lesser extent $\text{SiH}(\text{OR})_3$ ($\text{R} = \text{Me}$ or Et), the dehydrogenative hydrosilylated material, the vinylsilane $\text{PhCH}=\text{CHSiX}_3$, was the principal product with isomeric 1/1 adduct byproducts; with allylbenzene, likewise, $\text{PhCH}_2\text{CH}=\text{CHSiX}_3$ was a significant, but less important, component of the reaction mixture. Mechanistic pathways are proposed; for the dehydrogenative

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hydrosilylation of styrene, crucial steps are styrene insertion into a $\text{Rh}^{\text{III}}\text{-SiX}_3$ bond and a subsequent intramolecular hydrogen transfer, which are consistent with both a labelling experiment using SiDEt_3 and the lack of dehydrogenation (under the reaction conditions) of $\text{PhCH}_2\text{CH}_2\text{SiEt}_3$.

Introduction

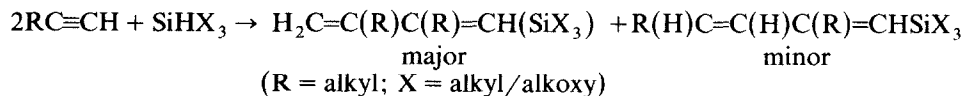
The use of a two component Ziegler catalyst for hydrosilylation goes back to 1972; $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ ($\text{acacH} = \text{MeCOCH}_2\text{COME}$) was particularly successful for the hydrosilylations of 1,3-dienes or terminal acetylenes, but the analogous Fe^{II} or Co^{II} systems were also active [1,2]. Of these catalysts only the Ni^{II} and Co^{II} showed low activity towards an α -olefinic substrate, and Cr^{III} , Mn^{III} , and Fe^{III} proved ineffective. Further studies have appeared dealing with such Ni^{II} [3–5] and Co^{II} [4–6] catalysts in the context of 1,3-dienes. One objective of the present work was to extend such researches to the noble metals, and specifically to the $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ system.

Rhodium complexes have featured as hydrosilylation catalysts, even of terminal alkenes, since 1968 [7,8], but generally in metal oxidation state +1. The most commonly used was $[\text{RhCl}(\text{PPh}_3)_3]$ or a simple analogue, see e.g., ref. 9, or for a carbenerhodium(I) complex [10,11]. Rhodium(II) chlorides [12] or acetate [13] have also been employed. Complexes of rhodium(III) as hydrosilylation catalyst have been $[\text{Rh}(\text{acac})_3]$ [13] (without a cocatalyst) and $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\mu\text{-Cl})\text{Cl}\}_2]$ [14]. A further objective of this study was to extend the range of hydrosilylation rhodium(III) catalysts to that of the $[\text{Rh}(\text{acac})_3]\text{-based}$ Ziegler systems, including that with AlEt_3 as cocatalyst.

Results and discussion

1. Hydrosilylation of alkynes

With the Ziegler catalyst $[\text{Rh}(\text{acac})_3]\text{-triethylaluminium}$, terminal alkynes were observed not to undergo hydrosilylation; however, considerable and rapid oligomerisation was found; the product was a flocculent precipitate. Other catalytic studies with Ziegler systems in their reactions with terminal alkynes have shown that (i) in hydrogenation, polymerisation is a competitive reaction [15], whilst (ii) in hydrosilylation Ziegler systems containing Cr^{III} , Mn^{II} , Fe^{III} , or Co^{II} pentadienoates are inactive, giving alkyne polymers containing no silyl groups [2,6] and $\text{Cu}^{\text{II}}(\text{acac})_2\text{-triethylaluminium}$ was inactive for both hydrosilylation and polymerisation [17]. Only the nickel(II) pentanedienoate–triethylaluminium catalyst has been shown to be active in hydrosilylation, but with simultaneous oxidative dimerisation of the alkyne [1,2], eq. 1.

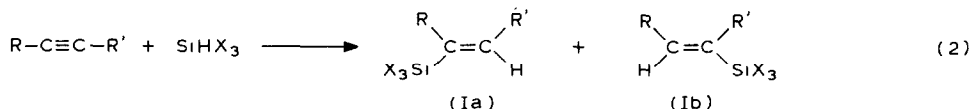


(1)

The $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ system thus compares unfavourably in this reaction to

other homogeneous catalysts; e.g., Rh^{I} complexes [8–12,18,19] or chloroplatinic acid [20] catalyse the hydrosilylation of terminal acetylenes in high yields. It also compares adversely with $[\text{Rh}(\text{acac})_3]$ alone, which shows reasonable catalytic activity with terminal alkynes [13].

The same Ziegler system $[\text{Rh}(\text{acac})_3]\text{--AlEt}_3$ does, however, catalyse the hydrosilylation of non-terminal alkynes with alkylsilanes to give vinylsilanes, eq. 2, but no reaction was observed with alkoxysilanes.



(X = Et and R = R' = Et or Pr^{n} , X = Et, R = Me or Et, R' = Bu^{n} ,

X = Et, R = Me, R' = $n\text{-C}_5\text{H}_{11}$, $\text{X}_3 = \text{MeEt}_2$, R = Me, R' = Bu^{n})

Since the symmetric internal alkynes oct-4-yne and hex-3-yne afforded single products (Table 1), it seems possible that this catalytic system behaves in a manner comparable to chloroplatinic acid, i.e., giving *cis*-addition [20–22], rather than in the way that has been observed using $[\text{RhCl}(\text{PPh}_3)_3]$ as catalyst. In the latter system, *trans*-addition was noted [23] yielding the *cis*-adducts, which, however, underwent slow isomerisation on heating to the thermodynamically more stable *trans*-isomers [20].

Addition to asymmetric internal alkynes, e.g., oct-3-yne, resulted in the formation of isomeric products in ca. equivalent proportions; their unambiguous identification proved difficult, but they are believed to be the adducts Ia and Ib, eq. 2 (R = Et and R' = Bu^{n}) and Table 1.

Yields and distribution of products in the hydrosilylation of internal alkynes by $[\text{Rh}(\text{acac})_3]\text{--AlEt}_3$ are shown in Table 1. Neither hydrosilylation of the adduct, as observed with chloroplatinic acid [24], nor isomerisation of the alkyne to a terminal alkyne, was observed during hydrosilylation.

