

Carboxylation of 1-Hexyne Catalyzed by Bis(triarylphosphine)nickel Dibromide

Yasumasa SAKAKIBARA, Tadashi OKAMOTO
and Hiroshi KURAUCHI*

(Kunichika Laboratory)

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The carboxylation of 1-hexyne with carbon monoxide was tried using bis(triarylphosphine)nickel dibromide catalysts, $\left[\left(\text{X}-\langle\text{C}_6\text{H}_4\rangle\text{P}\right)_2\right]_2\cdot\text{NiBr}_2$, to investigate the effects of substituent X (X=H, CH₃, OCH₃) and reaction conditions on reaction rate.

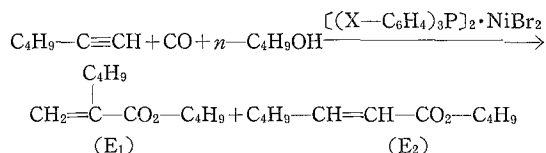
Reaction rate was promoted with an increase in the electron-donating power of X (H: CH₃:CH₃O=1.0:1.7:3.3). In the most effective catalyst of bis(trianisylphosphine)nickel dibromide, the maximum rate was obtained under 5 atm. of carbon monoxide, and the reaction rate was proportional to the first order of concentration of hexyne and catalyst, and was about 1.8 times faster at 200° than at 190°.

The maximum total yield of acrylic esters was 76.6%, and the product ratio of butyl α -butylacrylate to butyl β -butylacrylate was about 5:1.

INTRODUCTION

For the synthesis of acrylates by the carboxylation of acetylenic compounds, it is well known that two types of catalyst, namely, metal carbonyls and nickel halide complexes, are used and that the formers are especially popular.

The present authors reported already on the synthesis of methyl methacrylate from methylacetylene¹⁾ and allene²⁾, respectively, by catalytic reaction of nickel carbonyl under pressure of carbon monoxide. However, on the carboxylation by the second type of the catalysts, only a few literatures³⁾ have been published and the reaction mechanism is not clear. The authors, therefore, tried the carboxylation of 1-hexyne by catalytic reaction of nickel halide complexes, bis-(triarylphosphine)nickel dibromides $\left[\left(\text{X}-\langle\text{C}_6\text{H}_4\rangle\text{P}\right)_2\right]_2\cdot\text{NiBr}_2$ (X=H, CH₃, OCH₃).



On next items our attention was concentrated:

- (1) Effects of different substituent X and of reaction conditions on the reaction rate.
- (2) Comparison of the reaction rate in case of nickel carbonyl and that in the phosphine nickel complexes.

* 榑原 保正, 岡本 忠, 倉内 浩

As the starting materials, 1-hexyne and *n*-butanol were used in considering that their lower vapor pressure gives an easy and accurate measurement of absorbed amount of carbon monoxide.

EXPERIMENTAL

1) Materials

Hexyne-1 was prepared according to the ordinary method⁴⁾; b.p. 71~72°, n_D^{20} 1.3989. The purity was shown to be 99.5% by gas chromatography.

Carbon monoxide (99.7 mol.% pure) was purchased from the Takachiho Chemical Co.

Triarylphosphines. The three kinds of triarylphosphines ($(X-\text{C}_6\text{H}_4)_3\text{P}$; (X=H, CH₃; CH₃O) were prepared from the corresponding arylmagnesium bromides and phosphorous trichloride, respectively⁵⁻⁷⁾.

$(X-\text{C}_6\text{H}_4)_3\text{P}$	m.p. (°C)	Anal.			
		Calcd.		Found	
		C	H	C	H
X=H	79 (lit. 78~79) ⁶⁾	82.40	5.72	82.33	5.76
CH ₃	145 (lit. 146~147) ^{5,6)}	82.90	7.01	82.80	7.04
CH ₃ O	131 (lit. 131~132) ⁷⁾	71.60	6.02	71.28	5.98

Bis(triarylphosphine)nickel dibromides. The three kinds of bis(triarylphosphine)nickel dibromides were prepared by heating the mixture of 0.04 mole of the corresponding phosphines and 0.02 mole of nickel dibromide in 100 ml. of *n*-butanol.

