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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS—XLVIII[1]

CARBONYLATION OF BUTADIENE CATALYZED BY PALLADIUM-PHOSPHINE COMPLEXES

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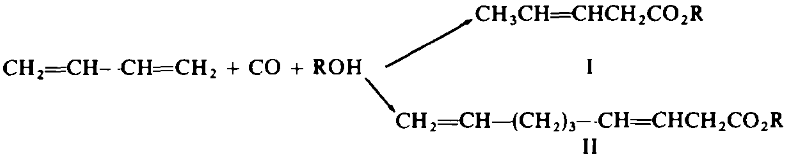
Abstract— Two moles of butadiene react with one mole of carbon monoxide in alcohol in the presence of palladium–phosphine complexes to give the 3,8-nonadienoate. The absence of halide coordinated to the palladium is essential for the catalytic carbonylation to form nonadienoate. In the presence of halide, one mole of butadiene reacts with one mole of carbon monoxide to give the 3-pentenoate.

Palladium is a versatile catalyst for carbonylation of various types of olefinic and acetylenic compounds.[2] Studies on palladium catalyzed carbonylations reveal that the presence of a small amount of hydrogen halide is essential for the palladium catalyzed carbonylation of olefinic and acetylenic compounds. In the absence of hydrogen halide, no carbonylation takes place. Sometimes, the reactions proceed satisfactorily by using palladium chloride as catalyst without addition of hydrogen chloride, showing that a halide ion coordinated to the palladium is essential. We have reported that carbonylation of butadiene catalyzed by palladium chloride gives the 3-pentenoate (I).[3] We have now found a new type of butadiene carbonylation; namely halide free palladium complexes catalyze the carbonylation of butadiene to give the 3,8-nonadienoate (II).



$$CH_2{=}CH{-}CH{=}CH_2 + CO + ROH \begin{cases} CH_3CH{=}CHCH_2CO_2R & \text{I} \\ CH_2{=}CH{-}(CH_2)_3{-}CH{=}CHCH_2CO_2R & \text{II} \end{cases}$$

We have briefly reported the reaction[4] but the details of this dimeric carbonylation reaction are presented here. Recently Billups *et al.* gave a brief report on a similar method.[5]

RESULTS AND DISCUSSION

It is apparent that both the 3-pentenoate and the 3,8-nonadienoate are formed by the palladium catalyzed carbonylation of butadiene. An essential factor which differentiates the monomeric and dimeric carbonylations was found to be the presence or absence of a halide ion coordinated to the palladium. The dimeric carbonylation reaction proceeded satisfactorily with halide free palladium phosphine complexes. Most conveniently, easily available palladium acetate or palladium acetylacetonate was used with phosphine. With these halide free complexes, the 3,8-nonadienoate was obtained almost selectively. When halide containing divalent palladium compounds were used as catalyst, the 3-pentenoate was the main product. The addition of base (KOAc or NaOAc) to these halide containing complexes deprives the halide from the coordination sphere of the palladium and the resulting complex catalyzes the dimeric carbonylation. The results of the reaction using various catalyst systems are shown in Table 1.

TABLE 1. CATALYST SYSTEMS[a]

Catalyst system (molar ratio)	ethyl 3,8-nonadienoate (g)
$Pd(OAc)_2$–PPh_3 (1:2)[b]	29·5
$Pd(OAc)_2$–$^nBu_3P$ (1:2)[b]	31·4
$Pd(AcAc)_2$–PPh_3 (1:2)	7·8
$PdCl_2(PPh_3)_2$–AcOK (1:5)	14·4
$PdCl_2(PPh_3)_2$–AcOK (1:20)	trace
$PdCl_2(PPh_3)_2$–AcONa (1:5)	9·7
(π-allyl $PdCl)_2$–PPh_3–AcOK (1:2:5)	10·3

[a] Carried out with butadiene (20g), EtOH (30 ml), Pd complex (1·33 mmol), phosphine, base, and CO (100 atm) at 110° for 16 hr

[b] Carried out under 50 atm of CO press.