The catalyst system $[\text{Rh}(\text{acac})_3]\text{--AlEt}_3$ showed little variation in activity in the temperature range 60–120°C; after 5 h essentially quantitative hydrosilylation was

TABLE 1
YIELDS (%) OF HYDROSILYLATION PRODUCTS OF DISUBSTITUTED ALKYNES $\text{R--C}\equiv\text{C--R}'$ AT 60°C USING $[\text{Rh}(\text{acac})_3]\text{--AlEt}_3$ AS CATALYST^a

R	R'	Silane ^b	Time (h)	Yield (%) ^c
Pr^{n}	Pr^{n}	SiHEt_3	11	94
Et	Bu^{n}	SiHEt_3	10	27
Me	$n\text{-C}_5\text{H}_{11}$	SiHEt_3	10	32
Et	Et	SiHEt_3	8	31
Me	Bu^{n}	SiHEt_3	8	35
Me	Bu^{n}	SiHEt_2Me	12	45
Pr^{n}	Pr^{n}	$\text{SiH}(\text{OEt})_3$ ^d	18	0

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; maintained on oil bath at 60°C. ^b Silane, 6.3 mmol; $\text{R--C}\equiv\text{C--R}'$, 18 mmol. ^c Based on silane; calculated by quantitative GLC. Where two figures are given, these refer to the two isomers Ia and Ib (eq. 2). ^d Silane, 5.5 mmol; $\text{R--C}\equiv\text{C--R}'$, 15 mmol.

TABLE 2
EFFECT OF TEMPERATURE ON YIELD (%) IN THE $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ CATALYSED HYDROSILYLATION OF OCT-4-YNE WITH TRIETHYLSILANE ^a

Temperature (°C) ^b	Yield ^c
20	0
60	94
100	98
120	96

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; SiHEt_3 , 6.3 mmol; oct-4-yne, 18 mmol. ^b Maintained on oil bath at the recorded temperature for 5 h. ^c Based on silane; calculated by quantitative GLC.

observed, although negligible reaction occurred below 60°C (Table 2, for the oct-4-yne- SiHEt_3 reaction).

2. Hydrosilylation of dienes

The Ziegler catalyst $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ has proved to be efficient for the hydrosilylation of acyclic dienes giving 1/1 diene/silane adducts, eq. 3, and Tables 3 and 4. The latter comprise both the products of 1,4- (II) and 1,2- (IIIa) and (IIIb) addition. By contrast, hydrosilylation using nickel salts in the presence of triethylaluminium, yielded only a 1,4-adduct [2], as found with chloroplatinic acid [25,26]. The complex $[\text{RhCl}(\text{PPh}_3)_3]$ also gave 1,2- and 1,4-adducts [27], as did the Ziegler

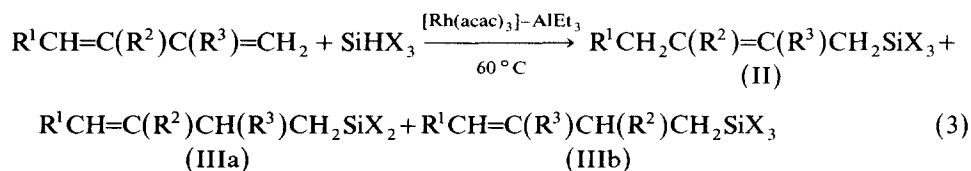


TABLE 3
HYDROSILYLATION OF ISOPRENE AT 60°C USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ AS CATALYST ^a

Silane	Mmol	Time (h)	Yield ^b (%)	Adduct ^{c,d}
SiHEt_3	6.3	12	44	II
			41	IIIa,IIIb
$\text{SiH}(\text{OEt})_3$	5.5	15	43	II
			6	IIIa,IIIb
$\text{SiHMe}(\text{OSiMe}_3)_2$	4.4	15	20	II
			18	IIIa,IIIb
SiHEt_2Me	6.3	12	60	II
			13	IIIa,IIIb
SiHPh_3	5.0	18	0	

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; maintained on oil bath at 60°C. ^b Based on silane; calculated by quantitative GLC. ^c See eq. 3, $\text{R}^1 = \text{H} = \text{R}^2$, $\text{R}^3 = \text{CH}_3$. ^d The isomers IIIa and IIIb were not isolated, but were identified by their mass spectra (by GLC/MS) and by comparison of their GLC retention times with authentic samples of the 1,2-adducts, prepared by hydrosilylation of isoprene using $[\text{Co}_2(\text{CO})_8]$ as catalyst [33].

TABLE 4
HYDROSILYLATION OF DIENES USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ ^a

Diene	Silane ^b	Time (h)	Yield ^c (%)	Adduct
2,3-Dimethylbuta-1,3-diene (DMBD)	SiHEt_3	12	54	II ^d
DMBD	$\text{SiH}(\text{OEt})_3$	15	6	IIIa ^d
			40	II ^d
			7	IIIa ^d
1,4-Dimethylcyclopenta-1,3-diene	SiHEt_3	20	0	
<i>cis</i> / <i>trans</i> -Penta-1,3-diene	SiHEt_3	10	41	IV
Cyclohexa-1,3- or -1,4-diene	SiHEt_3	15	64	V
Cyclo-octa-1,5-diene	SiHEt_3	2	0	
Cycloocta-1,3-diene	SiHEt_3	15	0	

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; maintained on oil bath at 60 °C. ^b SiHEt_3 , 6.3 mmol; diene, 18 mmol. ^c Based on silane; calculated by quantitative GLC. ^d See eq. 2; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3 = \text{R}^3$.

catalysts containing cobalt(II) [6] or iron(III) pentanedienoates [16]. In the present experiments, only penta-1,3-diene did not apparently give 1,2-adducts (Table 4).

Diene/silane (1/2) adducts, $\text{X}_3\text{SiCH}(\text{R}^1)\text{CH}(\text{R}^2)\text{CH}(\text{R}^3)\text{CH}_2\text{SiX}_3$, if formed, were present only in trace amounts in the $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ system. By contrast, hydrosilylation with complexes of nickel [28–30], palladium [28,31,34] or platinum [32,33], invariably gave such adducts, sometimes as the major products [34]. Oligomerisation, which often accompanies hydrosilylation of dienes with Ziegler catalysts [4,5], although not with $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ [3,6,35], was not observed using $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$. However, the Al/Rh ratio needs to be > 3 for polymerisation to be significant [36].

$[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ is evidently an active catalyst for the hydrosilylation of dienes with a variety of silanes SiHX_3 , although the data of Table 3 do not show clear trends other than the unreactivity of SiHAr_3 .

