Specific Polar Solvents as Organocatalysts for the Hydrosilylation of Isoprene

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Abstract: Isoprene was hydrosilylated in the absence of transition metals by using specific organic solvents as both reaction media and organocatalysts. A highly selective reaction with successful catalyst recycling could be performed by using propylene carbonate as the reaction medium.

Key words: hydrosilylations, homogeneous catalysis, solvent effects, dienes, silanes

The hydrosilylation of conjugated 1.3-dienes is a wellknown synthetic method for preparing allylic silanes. In particular, the hydrosilylation of isoprene (2-methylbuta-1,3-diene) has been studied extensively because of the regioselectivity for 1,2- or 1,4-addition and the production of head or tail products. This hydrosilylation reaction was the subject of a comprehensive review in 1993.¹ Complexes of various transition metals catalyze the hydrosilylation of isoprene. For example, rhodium catalysts give head and tail 1,4-products, and the effects of various reaction conditions, such as the choice of ligand,² the presence of oxygen,³ the temperature, and the solvent⁴ have been investigated. It is also possible to use immobilized rhodium/polyamide catalysts for the hydrosilylation reaction.⁵ The hydrosilylation can also be catalyzed by rhodium carbonyl or mixed rhodium–nickel carbonyl complexes.⁶ A series of 1,2-hydrosilylation products can be synthesized stereoselectively by using the Speier catalyst hexachlorodihydroplatinum hexahydrate (H₂PtCl₆·6H₂O),⁷ whereas there is an increased selectivity toward the tail 1,4product when a cobalt catalyst is used.⁸ Palladium phosphine complexes or light-activated chromium carbonyl complexes are also suitable for this reaction.⁹⁻¹¹ Furthermore, the formation of unsaturated bis(silyl)alkenes by the hydrosilylation of isoprene has been observed.^{12–16}

The allylic silane products of this hydrosilylation reaction are valuable because they can be used as monomers or comonomers for the synthesis of polysilanes^{17,18} or as building blocks in organic synthesis.^{19,20}

Besides transition-metal catalysts, Brønsted acids and Lewis acids and bases are known to catalyze hydrosilylation reactions.^{21–23} Recently, a wide range of organocatalysts for various reactions have been described in the literature, but none have been used in the hydrosilylation reaction.²⁴

SYNTHESIS 2012, 44, 575–578 Advanced online publication: 16.01.2012 DOI: 10.1055/s-0031-1289669; Art ID: T87911SS © Georg Thieme Verlag Stuttgart · New York Initially, we investigated the hydrosilylation of isoprene (1) with triethylsilane (2) by using rhodium trichloride monohydrate (RhCl₃·H₂O) as a catalyst, which led to the tail and head 1,4-products **3** and **4**, respectively (Scheme 1). Furthermore, the unsaturated bis(silyl)alkene **5** was obtained together with byproducts **6** and **7**, formed by oxidation and hydrolysis of triethylsilane. Only trace amounts of the corresponding 1,2-addition products were observed.



Scheme 1 Reaction products of the hydrosilylation of isoprene with triethylsilane. *Reaction conditions*: isoprene (20 mmol), Et_3SiH (20 mmol), $RhCl_3 \cdot H_2O$ (0.12–0.68 mmol), propylene carbonate (30 mL), 80 °C, 3 h.

In our first experiments, we used rhodium trichloride hydrate (RhCl₃·H₂O) (0.25 mol%) as the catalyst, because this has been described as a simple and efficient catalyst for the hydrosilylation of isoprene that operates under oxygenated or atmospheric reaction conditions.³ Propylene carbonate (4-methyl-1,3-dioxolan-2-one) was used as the solvent because it forms a biphasic system with isoprene, triethylsilane, and the reaction products, permitting the solvent to be easily recycled by phase separation.

The reaction temperature had a marked effect on the regioselectivity of the reaction.⁴ Experiments in which the temperature was varied between 20 and 100 °C showed that a 99% conversion of triethylsilane can be achieved in three hours at temperatures above 50 °C. At 80 °C, the highest yields of products **3** and **4** were 10% and 65%, respectively. The effects of the catalyst concentration on the product formation were also examined, and the results are shown in Table 1.

Surprisingly, the desired hydrosilylation reaction took also place in the absence of the metal catalyst (Entry 1). In addition, the formation of the byproducts **6** and **7** occurred only in the presence of rhodium trichloride hydrate. A selective synthesis of the desired products 3-5 can, therefore, be carried out by using propylene carbonate as both the solvent and the catalyst.

Entry	Concn of RhCl ₃ ·H ₂ O (mol%) Conv. (%) of 2	Yield (%) of 3	Yield (%) of 4	Yield (%) of 5	Yield (%) of 6 + 7		
1	0	96	10	82	4	_		
2	0.12	99	15	48	-	36		
3	0.25	99	10	65	-	24		
4	0.68	99	14	15	6	64		

Table 1Effects of Changing the Catalyst Concentration in the Hydrosilylation of Isoprene in the Presence of Rhodium Trichloride Hydratein Propylene Carbonate at $80 \, ^{\circ}C^a$

^a Reaction conditions: isoprene (20 mmol), Et₃SiH (20 mmol), RhCl₃·H₂O (0.12–0.68 mmol), propylene carbonate (30 mL), 80 °C, 3 h.

