The Cobalt Carbonyl-catalyzed Hydroesterification of Butadiene with Carbon Monoxide and Methanol

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The cobalt carbonyl-catalyzed hydromethoxycarbonylation of butadiene is studied. The reaction proceeds in the presence of a pyridine base to give methyl 3-pentenoate. Isoquinoline is found to be a better solvent for the production of methyl 3-pentenoate than pyridine, not only because the yield of the ester is somewhat higher in the presence of isoquinoline than in the presence of pyridine, but also because it is far less volatile than pyridine, so that the product can be easily separated from the solvent and the catalyst by distillation. Also, the hydromethoxycarbonylation of methyl 3-pentenoate under somewhat different conditions is found to give a good yield of dimethyl adipate. The hydroformylation of methyl 3-pentenoate is studied as well. The effect of such a solvent as THF, benzene, and acetonitrile in increasing the selectivity to methyl 5-formylpentanoate is found to increase in this order: acetonitrile$<$benzene$<$THF.

In the first paper of this series it was reported that the initial rate of the cobalt carbonyl-catalyzed hydroesterification of propylene was remarkably promoted by the presence of a small amount of hydrogen and an excess of pyridine.[1] In a following paper concerning the hydroesterification of acrylonitrile, the reaction mechanism was discussed on the bases of the kinetic results and the IR study of the reaction intermediates.[2]

The present investigation will deal with the hydroesterification of butadiene. The results varied in some respects from those of previous studies which dealt only with mono-olefins.[1,2] For example, in the hydroesterification of mono-olefins, hydrogen added in the synthesis gas played a significant role in accelerating the reaction.[1,2] However, in the present hydroesterification of butadiene, hydrogen exerted essentially no effect on the reaction rate. On the other hand, the effect of pyridine on the hydroesterification of butadiene was remarkable in that both the reaction rate and the selectivity to methyl 3-pentenoate steadily increased with an increase in the concentration of pyridine. The inhibition by a large excess of pyridine which is usually observed in the case of mono-olefins[1,2] did not appear at all in this experiment. The reaction proceeded in pyridine at a relatively low temperature (100—140°C), and methyl 3-pentenoate was selectively produced.

It has already been found by Imyanitov et al. that the hydrocarboxylation of butadiene also proceeded in the presence of pyridine to give 3-pentenoic acid.[3] They also reported the results of their hydroesterification of butadiene in the presence of pyridine;[4] they carried out the reaction at a higher temperature (210 °C), and obtained a mixture of unsaturated and saturated mono esters and saturated diesters. On the other hand, in the present investigation a better method for the selective production of methyl 3-pentenoate by the hydroesterification of butadiene was explored. As a result, it was found that isoquinoline was a better solvent than pyridine for this purpose, not only because the yield of methyl 3-pentenoate was somewhat improved when the reaction was carried out in the presence of isoquinoline instead of pyridine, but also because isoquinoline (bp 240°C) is less volatile than pyridine (bp 115°C), so methyl 3-pentenoate can be easily removed from the reaction mixture by vacuum distillation at a low temperature, the catalyst and isoquinoline being left as a residue.

The hydroesterification and the hydroformylation of the resulting methyl 3-pentenoate to give the corresponding diesters and formyl esters were also examined.

Experimental

Such reagents as butadiene, carbon monoxide, methanol, and pyridine were obtained commercially. The butadiene was 99% pure. The carbon monoxide was 99.5% pure, containing 0.018% hydrogen. The amount of butadiene remaining in the gas phase after the reaction was analyzed by passing the gas through methanol cooled by dry ice, followed by the gas-chromatographical analysis of the methanol solution. The amount of the dissolved butadiene and that of each product in the liquid product were also gas-chromatographically analyzed. The gas-chromatographical analyses were performed with a 9-m column of propyleneglycol–adipic acid polyester at the column temperature of 150°C (2-ethylhexyl acetate was added as an internal standard when necessary). Standard samples for the gas-chromatographical analyses were prepared as follows. Dimethyl adipate, methyl *n*-pentanoate, and methyl 4-pentenoate were prepared by the esterification of commercially-obtained adipic acid, *n*-pentanoic acid, and 4-pentenoic acid with methanol. The others were prepared by the distillation of the reaction products with a rectifier of the spinning-band type, followed by separation with a preparative gas-chromatograph (Perkin-Elmer F-21). These samples were identified by means of their IR and NMR spectra.

