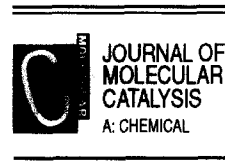




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Regiospecific hydroesterification of vinylsilanes catalyzed by palladium–montmorillonite

Byeongno Lee, Howard Alper *

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada

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Abstract

The hydroesterification of vinylsilanes, catalyzed by a palladium complex intercalated into montmorillonite, in the presence of an appropriate amount of triphenylphosphine and *p*-toluenesulfonic acid, afforded β -silyl esters in high yield with excellent regioselectivity. The hydroesterification reaction of trimethylvinylsilane in the presence of a diol gives the monoesterification product in a selective manner.

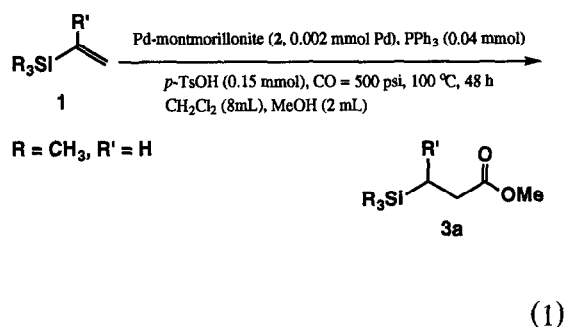
The hydroesterification of unsaturated organic compounds, catalyzed by transition metal complexes, has been extensively studied probably because the reaction is one of the most practical ways to prepare esters from olefins [1]. Little is known about the catalytic carbonylation (hydroformylation and hydroesterification) of vinylsilanes, although the carbonylation of such substrates gives useful products, organosilicon aldehydes or esters, which are important in organic synthesis [2,3]. Conventional methods to produce organosilicon esters (or aldehydes) show some disadvantages including low selectivity [4]. The monohydroesterification of diols, on the other hand, is an exceedingly simple method for preparing diol monoesters which are of significant industrial value [5]. It is known that the hydroesterification of vinylsilanes with ethanol can be catalyzed by homogeneous palla-

dium(II) complexes in high regioselectivity to give linear organosilicon esters [6] along with a small amount of branched ester as the by-product. The practical difficulties of homogeneous catalysis, such as the purification of the product and recovery of the catalyst, results in the reduction in product yields. There is no publication, to our knowledge, for the monoesterification of diols in the hydroesterification reaction of vinylsilanes. Recently, one of us described the hydroformylation of vinylsilanes using chloro(1,5-cyclooctadiene)rhodium(I) dimer, intercalated into montmorillonite, as the catalyst [7]. We now report the regiospecific hydroesterification of vinylsilanes with the heterogenized homogeneous catalyst, palladium–montmorillonite [8] to give organosilicon monoesters of monoalcohols and diols.

Initial studies were conducted using trimethylvinylsilane (1): $R = \text{CH}_3$, $R' = \text{H}$) as the reactant and MeOH as the alcohol. The hydroesterification of trimethylvinylsilane is catalyzed by

* Corresponding author. Tel.: +1-613-5625270; fax: +1-613-5625271.

Pd–clay (**2**) [8] in the presence of PPh₃ and *p*-TsOH in CH₂Cl₂ and MeOH, at 500 psi of CO, to give the corresponding linear ester (**3a**): R = CH₃, R' = H) as the only product in 81% isolated yield:



The influence of additional ligands, PPh₃ and 1,4-bis(diphenylphosphino)butane (dppb), and the role of *p*-TsOH, was examined and the results are summarized in Table 1. Both PPh₃ and *p*-TsOH are necessary in order to obtain the linear ester (**3a**) (Table 1, entries 1–4), and the appropriate amount of PPh₃ (0.04 mmol) and *p*-TsOH (0.15 mmol) is crucial for complete conversion of **1** within 48 h (Table 1,

entries 5 and 6). Previous studies demonstrated that the palladium catalyzed hydrocarboxylation of alkynes with formic acid was improved by the presence of both PPh₃ and dppb [9]. However, it was found that the hydroesterification reaction of trimethylvinylsilane was significantly retarded by the presence of dppb (entries 7–9), and the selectivity to the linear ester, **3a**, was decreased: branched ester (Me₃SiCH(Me)C(O)OMe, **3b**) is produced when dppb is used together with PPh₃ (Table 1, entries 8 and 9).

The hydroesterification of **1** (R = CH₃, R' = H) with other alcohols was examined using the palladium–montmorillonite catalyst under the same reaction conditions, and the results are listed in Table 2. Only linear esters were obtained from the hydroesterification reaction of **1** (Table 2, entries 1–5). It should be noted that the hydroesterification reaction of **1** with a diol give monoesterification products (Table 2, entries 3–5) and a small amount of an unknown by-product(s). The use of the correct amount of diol (1/diol = 1/1) is important in order to obtain the product in good yield: unknown products were produced when a large excess of diol (1/diol = 1/10) was used for the reaction.

