

HYDROSILYLATION OF 1,3-DIENES WITH METHYLDICHLOROSILANE IN THE PRESENCE OF Ni CATALYST SYSTEMS

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Hydrosilylation of 1,3-dienes with halohydrosilanes takes place in the presence of Pt, Pd, and Rh catalyst systems [1-3], the structure of the end product depending on the catalyst used. It has recently been found that Ni phosphine catalysts are also effective catalysts for this reaction [4].

The present work is concerned with investigating the reaction of methyldichlorosilane with 1,3-dienes in the presence of Ni catalyst systems. The process was studied in the presence of Et_3Al or $i\text{-Bu}_3\text{Al}$ and in their absence. In the latter case, MeCl_2SiH was used both as a hydrosilylating agent and as a reducing agent. All reactions were performed in the presence of triphenylphosphine.

The reaction of butadiene with MeCl_2SiH gives a mixture of 1-methyldichlorosilyl-cis-2-butene (I), 1-methyldichlorosilyl-trans-2-butene (II), and 1,4-bismethyldichlorosilyl-cis-2-butene (III). The ratio between (I), (II), and (III) depends on the reducing agent used and the reaction conditions. From data on the hydrosilylation of butadiene with various catalyst systems (Table 1) it can be seen that the process takes place at room temperature when Et_3Al and $i\text{-Bu}_3\text{Al}$ are used. Increasing the temperature reduces the selectivity of the process. As well as the cis adduct (I), up to 15% of the trans isomer (II) is formed. The structure of (I) and (II) was confirmed by the PMR spectra of their methylation products, viz., cis- and trans-1-trimethylsilyl-2-butenes (Ia) and (IIa), which were separated by GLC. The PMR spectrum of (IIa) contains two doublets (δ 1.29 and 1.55 ppm), corresponding to the CH_2 and CH_3 protons. In the PMR spectrum of (Ia), the signals from these protons appear in the form of a multiplet at 1.50 ppm. It is characteristic that the signals from the analogous butenyl protons in the spectrum of (I) are shifted to weaker field owing to the influence of the Cl atom (1.51 and 2.00 ppm).

An interesting feature of the reaction of butadiene with MeCl_2SiH is the formation of compound (III). The structure of (IIIa) was confirmed by its PMR spectrum, which contains a doublet at 2.10 ppm ($J = 7$ Hz) corresponding to the four methylene protons at C^1 and C^4 . The six methyl protons on the Si atoms gives a singlet at 0.75 ppm. In addition, methylation of (III) gives the known 1,4-bis(trimethylsilyl)-cis-2-butene (IIIa) [4].

Isoprene reacts similarly with MeCl_2SiH to give 1-methyldichlorosilyl-3-methyl-2-butene (IV), which is described in [1], and 1,4-bis(methyldichlorosilyl)-3-methyl-2-butene (V). Depending on the type of reducing agent used, the reaction can be directed towards (IV) or (V) (see Table 1). The structure of (IV) and (V) was confirmed by their mass spectra and PMR spectra. In particular, the spectrum of (IV) contains a triplet signal from the vinyl proton (5.15 ppm), the splitting of which is due to its coupling with the two protons of the CH_2 group, and the spectrum of (V) contains two singlets at 0.65 and 0.66 ppm, corresponding to six methyl protons on Si. The formation of (III) and (V) in the reactions of butadiene and isoprene with MeCl_2SiH evidently takes place, according to [5], via an intermediate complex containing a Si-N-Si fragment.

In contrast to butadiene and isoprene, only 1-methyldichlorosilyl-cis-2-pentene (VI) is obtained from piperylene and MeCl_2SiH . This result is in accord with the data in [6]. The yield of (VI) is 40-50% in the presence and absence of Et_3Al , increasing to 70% in the presence of $i\text{-Bu}_3\text{Al}$.

