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SYNTHESIS OF VINYLSILANES BY PALLADIUM-CATALYZED REACTION OF TRIMETHYLSILYLALLYL ACETATES WITH NUCLEOPHILES

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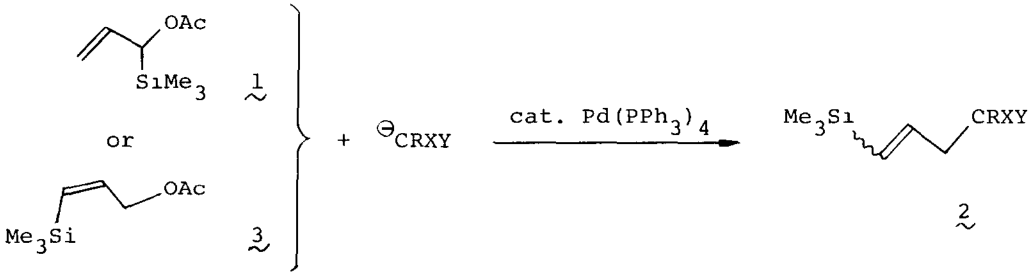
Summary: Treatment of 1-trimethylsilylallyl and 3-trimethylsilylallyl acetates with nucleophiles (active methylene compounds and enamines) in the presence of a catalytic amount of $Pd(PPh_3)_4$ affords vinylsilane derivatives selectively.

The palladium-catalyzed substitution reaction of allylic esters with nucleophiles has been recently developed as a useful synthetic methodology.[1] The carbon-carbon bond formation by this method is applied to the synthesis of natural products.[2] Studies on the regioselectivity of the allylic exchange reaction, however, are scanty. This prompts us to investigate that introduction of a functional group to an allylic part effects the regioselectivity of the reaction Herein, we wish to report the reaction of trimethylsilylallyl acetates with some nucleophiles to afford vinylsilanes selectively.

Treatment of 1-trimethylsilylallyl acetate (1) with sodium diethyl malonate in the presence of 5mol% of tetrakis(triphenylphosphine)palladium and 10mol% of triphenylphosphine at room temperature for 9h exclusively gave the vinylsilane 2a in 72% yield (E/Z 22:78). No allylsilane derivative could be obtained. Acetoacetate also reacted with 1 to produce only the vinylsilane 2b.

The reaction of 3-trimethylsilylallyl acetate (3) with malonate selectively yielded the same vinylsilane 2a. Some results are summarized in Table 1.

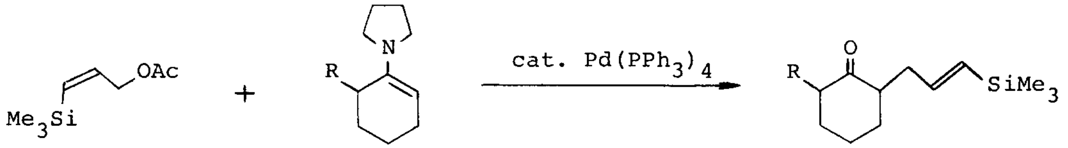


In either of the reactions, the regioselective attack of nucleophiles occurred at the γ carbon from the silyl group. The E/Z ratio of the products, 2a or 2b, obtained from 1 and 3 was almost the same (runs no. 1 and 3, 2 and 4), indicating that the present reactions of 1 and 3 are thought to proceed via the same π-allylpalladium complex intermediate. Interestingly, the main product of the vinylsilane 2a had Z form (runs no. 1 and 3) in contrast to predominant formation of (E)-vinylsilane from acetoacetate (runs no. 2 and 4), though the reason for this difference has not been clarified.

Table 1. Synthesis of Vinylsilanes

Run no.	Acetates	Nucleophiles R	X	Y	Reaction Time (h)	Temp.(°C)	Products	Yield (%)	E/Z
1	1	H	CO_2Et	CO_2Et	9	rt	2a	72	22/78
2	1	H	CO_2Et	COMe	19	rt	2b	32	85/15
3	3	H	CO_2Et	CO_2Et	43	rt	2a	65	27/73
4	3	H	CO_2Et	COMe	24	rt	2b	51	89/11
5	3	H	CO_2Et	SO_2Ph	27	rt	2c	54	41/59
6	3	$(CH_2)_2OCO$		CO_2Et	21	rt	2d	74	88/12
7	3	$(CH_2)_4CO$		CO_2Et	24 1	rt 66	2e	49	87/13

Furthermore, the reaction of 3 with cyclohexanone enamine[3] was carried out to lead a good yield of the vinylsilane 4 selectively. In these cases, only (E)-vinylsilanes were formed.



4 R=H 65% (rt, 46h)
Me 71% (66°C, 28h)

Vinylsilanes are employed as valuable synthetic intermediates.[4] The present palladium-catalyzed reaction provides a useful method for the synthesis of vinylsilanes. Further studies are in progress now.

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