Methyl 3-Pentenoate: IR spectrum: C=O (ester) 1744 cm^{-1}, NMR spectrum: CH_3 τ 8.33, CH_2 τ 7.05, OCH_3 τ 6.40 (singlet), CH τ 4.50 (the NMR spectrum was complex because the sample was a mixture of *cis*- and *trans*-forms)

Methyl 2-Pentenoate: IR spectrum: C=O (ester) 1730 cm^{-1}, C=C (conjugated with C=O) 1662 cm^{-1}. NMR spectrum: CH_3 τ 8.88 (triplet), CH_2 τ 7.76 (quintet), OCH_3 τ 6.34 (singlet), CH($-COOCH_3$) τ 4.27 (sextet), CH($-CH_2$) τ 3.07 (sextet)

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[1] A. Matsuda and H. Uchida, This Bulletin, **38**, 710 (1965)

[2] A. Matsuda, *ibid.*, **40**, 135 (1967).

[3] N. S. Imyanitov and D. M. Rudkovskii, *J. Applied Chemistry of USSR* (English translation), **41**, 157 (1968).

[4] N. S. Imyanitov and D. M. Rudkovskii, *Zh. Prikl. Khim.*, **39**, 2335 (1966).

Dimethyl α-Methylglutarate: IR spectrum: C=O (ester) 1742 cm^{-1}. NMR spectrum: CH_3 τ 8.83 (doublet), CH_2-(-CH) τ 8.19 (quintet), CH_2 (-$COOCH_3$) τ 7.73 (triplet), CH τ 7.45—7.8 (multiplet), OCH_3 τ 6.38, 6.40.

Dimethyl Ethylsuccinate: IR spectrum: C=O (ester) 1740 cm^{-1}. NMR spectrum: CH_3 τ 9.06 (triplet), CH_2(-CH_3) τ 8.39 (quintet), CH(-$COOCH_3$) τ 7.35—7.75 (multiplet), CH_2(-$COOCH_3$) τ 7.35 (doublet), OCH_3 τ 6.36, 6.38.

Methyl 5-Formylpentanoate: IR spectrum: C=O (ester and aldehyde) 1720—1740 cm^{-1}. NMR spectrum: CH_2CH_2 (-CH_2COOCH_3) τ 8.2—8.4 (overlapped multiplet), CH_2-(-$COOCH_3$), CH_2(-CHO) τ 7.4—7.8 (overlapped multiplet), OCH_3 τ 6.37 (singlet), CHO τ 0.23 (triplet). The structure of this compound was further confirmed by its oxidation with air, followed by esterification with methanol into dimethyl adipate.

Methyl 4-Formylpentanoate: IR spectrum: C=O (ester and aldehyde) 1740, 1710 cm^{-1}. NMR spectrum: CH_3(-CH-CHO) τ 8.88 (doublet), CH_2(-CH_2COOCH_3) τ 7.9—8.5 (multiplet), CH_2(-$COOCH_3$) τ 7.67 (triplet), CH(-CHO) τ 7.5—7.9 (overlapped multiplet), OCH_3 τ 6.39 (singlet), CHO τ 0.39 (doublet). The structure of this compound was further confirmed by its oxidation with air and by its subsequent esterification with methanol into dimethyl α-methylglutarate.

Methyl 3-Formylpentanoate: IR spectrum: C=O (ester and aldehyde) 1740, 1710 cm^{-1}. NMR spectrum: CH_3(-CH_2) τ 9.02 (triplet), CH_2(-CH_3) τ 8.1—8.6 (multiplet), $CHCH_2$-(-$COOCH_3$) τ 7.2—7.8 (multiplet), OCH_3 τ 6.40 (singlet). CHO τ 0.35. The structure of this compound was further confirmed by its oxidation with air and by its subsequent esterification with methanol into dimethyl ethylsuccinate.

The reactions were carried out with a 300-ml (or a 100-ml) stainless steel autoclave. The catalyst, $Co_2(CO)_8$, was put into a small Teflon cup and placed on a wing of the stirrer so that the reaction would not start until the stirring (an up-and-down motion) began. For the measurement of the initial rate, a small portion of the reaction mixture was withdrawn a short, definite time after the stirring began; this portion was gas chromatographically analyzed with the aid of an internal standard (methyl benzoate or benzonitrile) which had been added to the reaction mixture before the reaction.[5]

The effect of bases was examined by carrying out the reaction in the presence of various bases. In control experiments carried out in the absence of a base (in toluene or acetonitrile), the reaction products were confirmed, by the measurement of the IR spectra, not to contain any carbonylated product (there was an absence of absorption at 1700—1800 cm^{-1}). The effect of the pyridine concentration was examined by varying the concentration of pyridine in a solvent mixture (acetonitrile plus pyridine) from zero to 100%.

