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Palladium-Catalyzed, Atmospheric Pressure Carbonylation of Allylic Chlorides in Two-Phase Aqueous Sodium Hydroxide-Organic Solvent Media

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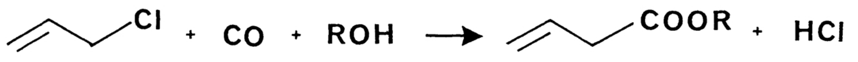
The palladium-catalyzed, atmospheric pressure carbonylation of allylic chlorides is realized in aqueous NaOH/benzene. Phosphine complexes $PdCl_2L_2$ (I) (a, $L=Ph_2P(m\text{-}C_6H_4SO_3Na)$; b, $L=Ph_3P$), or Na_2PdCl_4 can be used as the catalyst.

The transition metal-catalyzed carbonylation of allylic compounds offers a synthetic method of β,γ-unsaturated acid. Though organic synthesis with transition metal compounds has attracted much attention,[1,2] the carbonylation has found less application in organic synthesis. The reason is that it requires a high carbon monoxide pressure and the yield of the β,γ-unsaturated acid is moderate.[3-8] Several years ago Tsuji et al.[9] have developed the atmospheric decarbonylation-carbonylation of allylic carbonates with $Pd(OAc)_2$-Ph_3P and obtained β,γ-unsaturated esters in high yields. Milstein[10] has succeeded in low pressure (3.4 atm) carbonylation of π-allylpalladium complexes, which are proved to be a key intermediate of the catalytic carbonylation, in the presence of carboxylic acid anions.

Allyl chloride is a versatile starting material. It is apparent that its carbonylation offers a highly promising synthetic route to 3-butenoic acid. The carbonylation of allyl chloride in a protic solvent is expressed by Eq. 1.



(1)

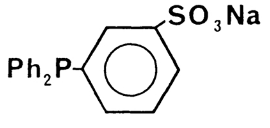
R; H, CH_3, C_2H_5, etc.

Accumulation of hydrogen chloride is not favorable for the high pressure reaction at high temperature. This disadvantage was overcome by using tetrahydrofuran as the solvent and 4-chlorobutyl 3-butenoate was obtained in a high yield, though the reaction was performed under high pressure.[11]

Since organotransition metal complexes are hydrophobic, water has been considered undesirable for the reactions catalyzed by them. If a water-soluble catalyst is used, the catalyst can easily be separated from the products which are immiscible with water. Therefore, the use of water is attractive for the organic reactions.[12,13] For this purpose, we have prepared water-soluble phosphines[14] and used as the ligand of the transition metal catalysts in two-phase water-organic solvent media.[15)] In the course of the studies we have found that the palladium-catalyzed carbonylation of allyl chloride, which had required high pressure of carbon monoxide, proceeds smoothly in two-phase aqueous sodium hydroxide/benzene medium under atmospheric pressure at room temperature and 3-butenoic acid is formed in a high yield.

Phosphine complexes $PdCl_2L_2$ (I) (a, $L=Ph_2P(m-C_6H_4SO_3Na)$; b, $L=Ph_3P$) and Na_2PdCl_4 (II) were used as the catalyst. While Ia and II are water-soluble, Ib is not soluble in water but in benzene.

A typical experimental procedure is as follows. In a 50 ml two-necked flask, of which one side neck was fitted with a three-way stopcock and the other was connected to a gas buret filled with decalin, palladium catalyst was placed. After the atmosphere was replaced with carbon monoxide, benzene (7-10 ml), aqueous NaOH (2.5 mol dm^{-3}) and allyl chloride were added, and the mixture was stirred vigorously. After the absorption of carbon monoxide ceased, the aqueous layer was acidified and extracted with ether.



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The absorption rates of carbon monoxide are shown in Fig. 1. Characteristic features of this reaction are summarized as follows. First, the carbonylation occurs under very mild conditions; under atmospheric pressure and at room temperature. Second, either catalyst, no matter whether it is soluble in water or not, can be used. Third, it is not necessary to add phosphorus ligand. Phosphines seems to protect molecular palladium against aggregation to metallic one. When Na_2PdCl_4 was used, palladium was recovered as a black precipitate and both aqueous and organic layers were colorless. And lastly, the presence of hydroxide ion is essential; namely, in the absence of hydroxide ion carbon monoxide was not absorbed at all.

