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Palladium-Catalyzed Reactions of Alkenyloxiranes with Carbon Monoxide

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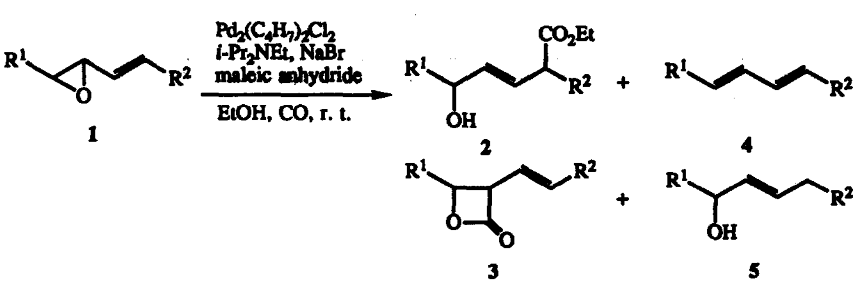
Abstract: Reaction of alkenyloxiranes with carbon monoxide in the presence of palladium catalysts gives unsaturated esters, β-lactones, dienes, and allylic alcohols. The selectivity of the reaction depends on the nature of the alkenyloxiranes. Carbonylation products were obtained in the reaction of terminal alkenyloxiranes and alkenyloxiranes having electron-donating substituents, whereas carbonylation scarcely took place in the reaction of alkenyloxiranes having electron-withdrawing groups; dienes and allylic alcohols were produced instead of carbonylation products.

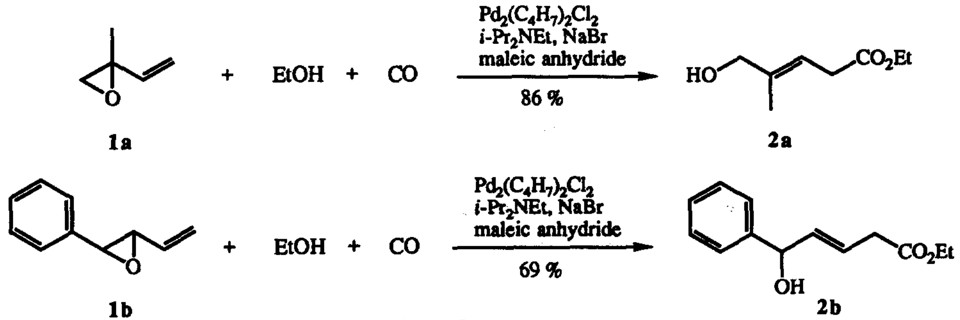
Carbonylation of allylic compounds is a useful tool for organic synthesis. Allylic carbonates, halides, acetates, phosphates, and others are known to be carbonylated with palladium catalysts to give β,γ-unsaturated esters through processes proceeding via π-allylpalladium complexes.[1a)-1d)] Alkenyloxiranes react with palladium compounds to give π-allylpalladim complexes, which undergo isomerization,[2)] nucleophilic reaction,[3)] or reduction.[4)] However, no carbonylation of alkenyloxiranes promoted by palladium catalysis has been documented.

We report here on the results of our study on the palladium-catalyzed reaction of alkenyloxiranes with carbon monoxide. The reaction course was found to vary depending on the nature of the alkenyloxiranes employed. Four types of products (2-5 in Scheme 1) are produced depending on the nature of the substituents R^2 of the alkenyloxirane 1.



Scheme 1

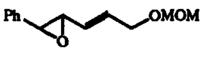
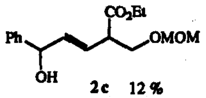
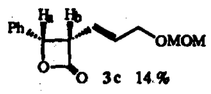
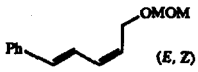
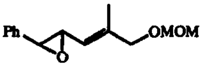
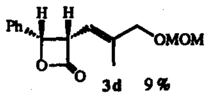
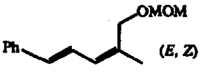
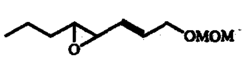
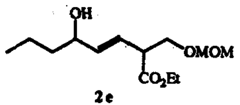
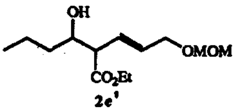
Reaction of isoprene monoxide **1a** with CO (30 atm) in ethanol in the presence of $Pd_2(C_4H_7)_2Cl_2$, *i*-Pr_2NEt, NaBr, and maleic anhydride at room temperature for 12 h gave ethyl (*E*)-5-hydroxy-4-methyl-3-pentenoate **2a** in 86 % yield after purification on column chromatography.[1c] Similarly, (*E*)-5-hydroxy-5-phenyl-3-pentenoate **2b** was obtained in 69 % yield by the carbonylation of the terminal alkenyloxirane **1b** (Scheme 2).



