Tetrahedron Letters,Vol.23,No.46,pp 4809-4812,1982 0040-4039/82/464809-04$03.00/0
Printed in Great Britain

FACILE PALLADIUM CATALYZED DECARBOXYLATIVE ALLYLATION OF ACTIVE METHYLENE COMPOUNDS UNDER NEUTRAL CONDITIONS USING ALLYLIC CARBONATES

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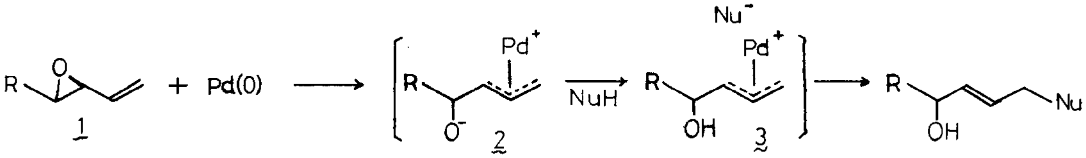
Summary: Palladium catalyzed decarboxylative allylation of active methylene compounds proceeded under mild neutral conditions using allylic carbonates, which are much more reactive than allylic acetates or phenoxides used commonly in the reaction.

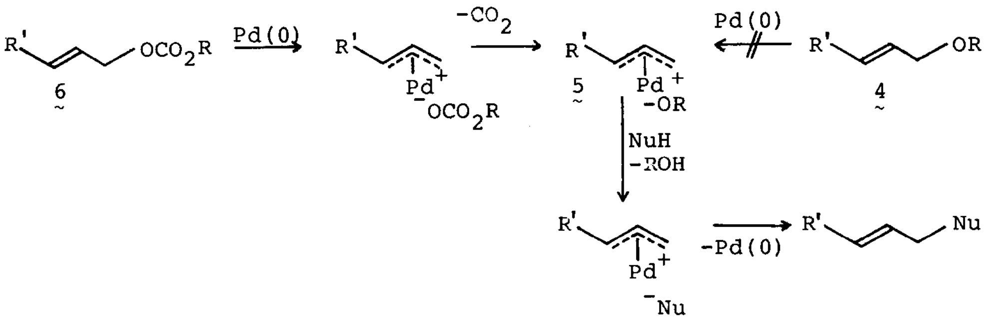
Palladium catalyzed allylation of carbanions is a useful method for carbon-carbon bond formation.[1,2] Allylic acetates are commonly used as a precursor of π-allylpalladium intermediate. In this reaction, generally a stoichiometric amount of bases such as NaH is used for carbanion generation to carry out the reaction smoothly. Although the allylation is a very useful reaction, it would be much more valuable if it can be carried out under neutral conditions without attacking base-sensitive functional groups present in the same molecule. We have reported the palladium catalyzed regioselective nucleophilic 1,4-addition to 1,3-diene monoxides **1** under neutral conditions.[3,4]



1 2 3

In this reaction alkoxides **2** are generated *in situ* by the oxidative addition of Pd(0) species to the epoxides, and abstract proton from nucleophiles to form carbanions **3**. From this result, we speculated that the allylation can be achieved without addition of bases by using allylic ethers **4**, from which alkoxides **5** are generated. But aliphatic allylic ethers hardly react with palladium-phosphine complexes.[5]

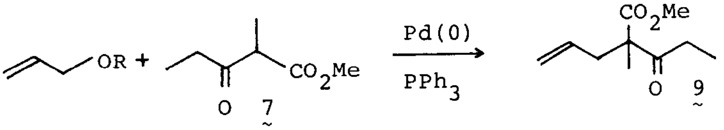
In our continuous effort to achieve the efficient allylation, particularly in the absence of bases, we found that allylic carbonates **6** show very high reactivity in the palladium catalyzed allylation reaction. More importantly the reaction proceeds under neutral conditions since the alkoxides **5** are generated *in situ* after oxidative addition, and subsequent facile decarboxylation. In this paper, we wish to report the facile allylation reaction under mild conditions using allylic carbonates **6**.



At first the allylation of the β-keto ester 7 was carried out using various allylic compounds in order to compare their reactivity (Table 1). Diallyl carbonate (8) was the most reactive and the allylation was completed without addition of NaH at 30°C in 10 min (Run 1). In contrast, in the absence of NaH, reaction hardly took place with allyl acetate (9) and allyl diethyl phosphate (11),[6)] which reacted smoothly only in the presence of stoichiometric amounts of NaH (Runs 2, 3, 7, 8). Allyl phenyl ether reacted at 65°C in 62% yield, but no allylation took place at 30°C (Runs 4-6).

Another evidence for high reactivity of allyl carbonates was obtained by the following competitive reactions. The reaction of a mixture of allyl acetate (10) and methallyl methyl carbonate (12) with 7 (1 : 1 : 1) in THF for 20 min gave 14 in 84% yield and 13 in 16% yield (GLC analysis). Also high chemoselectivity was observed in the reaction of 4-acetoxy-2-butenyl methyl carbonate (15) and 7 at 25°C for 2 h to give 16 in 77% yield after chromatographic purification.