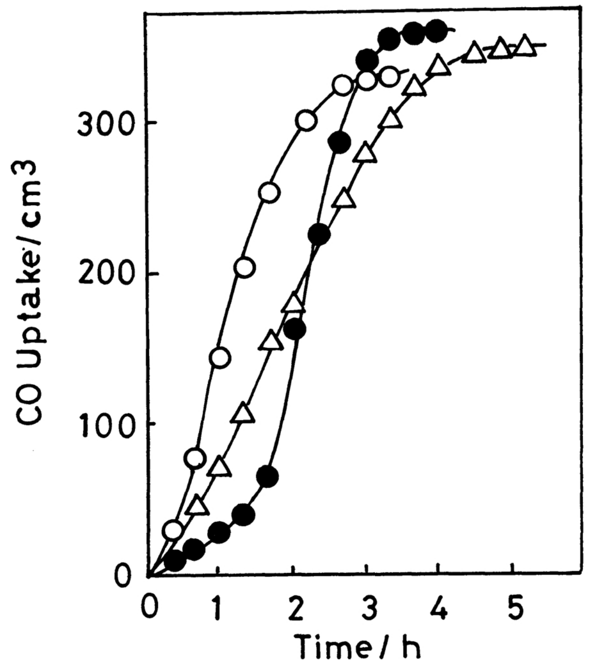

Fig. 1. Carbonylation of allyl chloride catalyzed by Ia(-○-), Ib(-△-), and II(-●-). Reaction conditions, see Table 1.

This reaction requires 2 mol of sodium hydroxide. In the carbonylation of allyl chloride 2-butenoic acid, which was formed by the base-catalyzed isomerization of 3-butenoic acid, was obtained in 10-20 % yields under these two-phase conditions. The formation of the α,β-unsaturated isomer is not a characteristic of the reaction but depends upon the concentration of the base during the reaction. In fact, the isomerization was suppressed by continuous addition of aqueous sodium hydroxide in order to keep the concentration of the base lower (Table 1, Entry 4).

Other allylic chlorides were carbonylated under atmospheric pressure.

Low molecular weight compounds such as methallyl chloride were readily carbonylated. Cinnamyl and geranyl chlorides gave the corresponding β,γ-unsaturated acids in moderate yields. On the carbonylation of cinnamyl chloride 1,4-diphenyl-1,5-hexadiene[16)] was formed in a comparable yield. To improve the reaction of cinnamyl chloride, tetrahydrofuran or butanol, which is more polar than benzene and heptane, was used as the organic solvent of the two-phase reaction. In this case, however, the yield of 4-phenyl-3-butenoic acid did not exceed 50%.

Table 1. Carbonylation of Allylic Chlorides in Two-phase System[a)]

Entry	Chloride (mmol)	Catalyst (mmol)	NaOH[b)] mmol	Organic solvent	Yield of acid/% (β,γ/α,β)[c)]
1	allyl(15)	Ia (0.1)	38	benzene	77 (87/13)
2	allyl(15)	II (0.1)	38	benzene	86 (79/21)
3	allyl(15)	Ib (0.1)	38	benzene	90 (76/24)
4	allyl(15)	Ib (0.1)	30[d)]	benzene	70 (96/4)
5	methallyl(15)	Ia (0.1)	25	heptane	63
6	geranyl(6)	Ia (0.05)	38	heptane	48
7	cinnamyl(15)	Ia (0.1)	25	heptane	19
8	cinnamyl(15)	Ia (0.1)	25	THF	40

a) Entries 1-4, at 30 °C ; 5-8, at 50 °C.

b) Aqueous NaOH (2.5 mol dm^{-3})

c) Only when the formation of the α,β-isomer was shown by the NMR spectrum, the ratio is given in parentheses.

d) 25 mmol of them were added slowly during 3 h.

Since this carbonylation occurred in the absence of transfer agent, it is not a phase transfer reaction. It is likely that the reaction occurs at the liquid-liquid interface. Furthermore, though somewhat speculative, the reaction proceeds through a carboxypalladium intermediate. The product-forming step is probably the reductive elimination of the allyl and carboxy groups and not CO insection into the allyl-Pd followed by hydrolysis.

More work is needed to define the pathway of this reaction.

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concentration significantly influences the yield and product distribution. Under optimum conditions, where higher yields of butenoic acids are attained, conjugated 2-butenoic acid is produced as the major one.

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16) Isolated by gas chromatography, ^{1}H NMR($CDCl_3$) : δ 2.65(t, 2H), 3.45(q, 1H), 5.0-5.1(m, 2H), 6.0-6.2(m, 2H), 6.40(d, 1H), 7.25(aromatic protons, 10H).

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