

THE CARBONYLATION OF ACETYLENIC COMPOUNDS
CATALYZED BY PALLADIUM-BLACK

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Palladium-black is a highly active catalyst in the presence of hydrogen iodide in methanol for α -monocarbonylation of phenylacetylene, methylacetylene, and acetylene to give methyl atropate, methyl methacrylate, and methyl acrylate respectively. Triphenylphosphine or triphenylarsine added to the reaction mixture increases the selectivity to β -carbonylated products.

Palladium chloride is known to be a highly active catalyst for the trimerization and oligomerization of acetylenic compounds.¹⁾ In the presence of carbon monoxide in the reaction medium, however, a palladium-carbonyl complex which is active for carbonylation and dimerization of acetylenic compounds, but not active enough for their trimerization and oligomerization, seems to be formed, being responsible for the carbonylation of acetylenic compounds, e.g., acetylene to give maleate and fumarate in methanol²⁾ and also muconyl chloride in benzene,³⁾ diphenylacetylene to give α,β -diphenyl- γ -crotonolactone,⁴⁾ and acetylenic mono- and diesters to give several polycarboxylates.⁵⁾ True catalytic species in the reaction medium is not known. Tsuji et al. suggested that the characteristic of these palladium-catalyzed carbonylation was an extensive dicarbonylation, rather than monocarbonylation, and that the true catalyst of these carbonylation was metallic palladium and hydrogen chloride.

On the other hand, it was reported that the carbonylation of acetylene catalyzed by palladium salts in alcohol gave acrylates as the major product when a small amount of hydrogen iodide was added to the reaction mixture.⁶⁾ Tetrakis(triphenylphosphine)-palladium in a mixture of chloroform and alcohol reportedly gives acrylate from acetylene under a mild condition.⁷⁾ The selectivity to the monocarbonylation product from acetylene, however, seems to depend considerably on the reaction conditions. Fenton obtained methacrylic acid from the carbonylation of methylacetylene with the palladium dichloride-triphenylphosphine system in acetic acid,⁸⁾ though the yield was as low as 17 %.

In our preceding paper,⁹⁾ it was shown that palladium-black effectively catalyzes the arylation of olefins with iodobenzene (for example, $C_6H_5I + CH_2=CH_2 \rightarrow C_6H_5CH=CH_2 + HI$) and also the carbonylation of iodobenzene in methanol ($C_6H_5I + CO + CH_3OH \rightarrow C_6H_5COOCH_3 + HI$)¹⁰⁾ in the presence of a base such as potassium acetate or tertiary amine to accept the produced hydrogen iodide. In this letter, we wish to report that palladium-black is a highly active catalyst for the monocarbonylation of phenylacetylene, methylacetylene, and acetylene in the presence of hydrogen iodide in methanol to give methyl atropate, methyl methacrylate, and methyl acrylate respectively, and also the

Table 1. Effect of Halide

$C_6H_5C\equiv CH$ 60 mmol, MeOH 20 ml, Pd-black 0.5 mmol, P_{CO} 20 kg/cm² at room temp. and Time 2 hr.

run	Halide (mmol)	Temp. (°C)	Conv. (%)	Product mmol, (Select. %)				Residual CH_3I ^{d)} (%)
				Methyl atropate		Methyl cinnamate		
1	CH_3I 20	110	51	19.2	(63)	0.9	(2.9)	94
2	CH_3I 20	110	76	30	(66)	0.7	(1.5)	91
3	H_2O HI ^{a)} 10	60	85	39.8	(78)	0.7	(1.4)	71
4	HBr ^{b)} 10	60	22	5.8	(44)	0	(0)	—
5	HCl ^{c)} 10	60	13	1.3	(17)	0	(0)	—
6	HBr ^{b)} 10	60	90	37.4	(67)	0.7	(1.3)	91
7	NaI 20 HCl ^{c)} 10	60	88	37.7	(72)	0.9	(1.7)	89
8	NaI 20 AcOH 86	60	9.5	0.3	(1.3)	0	(0)	trace
9	NaI 20	60	8.5	trace	(—)	0	(0)	trace

a) 57 % HI aq. b) 47 % HBr aq. c) 35 % HCl aq. d) Based on CH_3I or HX employed.

effect of additives on the catalytic activity of palladium and the selectivity to monocarbonylation products.