Hydrosilylation of 3-methyl-1,4,6-heptatriene gives a 50-60% yield of the 1,4-adduct

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TABLE 2. Properties of the Hydrosilylation Products of Dienes with MeCl_2SiH and Their Methylation Products

Compound	bp, °C (P, mm Hg)	n_D^{20}	Mass spectrum m/e (M^+)	PMR spectrum (δ , ppm, signal type, assignment)
SiMeCl_2 (I)	50–51 (20)	1,4525	168	0,62s (3H, Si-CH ₃), 1,51d (3H, CH ₃ -CH, $J=6\text{Hz}$), 2,00d (2H, Si-CH ₂ , $J=7\text{Hz}$), 5,35m (2H, CH=CH),
SiMe_3 (IIa)	31–32 (35)	1,4163	128	–0,03s (9H, Si-CH ₃), 1,29d (2H, Si-CH ₂ , $J=7\text{Hz}$), 1,55d (3H, CH ₃ -CH, $J=6\text{Hz}$), 5,20m (2H, CH=CH)
Cl_2MeSi SiMeCl_2 (III)	110–111 (2)	1,4802	282	0,75s (6H, Si-CH ₃), 2,40d (4H, Si-CH ₂ , $J=7\text{Hz}$), 5,65t (2H, CH=CH, $J=7\text{Hz}$)
Me_3Si SiMe_3 (IIa)	60–61 (1)	1,4420	200	–0,03s (18H, Si-CH ₃), 1,35d (4H, Si-CH ₂ , $J=7\text{Hz}$), 5,15t (2H, CH=CH, $J=7\text{Hz}$)
Cl_2MeSi SiMeCl_2 (IV)	92–94 (10)	1,4600	182	0,62s (3H, Si-CH ₃), 1,53s (3H, CH ₃ -C), 1,65s (3H, CH ₂ -C), 1,96d (2H, Si-CH ₂ , $J=6\text{Hz}$), 5,15t (4H, CH=C, $J=6\text{Hz}$)
Cl_2MeSi SiMeCl_2 (V)	70–71 (2)	1,4768	294	0,65s, 0,66s (6H, Si-CH ₃), 1,75s (3H, CH ₃ -C at C ²), 2,10s (2H, Si-CH ₂ at C ¹), 1,87d (2H, Si-CH ₂ at C ⁴ , $J=6\text{Hz}$), 5,25t (4H, $J=6\text{Hz}$)
Me_3Si SiMe_3 (Va)	74–74,5 (5)	1,4480	186	–0,04s (9H, Si-CH ₃ at C ¹), 0,08s (9H, Si-CH ₃ at C ⁴), 1,30d (2H, Si-CH ₂ at C ² , $J=7\text{Hz}$), 1,45s (2H, Si-CH ₂ at C ¹), 1,65s (3H, CH ₃ -C), 5,10 (4H, CH=C, $J=7\text{Hz}$)
SiMeCl_2 (VI)	75–76 (38)	1,4546	182	0,62s (3H, Si-CH ₃), 0,91t (3H, CH ₃ -CH ₂ , $J=7\text{Hz}$), 1,67–2,07m (2H, CH-CH ₂ -CH ₃), 1,87d (2H, Si-CH ₂ , $J=7\text{Hz}$), 5,15m (2H, CH=CH)
SiMeCl_2 (VII)	80–81 (2)	1,4690	222	0,60s (3H, Si-CH ₃), 1,05d (3H, CH ₃ -CH, $J=7\text{Hz}$), 1,65m (3H, CH-CH ₂), 2,13d (2H, Si-CH ₂ , $J=6\text{Hz}$), 4,40–5,25m (5H, CH ₂ =CH, CH=CH)
SiMeCl_2 (VIII)	90–92 (2)	1,4780	222	0,68s (3H, Si-CH ₃), 1,50d (3H, CH ₃ -CH, $J=6\text{Hz}$), 1,57s (3H, CH ₃ -C), 2,05d (2H, Si-CH ₂ , $J=7\text{Hz}$), 2,50d (2H, C-CH ₂ -CH, $J=6\text{Hz}$), 5,10m (3H, CH=C, CH=CH)
SiMe_3 (VIIIa)	60–61 (2)	1,4644	182	–0,03s (9H, Si-CH ₃), 1,42d (2H, Si-CH ₂ , $J=7\text{Hz}$), 1,50d (3H, CH ₃ -CH, $J=6\text{Hz}$), 1,57s (3H, CH ₃ -C), 2,55d (2H, C-CH ₂ -CH, $J=6\text{Hz}$), 5,15m (3H, CH=C, CH=CH)