Table 1
Hydroesterification of trimethylvinylsilane (**1**) catalyzed by palladium–montmorillonite (**2**)^a

Entry	Additive (mmol)			Time (h)	Conv. (%)	Product(s) ^b	Isolated yield (%)
	<i>p</i> -TsOH	PPh ₃	dppb				
1	0.15	0.04	–	48	100	3a	81
2	–	0.04	–	48	0	–	–
3 ^c	–	0.04	–	48	0	–	–
4	0.15	–	–	48	0	–	–
5	0.15	0.02	–	72	< 10	3a	–
6	0.05	0.04	–	48	45	3a + unknown	–
7	0.15	0.02	0.01	60	0	–	–
8	0.15	0.02	0.02	65	40	3a / 3b (2.5/1)	27
9	0.15	0.01	0.01	72	< 10	3a / 3b (3/1)	–



^a General procedure: A mixture of **1** (2.0 mmol), PPh₃ (0.04 mmol), *p*-TsOH (0.15 mmol) and palladium–montmorillonite (**2**, 100 mg; 0.002 mmol Pd) in CH₂Cl₂ (8 ml) and MeOH (2 ml) was placed in a 45 ml autoclave. The autoclave was flushed thoroughly with CO, pressurized (500 psi CO), and then heated in an oil bath to 100°C. After the time indicated in the Tables, the reaction mixture was cooled to room temperature, and the products were isolated by removal of the catalyst filtration, followed by Kugelrohr distillation.

^b The product ratio was determined by ¹H-NMR.

^c P_{CO}/P_{H₂} = 500/300 psi.

Table 2

Hydroesterification of vinylsilanes catalyzed by palladium–montmorillonite (**2**)^a

Entry	Substrate	Alcohols	Time (h)	Conv. (%)	Product(s) ^b	Isolated yield (%)
1	Me ₃ SiCH=CH ₂	MeOH	48	100	Me ₃ SiCH ₂ CH ₂ C(O)OMe	89
2	Me ₃ SiCH=CH ₂	EtOH	48	100	Me ₃ SiCH ₂ CH ₂ C(O)OEt	89
3	Me ₃ SiCH=CH ₂	HOCH ₂ CH ₂ OH	72	100	Me ₃ SiCH ₂ CH ₂ C(O)OCH ₂ CH ₂ OH	95 ^{c,d}
4	Me ₃ SiCH=CH ₂	HO(CH ₂) ₅ OH	72	94	Me ₃ SiCH ₂ CH ₂ C(O)O(CH ₂) ₅ OH	78 ^{c,d}
5	Me ₃ SiCH=CH ₂	HO-  -OH	20	75	Me ₃ SiCH ₂ CH ₂ C(O)O-  -OH	69 ^{c,e}
6	Et ₃ SiCH=CH ₂	MeOH	24	100	Et ₃ SiCH ₂ CH ₂ C(O)OMe	83
7	Ph ₃ SiCH=CH ₂	MeOH	48	100	Ph ₃ SiCH ₂ CH ₂ C(O)OMe	94
8	Me ₃ SiC(Ph)=CH ₂	MeOH	20	75	Me ₃ SiC(Ph)HCH ₂ C(O)OMe	51 ^f
9	(MeO) ₃ SiCH=CH ₂	MeOH	44	100	(MeO) ₃ SiCH ₂ CH ₂ C(O)OMe (MeO) ₃ SiCH(CH ₃)C(O)OMe CH=CH ₂ Si(MeO) ₂ OSiCH ₂ CH ₂ C(O)OMe	69 ^c 8 22

^a Reaction conditions: **1**, 2.0 mmol; Pd–montmorillonite (**2**, 100 mg (0.002 mmol Pd)); CH₂Cl₂, 10 ml; a MeOH or EtOH=2 ml; other diols = 2.0 mmol; P_{CO} = 500 psi.; reaction temp. of 100°C; PPh₃ = 0.04 mmol; *p*-TsOH = 0.15 mmol.

^b The products were identified by comparison of spectral data with literature results. New trimethylsilyl hydroxyesters were characterized by analytical and spectral data.

^c ¹H-NMR yield.

^d A small amount of unknown compound(s) was detected, and the ratio was calculated by comparing the protons of the trimethyl silyl group and methylene protons in the Si–CH₂CH₂ moiety with the methylene protons in the alkoxy group.

^e A small amount of unknown compound(s) was observed, and the ratio was calculated by comparing the protons in the trimethyl silyl group and methylene protons with the CH of the alkoxy group.

^f ¹H-NMR yield, and the ratio was determined by comparison of the phenyl protons with the protons of CH₂C(O) group as well as Me₃Si protons.

The hydroesterification of other vinylsilanes was carried out using the same catalyst and reaction conditions. When triethylvinylsilane, triphenylvinylsilane or 1-phenylvinylsilane was employed as the reactants, linear esters were obtained in 51–94% yield (Table 2, entries 6–8). Steric factors can not alone account for these results, and the β-effect of silicon should also be considered to explain the selectivity [10]. The reaction of trimethoxyvinylsilane gave a mixture of linear and branched esters in a 9:1 ratio, and the disilicon compound (CH₂=CHSi(OMe)₂–O–SiCH₂CH₂C(O)OMe) (Table 2, entry 9). Electronic effects of Si(OMe)₃ versus SiMe₃ may be responsible, at least in part, for the formation of the branched-chain ester. It should be noted that the hydroformylation of trimethoxyvinylsilane gave the linear and branched aldehyde in a ratio of 1:4 and the 1,3-Si shift product. The 1,3-Si shift reaction was not observed in the hydroesterification reaction catalyzed by Pd–montmorillonite (**2**).

In conclusion, the palladium–montmorillonite (**2**) catalyzed hydroesterification of vinylsilanes is usually regiospecific, and selective reaction in the presence of a diol afforded monoesterification products. This hydroesterification reaction is a useful method for preparing organosilicon esters and organosilicon ester alcohols which are of value in organic synthesis.

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