Phenylacetylene (60 mmol), methanol (20 ml), palladium-black (0.5 mmol) and a given amount of halide (either methyl iodide, sodium iodide, or hydrogen halide) were placed in a titanium alloy autoclave (100 ml) equipped with a magnetic stirrer. Carbon monoxide was introduced up to 20 kg/cm² into the autoclave at room temperature. The autoclave was then heated up to the reaction temperature within 20 min. After a 2 hr run at constant temperature and pressure, the autoclave was rapidly cooled by water and carbon monoxide was purged out. The reaction product was analyzed by gas chromatography. The results are summarized in Table 1. No carbonylation was observed in the absence of halide. When water was added to methyl iodide, the yield of methyl atropate increased (run 2). This suggested that hydrogen iodide was supplied from the hydrolysis of methyl iodide. In fact, the addition of hydrogen iodide in place of methyl iodide increased the yield of methyl atropate even at lower temperature, although hydrogen iodide was almost quantitatively converted to methyl iodide after the reaction (run 3). The effectiveness of hydrogen halide decreased in the order $HI \gg HBr > HCl$ (run 3-5). Practically no reaction was observed when sodium iodide was added with or without acetic acid (run 8,9). However, when sodium iodide was added together with hydrogen bromide or hydrogen chloride (run 6,7), the yield of methyl atropate became almost the same as that obtained on the addition of hydrogen iodide (run 3). In these cases, methyl iodide was also detected after the reaction. Thus it is concluded that hydrogen iodide plays an essential role in this reaction to give methyl atropate.

On the other hand, when a catalytic amount of triphenylphosphine or triphenylarsine was added to this catalyst system, the yield of methyl atropate decreased and that of methyl cinnamate increased as shown in Table 2. The conversion of phenylacetylene slightly increased at high temperature (100 °C or 110 °C) by adding triphenyl-

Table 2. Effect of Triphenylphosphine or Triphenylarsine

$C_6H_5C\equiv CH$ 60 mmol, MeOH 20 ml, Pd-black 0.5 mmol, P_{CO} 20 kg/cm² at room temp., and Time 2 hr.

Additives (mmol)	HI (mmol)	Temp. (°C)	Conv. (%)	Product mmol (Select. %)			
				Methyl atropate		Methyl cinnamate	
—	1	110	40	14.8	(62)	0.3	(1.3)
$P\phi_3$	1	110	53	3.5	(11)	6.3	(20)
$P\phi_3$	3	110	55	9.9	(30)	8.4	(25)
$As\phi_3$	1	100	51	14.5	(47)	8.1	(26)
$As\phi_3$	3	100	61	13.2	(37)	12.7	(35)
—	10	60	85	39.8	(78)	0.7	(1.4)
$P\phi_3$	1	60	54	17.9	(56)	7.7	(24)
$P\phi_3$	3	60	39	3.8	(16)	7.4	(32)
$As\phi_3$	1	60	9.0	trace	(—)	trace	(—)
$As\phi_3$	3	60	7.0	trace	(—)	0	(0)

ϕ = phenyl

Table 3. Carbonylation of Methylacetylene and Acetylene

HI 10 mmol, MeOH 20 ml, Pd-black 0.5 mmol, P_{CO} 15 kg/cm² at room temp., and Time 2 hr.

Acetylenic Compounds (mmol)	Temp. (°C)	Conv. (%)	Product mmol (Select. %)			
			MMA		MC	
Methylacetylene	90	80	30.9	(48)	3.7	(5.7)
Methylacetylene	90	55	20.5	(91)	2.1	(9.0)
Acetylene	53	80	13.3	(40)		
Acetylene	56	55	12.2	(52)		

MMA = Methyl methacrylate, MC = Methyl crotonate, MA = Methyl acrylate.

phosphine or triphenylarsine, while considerably decreased at low temperature (60 °C).

The carbonylation of acetylene and methylacetylene was also examined. Palladium-black (0.5 mmol), hydrogen iodide (10 mmol), and methanol (20 ml) were placed in the autoclave. The autoclave was then cooled by Dry ice-methanol bath and a given amount of acetylene or methylacetylene was introduced in the autoclave from a gas burette (1000 ml). Carbon monoxide was introduced up to 15 kg/cm² at room temperature. The procedure for the reaction was the same as for phenylacetylene. The gaseous materials were discharged through two traps containing acetone (40 ml and 20 ml) cooled with Dry ice-methanol. The trapped and liquid materials were analyzed by gas chromatography. The results are summarized in Table 3. Methylacetylene gave almost exclusively methyl methacrylate at lower temperature. Acetylene also gave monocarbonylation product predominantly, no dicarbonylation product being detected.

The above-mentioned carbonylation can be carried out under milder conditions. Recovery of the palladium catalyst seems to be easy, since most of palladium is present in the form of palladium-black in the reaction mixture. These results suggest that the carbonylation of methylacetylene catalyzed by palladium-black in the presence of hydrogen iodide can be a useful synthetic procedure for methyl methacrylate.

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