Scheme 2

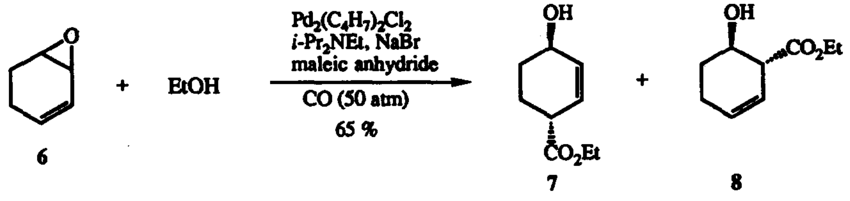
Carbonylation of alkenyloxiranes which have internal olefins (**1**, R^2=alkyl) also took place to give the corresponding hydroxy esters and β-lactones but considerable amounts of 1,3-dienes were formed as shown in Table 1. The stereochemistry of the β-lactone **3c** is assigned on the basis of the proton NMR spectrum where H_a (δ: 5.26) couples with H_b (δ: 4.89) with coupling of J=7.9 Hz, indicative of a cis relationship. The stereochemistry of the diene formed (**4c**) was (*E* , *Z*) as depicted in Table 1. The (*E*)-olefin of the starting materials were inverted. But, the diene **4e** obtained in the reaction of **1e** with CO was a mixture.

Table 1 Palladium-Catalyzed Reaction of Alkenyloxiranes with Carbon Moxide

Run	Alkenyloxirane 1	Product (isolated yield)		
1	 1c	 2c 12 %	 3c 14 %	 (E, Z) 4c 44 %
2	 1d		 3d 9 %	 (E, Z) 4d 55 %
3	 1e MOM = CH_2OCH_3	 2e	 2e' 35 % (2e : 2e' = 5 : 2)	 4e 13 %

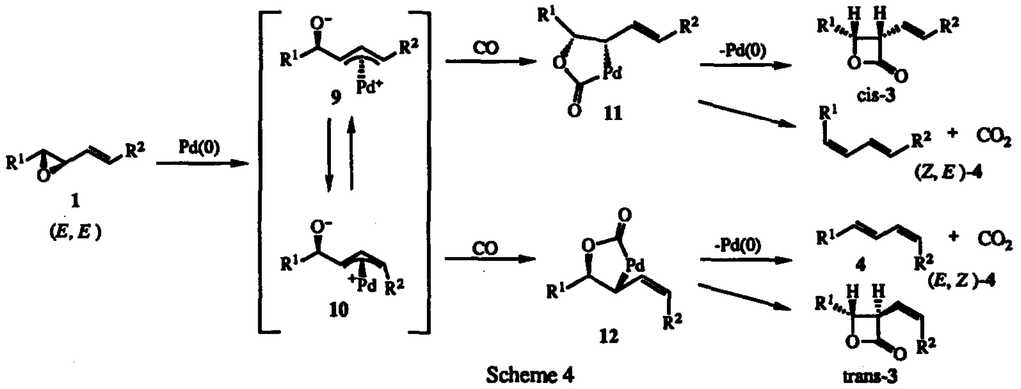
Reaction Conditions : $Pd_2(C_4H_7)_2Cl_2$ 5 mol%, NaBr 1 eq., *i*-Pr_2NEt 1eq., maleic anhydride 10 mol%,
EtOH 5 ml, CO 30 atm, r. t.

The carbonylation of 1,3-cyclohexadiene monoepoxide **6** proceeded stereoselectively and gave a mixture of hydroxy esters **7** and **8**. But neither β-lactone nor 1,3-diene was formed in this case (Scheme 3). The ethoxycarbonyl and hydroxy groups in both 7 and 8 were trans. The trans stereochemistry was assigned from the proton NMR spectrum after hydrogenating **7** and **8** respectively. The stereochemistry of **8** indicates that the carbonylation proceeds with inversion of configuration at the allylic carbon.