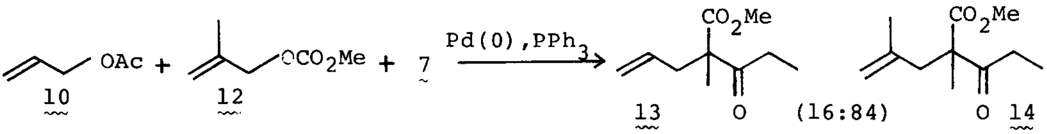
Table 1. Pd-Catalyzed Allylation of Methyl 2-Methyl-3-oxopentanoate (7)[a]



Run	Allylic Compound	Base	Reaction Time	Yield (%)[b]
1	$(CH_2{=}CHCH_2O)_2CO$ (8)	-	10 min	98
2	$CH_2{=}CHCH_2OAc$ (10)	-	22 h	24
3	$CH_2{=}CHCH_2OAc$	NaH	30 min	95
4	$CH_2{=}CHCH_2OPh$	-	19 h	0
5[c]	$CH_2{=}CHCH_2OPh$	-	7.5 h	62
6	$CH_2{=}CHCH_2OPh$	NaH	4 h	5
7	$CH_2{=}CHCH_2OPO(OEt)_2$ (11)	-	24 h	6
8	$CH_2{=}CHCH_2OPO(OEt)_2$	NaH	1.5 h	96

a) Carried out using 7 (1 mmol), allylic compound (2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.05 mmol) and PPh_3 (0.2 mmol) in THF (3 mL) at 30°C under argon.

b) GLC analysis. c) Reaction at 65°C.



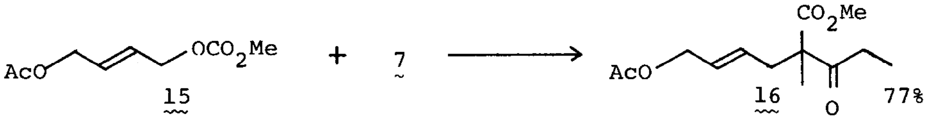
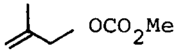
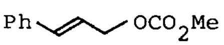
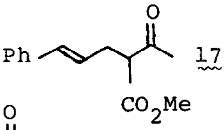
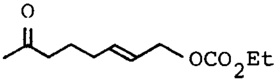
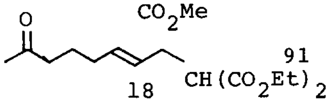
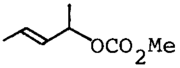
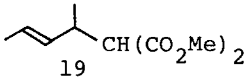
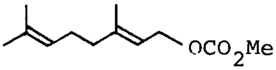
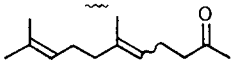
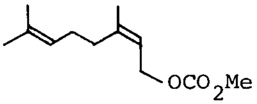
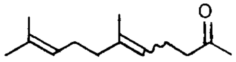
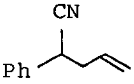
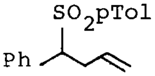
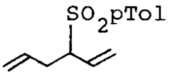


Table 2. Reaction of allylic carbonates and carbonucleophiles[a]

Run	Allylic carbonate	Nucleophile	Ligand	Temp.	Time(h)	Product	Yield(%)[b]
1		7	PPh_3	30°C	0.2	14	92
2		$CH_3COCH_2CO_2Me$	PPh_3	25	1	 17	90
3		$CH_2(CO_2Et)_2$	dppe	30	0.5	 18	91
4		$CH_2(CO_2Me)_2$	PPh_3	30	3	 19	64
5		$CH_3COCH_2CO_2Me$	dppe	50	3		74[c,d]
6		$CH_3COCH_2CO_2Me$	dppe	50	3		54[c,e]
7[f]	$(CH_2=CHCH_2O)_2CO$ (8)	$PhCH_2CN$	dppe	65	2		91
8[f]	8	$PhCH_2SO_2pTol$	dppe	65	3		92
9[f]	8	$CH_2=CHCH_2SO_2pTol$	dppe	65	2		57[g]

a) Reactions were carried out using $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) and phosphine (10-20 mol%) in THF under argon. b) Isolated yield. c) After decarboxylation (5% NaOH, then H_3O^+). d) E/Z=92/8 (GLC analysis). e) E/Z=52/48 (GLC analysis). f) 5 mol% of $Pd_2(dba)_3 \cdot CHCl_3$ and 10 mol% of dppe were used. g) Diallylated compound was obtained. (12%)

Results of the reactions of other allylic carbonates with various carbonucleophiles are summarized in Table 2. The allylation proceeded in good yields with β-keto esters and malonates (entries 1-6). Phenylacetonitrile, benzylsulfone and allylsulfone were also allylated in good yields without base using bis(diphenylphosphino)ethane (dppe) as the ligand (entries 7-9). Starting from E olefins (15, Runs 2, 3, 4) only single products which have E forms were obtained. The E forms were confirmed by NMR [for 17; (CCl_4) δ 6.40 (d, J = 20 Hz, 1 H, PhCH=), and 5.95 ppm (dd, J = 7, 20 Hz, 1 H, =CH-CH_2-)] and IR [(for 16; 970 (C=C-H), 17; 970 (C=C-H), 18; 970 (C=C-H), and 19; 970 cm^{-1} (C=C-H)]. The reaction of geranyl or neryl carbonate with Pd-dppe at 50°C for 3 h, followed by demethoxycarbonylation gave mixtures of geranyl- and nerylacetone (entries 5 and 6). These results are explained by syn $\rightleftharpoons$ anti isomerization of π-allylpalladium intermediate before the nucleophilic attack.

It was reported that treatment of allylic carbonates with Pd-phosphine catalyst gave allylic ethers.7) But it should be noted that the attack of carbonucleophiles on the π-allylpalladium complexes is faster than that of alkoxides. No allylic ether was obtained in the reactions described above.

Since allylic carbonates are easily prepared from the corresponding allylic alcohols and chloroformates, the palladium catalyzed allylation using allylic carbonates has wide application in organic synthesis. Further studies on the synthetic application of this reaction are in progress.8)

Acknowledgment: This research was supported by grant-in-aid administered by the Ministry of Education, Japanese Government (No. 56750588).

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(Received in Japan 26 July 1982)