The methyl 3-pentenoate for the hydroesterification and hydroformylation experiments was continuously produced by the hydroesterification of butadiene, using isoquinoline as the solvent. A solution consisting of 5.4 g of $Co_2(CO)_8$, 8.6 g of methanol, and 34 g of isoquinoline was pumped into a 100 ml stainless steel autoclave, and the autoclave brought to the condition of 130°C and 300 kg/cm^2 by heating and by introducing carbon monoxide from a pressure reservoir; the stirrer was started, and then butadiene was continuously fed from the bottom of the autoclave at a rate of 0.05 mol/hr, the carbon monoxide being supplied from the pressure reservoir to keep the pressure constant. Three hours after the start of the reaction, the reaction was interrupted and reaction mixture was totally withdrawn from the bottom of the autoclave through a cooling tube. The volatile components including methyl 3-pentenoate were then separated from the reaction mixture by vacuum distillation at a low temperature (below 50°C), while an isoquinoline solution of cobalt carbonyl was recovered as a residue. This recovered isoquinoline solution of cobalt carbonyl was catalytically active, and was used again in the next run. The effect of recycling the catalyst solution is illustrated in Table 1.

TABLE 1. THE EFFECT OF RECYCLING THE CATALYST SOLUTION

Exp. No.	Conversion of butadiene (%)	Selectivity (%)[a] M3P	VC
1	92	87	8.7
2	94	89	11
3	85	88	12
4	90	89	11
5	81	86	8.2

a) *cf.* Table 3.

Results

The Addition of Bases. The effectiveness of bases in increasing the yield of methyl 3-pentenoate decreased in this order: γ-picoline>isoquinoline>pyridine>3,4-lutidine>β-picoline>4-vinylpyridine>α-picoline, quinoline, 4-cyanopyridine>triethylamine (Table 2). Triethylamine was almost ineffective. In the absence of pyridine bases, methyl 3-pentenoate was not produced, while only the conversion of bu-

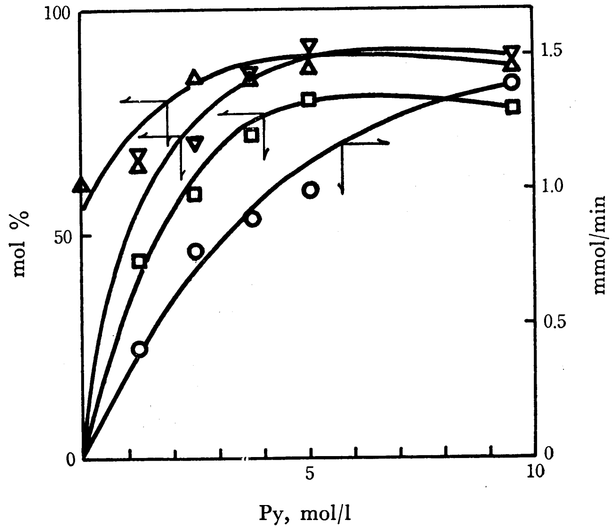

Fig. 1. The effect of the pyridine concentration.
—○—: Initial rate (mmol/min)
—△—: Conversion of butadiene (%)
—□—: Yield of methyl 3-pentenoate (%)
—▽—: Selectivity to methyl 3-pentenoate (%)
The abscissa is expressed in terms of the concentration at room temperature in 50 ml solution containing methanol (8 g), methyl benzoate (1 g), pyridine and acetonitrile. Experimental methods are same as described in Table 2.

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[5] The use of 2-ethylhexyl acetate as an internal standard was avoided, since it can undergo transesterification with methanol under the reaction condition. The effect of the addition of a small amount of methylbenzoate (or benzonitrile) on the results of the reaction was negligible.

Table 2. The effect of the added bases on the hydroesterification of butadiene
methanol (8 g), methyl benzoate (1 g), base (10 g), diluted with acetonitrile to 50 ml (room temp.); 0.1 mol butadiene, 4 mmol $Co_2(CO)_8$; reaction temp. 140°C, pressure (constant) 300 kg/cm², reaction time 3 hr

%	Initial rate[a] (mmol/min)	Conversion (%)	methyl 3-pentenoate	
			Yield (%)	Selectivity (%)
None	0	61	0	0
Pyridine	0.77	85	59	70
γ-Picoline	0.67	90	77	86
Isoquinoline	0.60	89	65	73
3,4-Lutidine	0.44	76	56	74
β-Picoline	0.34	83	45	54
4-Vinylpyridine	0.20	74	37	50
α-Picoline	0.13	53	4.7	8.9
Quinoline	0.075	56	4.6	8.2
4-Cyanopyridine	0.035	—	5.0	5.0
Triethylamine	—	31	0.3	1.0

a) The initial rate was calculated from the analysis of a sample withdrawn 10 min after the reaction started.