$[(X-\text{C}_6\text{H}_4)_3\text{P}]_2 \cdot \text{NiBr}_2$	m.p. (°C)	Anal.			
		Calcd.		Found	
		C	H	C	H
X=H	222~4 (lit. 221~3) ^{3b,9)}	58.21	4.04	58.57	4.07
CH ₃	236~8 (lit. 236~8) ⁹⁾	60.97	5.11	60.63	5.35
CH ₃ O	185~7 (lit. 185~7) ⁹⁾	54.20	4.55	53.89	4.49

2) Apparatus and Procedure

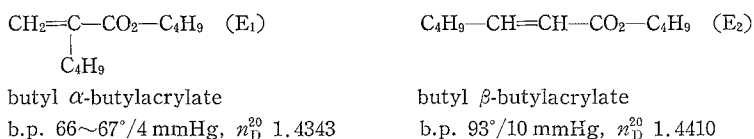
a) **Experiments with triarylphosphine complex catalysts.** In a 200 ml. magnet-rotating-type autoclave, *n*-butanol (50 ml.), hydroquinone (0.1 g.) and the specified amount of catalyst were put and air was swept away by nitrogen, and carbon monoxide was charged to the specified pressure. The vessel was heated, and when the temperature reached the reaction temperature, weighed amount of 1-hexyne was added by means of a pressure injection pump in a breath. Reaction pressure was kept at constant by continuous supply of carbon monoxide from a 120 ml. storage tank.

b) **Experiments with nickel carbonyl catalyst.** They were made almost similarly with the above case, except that the expelling of air was done at -50°.

3) Analytical Method

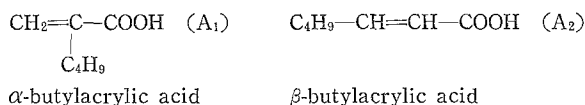
To confirm the components of the product by means of gas chromatography, the following presumable reagents were synthesized authentically.

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Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_2$: C, 71.69; H, 10.94

Found: C, 71.81; H, 11.08 (E_1), Found: C, 71.12; H, 10.94 (E_2).



E_1 and E_2 were determined gas-chromatographically using a 2 m. column of 30% silicone DC 703 on celite 545 at 150°, with a flow speed of 80 ml./min. of hydrogen as a carrier gas. Benzyl propionate was selected as the internal standard. The retention times of E_1 , E_2 , and benzyl propionate were 7.9, 14.8, and 12.5 min., respectively.

A_1 and A_2 were analyzed by a combination of a titration using 0.05 *N* sodium hydroxide solution and gas chromatography under the same conditions with those in the analysis of the esters.

Unreacted 1-hexyne was determined gas-chromatographically by a 2.5 m. column of 30% DOP at 100° with 40 ml./min. of hydrogen, using benzene as the internal standard. The retention times of 1-hexyne, benzene, and *n*-butanol were 4.1, 6.6, and 9.9 min., respectively.

Nickel carbonyl in the reaction mixture was driven off with nitrogen into a mixed solution of bromine, carbon tetrachloride and water, and was determined by the nickel dimethylglyoxime method.

RESULTS AND DISCUSSION

The main product is butyl α -butylacrylate and the main by-product is butyl β -butylacrylate. The ratio of these esters was about 4.5~5:1 in all cases.

Reaction rate was calculated from the initial absorption amount of carbon monoxide observed by pressure drop of the storage tank.

The results obtained with bis(triarylphosphine)nickel dibromides are listed respectively in Table 1 and, for comparison, in Table 2 those by nickel carbonyl catalyst.