TABLE 1. Reaction of 1,3-Dienes with Methylchlorosilane [diene:MeCl₂SiH:Ni(acac)₂:reducing agent:PPh₃ ratio = 1:1·10⁻³:10⁻²·10⁻³]

Diene	Reducing agent	Reaction conditions		Products and relative yields, %	Total yield, mole, %
		T, °C	time, h		
Butadiene	—	100	6	(I) 90, (III) 10	70
"	Et ₃ Al	100	5	(I) 35, (II) 15, (III) 50	40
"	Et ₃ Al	20	12	(I) 80, (III) 20	50
"	<i>i</i> -Bu ₃ Al	20	12	(I) 90, (III) 10	60
"	<i>i</i> -Bu ₃ Al	100	6	(I) 30, (III) 70 *	60
Isoprene	—	100	6	(IV) 90, (V) 10	70
"	Et ₃ Al	20	12	(IV) 82, (V) 18	75
"	<i>i</i> -Bu ₃ Al	20	12	(IV) 85, (V) 15	70
"	<i>i</i> -Bu ₃ Al	100	6	(IV) 35, (V) 65 *	70
Piperylene	—	60	6	(VI) 100	50
"	Et ₃ Al	20	12	(VI) 100	40
"	<i>i</i> -Bu ₃ Al	20	12	(VI) 100	70
3-Methyl-1, 4, 6-heptatriene	—	100	6	(VII) 98, (VIII) 2	50
"	Et ₃ Al	20	12	(VII) 90, (VIII) 10	60
"	<i>i</i> -Bu ₃ Al	20	12	(VII) 90, (VIII) 10	65
"	<i>i</i> -Bu ₃ Al	20	24	(VII) 15, (VIII) 85	60

* Experiments performed with twice the amount of silane.

1-methyldichlorosilyl-5-methyl-cis-2,6-heptadiene (VII), the structure of which was confirmed by its PMR spectrum. Increasing the reaction time to 24 h results in total isomerization of (VII) to 1-methyldichlorosilyl-5-methyl-cis-2,5-heptadiene (VIII). In the PMR spectrum of (VIII), the doublet at 1.05 ppm assigned to the CH₃ protons at C⁵ is absent and new methyl proton signals appear at 1.57 ppm (singlet, 3H) and 1.50 ppm (doublet, 3H, J = 6 Hz). The IR spectrum of (VIII) contains no absorption bands characteristic of a vinyl group in the 920 and 1000 cm⁻¹ region. As in the case of the hydrosilylation of piperylene, the reaction of MeCl₂SiH with 3-methyl-1,4,6-heptatriene does not give bis-silylated products. This reaction is evidently uncharacteristic for 1-substituted dienes.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were obtained with Tesla BS-487B and Jeol C-60 instruments using CCl₄ solutions with HMDS as internal standard. The mass spectra were recorded using an MKh-13-03 spectrometer with an electron ionization energy of 50 eV and an ionization temperature of 200°C. The GLC analyses were performed using an XT instrument with a 3 m × 4 mm column containing 10% KhE-60 on Chromaton N, with a carrier gas (N₂) flow rate of 40 ml/min.

The IR spectra of all the alkenylmethyldichlorosilanes contain characteristic absorption bands (ν, cm⁻¹) at 480, 540, 560, 670 (Si-Cl), 830 (Si-CH₂), and 1247 (Si-CH₃).