Table 3. The effect of pressure (I)
0.25 mol methanol, 1 g benzonitrile, 0.48 mol pyridine, 0.1 mol butadiene, 4 mmol $Co_2(CO)_8$; reaction temp. 100°C, reaction time 18 hr; in 300 ml autoclave.

Pressure (constant)	Initial rate[a] (mmol/min)	Conversion (%)	Selectivity (%)[b]	
			M3P	VC
100	0.029	33	87	13
150	0.065	63	94	4.4
200	0.12	66	95	5.0
300	0.12	63	92	7.5

a) The initial rate was calculated from the analysis of a sample withdrawn 60 min after the reaction started.
b) Abbreviations M3P and VC stand for methyl 3-pentenoate and 4-vinyl 1-cyclohexene.

tadiene increased. This increase in the conversion is due to the polymerization, not to the hydroesterification of butadiene (cf. Experimental section).

The Effect of the Pyridine Conecntration. The initial rate increased with the increase in the concentration of pyridine (Fig. 1). The conversion of butadiene, and the yield of, and the selectivity, to methyl 3-pentenoate all increased with the increase in the concentration of pyridine; however, they reached a maximum at the concentration of 5 mol/l and remained essentially unchanged thereafter.

The Effect of the Carbon Monoxide Partial Pressure. The effect of the pressure was examined at two different temperatures (100 and 140°C). The results are shown in Tables 3 and 4. The initial rate at 100°C increased with the increase in the pressure; it reached a maximum at 200 kg/cm² and leveled off thereafter. The conversion of butadiene and the selectivity to methyl 3-pentenoate both increased with the increase in the pressure, reached a maximum at 200 kg/cm², and declined thereafter. The selectivity to 4-vinyl 1-cyclohexene decreased as the pressure was increased. from 100 to 150 kg/cm², reached a minimum at 150—200 kg/cm², and then increased. At 140°C, on the other hand, the conversion of butadiene and the selectivity to methyl 3-pentenoate both increased, while the selectivity to 4-vinyl 1-cyclohexene decreased with the increase in the pressure in the range from 150 to 600 kg/cm².

Table 4. The effect of pressure (II)
0.25 mol methanol, 0.15 mol pyridine, 0.1 mol butadiene, 1 mmol $Co_2(CO)_8$; reaction temp. 140°C, reaction time 1.5 hr; in 100 ml autoclave.

Initial pressure (kg/cm²)	Conversion (%)	Selectivity (%)[a]	
		M3P	VC
150	20	46	30
300	44	63	22
600	87	87	7.2

a) *cf.* Table 3.

The Effect of the Hydrogen Partial Pressure. Two hydroesterification runs of butadiene were carried out, with and without hydrogen, and the results were compared. Of the two experiments (listed in Table 5), one was carried out in the absence of hydrogen, while the other one was carried out with an initial hydrogen pressure of 137 kg/cm² under identical conditions; these experiments were carried out with the same carbon monoxide partial pressure, the initial pressure in the former experiment being 380 kg/cm², while that in the latter experiment was 517 kg/cm² (380+137). In the presence of hydrogen, the resulting methyl 3-pentenoate was partly hydrogenated into methyl *n*-pentanoate. Also, the dimerization of butadiene into 4-vinyl 1-cyclohexene and the polymerization of butadiene into unidentified polymers were accelerated and the selectivity to methyl 3-pentenoate decreased. Clearly hydrogen has no accelerating effect on the hydroesterification of butadiene, since the yield of methyl 3-pentenoate plus its hydrogenation product, methyl *n*-pentanoate, did not increase with the presence of hydrogen.

The Hydroesterification of Methyl 3-Pentenoate. The cobalt carbonyl-catalyzed hydroesterification of methyl

Table 5. The effect of hydrogen

0.25 mol methanol, 0.15 mol pyridine, 0.1 mol butadiene, 1 mmol $Co_2(CO)_8$, reaction temp. 140°C, reaction time 2.5 hr

Initial pressure (kg/cm²)		Conversion (%)	Selectivity (%)[a]			
Pressure,	P_{H_2}		M3P	MP	VC	Residue
380	0	71	79	—	5.8	15
517	137	78	55	6.3	20	19

a) Abbreviation MP stands for methyl *n*-pentanoate. For others *cf.* Table 3.