1) Reaction Rate

a) **Effect of substituent on reaction rate.** The results are shown in Fig. 1. The reaction rate varied in the different substituent X in $\left[\left(\text{X}-\langle \text{C}_6\text{H}_4 \rangle \right)_3\text{P} \right]_2 \cdot \text{NiBr}_2$ as follows:

X	Initial rate %/min.	Relative rate
H	0.90	1
CH_3	1.5	1.7
CH_3O	3.0	3.3

This result corresponds with the order of increase in electron donating power

Table 1. Reaction by $\left[\left(\text{X}-\langle\text{C}_6\text{H}_4\rangle\text{P}\right)_2\text{NiBr}_2\right]$ catalyst.
 Autoclave 200 ml.; *n*-butanol 50 ml.; hydroquinone 0.1 g.

Run No.	Hexyne (g.)	Catalyst (g.)	CO		React. temp. ^{b)} (°C)	React. time (hr.)	Unreacted hexyne (g.)	Ni(CO) ₄ formed (g.)	Product ^{c)}	
			Initial (atm.)	Absorbed ^{a)} (%)					E ₁ (g.)(%)	E ₂ (g.)(%)
		X=H								
1	6.0	1.7	5	39.1	190	3.0	trace	trace	3.21(23.8)	0.76(5.6)
2	6.0	1.7	10	70.1	190	5.0	trace	0.048	4.58(34.0)	1.05(7.8)
3	6.0	1.7	15	62.5	190	8.0	0.68	0.058	5.52(41.0)	1.54(11.5)
4	6.0	1.7	10	47.6	210	6.0	—	0.024	3.37(25.0)	0.95(7.1)
		X=CH ₃								
5	6.0	1.9	5	54.6	190	5.0	trace	trace	3.48(25.9)	1.04(7.8)
6	6.0	1.9	10	76.6	190	4.5	trace	0.018	6.01(44.6)	1.87(14.0)
7	6.0	1.9	15	72.0	190	6.0	0.53	0.088	7.15(53.2)	1.81(13.5)
8	6.0	1.9	10	60.0	210	5.0	0.55	0.021	5.09(37.8)	0.86(6.4)
		X=OCH ₃								
9	6.0	2.1	2	59.1	190	2.0	0.22	trace	2.72(20.2)	0.75(5.6)
10	6.0	2.1	5	58.0	190	2.5	trace	0.034	4.81(35.8)	1.06(7.9)
11	6.0	2.1	10	76.5	190	4.0	0.23	0.210	6.05(45.0)	1.47(10.9)
12	6.0	2.1	15	78.5	190	5.5	0.28	0.140	6.57(48.8)	1.37(10.2)
13	6.0	2.1	10	75.0	180	7.0	0.15	0.100	7.62(56.6)	1.46(10.8)
14	6.0	2.1	10	79.8	200	1.5	0.45	0.100	9.05(67.3)	1.25(9.3)
15	9.0	2.1	10	70.6	190	3.0	0.25	0.061	9.10(45.0)	2.36(11.7)
16	12.0	2.1	10	74.0	190	4.0	0.27	0.160	11.10(41.2)	2.56(9.5)
17	15.0	2.1	10	60.4	190	5.0	0.33	0.046	12.20(33.3)	2.56(7.6)
18	6.0	1.0	10	70.9	190	6.0	trace	0.034	5.80(43.1)	1.42(10.5)
19	6.0	1.6	10	75.4	190	4.0	0.25	—	7.05(52.5)	1.53(11.4)
20	6.0	3.0	10	75.0	190	2.5	0.35	0.130	6.85(50.9)	1.41(10.5)

- a) Absorbed amount of CO indicates percentage for hexyne used.
 b) Reaction temp. was controlled within $\pm 1^\circ$.
 c) The values in parentheses show the theoretical yield for hexyne used.
 E₁ butyl α -butylacrylate; E₂ butyl β -butylacrylate.