Scheme 3 (7 : 8 = 9 : 5)

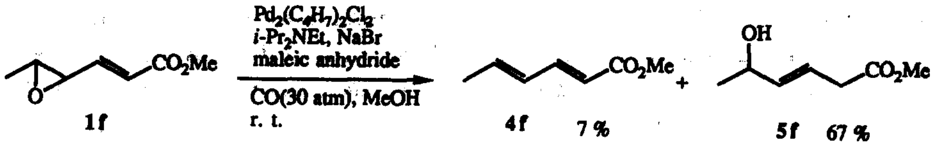
The mechanisms illustrated in Scheme 4 are proposed to consistently account for the formation of β-lactone **3** and 1,3-diene **4**. The ring-opening reaction of alkenyloxirane **1** with palladium complex proceeds stereoselectively in an S_N2 manner to afford π-allylpalladium complex **9**.[4)] The syn π-allylpalladium complex **9** is converted into anti π-allylpalladium complex **10** by the π–σ–π interconversion. Coordination of CO to the palladium complex followed by attack of the oxide anion to the coordinated CO gives five-membered metalacycles **11** and **12** respectively. The reductive elimination of palladium out of **11** affords β-lactone cis-**3**, whereas (*E*, *Z*)-diene **4** is obtained by the decarboxylation from complex **12**. The selectivity between reductive elimination and decarboxylation may depend on the stereochemistry of the intermediate **11** or **12**. However, stereochemical requirements for these reactions are not obvious.



Scheme 4

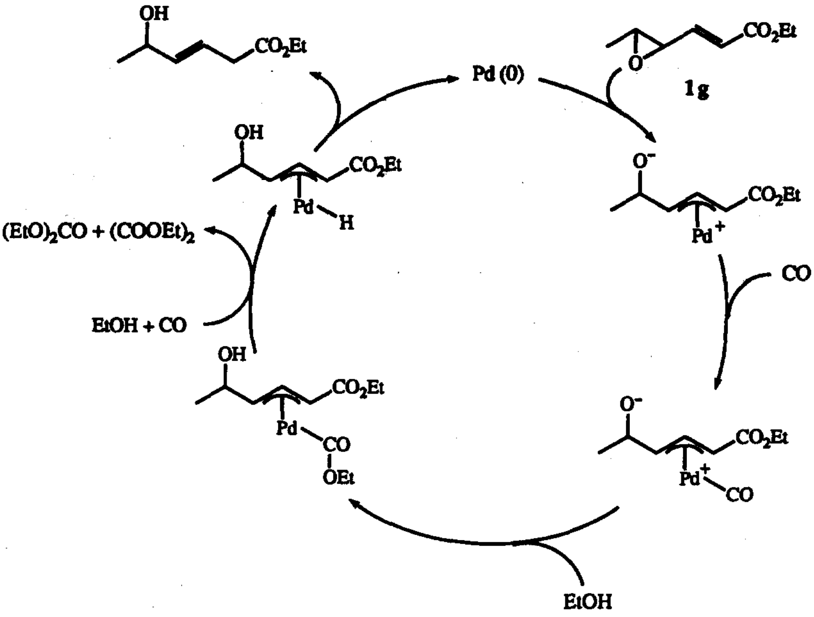
Since the intramolecular participation of the oxide anion to CO coordinated to the palladium (**11** or **12** in Scheme 4) is impossible in the reaction of cyclic alkenyloxirane **6**, neither β-lactone nor diene was formed in this case.

When alkenyloxiranes having electron-withdrawing substituent R^2 such as alkoxycarbonyl group were subjected to the reaction with CO, no carbonylation product was formed and allylic alcohol and diene were produced as reduction products of the oxirane (Scheme 5). The ratio of the allylic alcohol **5f** to the diene **4f** increased on decrease of the CO pressure employed. Indeed, allylic alcohol **5f** was obtained selectively at atmospheric CO pressure. The presence of CO, however, is essential for reduction of **1f** to **4f** and **5f**. When the reaction of **1f** was carried out in the absence of CO, no reaction proceeded and **1f** was recovered.



Scheme 5

Although the role of CO and the precise mechanisms for the reduction are not known, involvement of an alkoxycarbonyl complex and its reaction with alcohol to give π-allylpalladium hydride complex are probable. Indeed, formation of diethyl carbonate and diethyl oxalate in the reaction of **1g** was confirmed by GC-mass spectroscopy (Scheme 6).



Scheme 6

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