Table 6. The hydroesterification of methyl 3-pentenoate

0.05 mol methyl 3-pentenoate, 0.125 mol methanol

Diluent(g)	$Co_2(CO)_8$ (mmol)	Py (mmol)	Temp. (°C)	Initial press. (kg/cm²)	Time (hr)	Conv. (%)	Selectivity (%)[a]					
							MP	M2P	M4P	E1	E2	E3
Toluene 15	2	16	160	130	4	87	1.7	—	—	81	13	3.0
Toluene 10	2	127	200	300	1	100	15	—	—	68	12	3.3
Benzene 10	1	127	180	200	2	90	13	—	—	69	9.1	1.7
n-Heptane 10	1	127	180	200	2	94	14	—	—	68	10	2.1
Benzene 10	1	0	180	200	2	64	12	56	9.4	5.3	3.9	2.6
None	1	127	180	200	2	21	—	—	—	3.7	—	—

a) Abbreviations M2P, M4P, E1, E2, and E3 stand for methyl 2-pentenoate, methyl 4-pentenoate, dimethyl adipate, dimethyl α-methylglutarate, and dimethyl ethylsuccinate. For another *cf.* Table 5.

Table 7. The effect of the reaction temperature of the first stage on the direct syntheses of diesters

0.25 mol methanol, 0.15 mol pyridine, 0.1 mol butadine, 4 mmol $Co_2(CO)_8$; Initial pressure of the first stage 500 kg/cm²; Temperature of the second stage 200°C; Reaction time 3 hr (first stage), 1 hr (second stage)

Temperature (first stage) (°C)	Initial press. (second stage) (kg/cm²)	Conv. (%)	Selectivity (%)[a]					
			MP	M2P	M3P	E1	E2	E3
130	520	94	12	1.4	7.4	47	9.5	2.5
120	526	93	9.9	1.0	5.7	49	9.9	2.5
110	530	95	11	1.1	5.8	51	12	3.1

a) *cf.* Table 6.

3-pentenoate proceeded at 160—200°C in the presence of pyridine and such a solvent as benzene, toluene, or *n*-heptane; dimethyl adipate was produced in a good yield, while dimethyl α-methylglutarate and dimethyl ethylsuccinate were produced in minor amounts. The results are summarized in Table 6. Methyl 3-pentenoate was partly hydrogenated to methyl *n*-pentanoate in spite of the fact that the reaction was carried out in the absence of hydrogen. Hydrogen can be formed from methanol and carbon monoxide in the presence of cobalt carbonyl.[6] In fact, it was confirmed that hydrogen was produced from methanol and carbon monoxide under the conditions of Table 6, and that carbon dioxide and methyl acetate were produced, together with hydrogen, without the formation of dimethylether:

$$2CH_3OH+2CO \longrightarrow CH_3COOCH_3+CO_2+H_2$$

In the presence of a small excess of pyridine($Py/Co_2(CO_8)=8$), the reaction proceeded at 160°C. In the presence of a large excess of pyridine ($Py/Co_2(CO)_8=127$), however, a higher temperature (180—200°C) and the use of such a solvent as has been mentioned above were necessary for the reaction to proceed. In the absence of pyridine, on the other hand, only the isomerization of methyl 3-pentenoate into methyl 2-pentenoate and methyl 4-pentenoate took place, with the hydroesterification occurring very sparingly.

The Direct Synthesis of Dimethyl Adipate from Butadiene, Carbon Monoxide, and Methanol. It has been found that the hydroesterification of butadiene proceeded in the presence of pyridine at 100—140°C to give methyl 3-pentenoate, but the further hydroesterification of methyl 3-pentenoate did not occur at these temperatures. On the other hand, in the experiments cited in Table 6, it has also been found that the hydroesterification of methyl 3-pentenoate proceeded in the presence of pyridine at 160—200°C to give diesters. Therefore, it should be possible, by the combination of the above two results, to synthesize diesters directly from butadiene, i. e., by merely carrying out the reaction in two steps, at two different temperatures. For example, the hydroesterification of butadiene was carried out at 110—130°C as the first-stage reaction, and then the temperature was raised to 200°C to carry out the reaction of the second stage(Table 7). The selectivity to each diester increased as the temperature of the first stage decreased; this is probably because

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[6] G. Natta, P. Pino, and R. Ercoli, *J. Amer. Chem. Soc.*, **74**, 4496 (1952).