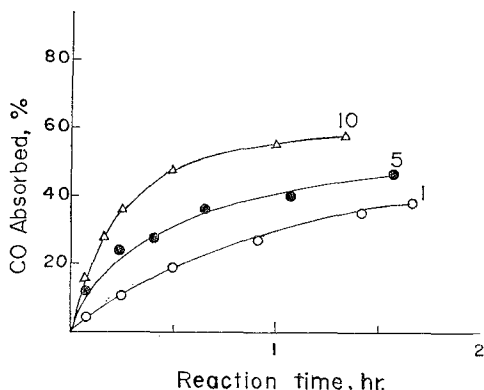


Fig. 1. Effect of substituent on reaction rate. Hexyne, 6 g.; CO, 5 atm.; temp., 190°C
 ○: X=H; ●: CH₃; △: CH₃O (Curve number corresponds with Run No. in Tables.)

of the substituent X and it is considered that the effect of substituent on reaction rate is due to the increase of electron density on the phosphorus atom. In the cases of X=H and X=CH₃, the reaction was not initiated at 180°, but in the case of X=OCH₃, the reaction proceeded considerably at that temperature, as shown in Fig. 2.

Hereafter, therefore, the authors investigated the effect of reaction conditions by this X=OCH₃ catalyst.

b) **Effect of reaction temperature.** Using fixed amounts of 1-hexyne and the catalyst, and charging a constant initial pressure of carbon monoxide (10 atm. at room temperature), the reaction was performed at 180°, 190°, and 200°, respectively. The results are shown in Fig. 2, and the relative initial reaction rates are as follows: 180°:190°:200°=1:2:3.6.

c) **Effect of carbon monoxide pressure.** Under the same conditions, only

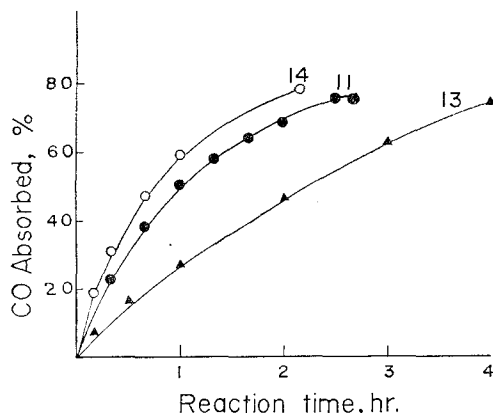


Fig. 2. Effect of reaction temperature. Hexyne, 6 g.; CO, 10 atm.; catalyst (X=CH₃O), 2.1 g.
 ○: 200°C; ●: 190°C; ▲: 180°C

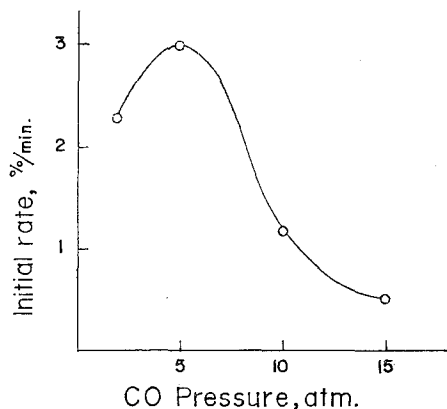


Fig. 3. Effect of pressure of carbon monoxide. Hexyne, 6.0 g.; catalyst (X=CH₃O), 2.1 g.; temp., 190°C

varying the pressure of carbon monoxide, the reaction was tried and the results are shown in Fig. 3 (Run Nos. 9, 10, 11, and 12 in Table 1).

In Fig. 3, the maximum rate was obtained at about 5 atm. (Run No. 10). The existence of the maximum rate suggests that a true catalyst for the carboxylation, supposed to be $\text{LNiH}(\text{CO})^{**}$, may be converted partly into low active species, $\text{L}'\text{NiH}(\text{CO})_2$ or $\text{L}'\text{Ni}(\text{CO})_2$ (?), under higher pressure of carbon monoxide. Further studies are desired on these problems.

d) **Effect of concentration of 1-hexyne.** The reaction rate was observed varying the concentration of 1-hexyne. Fig. 4 shows the results.

To 12 g. of 1-hexyne, the rate was almost proportional to the first order of 1-hexyne concentration, but it decreased above that value. In the case of higher concentration of 1-hexyne, the yield of esters was lower and polymeric substance was found. Perhaps side reactions such as polymerization would proceed competitively.