Next, we investigated the catalytic efficiency of some other solvents (Table 2).

This study showed that a solvent is essential for the reaction; without a solvent, the yield of the hydrosilylation products is very low. Neither nonpolar solvents nor polar solvents with an acidic proton catalyzed the reaction. Polar solvents containing a sulfur atom (dimethyl sulfoxide and sulfolane) showed no catalytic activity for the reaction, whereas nitrogen-containing solvents (for example, *N*,*N*-dimethylformamide or *N*-methylpyrrolidin-2-one) showed a relatively low reactivity. In N-methylpyrrolidin-2-one, the hydrolysis products 6 and 7 were formed in large amounts. The polar oxygen-containing solvents tetrahydrofuran, 1,4-dioxane, ethyl acetate, acetone, and propylene carbonate gave near-quantitative conversions of triethylsilane, and the byproducts 6 and 7 were formed in only trace amounts. Surprisingly, compounds that are structurally similar to propylene carbonate, such as butylene carbonate or γ -butyrolactone, showed no catalytic activity. Obviously, only small, nearly planar solvents are suitable as catalysts for the hydrosilylation of isoprene.

The reaction system (isoprene, triethylsilane, propylene carbonate, and the formed products) is biphasic, which enabled the propylene carbonate phase to be readily recycled (Table 3).

The recycling process proved to be very convenient. The propylene carbonate phase was simply separated from the product phase and then used in a new reaction by adding fresh isoprene and triethylsilane. No loss of propylene carbonate into the product phase was observed.

Table 3 Effects of Catalyst Recycling on the Hydrosilylation of Iso-prene with Triethylsilane in Propylene Carbonate

Run ^a	Conv. (%) of 2	Yield (%) of 3	Yield (%) of 4	Yield (%) of 5	Yield (%) of (6 + 7)
1	96	10	82	4	0
2	97	10	83	4	0
3	97	10	79	8	0

^a Reaction conditions: isoprene (20 mmol), Et₃SiH (20 mmol), propylene carbonate (30 mL), 80 °C, 3 h.

Table 2 Effects of Changing the Solvent on the Hydrosilylation of Isoprene in the Absence of a Transition-Metal Catalyst

Type of solvent	Solvent	Conv. (%) of 2	Yield (%) of 3	Yield (%) of 4	Yield (%) of 5	Yield (%) of (6 + 7)
_	none ^a	10	1	8	1	0
polar with acidic proton	MeOH ^a	0	0	0	0	0
	BuOH ^a	0	0	0	0	0
polar without acidic	DMSO ^a	0	0	0	0	0
proton	sulfolane ^a	0	0	0	0	0
	CH ₂ Cl ₂ ^a	0	0	0	0	0
	NMP ^a	60	8	2	1	49
	DMF ^a	5	1	3	1	0
	MeCN ^a	0	0	0	0	0
	<i>i</i> -Pr ₂ O ^a	0	0	0	0	0
	MTBE ^a	0	0	0	0	0
	THF ^a	>99	13	87	0	0
	1,4-dioxane ^b	93	19	74	0	0
	EtOAc ^b	99	13	86	1	0
	acetone ^b	99	12	84	3	0
	propylene carbonate ^b	96	10	82	4	0
	butylene carbonate ^a	0	0	0	0	0
	γ-butyrolactone ^a	0	0	0	0	0
nonpolar	toluene ^{a,b}	0	0	0	0	0
-	cyclohexane ^a	0	0	0	0	0

^a Reaction conditions: isoprene (5.5 mmol), Et₃SiH (5.5 mmol), solvent (8 mL), 80 °C, 3 h.

^b Reaction conditions: isoprene (20 mmol), Et₃SiH (20 mmol), solvent (30 mL), 80 °C, 3 h.

In summary, we report the hydrosilylation of isoprene with triethylsilane without the need for expensive transition-metal catalysts. However, only a handful of solvents were effective catalysts for this reaction, of which propylene carbonate proved to be the most efficient. Because of the biphasic nature of the reaction system, recycling of the propylene carbonate phase was possible and the system remained active over several catalytic cycles. We have therefore developed a new, easy, and inexpensive method for the continuous production of allylic silanes.

Isoprene (purity 98%), Et₃SiH, and the solvents were obtained from Acros Organics. The catalyst RhCl₃·H₂O was obtained from Umicore. The gas chromatographic analyses were carried out on an HP 6890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with an FI detector and an HP-5 capillary column (30 m, diameter 250 μ m, film thickness 0.25 μ m) connected to an autosampler. Di-*n*-butyl ether was used as internal standard. The products were characterized by mass spectrometry using an HP Series 5973 GC-MS (Hewlett-Packard GmbH, Waldbronn, Germany) with 70 eV and NMR spectroscopy with a Bruker Avance DRX-400 (400 MHz) instrument. For the NMR analyses, CDCl₃ was used as solvent.