The 1,4-adduct (II) ($\text{R}^1 = \text{H} = \text{R}^2$, $\text{R}^3 = \text{Me}$) in the hydrosilylation of isoprene with triethylsilane was identified by ^1H NMR data and comparison with published data [13].

The Rh/Al hydrosilylation of penta-1,3-diene (PD) gave solely the 1,4-adduct IV ($\equiv$ II) with $\text{R}^1 = \text{Me}$ and $\text{R}^2 = \text{H} = \text{R}^3$) eq. 4. Identification was by ^1H NMR (Table

TABLE 5
 ^1H NMR CHEMICAL SHIFT DATA FOR $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{SiEt}_3$ ^a

$\text{CH}=\text{CH}$	$\text{CCH}_2\text{C}=\text{C}$	$\text{C}=\text{CCH}_2\text{Si}$	$\text{CH}_2\text{CC}=\text{C SiCH}_2\text{CH}_3$
5.0–5.5	1.8–2.2	1.4–1.8	0.4–1.1

^a Chemical shifts in δ (ppm) with appropriate integration.

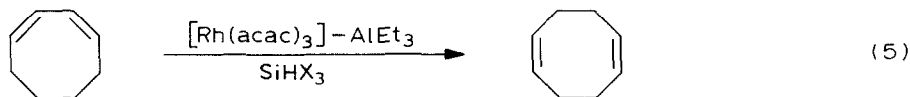
5) and by comparative GLC with an authentic sample, prepared by hydrosilylation of PD with $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ [2].



Of the cyclic dienes only cyclohexadienes (1,3- or 1,4-) were hydrosilylated by triethylsilane using $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$, to give exclusively cyclohex-2-enyltriethylsilane, (V). Identification was by ^1H NMR (using similar data for cyclohex-2-enyltrimethylsilane [37]). Cyclohexa-1,4-diene gave both V and its 3-isomer using $[\text{RhCl}(\text{PPh}_3)_3]$ [38].

The Ziegler system $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ proved not to be an effective catalyst for the hydrosilylation of 2,5-dimethylhexa-2,4-diene; however, in contrast to $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ (this work), there was no reduction to metal. Such lack of reactivity may be due to steric hindrance, because this conjugated diene is dimethylated at both termini. (Similarly hydrosilylation of a trisubstituted alkene with this catalyst also proved unsuccessful.)

Cycloocta-1,3-diene was isomerised during attempts at hydrosilylation eq. 5. By contrast, isomerisation was not observed upon treating cycloocta-1,3-diene in identi-



cal fashion except for the absence of triethylsilane. Presumably, the silane functions here merely as a reducing agent.

The catalytic polymerisation of bicyclo[2.2.1]heptadiene (norbornadiene) was effected using $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$, as had previously been observed with $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ [2].

Variations in the nature of the cocatalyst in the hydrosilylation of 2,3-dimethylbuta-1,3-diene by SiHET_3 had only minor influence on yields (Table 6). However, as

TABLE 6
EFFECT OF COCATALYST ON THE HYDROSILYLATION OF 2,3-DIMETHYLBUTA-1,3-DIENE (DMBD) BY TRIETHYLSILANE USING $[\text{Rh}(\text{acac})_3]\text{-COCATALYST}$ AT 60°C ^a

Reducing agent ^b (cocatalyst)	Quantity (mmol)	Yield ^c (%)
AlEt_3 ^d	1	62
$\text{AlEt}_2(\text{OEt})$ ^d	1	59
$\text{Al}(\text{Cl})\text{Et}_2$ ^d	1	59
Redal ^d	1	64
$\text{Na}[\text{BH}_4]$	2	7
$\text{Na}[\text{BH}_4]$ ^e	2	29
$\text{Li}[\text{AlH}_4]$	2	16
$\text{Li}[\text{AlH}_4]$ ^e	2	38

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; DMBD, 18 mmol; SiHET_3 , 6.3 mmol; maintained on oil bath at 60°C for 5 h.

^b Empirical formulae used for convenience. ^c Diene/silane (1/1) adducts; based on silane; calculated by quantitative GLC. ^d Redal = $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$; as 1 molar solutions in benzene. ^e In solution in OEt_2 .

TABLE 7
EFFECT OF SOLVENT ON YIELDS (%) IN THE HYDROSILYLATION OF DIENES BY TRIETHYLSILANE USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ AT 60°C ^a

Solvent ^b	Diene	Yield of 1/1 adduct ^c (%)
THF	Isoprene (IP)	99 (4) ^d
OEt ₂	IP	83 (4)
n-pentane	IP	83 (4)
THF	2,3-Dimethylbuta-1,3-diene (DMBD)	56 (9)
n-pentane	DMBD	52 (9)
OEt ₂	DMBD	52 (9)
Benzene	DMBD	56 (9)

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; maintained on oil bath at 60°C for 6 h. ^b Solvent, 2 cm³. ^c Based on silane; calculated by quantitative GLC. ^d Figures in parentheses represent ratio of 1,4 adduct/1,3 adduct (e.g., (4) means yield of II/yield of (IIIa + IIIb) = 4, see eq. 3).

to distribution, $\text{Li}[\text{AlH}_4]$ or $\text{Na}[\text{BH}_4]$ in the presence of ethoxyethane as solvent, gave only 1,4-adducts. This was shown not to be primarily a solvent effect. Indeed, solvents have little or no influence on yields or product distributions (Table 7), as had previously also been found for the $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ catalyst system [16].