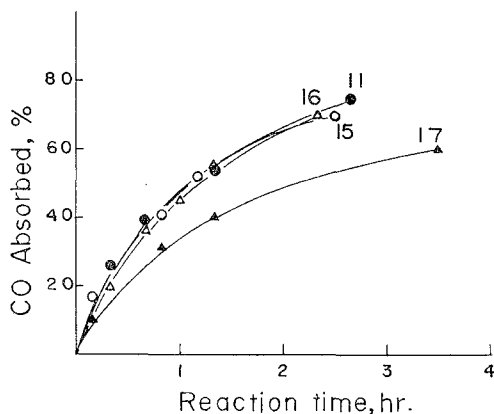


Fig. 4. Effect of hexyne concentration.
CO, 10 atm., catalyst ($\text{X}=\text{CH}_3\text{O}$), 2.1 g.; temp.,
190°C
Hexyne ●: 6.0; ○: 9.0; △: 12.0; ▲: 15.0g.

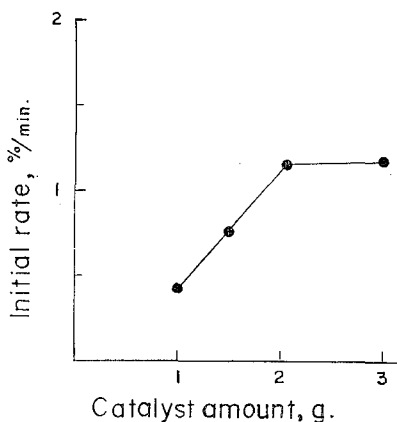


Fig. 5. Effect of catalyst concentration.
Hexyne, 6 g.; CO, 10 atm.; temp.,
190°C

e) **Effect of catalyst concentration.** The results are shown in Fig. 5.

To 2.1 g. of the catalyst, the rate was proportional to the first order of catalyst concentration (Run Nos. 18, 19, 11, and 20 in Table 1), but no effect was found above the amount. The authors tried blank test as follows: in a sealed glass tube, each 1/50 amount of 1-hexyne, *n*-butanol, and the catalyst in Run Nos. 19, 11, and 20 in Table 1 were put and heated at 190° in silicon oil bath for about 4 hours under stirring. In the cases of the former two runs, the catalyst was dissolved and a clear solution was obtained, but in the last case the catalyst was not dissolved completely. This fact would explain the result for higher amounts

** L and L' show ligands such as phosphine and bromine. In the 152nd Annual Meeting of the American Chemical Society, New York, September, 1966, and private communications, Dr. Bailar *et al.* indicated that bis(triphenylphosphine)nickel halides are hydrogenation catalysts which can utilize alcohol as hydrogen source and that the complexes appear to act as the hydrido form. RH^* (R=catalyst).

Table 2. Reaction by nickel carbonyl catalyst.

Autoclave 200 ml.; hexyne 6.0 g.; *n*-butanol 50 ml.; nickel carbonyl 2.0 g.; hydroquinone 0.1 g.

Run No.	Co-catalyst		CO		React. temp. (°C)	React. time (hr.)	Unreacted hexyne (g.)	Ni(CO) ₄ decomp. (g.)	Catalytic level ^{b)} (%)	Product ^{c)}			
	AcOH (g.)	H ₂ O (g.)	Initial (atm.)	Absorbed ^{a)} (%)						A ₁ (g.)(%)	A ₂ (g.)(%)	E ₁ (g.)(%)	E ₂ (g.)(%)
21	3	2	10	91.8	150(+1)	2.2	0	trace	98.8	5.17(55.1)	0.59(6.2)	2.90(21.6)	0.92(6.8)
22	3	2	15	82.6	150(±1)	4.5	0	trace	92.6	3.28(35.1)	1.10(11.7)	4.73(35.1)	1.13(8.4)
23	3	—	10	77.2	150(±1)	5.5	0	trace	94.0	1.58(16.9)	trace	6.15(45.7)	1.39(10.3)
24	3	2	5	—	150(±1)	2.0	—	1.8	—	—	—	—	—

a) Absorbed amount of CO indicates percentage for hexyne used.

b) Catalytic level means : $\frac{\text{free CO}}{\text{free CO} + \text{CO from Ni(CO)}_4} \times 100$.