General Method of Hydrosilylating 1,3-Dienes. A cooled autoclave was flushed with argon and charged with 0.1 mole of the 1,3-diene, 0.1 mole of MeCl₂SiH, 5·10⁻⁴ mole of Ni(acac)₂, 1·10⁻³ mole of reducing agent (if used), and 1·10⁻³ mole of PPh₃. The mixture was maintained under the conditions indicated in Table 1 and then distilled under vacuum. Methylation with methylmagnesium bromide gave the corresponding trimethylsilyl derivatives, the constants of which were compared with known values [7]. The properties and spectra of the products are given in Table 2.

CONCLUSIONS

The Ni(acac)₂-Et₃Al and Ni(acac)₂-*i*-Bu₃Al systems effectively catalyze with 1,4-addition of methyldichlorosilane to 1,3-dienes at 20-25°C. In the case of butadiene and isoprene, the reaction is accompanied by the formation of appreciable amounts of bis-silylated products, viz., 1,4-bis(methyldichlorosilyl)-cis-2-butene and 1,4-bis(methyldichlorosilyl)-3-methyl-2-butene.

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REACTION OF ETHYL VINYL SULFIDE AND DIVINYLSULFIDE WITH TRIETHYL- AND TRIETHOXYSILANE

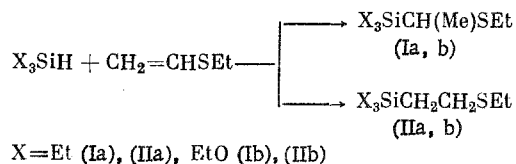
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Data on the hydrosilylation of alkenyl sulfides are scarce, and the characteristics of this reaction have not been studied sufficiently. According to [1], the reaction of dialkenyl sulfides of formula $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{SCH}=\text{CH}_2$ ($n = 1$ or 2) with compounds of the type R_3SiH only involves the double bond not conjugated with the sulfur atom. Hydrosilylation of the $\text{CH}_2=\text{CHS}$ group in vinyl trialkylsilylmethyl sulfides is accompanied by secondary reactions, one of which comprises cleavage of the C-S bond [2]. In contrast to this, divinyl sulfide (DVS) reacts with diethylsilane [3] and dialkylfluorosilanes [4] without any appreciable secondary reactions.

We have studied the reaction of ethyl vinyl sulfide (EVS) and DVS with triethyl- and triethoxysilanes of formula X_3SiH ($\text{X} = \text{Et}$ or EtO) in the presence of catalysts comprising $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol and $(\text{Ph}_3\text{P})_3\text{RhCl}$. The reactions were carried out at 100-170°C for 8-48 h.

In the case of the hydrosilylation of EVS, increasing the temperature and reaction time from 100-120°C (8 h) to 150-160°C (44-46 h) increases the X_3SiH conversion from 10 to 60% when $\text{X} = \text{Et}$ and from 30 to 60% when $\text{X} = \text{EtO}$. The hydrosilylation of EVS in the presence of H_2PtCl_6 and $(\text{Ph}_3\text{P})_3\text{RhCl}$ proceeds nonselectively, giving the isomeric adducts (Ia,b) and (IIa,b) in yields of 2.5-3 and 35-42%, respectively



In all cases, besides the indicated adducts, compounds of the type EtSSiX_3 (IIIa,b) are isolated, indicating that the $=\text{CH-S}$ bond is broken under the hydrosilylation conditions. No products formed by cleavage of the S- CH_2 bond were detected. In accordance with this, diethyl sulfide hardly reacts with X_3SiH at all in the presence of H_2PtCl_6 under the same conditions (the EtSSiX_3 yield is $\leq 2\%$ according to GLC).

In the case of the hydrosilylation of DVS with X_3SiH in the presence of H_2PtCl_6 , the cleavage of the C-S bond is the dominant reaction. One of the main products in this case is the corresponding vinylthiosilane derivative (IVa,b)

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