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STEREOCHEMISTRY OF ALLYLIC CARBON-OXYGEN AND CARBON-CARBON BOND FORMATION IN PALLADIUM-CATALYZED DECARBOXYLATION OF ALLYLIC CARBONATES AND ACETOACETATES

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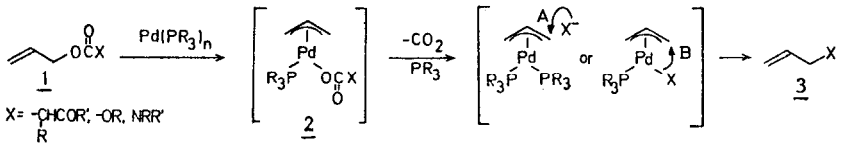
Summary: Palladium-catalyzed decarboxylation of allylic carbonates(cis- and trans-4)and allylic acetoacetates(cis- and trans-5)results in carbon-oxygen and carbon-carbon bond formation with both retention and inversion of configuration at the allylic position. The reaction of the cis-substrates proceeds with predominant retention, whereas the reaction of the trans substrates is nonstereospecific.

Nucleophilic attack on π-allylpalladium complexes is an important reaction for creating new carbon-carbon, carbon-oxygen, and carbon-nitrogen bonds.[1] Mechanistic studies have shown that stabilized carbon nucleophiles and most heteronucleophiles add with trans stereochemistry.[2-4] However, we recently found that acetate can add also via a cis-migration pathway.[3,5] By ligand control it was possible to completely control the stereochemistry of the acetate attack and obtain either a stereospecific cis-attack or a stereospecific trans-attack.[3]

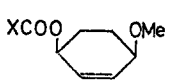
Recently there has been some interest in reactions where allylic substrates 1 undergo a palladium-catalyzed decarboxylation to give 3 (eq. 1).[6,7] In analogy with related palladium-cata-



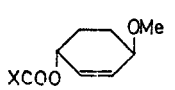
X= -CHCOR', -OR, NRR'

(eq. 1)

lyzed reactions of allylic substrates[1] the decarboxylation of 1 to give 3 involves the formation of a π-allylpalladium intermediate 2. Decarboxylation of 2 followed by nucleophilic addition of X then yields 3. An important question concerning the mechanism of the reactions in equation 1 is whether the nucleophilic group X is introduced on the π-allyl group via a trans-attack (path A) or a cis-attack (path B). In order to answer this question we studied the stereochemistry of the palladium-catalyzed decarboxyalation of allylic carbonates 4[8] and acetoacetates 5.[9]



cis-4 (X= OMe)
cis-5 (X= CH_2COMe)



trans-4 (X= OMe)
trans-5 (X= CH_2COMe)

Treatment of the carbonate cis-4 with $Pd(OAc)_2$ and triphenylphosphine in benzene at 55°C, following the procedure described by Guibe and Saint M'Leux,[7a] gave a low yield of 1,4-dimethoxy-2-cyclohexene. ^1H NMR analysis of the product showed that it was mainly the cis-isomer (cis:trans = 91:9). The corresponding reaction of trans-4 was not stereospecific and gave a 64:36 mixture of cis- and trans-1,4-dimethoxy-2-cyclohexene (Table 1).

Similar reactions of cis- and trans-5 gave in each case a mixture of cis- and trans-1,4-isomers and 1,2-isomer (Table 1). The results in Table 1 from these reactions show that there is

Table 1. Palladium-catalyzed decarboxylation of allylic carbonates and acetoacetates.[a]

substrate	relative yield of products[a,b,c]			cis/trans for 1,4-isomer
XCOO–⟨⟩–OMe	X–⟨⟩–OMe	OMe–⟨⟩–X	OMe–⟨⟩–X	
cis-4 (X = OMe)	91	9	–[d]	91/9
trans-4 (X = OMe)	64	36	–[d]	64/36
cis-5 (X = CH_2COMe)	61	14	23[e]	81/19
trans-5 (X = CH_2COMe)	51	26	23[e]	66/34

a. Absolute yields were 10-15% from 4 and 50-60% from 5; b. Relative yields were determined by ^1H NMR and GLC; c. ^1H NMR ($CDCl_3$) δ 1,4-dimethoxy-2-cyclohexene, cis: 5.93 (s, CH=CH), 3.70 (m, CH-O(W_H=11Hz)), 3.37 (s, MeO), 1.8 (m, CH_2CH_2); trans 5.90 (s, CH=CH), 3.82 (m, CH-O(W_H=14Hz)), 3.37 (s, MeO), 2.1 and 1.5 (m, CH_2CH_2); 1-acetonyl-4-methoxy-2-cyclohexene, cis: 5.9-5.7 (m, CH=CH), 3.67 (m, CH-O(W_H=10Hz)), 3.36 (s, MeO), 2.59 (m, CH) 2.47 (CH_2) 2.15 (s, Me) 1.9-1.5 (m, CH_2CH_2); trans: 5.8-5.6 (m, CH=CH), 3.79 (m, CH-O(W_H=16Hz)), 3.36 (s, MeO), 2.68(m, CH), 2.40 and 2.41 (CH_2), 2.15 (s, Me), 2.1-1.5 (m, CH_2CH_2); d. 1,2-Isomer not observed; e. Stereochemistry not determined for the 1,2-isomer.

a loss of stereospecificity in the formation of the new carbon-carbon bond.

The figures in Table 1 show that there is a preference for overall retention in the reactions of the cis-isomers. This is consistent with a displacement of the X-COO- group by Pd(0) with inversion of configuration[1] followed by a trans-attack by X on the allylic ligand. It is likely that the low stereospecificity in the reactions is due to isomerization of the starting material.[10] Accordingly, isolation of unreacted 4 from an incomplete palladium-catalyzed reaction of trans-4 showed that it consisted of cis- and trans-4 in an approximate ratio of 1:1.7.

Although we cannot exclude some cis-migration of MeO^- and $MeCOCH_2^-$ (cf. eq. 1), we conclude that the results are best explained by an external trans-attack by these nucleophiles on an intermediate π-allylpalladium complex, with a disturbing isomerization of the starting material.[11]

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8. Prepared by treatment of the corresponding 4-methoxycyclohex-2-ene-1-ol[3,5] with methyl chloroformate in THF at room temperature in the presence of pyridine. Because of decomposition of the methyl chloroformate it was necessary to add it in excess in intervals.
9. Prepared from the corresponding 4-methoxycyclohex-2-ene-1-ol[3,5] and diketene according to W. Kimel and A.C. Cope, *J. Am. Chem. Soc.*, 65, 1992 (1943).
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