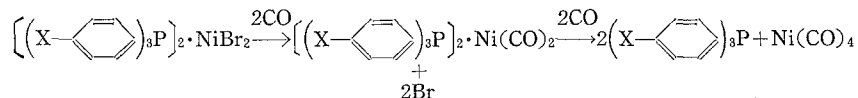
c) The values in parentheses show the theoretical yield for hexyne used.

A₁ CH₂=C—COOH; A₂ C₄H₉—CH=CH—COOH.
$$\begin{array}{c} | \\ \text{C}_4\text{H}_9 \end{array}$$

of the catalyst, shown in Fig. 5.

2) Stability of Catalyst

As X was varied to H, CH₃, OCH₃, the reaction rate increased as mentioned above, and the amount of nickel carbonyl (cited in Table 1), produced by side reaction, increased with the same order (for example, Run Nos. 3, 7, and 12). Of course, nickel carbonyl is an unstable catalyst and triarylphosphine nickel complexes also are considerably unstable, though the latter are much more stable than the former. The formation of nickel carbonyl from triarylphosphine nickel halide complexes is supposed to be made according to the following route,



though it is uncertain.

3) Catalytic Carboxylation by Nickel Carbonyl

For comparison with triarylphosphine nickel halide complexes, the results obtained by nickel carbonyl are listed in Table 2 and Fig. 6.

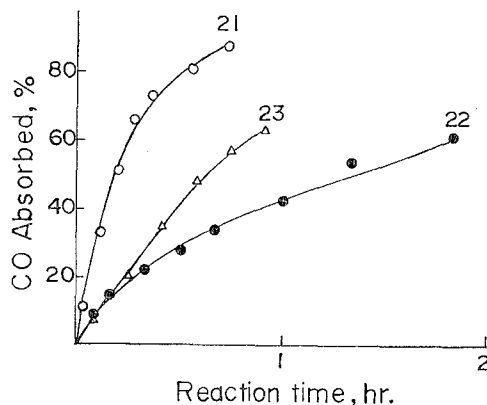


Fig. 6. Carboxylation by nickel carbonyl.
 Curve number corresponds with Run No. in Table 2.
 Hexyne, 6 g.; nickel carbonyl, 2 g.; temp., 150°C
 ○; CO, 10 atm.; co-catalyst AcOH+H₂O
 ●; CO, 15 atm.; co-catalyst AcOH+H₂O
 △; CO, 10 atm.; co-catalyst AcOH

In this case the effect of carbon monoxide pressure might be the most serious factor, as shown in the catalytic carboxylation of methylacetylene by nickel carbonyl¹⁾. Here, this effect was examined mainly.

As shown in Table 2, under 5 atm. partial pressure of carbon monoxide, the absorption of carbon monoxide was not observed almost at all and the most part of nickel carbonyl decomposed owing to violent reaction (Run No. 24). At 10 atm. of carbon monoxide the initial absorption rate was about 2.5 times that at 15 atm. (Run Nos. 21 and 22).

These results indicate that carbon monoxide pressure acts a very effective

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roll in this case. Moreover, there are some differences between these two kinds of catalysts, as follows:

a) In the case of nickel carbonyl, the presence of co-catalyst such as water and acetic acid was necessary for the carboxylation¹⁾. In cases of the catalysts of the triarylphosphine complex series, the conditions are different completely.

b) In nickel carbonyl catalyst, it is fairly difficult to allow the catalytic reaction to proceed smoothly under low carbon monoxide pressure, owing to the instability of nickel carbonyl, while the catalysts of the phosphine complex series were fairly stable and used easily even under a low pressure of 2 atm.

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