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PALLADIUM-CATALYZED REGIOSELECTIVE REACTIONS OF SILYL-SUBSTITUTED ALLYLIC CARBONATES AND VINYL EPOXIDE

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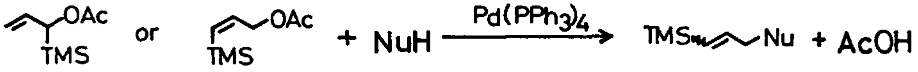
Summary: Palladium-catalyzed reaction of α-substituted γ-trimethylsilylated allylic carbonates with carbonucleophiles took place regioselectively at the α-carbon. Reaction of formic acid took place at γ-carbon to afford allylic silanes. Methyl acetoacetate attacked regioselectively at 2-carbon of 1,2-epoxy-4-trimethylsilyl-3-butene.

The palladium-catalyzed substitution reaction of allylic compounds via π-allylpalladium complexes with various nuclephiles is a well-established synthetic method, and used extensively in organic syntheis.1) Nucleophilic substitution of monosubstituted allylic compounds takes place regioselectively at unsubstituted side of allylic system. On the other hand, reaction of α,γ-disubstituted allylic compounds gives a mixture of regioisomers of α- or γ-substituted products. The ratios depend on steric size of the substituents, and it is difficult to achieve high regioselectivity. We now wish to report highly regioselective substitution reaction of allylic compounds substituted with trimethylsilyl (TMS) group at the γ-side to give vinylsilane derivatives.

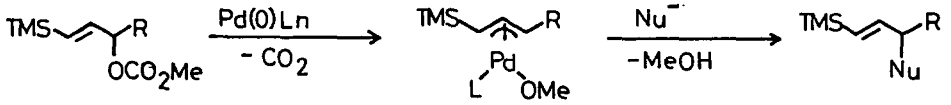
Facile synthesis of α-substituted γ-silylated allylic alcohols is now possible particularly in optically active forms.2) Then we wanted to test the effect of the silyl group on the palladium-catalyzed substitution reactions after converting them to allylic carbonates. Palladium-catalyzed reaction of allyl acetate substituted by TMS at α or γ carbon with carbonucleophiles is known to give vinylsilane derivatives regioselectively as expected<Scheme 1>.3,4) But no studies on regioselectivity has been carried out with allyl esters substituted at both α and γ carbons.

<SCHEME 1>



As shown in <SCHEME 2>, we found that it is possible to synthesize vinylsilanes via regioselective substitution of trimethylsilylallyl methyl carbonates (**1a,b**) with nucleophiles.

<SCHEME 2>



1a; R=pentyl
1b; R=Ph

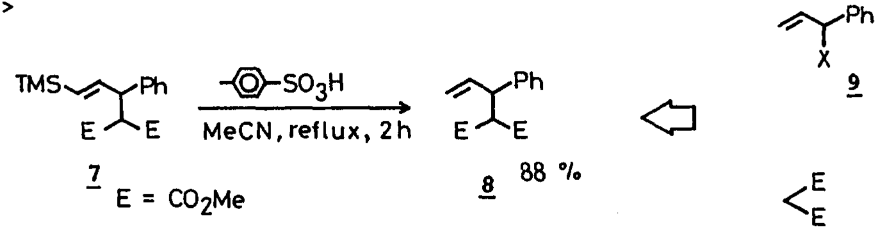
Results of the palladium-catalyzed reactions of trimethylsilylallyl carbonates with some soft carbonucleophiles are summarized in <TABLE 1>. The allylic carbonate **1a** (R=pentyl) smoothly reacted with acetoacetate and malonate in the presence of 5 mol% of palladium catalyst to afford the vinylsilanes **2** and **4** in 81 % and 65 % yields respectively (Runs 1 & 3). No regioisomers were detected by GLC, TLC and NMR analyses. In this reaction, PBu_3 and dppe were suitable phosphine ligands. When PPh_3 was employed, β-elimination of π-allyl intermediate took place to give a considerable amount of the diene **3** (Run 2).

The carbonate **1b** (R=Ph) reacted with acetoacetate to afford the vinylsilane **5** in a good yield. But with malonate, a similar substitution did not take place under neutral conditions and the product was the desilylated compound **6**.$^{5)}$ But when sodiomalonate is used, the vinylsilane **7** was obtained. The reaction of the carbonate, which has a t-butyl group at α-carbon, with acetoacetate in refluxing THF for eight h did not proceed.

These regioselectivities cannot be explained by simple comparison of steric bulkiness of the substituents. Because when the carbonate **1b**, which has a bulky phenyl group was employed, nucleophiles attacked the carbon close to the phenyl group exclusively. Considering the completely controlled regioselectivity, electronic factors seem to play an important role in the π-allylpalladium complex. Thus in the nucleophilic substitution of 1,3-disubstituted π-allylpalladium intermediate, introduction of trimethylsilyl group apparently resulted in the excellent regioselectivity.