3. Hydrosilylation of alkenes

Rhodium(III) pentanedienoate-triethylaluminum is now shown to be an active catalyst for the hydrosilylation of disubstituted internal straight-chain alkenes (i.e., $\text{RCH}=\text{CHR}'$, where R and R' = an n-alkyl group). Trisubstituted alkenes, e.g.,

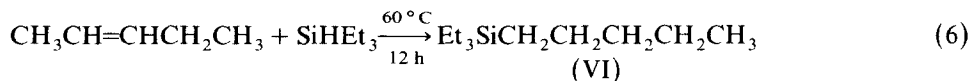
TABLE 8
YIELDS (%) OF HYDROSILYLATION PRODUCTS OF ALKENES USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$, AlBu_3 OR $\text{Al}(\text{Cl})\text{Et}_2$ AT 60°C ^a

Olefin	Silane	Time (h)	Yield ^b (%)	Adducts
Oct-1-ene	SiHET_3 ^c	18	94	4 isomers ^f
Oct-1-ene	SiHET_3 ^{c,f}	18	82	4 isomers ^f
Oct-1-ene	SiHET_3 ^{c,g}	18	87	4 isomers ^f
Oct-1-ene	$\text{SiH}(\text{OEt})_3$ ^d	20	60	$\text{n-C}_8\text{H}_{17}\text{Si}(\text{OEt})_3$
Oct-1-ene	SiHPh_3 ^e	10	45 ^h	$\text{n-C}_8\text{H}_{17}\text{SiPh}_3$
Hex-1-ene	SiHET_3 ^c	18	64	3 isomers
cis/trans-Pent-2-ene	SiHET_3 ^c	12	57	$\text{n-C}_5\text{H}_{11}\text{SiEt}_3$
cis/trans-Oct-2-ene	SiHET_3 ^c	12	24	$\text{n-C}_8\text{H}_{17}\text{SiEt}_3$
cis-Oct-2-ene	SiHET_3 ^c	12	24	$\text{n-C}_8\text{H}_{17}\text{SiEt}_3$
trans-Oct-2-ene	SiHET_3 ^c	12	52	$\text{n-C}_8\text{H}_{17}\text{SiEt}_3$
Cyclohexene	SiHET_3 ^c	20	0	
Diisobutylene	SiHET_3 ^c	20	0	

^a $\text{Rh}(\text{acac})_3$, 0.05 mmol; AlEt_3 , 0.1 mmol (unless otherwise stated, see *f* and *g*); maintained on oil bath at 60°C . ^b Based on silane; calculated by quantitative GLC. ^c SiHET_3 , 6.3 mmol; olefin, 18 mmol. ^d $\text{SiH}(\text{OEt})_3$, 5.5 mmol; alkene, 15 mmol. ^e SiHPh_3 , 5 mmol; olefin, 15 mmol. ^f AlBu_3 , 0.1 mmol, instead of AlEt_3 . ^g $\text{Al}(\text{Cl})\text{Et}_2$, 0.1 mmol, instead of AlEt_3 . ^h Based on silane; calculated gravimetrically. ⁱ VII, VIII, IX, and X, eq. 8; yields (%): 48.1, 28.3, 18 (AlEt_3); 57, 12, 13 (AlBu_3); and 49, 19, 19 [$\text{Al}(\text{Cl})\text{Et}_2$] for VII, VIII, and IX and X combined, respectively.

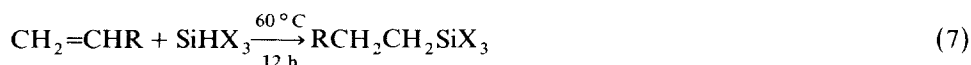
2-methyl-4,4-dimethyl-pent-2-ene (diisobutylene), tetrasubstituted alkenes, or cyclic alkenes, e.g., cyclohexene, were not hydrosilylated using this system.

Internal alkenes were hydrosilylated by alkylsilanes to give terminal adducts; e.g., eq. (6), in low yields (20–60%, Table 8). Thus, products such as VI may be regarded as having been derived by a combination of hydrosilylation and isomerisation of the substrate.

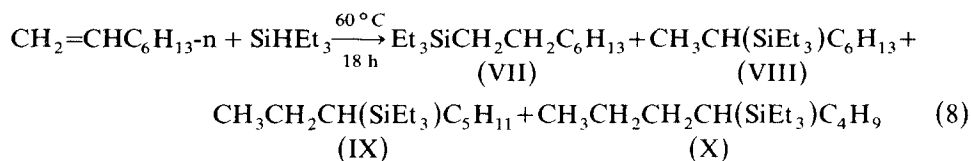


Similar formation of the terminal adducts, e.g. VI, is commonly found in hydrosilylation by homogeneous catalysts of rhodium [39,40] or platinum [41–43]; isomerisation of the internal alkene to the terminal alkene is considered to be rate-limiting [44] and responsible for yields lower than for those observed in the hydrosilylation of the terminal isomer.

The $[\text{Rh}(\text{acac})_3] - \text{AlEt}_3$ system is also active as catalyst for the hydrosilylation of terminal alkenes. Alkoxy- or aryl-silanes gave terminal adducts in high yields, eq. 7 ($\text{X} = \text{aryl or alkoxy}$, $\text{R} = \text{alkyl}$), Table 8.

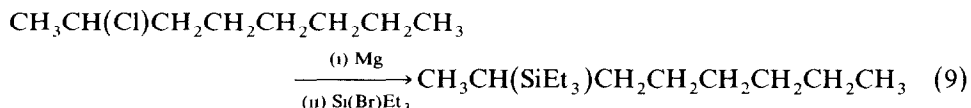


The addition of an alkylsilane to a terminal alkene afforded a mixture of structural isomers (VII–X), with the *n*-alkylsilane (VII) predominating, eq. 8 (for the case of $\text{R} = n\text{-C}_6\text{H}_{13}$).



Separation of the isomers by preparative GLC was not achieved. Compound VII, and the equivalent component from the hydrosilylation of hex-1-ene, was identified by comparison by GLC with an authentic sample prepared by the hydrosilylation of the appropriate $\text{CH}_2=\text{CHR}$ using $[\text{RhCl}(\text{PPh}_3)_3]$ as catalyst [1]. ^1H NMR spectra of the mixtures were recorded, but were of little value, showing only a broad singlet for the octyl or hexyl protons (0.95 and 1.1 ppm, respectively) and characteristic signals of the triethylsilyl protons. No resonances were observed in the region 4–6 ppm indicating that olefinic products were absent; by contrast, olefinic substitution products have been found with other catalysts (see discussion of mechanisms, below).

The silane $\text{CH}_3\text{CH}(\text{SiEt}_3)\text{C}_6\text{H}_{13}$ (VIII) was identified by GLC, using as reference a sample prepared by an unequivocal route, eq. 9.