Another essential component of the catalyst is phosphine. Palladium chloride catalyzed carbonylations of olefins and acetylenes are possible even in the absence of phosphine but addition of triphenylphosphine enhances catalytic activity and efficiency. However it was confirmed that in the palladium acetate catalyzed dimeric carbonylation, no reaction took place in the absence of phosphine. Both triphenylphosphine and tributylphosphine can be used. Catalytic activity varied with the relative ratio of palladium and phosphine as shown in Table 2. The highest activity was observed when the ratio was 1/4.

TABLE 2. EFFECT OF RELATIVE AMOUNTS OF PPh_3[a]

PPh_3/Pd molar ratio	ethyl 3,8-nonadienoate (g)
0	trace
1	10·2
2	34·9
4	57·5
8	47·0

[a] Butadiene (43·2 g), EtOH (36·8 g), $Pd(OAc)_2$ (0·45 g), PPh_3, and CO (50 atm) at 110° for 16 hr.

The reaction can be carried out in alcohol under carbon monoxide pressure. The results of the reactions in various alcohols are shown in Table 3. Methanol was somewhat exceptional, low yield, but a satisfactory yield was obtained by diluting the MeOH with MeCN. Surprisingly, steric factors for the alcohols are not important.

TABLE 3. CARBONYLATION OF BUTADIENE IN ALCOHOLS[a]

ROH	yield of alkyl 3,8-nonadienoate
R : Et-	29·5 g (87·6 %)[d]
i-Pr	32·5 g (89·7 %)
t-Bu[b]	40·7 g (91·5 %)
Me-	2·8 g (9·2 %)
Me-[c]	64·5 g (96·0 %)

[a] Carried out with butadiene (20 g), alcohol (30 ml), $Pd(OAc)_2$ (0·30 g), PPh_3 (0·70 g), and CO (50 atm) at 110° for 16 hr.

[b] 23 g butadiene used.

[c] Butadiene (43·2 g), MeOH (12·8 g), MeCN (50 ml), $Pd(OAc)_2$ (0·90 g), PPh_3 (4·19 g) and CO (50 atm) at 110° for 16 hr.

[d] Based on butadiene.

For example the reaction proceeded smoothly even in t-BuOH to give the t-butyl ester in a high yield. However, it should be noted that the rate of the dimeric carbonylation reaction in general is slower than that of the carbonylation of simple olefins catalyzed by palladium chloride and triphenylphosphine in the presence of hydrogen chloride.

Carbon monoxide pressure has an important effect on the reaction, higher pressure tending to decrease yield. Its effect is shown in Table 4.

TABLE 4. EFFECT OF CO PRESSURE[a]

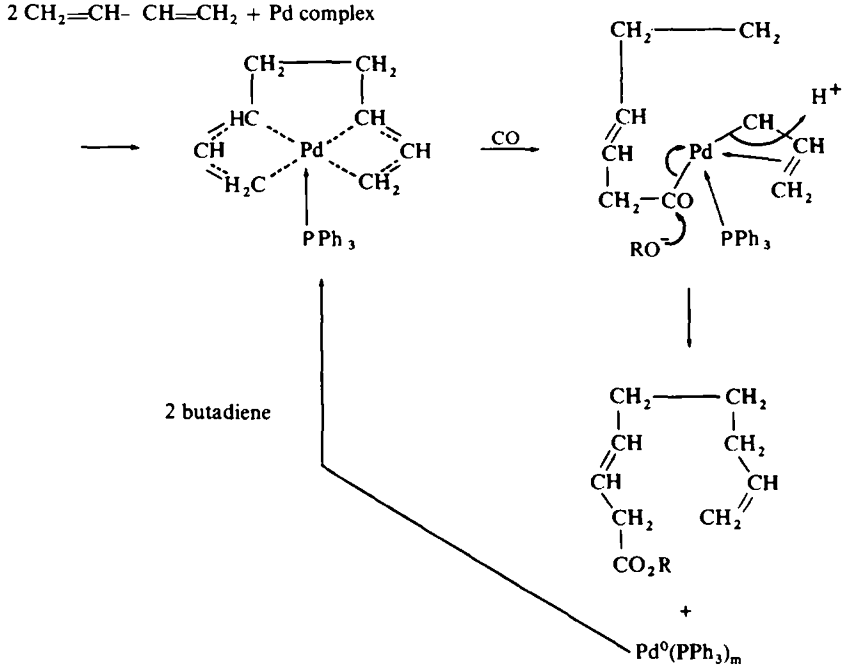
CO press (atm)	isopropyl 3,8-nonadienoate (g)
50	32·5
100	11·0
150	1·9

[a] Carried out with butadiene (20 g), i-PrOH (30 ml), $Pd(OAc)_2$ (0·30 g), PPh_3 (0·70 g) at 110° for 16 hr.