Furthermore, the treatment of the vinylsilane **7** with p-toluenesulphonic acid (0.5 eq.) in refluxing CH_3CN for two h gave the desilylated product **8** in 88 % yield,$^{6)}$ which is equivalent to the product obtained from the monosubstituted allylic compound **9** with malonate. This means that nucleophilic substitution at more substituted side of π-allylpalladium intermediate can be achieved indirectly by these reactions.

<SCHEME 3>

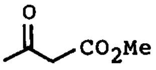
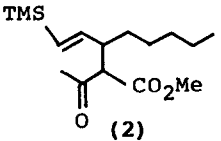
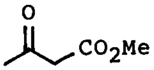
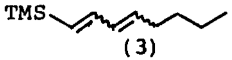
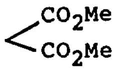
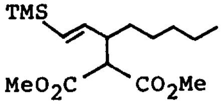
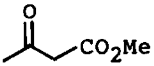
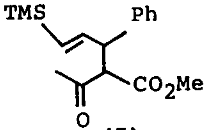
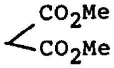
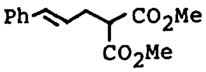
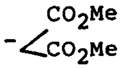
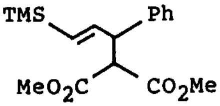


7 E = CO$_2$Me

8

9

<TABLE 1> Palladium-Catalyzed Substitution of Trimethylsilylallyl Methyl Carbonates with Nucleophiles$^{a)}$

Run	R	Nucleophile	Ligand	Temp(^{o}C)	Time(h)	Product$^{b,c)}$ &	Yield$^{d)}$
1	Am (1a)		PBu$_3$ dppe	65	0.5	 (2)	81%
2	1a		PPh$_3$	65	1	2 +  (3) (2.5 : 1)	
3	1a		PBu$_3$	65	0.5	 + 3 (4) 65% (5.7 : 1)	
4	Ph (1b)		PBu$_3$	20-25	2	 (5)	83%
5	1b		PBu$_3$	20-25	5	 (6)	56%
6	1b	Na$^+$ 	PBu$_3$	20-25	2	 (7)	80%

a) Reactions were carried out using allylic carbonate (1 mmol), nucleophile (1 mmol), $Pd_2(dba)_3CHCl_3$ (0.05 mmol) and phosphine ligand (0.20 mmol) in dry THF (5 mmol) under Ar atmosphere.

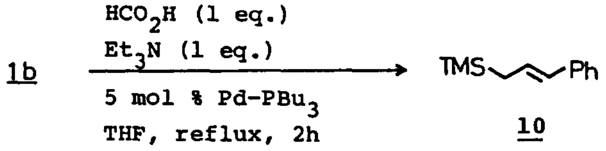
b) The ratio of the products was determined by GLC analyses.

c) The coupling constants of olefinic protons (15.8-18.5 Hz) support the trans-stereochemistry of the double bonds.

d) Isolated yields.

Then we carried out the palladium-catalyzed hydrogenolysis with formate, which is known to give olefins from allylic compounds with high regioselectivity.$^{7)}$ When the carbonate **1b** was treated with a 1:1 mixture of formic acid (1 eq.) and triethylamine in the presence of the palladium catalyst, the allylsilane **10** was obtained as a major product (81% GLC, 58% isolated yields). This means that the hydride derived from formate selectively attacked the γ-carbon.

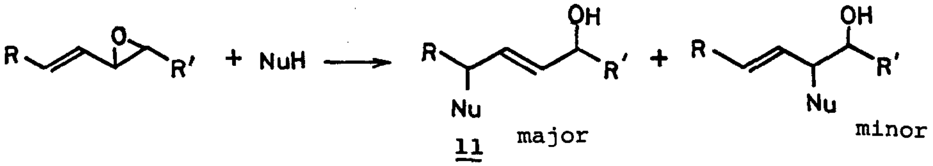
<SCHEME 4>



1b

10

It is known that palladium-catalyzed reaction of vinyl epoxides with carbonucleophiles proceeds with high regioselectivity to give 1,4-adducts 11.[8,9]



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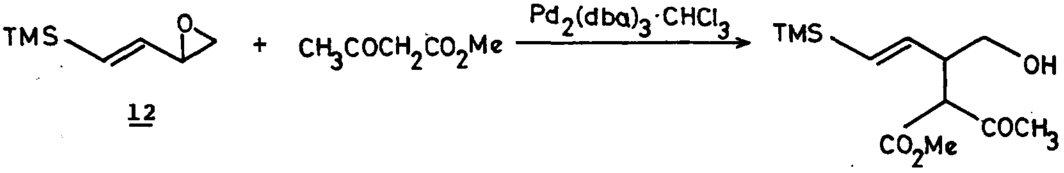
In order to investigate the effect of TMS group on the regioselectivity of this reaction, we carried out the reaction of 1,2-epoxy-4-trimethylsilyl-3-butene (12) with methyl acetoacetate at room temperature. A single product was obtained in 76% yield, which was found to be the 1,2-adduct. Thus the presence of TMS group again changed the regioselectivity.



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