GLC/MS showed all four components VII–X to have the same parent ion ($P^+ = 228$), and to have similar fragmentation patterns; thus identifying the remaining two components IX and X as structural isomers; however, there is no further

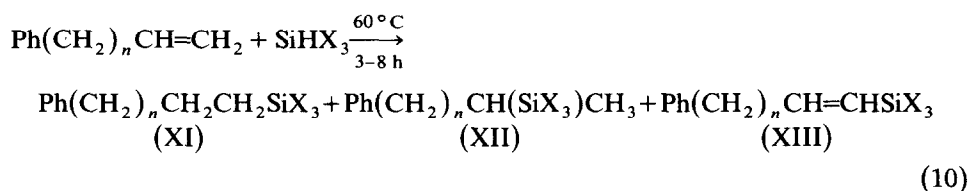
TABLE 9
YIELDS (%) OF HYDROSILYLATION PRODUCTS OF STYRENE USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ AT 60°C ^a

SiHX_3 ^b	$\text{PhCH}_2\text{CH}_2\text{SiX}_3$ (XI) ^c (%)	$\text{PhCH}(\text{SiX}_3)\text{CH}_3$ (XII) ^c (%)	PhCH=CHSiX_3 (XIII) ^c (%)
SiHEt_3	22	trace	50
SiHEt_3 ^d	24	0	75
$\text{SiH}(\text{OEt})_3$	39	7	15
$\text{SiH}(\text{OMe})_3$	40	10	10
SiHPh_3	94 ^e	0	0
SiHCl_3	0	0	0

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; maintained on oil bath at 60°C . ^b SiHEt_3 , 6.3 mmol, styrene, 18 mmol; $\text{SiH}(\text{OEt})_3$, 5.5 mmol, styrene, 15 mmol; $\text{SiH}(\text{OMe})_3$, 5.7 mmol, styrene, 15 mmol; SiHPh_3 , 15 mmol, styrene, 15 mmol; or SiHCl_3 , 8.3 mmol, styrene, 24 mmol.; ^c Yields based on silane; calculated by quantitative GLC; $n = 0$. ^d No AlEt_3 used. ^e Yield based on silane; calculated gravimetrically.

evidence for the formulae shown in eq. 8 for IX and X.

As was found in the hydrosilylation of aromatic substituted alkenes with triethylsilane catalysed by $[\text{Rh}(\text{acac})_3]$ alone [13], the hydrosilylation with $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ gave anomalous products, in that substitution, as well as addition, reactions were observed, eq. 10 ($n = 0$, X = alkoxy or alkyl; or $n = 1$, X = alkyl).



Hydrosilylation of styrene with triethylsilane, using $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$, as catalyst, afforded a high yield of the ω -substituted olefinic derivative (XIIIa) (Table 9);

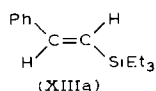


TABLE 10
EFFECT OF NEUTRAL LIGAND ON THE YIELDS (%) OF HYDROSILYLATION PRODUCTS OF STYRENE BY TRIETHYLSILANE, USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_2(\text{OEt})$ AS CATALYST ^a

Ligand	$\text{PhCH}_2\text{CH}_2\text{SiEt}_3$ (XI) ^b (%)	$\text{PhCH}(\text{SiEt}_3)\text{CH}_3$ (XII) ^b (%)	PhCH=CHSiEt_3 (XIII) ^b (%)
PPh_3 ^c	44	0	0
$\text{P}(\text{OPh})_3$ ^c	0	0	0
$\text{P}(\text{OEt})_3$ ^c	0	0	0
2,2'-Bipy ^d	2	0	5
Diphos ^d	70	0	16

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; $\text{AlEt}_2(\text{OEt})$, 0.1 mmol; SiHEt_3 , 6.3 mmol; styrene, 18 mmol; maintained on oil bath at 60°C for 5 h. ^b Yields based on the silane; calculated by quantitative GLC; $n = 0$, X = Et. ^c 0.1 mmol. ^d 0.05 mmol.

TABLE 11
EFFECT OF TEMPERATURE ON THE PRODUCT DISTRIBUTION FROM HYDROSILYLATION OF STYRENE WITH TRIETHYLSILANE USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ AS CATALYST^a

Temperature ^b (°C)	PhCH=CHSiEt_3 (XIII) ^c (%)	$\text{PhCH}_2\text{CH}_2\text{SiEt}_3$ (XI) ^c (%)
25	0	0
60	72	26
100	86	12
160	82	12

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; SiH_3Et_3 , 6.3 mmol; styrene, 18 mmol. ^b Maintained on oil bath at the recorded temperature for 5 h. ^c Yields (%) based on silane; calculated by quantitative GLC; $n = 0$, $X = \text{Et}$.

TABLE 12
YIELDS (%) OF HYDROSILYLATION PRODUCTS OF ALLYLBENZENE AT 60 °C USING $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ AS CATALYST^a

Silane ^b	$\text{PhCH}_2\text{CH}_2\text{CH}_2\text{SiX}_3$ (XI) ^c (%)	$\text{PhCH}_2\text{CH}(\text{SiX}_3)\text{Me}$ (XII) ^c (%)	$\text{PhCH}_2\text{CH=CHSiX}_3$ (XIII) ^c (%)
SiH_3Et_3	46	2	12
SiH_3Et_3 ^d	42	3	15
$\text{SiH}(\text{OEt})_3$	38	6	7

^a $[\text{Rh}(\text{acac})_3]$, 0.05 mmol; AlEt_3 , 0.1 mmol; maintained on oil bath at 60 °C. ^b SiH_3Et_3 , 6.3 mmol; allylbenzene, 18 mmol; or $\text{SiH}(\text{OEt})_3$, 5.5 mmol; allylbenzene, 15 mmol. ^c Yields (%) based on silane; calculated by quantitative GLC; $n = 1$. ^d No co-catalyst added.

this was identified by mass spectrometry and ^1H NMR as the *trans*-isomer, as previously characterised [13].

Table 9 lists results in which the silane and cocatalyst were varied. Alkylsilanes gave predominantly the substituted unsaturated compound XIII, with the terminal adduct XI as the only other product obtained in measurable quantity. Alkoxysilanes, however, showed preponderance of XI, and smaller proportions of XII and XIII. With triphenylsilane, no substitution occurred and only the adduct XI was formed.

Addition of a neutral phosphine ligand was shown to inhibit the formation of the substitution product XIII (Table 10); this is surprising, since in the absence of phosphine and cocatalyst, XIII was favoured (Table 9). Raising the temperature resulted in a maximisation in the ratio of XIII to XI (Table 11).

Allylbenzene showed similar hydrosilylation product distribution as found for styrene, with alkoxy- or alkyl-silanes, but with a much smaller proportion of the ω -substituted olefin (XIII) (Table 12).