Hydrosilylation of Isoprene: Typical Procedure

Isoprene (1.36 g, 2.00 mL, 20 mmol), Et_3SiH (2.33 g, 3.19 mL, 20 mmol), and propylene carbonate (30 mL) were transferred into a 70-mL Parr autoclave and heated at 80 °C for 3 h under argon (5 bar). The mixture was cooled and the two phases were separated. Both phases were analyzed by gas chromatography (Bu₂O internal standard).

Triethyl(3-methylbut-2-en-1-yl)silane (3)

The reaction solution was purified by column chromatography (silica gel, cyclohexane) to give the product as a light-yellow liquid.

¹H NMR (CDCl₃, 400 MHz): δ = 0.54–0.59 (q, J = 6.0 Hz, 6 H, Si–CH₂–CH₃), 0.95–0.98 (t, J = 6.0 Hz, 9 H, Si–CH₂–CH₃), 1.27 (d, J = 2.0 Hz, 2 H, CH₂–CH = Cq), 1.52 (s, 3 H, CH₃), 1.69 (s, 3 H, CH₃), 5.05–5.09 (q, J = 2.0 Hz, 1 H, HC–CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ = 3.7, 4.1, 7.4, 17.6, 26.2, 115.9, 134.0.

MS (EI, 70 eV): m/z (%) = 184 [M⁺] (9), 155 (4) (- C₂H₅), 127 (3), 115 (58) (- C₅H₉), 99 (5), 97 (4), 87 (100), 73 (5), 69 (6), 59 (37), 45 (7).

Anal. Calcd for C₁₁H₂₄Si: C, 71.7; H, 13.1. Found: C, 72.1; H, 13.2.

Triethyl(2-methylbut-2-enyl)silane (4)

The reaction solution was distilled (7.8 mbar, 110 $^{\circ}$ C) and the resulting crude product was purified by column chromatography (silica gel, cyclohexane) to give the product as a light-yellow liquid.

¹H NMR (CDCl₃, 400 MHz): $\delta = 0.52-0.57$ (q, J = 6.0 Hz, 6 H, Si-CH₂-CH₃), 0.90-0.96 (t, J = 6.0 Hz, 9 H, Si-CH₂-CH₃), 1.50 (s, 3 H, Cq-CH₃), 1.52 (s, 2 H, Si-CH₂-Cq), 1.67 (d, J = 2.0 Hz, 3 H, CH-CH₃), 5.02-5.07 (q, J = 2.0 Hz, 1 H, CH-CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ = 4.1, 7.4, 13.9, 17.5, 26.3, 115.8, 134.1.

MS (EI, 70 eV): m/z (%) = 184 [M⁺] (10), 155 (4) ($-C_2H_5$), 126 (2) ($-C_2H_5$), 15 (60) ($-C_5H_9$), 99 (4), 97 (4), 87 (100), 73 (4), 69 (4), 59 (33), 45 (7).

Anal. Calcd for C₁₁H₂₄Si: C, 71.7; H, 13.1. Found: C, 72.2; H, 13.2.

Triethyl[2-methyl-4-(triethylsilyl)but-2-en-1-yl]silane (5)

The reaction solution was distilled (7.8 mbar, 110 °C) to give a residue containing the raw product **5**, Et₃SiOH (**6**), and (Et₃Si)₂O (**7**). This residue was mixed with toluene (30 mL) and 20 wt% Pd/activated carbon then hydrogenated under 50 bar H₂ pressure for 6 h at 100 °C to give a mixture containing triethyl[2-methyl-4-(triethylsilyl)butyl]silane. (The spectra below relate to the hydrogenated product).

¹H NMR (CDCl₃, 400 MHz): δ = 0.35–0.44 (m, 2 H, CH₂), 0.49–0.56 (q, *J* = 6.0 Hz, 12 H, Si–CH₂–CH₃), 0.58–0.62 (m, 2 H, CH₂), 0.94 (t, *J* = 6.0 Hz, 21 H, CH₃), 1.10–1.28 (m, 2 H, CH₂), 1.43–1.51 (m, 1 H, CH–CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ = 3.3, 4.1, 8.5, 19.3, 22.5, 32.5, 34.8.

MS (EI, 70 eV): m/z (%) = 271 (>1) (-C₂H₅), 157 (2), 127 (6), 115 (100), 99 (4), 87 (43), 71 (2), 59 (25).

Triethylsilanol (6)

MS (EI, 70 eV): m/z (%) = 132 [M⁺] (2), 103 (86), 75 (8), 61 (5), 47 (37), 45 (46).

Hexaethyldisiloxane (7)

MS (EI, 70 eV): m/z (%) = 246 [M⁺] (0), 217 (100), 189 (79), 161 (52), 133 (22), 131 (9), 105 (27), 103 (17), 101 (3), 94 (8), 87 (8), 80 (13), 77 (10), 73 (6), 66 (16), 59 (17), 52 (5), 45 (3).

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