In connection with the reaction mechanism of the dimeric carbonylation, the following facts should be taken into consideration. It is well known that two moles of butadiene react with one mole of alcohol to give 2,7-octadienyl ether in the presence of a palladium complex of triphenylphosphine.[6] Also we have reported that various allylic ethers and alcohols are carbonylated with palladium catalyst to give βγ-unsaturated esters.[7] Based on these results, two mechanisms should be considered for the dimeric carbonylation of butadiene.

In one mechanism, at first butadiene and alcohol react to give 2,7-octadienyl ether and then the ether is carbonylated at the allylic position to give the 3,8-nonadienoate. However, this two step mechanism can be ruled out by the fact that an attempted carbonylation of ethyl 2,7-octadienyl ether with palladium acetate and triphenylphosphine did not proceed.

Another and more probable mechanism is as follows. Formation of a dimeric π-allylic complex from two moles of butadiene and the palladium complex is followed by carbon monoxide insertion at the allylic position to give an acyl palladium complex which then collapses to give the 3,8-nonadienoate by attack of the alcohol with regeneration of the palladium phosphine complex as shown below.



When chloride ion is coordinated to palladium, the formation of the above dimeric π-allylic complex is not possible, and only a monomeric π-allylic complex is formed. Then carbon monoxide insertion gives the 3-pentenoate.

EXPERIMENTAL

NMR spectra were determined on a Varian A-60 spectrometer in CCl_4 and are expressed in τ values. Molecular weight was determined by mass spectrometry. The carbonylation reaction was carried out in an autoclave with shaking. A typical example of the reaction is as follows.

A mixture of palladium acetate (0·30 g), triphenylphosphine (0·70 g) and isopropyl alcohol (30 ml) was placed in a 200 ml autoclave and then butadiene (20 g) and carbon monoxide (50 atm) were introduced. The autoclave was shaken at 110° for 16 hr. Distillation of the reaction product gave isopropyl 3,8-nonadienoate (32·5 g, b.p. 72–76°/1 mm).

Isopropyl 3,8-nonadienoate (Found: C, 73·54; H, 10·29; MW, 196. Calc. for $C_{12}H_{20}O_2$: C, 73·46; H, 10·20%; MW, 196). IR (cm^{-1}): 3085, 2990, 2930, 1736, 1645, 1110, 990, 966, 908. NMR: 3·86–4·60 (3H), 4·80–5·30 (3H), 7·08 (2H), 8·00 (4H), 8·50 (2H), 8·82 (6H).

Similarly, the following esters were obtained.

Ethyl 3,8-nonadienoate; b.p. 108–112°/18 mm (Found: C, 72·79; H, 10·01; MW, 182. Calc. for $C_{11}H_{18}O_2$: C, 72·52; H, 9·89%; MW, 182). IR (cm^{-1}): 3080, 2990, 2920, 1735, 1641, 1163, 992, 970, 912. NMR: 3·9–4·6 (3H), 4·7–5·2 (2H), 5·88 (2H), 7·02 (2H), 7·98 (4H), 8·43 (2H), 8·80 (3H).

t-Butyl 3,8-nonadienoate: b.p. 90–94°/1 mm. (Found: C, 74·09; H, 10·68; MW, 210. Calc. for $C_{13}H_{22}O_2$: C, 74·28; H, 10·48%; MW, 210). IR (cm^{-1}): 3080, 2990, 2930, 1735, 1642, 1150, 990, 968, 910. NMR: 3·9–4·55 (3H), 4·70–5·18 (2H), 7·10 (2H), 7·95 (4H), 8·40 (2H), 8·57 (9H).

Methyl 3,8-nonadienoate: b.p. 90–102°/18 mm. (Found: 71·57; H, 9·49. Calc. for $C_{10}H_{16}O_2$: C, 71·43; H, 9·52%).

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