Mechanisms

A general reaction pathway, Fig. 1, is proposed for the hydrosilylation of all the unsaturated species considered here (except PhCH=CH_2 or $\text{PhCH}_2\text{CH=CH}_2$), which is related to that suggested for the catalysis of hydrosilylation of various unsaturated compounds using $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ [2]. It involves a rhodium(I) intermediate and the role of the cocatalyst, such as AlEt_3 , is taken to be essentially that of a reducing agent.

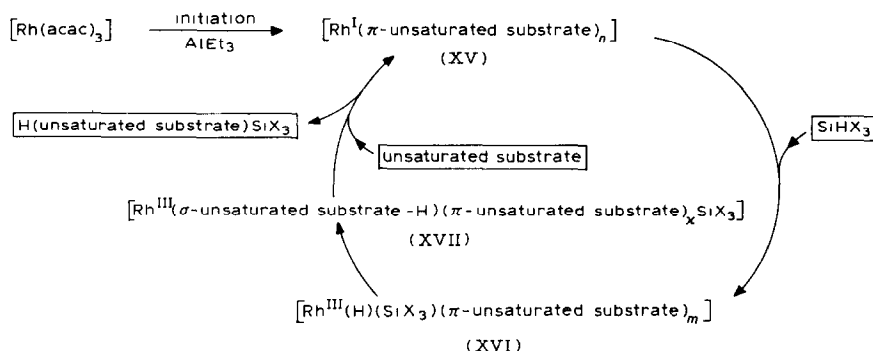


Fig. 1. Catalytic cycle for the hydrosilylation of an unsaturated organic substrate by SiHX_3 with $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ as catalyst.

Reaction of tris(pentanedionato)rhodium(III) with AlEt_3 is considered to lead to the rhodium(I) complex XV, which contains bound unsaturated substrate (this normally being present in excess). Compound XV might well arise via a reductive ethane-elimination from a hydrido(ethyl)rhodium(III) complex, itself formed by β -elimination of C_2H_4 from a di- or tri-ethylrhodium(III). The catalytic cycle (propagation) thus comprises successive oxidative addition of SiHX_3 to XV to yield XVI, insertion of the unsaturated moiety into the Rh-H bond of XVI to furnish XVII, and reductive elimination of the hydrosilylated organic substrate to regenerate the initiator.

For the case of hydrosilylation of an unsymmetric alkyne $\text{R-C}\equiv\text{C-R}'$ ($\text{R} \neq \text{R}'$, R and R' are similar, e.g., C_2H_5 and $n\text{-C}_4\text{H}_9$), the insertion step XVI $\rightarrow$ XVII is not expected to be regioselective. Hence the ultimate products Ia and Ib, and their isolation in similar yields, are accounted for via the intermediates $[\text{Rh}\{\text{C}(\text{R})=\text{CHR}'\}(\text{RC}\equiv\text{CR}')_x\text{SiX}_3]$ and $[\text{Rh}\{\text{C}(\text{R}')=\text{CHR}\}(\text{RC}\equiv\text{CR}')_x\text{SiX}_3]$.

The formation predominantly of 1,4-adducts in the hydrosilylation of a conjugated diene is considered to involve insertion of the diene into a rhodium-hydride bond to form a π -allyl [13]. For the case of isoprene, as proposed for its hydrosilylation using $[\text{Ni}(\text{acac})_2]\text{-AlEt}_3$ [2], this would lead, via a σ -but-2-enyl and silicon-carbon bond formation, to *cis*- and *trans*-2-methylbut-2-enylsilanes, cf., II ($\text{R}^1 = \text{H} = \text{R}^3$ and $\text{R}^2 = \text{Me}$) in eq. 3.

Formation of the 1,2-adducts is postulated to proceed through π -alkene complexes of type XV and XVI, then as in the hydrosilylation of an alkene (see below) [45].

The proposed pathway for the hydrosilylation of an alkene is also accommodated by the general scheme of Fig. 1. For a terminal alkene the insertion step XVI $\rightarrow$ XVII favours the thermodynamically more stable primary, rather than secondary, alkylrhodium(III) complex $[\text{Rh}(\text{CH}_2\text{CH}_2\text{R})(\eta\text{-CH}_2=\text{CHR})_x\text{SiX}_3]$ (XVIIa). In the case of an internal olefin, an intermediate isomerisation step is required (and is by precedent, probably rate-limiting), involving β -elimination from the potentially isomeric $[\text{Rh}(\text{CHRCH}_2\text{R}')(\eta\text{-RCH}=\text{CHR}')_x\text{SiX}_3]$ and readdition to yield XVIIa. Reductive elimination from compound XVIIa satisfactorily accounts for the formation of terminal adducts with an alkoxy- or aryl-silane and a terminal alkene, but does not explain the formation of non-terminal products with alkylsilanes. Here the

role of co-catalyst must be crucial, as this effect is not observed in the hydrosilylation using trispentanedionatorrhodium(III) alone [13]; moreover, the variations in product distribution as a function of co-catalyst (Table 8) points to the possibility of a bimetallic species being involved as the active catalyst in this instance.

The general mechanism of Fig. 1 likewise fails to account for the hydrosilylation behaviour of arylalkenes in the presence of $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$. A crucial feature there, eq. 10, is the formation not only of the "normal" hydrosilylation adducts XI and XII but also of the dehydrogenative substitution product, the vinylsilane XIII. Further mechanistic experimental data which are relevant are: (i) 2-phenylethyltriethylsilane is not dehydrogenated in the presence of the reaction system and indeed is unaffected; and (ii) the hydrogen atom of the silane SiHX_3 is not present in the substitution product $\text{Ph}(\text{CH}_2)_n\text{CH}_2\text{CH}_2\text{SiX}_3$ (XIII) (from ^2H labelling and ^1H NMR data, on the reaction product when using SiDEt_3); thus "normal" hydrosilylative addition followed by catalytic dehydrogenation (examples of these are found in refs. 46,47) seems improbable.

Since our earlier paper on the dehydrogenative silylation of styrene or allylbenzene using solely $[\text{Rh}(\text{acac})_3]$ as catalyst [13], others have appeared [14,48–52] which deal with a similar problem, but employ different catalysts and substrates. The most directly relevant concern (a) the $[\text{Ru}_3(\text{CO})_{12}]$ -catalysed formation of vinylsilanes from ArCH=CH_2 or $\text{PhOCH}_2\text{CH=CH}_2$ and SiHET_3 (or SiHMeEt_2 or SiHMe_2Ph) [50], (b) a similar reaction using $[\text{RhCl}(\text{PPh}_3)_3]$ as catalyst and PhCH=CH_2 , *trans*- PhCH=CHMe , or PhC(Me)=CH_2 as substrate [49], (c) system (b) but alternatively with $[\{\text{Rh}(\eta\text{-C}_2\text{H}_4)_2\text{Cl}\}_2]$ or $\text{H}_2[\text{PtCl}_6]$ as catalyst [48], (d) the $[\text{RhCl}(\text{PPh}_3)_3]$ -catalysed conversion of RCH=CH_2 ($\text{R} = \text{CF}_3$ or C_6F_5) into RCH=CHSiX_3 (not $\text{X} = \text{OEt}$) and $\text{RCH}_2\text{CH}_2\text{SiX}_3$ [52], and (e) the $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_4]$ -catalysed conversion of hex-1-ene and triethylsilane into (*E*)-hex-1-(and 2-)enyl(triethyl)silane [14]. Maitlis and coworkers observed that *n*-hexane was formed in an amount corresponding approximately to the total of hexenylsilanes [14], and ethylbenzene was likewise found as a coproduct in the earlier styrene reactions [48,50]. In the present study of the hydrosilylation of styrene or allylbenzene catalysed by $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$, we may therefore assume that PhCH_2CH_3 or $\text{PhCH}_2\text{CH}_2\text{CH}_3$ was a coproduct (although, unfortunately, this was not experimentally determined or indeed sought).

A propagation cycle consistent with the data of Tables 9–12, experiments (i) and (ii), and the formation of the hydrogenated substrate is shown in Fig. 2. The key steps (cf., refs. 14 and 52) are the proposal of (1) an insertion of $\text{Ph}(\text{CH}_2)_n\text{CH=CH}_2$ ($n = 1$ or 2) into a Rh-SiX_3 bond, $\text{XVIIb} \rightarrow \text{XVIII}$, and (2) the hydrogen-transfer reaction $\text{XVIII} \rightarrow \text{XVb} + \text{XIII}$; this involves an alternative pathway to that of $\text{XVIIb} \rightarrow \text{XVb} + \text{hydrosilylated adduct of Fig. 1}$ for the case of $\text{XVII} = \text{XVIIb}$ (i.e., the unsaturated substrate is $\text{Ph}(\text{CH}_2)_n\text{CH=CH}_2$, $n = 0$ or 1). The fact that the dehydrogenative pathway leading to a vinylsilane features prominently for the case of the substrate being styrene or allylbenzene (Tables 9 and 12) rather than oct-1-ene (Table 8) may be due to a weak $\eta\text{-Ph} \cdots \text{Rh}$ interaction in XVIII. Alternatively the hydrogen-transfer step (XVIII or $\text{XIX} \rightarrow \text{products}$ in Fig. 2) may be favoured by enhanced carbanionic character of the ligand $\overline{\text{C}}\text{H}_2(\text{CH}_2)_n\text{Ph}$ or $\overline{\text{C}}\text{H}(\text{Ph})(\text{CH}_2)_n\text{CH}_3$ as a consequence of the phenyl substituent; this postulate would favour XIX rather than XVIII, and might account for a similar behaviour of $\text{CF}_3\text{CH=CH}_2$ as substrate [52].

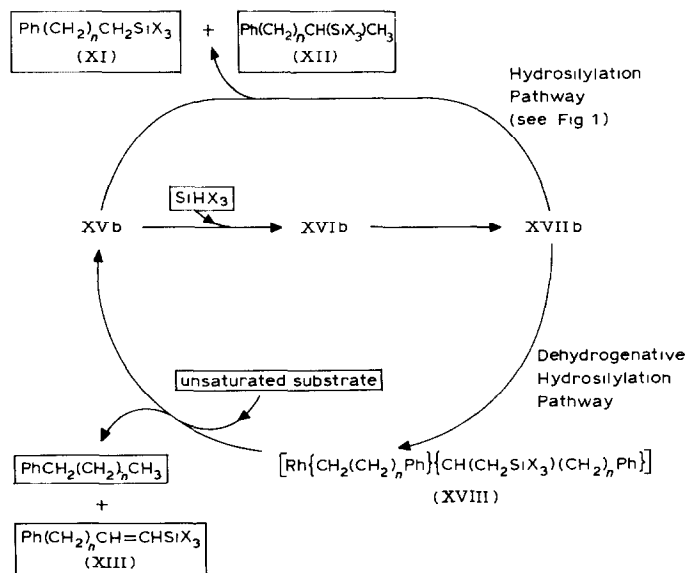


Fig. 2. Catalytic cycle for the hydrosilylation of styrene or allylbenzene by SiHX_3 with $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$ as catalyst; for formulae (XVb)–(XVIIb) see (XV)–(XVII), respectively in Fig. 1 [in which the unsaturated substrate is $\text{Ph}(\text{CH}_2)_n\text{CH=CH}_2$ ($n = 0$ or 1)]; an alternative to (XVIII) is the isomeric $[\text{Rh}\{\text{CH}(\text{Ph})(\text{CH}_2)_n\text{CH}_3\}\{\text{CH}(\text{Ph})(\text{CH}_2)_n\text{CH}_2\text{SiX}_3\}]$, (XIX).

The reduced yield of vinylsilane XIII when $\text{SiH}(\text{OR})_3$ ($\text{R} = \text{Me}$ or Et), rather than say SiHET_3 , was employed may be due to the stronger Rh-Si bond in XVII when $\text{X} = \text{OR}$ rather than $\text{X} = \text{Et}$, cf. ref. 22; likewise the absence of XIII when SiHCl_3 was the reagent is attributed to the strong Rh-SiCl_3 bond.

A $\text{Rh}^{\text{V}}\text{-SiX}_3$ intermediate in the cycles of Fig. 1 and 2 is an alternative or additional possibility; $[\text{Rh}^{\text{V}}(\eta\text{-C}_5\text{Me}_5)\text{H}_2(\text{SiEt}_3)_2]$ has been characterised [53].

Experimental

The hydrosilylations were carried out by the following general procedure. $[\text{Rh}(\text{acac})_3]$ (20 mg, 0.05 mmol) was reduced by triethylaluminium (0.2 mmol, calculated as monomer) in benzene (0.2 cm^3) in the presence of the unsaturated substrate (15–18 mmol).

The order of mixing the reagents is critical. If the rhodium(III) pentanedienoate was reduced in the absence of the unsaturated substrate, then formation of metallic rhodium occurred. Triethylaluminium also reacts with silanes [6], presumably by metallation. Thus, the silane was not added until the reduction by the trialkylaluminium had been completed. Thereafter the silane (15–18 mmol, depending on the silane used) was added and the mixture was warmed to 60°C on an oil bath. Analysis was carried out after the designated period by qualitative GLC, using an internal reference. (General procedures were as in ref. 11).

Hydrosilylation of oct-4-yne by triethylsilane

Rhodium(III) pentanedienoate (120 mg, 0.3 mmol) was reduced with triethylaluminium (0.6 mmol, in 0.6 cm^3 of benzene) in oct-4-yne (8.8 g, 80 mmol) under

argon. Triethylsilane (3.65 g, 31.5 mmol) was added and the reaction mixture was heated at 60°C, with stirring, for 12 h. Volatiles were then removed under reduced pressure. Vacuum distillation gave $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{SiEt}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ (5.17 g, 72.6%), b.p. 52°C/0.1 Torr. Analysis: Found: C, 74.1; H, 13.2. $\text{C}_{14}\text{H}_{30}\text{Si}$ calcd.: C, 74.3; H, 13.3%. ^1H NMR: (δ) 5.6 (1H, triplet, $J = 7$ Hz, $\text{HC}=\text{C}$), 1.8–2.2 and 0.2–1.5 ppm (29H, complex, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}=\text{CCH}_2\text{CH}_2\text{CH}_3$ and SiCH_2CH_3).

Hydrosilylation of isoprene by triethylsilane

$[\text{Rh}(\text{acac})_3]$ (120 mg, 0.3 mmol) was reduced with triethylaluminium (0.6 mmol, in 0.6 cm³ of benzene) in isoprene (5.4 g, 80 mmol) under argon. After 10 min, triethylsilane (3.65 g, 31.5 mmol) was added and the mixture was then heated, with stirring, to 60°C on an oil bath. After 6 h at 60°C the volatiles were removed under reduced pressure (~5 Torr) and the residue was fractionally distilled under reduced pressure to give $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{SiEt}_3$ (IIa) and the isomers $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{SiEt}_3$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SiEt}_3$ (7.4 g, 79.6%), b.p. 82–84°C/10 Torr. Analysis: Found: C, 71.7; H, 13.0. $\text{C}_{11}\text{H}_{24}\text{Si}$ calcd.: C, 71.5; H, 13.1%.

The isomer IIa was separated by preparative GLC. ^1H NMR: (δ) 5.51 (1H, quartet, J 6 Hz, $\text{CH}=\text{C}$), 1.3–1.7 (8H, complex, $\text{CH}_3\text{C}=\text{C}(\text{SiCH}_2\text{CH}_3)$), and 0.4–1.0 ppm (15H, complex, SiCH_2CH_3).

Hydrosilylation of isoprene by other silanes

The hydrosilylation of isoprene by triethoxy- or methyldiethyl-silane was carried out as described above for triethylsilane. The major isomer was isolated in a pure state by vacuum distillation. Total yields were > 70%, after purification.

Hydrosilylation of other 1,3-dienes

The hydrosilylations of 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene, or penta-1,3-diene, by triethyl- or triethoxy-silane were carried out as for isoprene. The major isomer was isolated, in each case, by fractional distillation.

Hydrosilylation of oct-1-ene by triethylsilane

$[\text{Rh}(\text{acac})_3]$ (120 mg, 0.3 mmol) in oct-1-ene (8.4 g, 75 mmol) was reduced using triethylaluminium (0.6 mmol, in 0.6 cm³ of benzene) under argon. After reduction, triethylsilane (3.65 g, 31.5 mmol) was added and the mixture was heated at 60°C for 18 h. Volatiles were then removed under reduced pressure and vacuum distillation gave a mixture of isomers of molecular formula $\text{C}_{14}\text{H}_{32}\text{Si}$ (6.54 g, 91%), b.p. 82°C/6 Torr. Analysis: Found: C, 73.6; H, 13.9. $\text{C}_{14}\text{H}_{32}\text{Si}$ calcd.: C, 73.7; H, 14.0%. Analytical GLC/MS showed the sample to be a mixture of four isomers, which were inseparable by preparative GLC.

Hydrosilylation of other olefins

The hydrosilylation of oct-1-ene by triethoxy- or triphenyl-silanes, and of hex-1-ene or pent-2-ene by triethylsilane were carried out in the manner described above for the hydrosilylation of oct-1-ene by triethylsilane; the products were isolated by fractional distillation under reduced pressure (except for $\text{C}_8\text{H}_{17}\text{SiPh}_3$ which was recrystallised from chloroform).

Hydrosilylation of styrene with triethoxysilane

Rhodium(III) pentanedienoate (120 mg, 0.3 mmol) was reduced with triethylaluminium (0.6 mmol, in 0.6 cm³ of benzene) in styrene (7.8 g, 75 mmol) under argon. Triethoxysilane (4.5 g, 27.5 mmol) was added and the mixture was stirred at 60 °C for 8 h. Vacuum distillation, after removal of volatiles, gave a mixture consisting of three products (3.2 g, 44%), b.p. 85 °C/0.5 Torr. Preparative GLC separation and ¹H NMR showed the products to be PhCH₂CH₂Si(OEt)₃, PhCH(CH₃)Si(OEt)₃, and PhCH=CHSi(OEt)₃.

Hydrosilylation of allylbenzene by triethylsilane

Allylbenzene (8.85 g, 75 mmol), [Rh(acac)₃] (120 mg, 0.3 mmol), and triethylsilane (3.6 g, 31.5 mmol) were heated together, with continuous stirring, at 60 °C for 12 h. After removal of volatiles under reduced pressure, vacuum distillation gave a liquid, b.p. 110 °C/0.1 Torr, which was shown by GLC to consist of three components. GLC/MS showed two of these to have a parent ion at *P*⁺ = 234, which corresponds to C₁₅H₂₆Si, and one at *P*⁺ = 232, due to C₁₅H₂₄Si.

Hydrosilylation of styrene by other silanes

The hydrosilylation of styrene by triethyl-, triphenyl- or trichloro-silane was carried out as described for triethoxysilane. The products from triethylsilane were separated by preparative GLC after initial distillation. Triphenylsilyl derivatives were obtained by removal of volatiles under reduced pressure and recrystallisation of the solid residue from a benzene/hexane mixture (20/80) at -30 °C.

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