TABLE 8. THE RESULTS OF THE HYDROFORMYLATION OF METHYL 3-PENTENOATE
methyl 3-pentenoate (0.1 mol) diluted with the solvent to 100 ml (room temp.), $Co_2(CO)_8$ 2 mmol (No. 1) 0.02 mmol (No. 2—11)

No.	Solvent	Temp. (°C)	Press. (kg/cm²)	Reaction time (min)	Conv. (%)	Selectivity (%)[a]					5F/(4F+3F)
						M2P	MP	5F	4F	3F	
1	Benzene	140	100	60	100	0	8.2	25	8.6	4.3	1.9
2	Benzene	200	250	60	99.6	0.09	19	34	16	8.6	1.4
3	Benzene[b]	200	250	60	99.3	0.23	18	32	16	7.5	1.4
4	Benzene[c]	200	250	30	90.0	6.5	17	41	23	10	1.2
5	Benzene[d]	200	250	30	95.7	5.8	18	40	27	10	1.1
6	Acetonitrile	200	250	60	92.7	9.1	20	33	25	9.3	0.96
7	THF	200	250	60	98.1	1.0	17	48	23	9.5	1.5
8	THF	170	150	210	98.9	1.2	15	48	20	8.7	1.7
9	THF[c]	170	150	90	84.0	21	11	40	23	9.0	1.3
10	Dioxane	200	250	60	100	0	21	41	20	10	1.4
11	Methyl acetate	200	250	60	96.2	2.6	18	40	21	8.7	1.3

a) Abbreviations 5F, 4F, and 3F stand for methyl 5-formylpentanate, methyl 4-formylpentanoate and methyl 3-formylpentanoate. For others *cf.* Table 6.

b) Carried out in the presence of 0.2 mmol of triphenyl phosphine.

c) Carried out in the presence of 20 mmol of pyridine.

d) Carried out in the presence of 200 mmol of pyridine.

the selectivity to methyl 3-pentenoate in the first stage increased as the temperature of that stage decreased.

The addition of a small amount of water (up to 10 mmol) had almost no effect on a similar reaction carried out in two stages (1st stage, 140°C, 600 kg/cm²: 2nd stage, 200°C, 600—610 kg/cm²), although the yield of dimethyl adipate decreased somewhat in the presence of 20 mmol of water.

The Hydroformylation of Methyl 3-Pentenoate. The hydroformylation of methyl 3-pentenoate was carried out in the presence of $Co_2(CO)_8$ at 140—200°C, under the synthesis gas ($Co/H_2=1$) pressure of 100—250 kg/cm². The effect of the solvent and such a ligand as pyridine or triphenylphosphine is shown in Table 8. In the presence of 2 mmol of $Co_2(CO)_8$, the reaction proceeded at 140°C (100 kg/cm²) and formylesters were produced, but the selectivity to formylesters was only 38 per cent, presumably because the formylesters easily polymerized under such a high concentration of $Co_2(CO)_8$.

When the amount of $Co_2(CO)_8$ was reduced to to 0.02 mmol, the reaction did not occur at 140°C; however, it proceeded at 200°C(250 kg/cm²) and the selectivity to formylesters increased to 59 per cent (No. 2). The addition of triphenylphosphine had almost no effect on the reaction(No. 3). The addition of pyridine increased the selectivity to formylesters to 74—77 per cent(No. 4,5); however, the selectivity to methyl 5-formylpentanoate did not increase so much(40—41%), as it worked to decrease the 5F/(4F+3F) ratio. On the other hand, when acetonitrile was used as a solvent(No. 6), the total selectivity to formylesters increased to 67 per cent while the 5F/(4F+3F) ratio decreased remarkably(0.69). When tetrahydrofuran(THF) was used as the solvent(No. 7,8), on the other hand, the selectivity to the total formylester increased(77—81%), together with the 5F/(4F+3F) ratio (1.5—1.7). When pyridine was added to the THF solvent(No. 9), the 5F/(4F+3F) ratio decresed to 1.3, the selectivity to methyl 5-formyl-pentanoate declining to 40 per cent as a result.

TABLE 9. THE EFFECT OF SOLVENTS ON THE INITIAL RATE OF THE ISOMERIZATION OF METHYL 3-PENTENOATE

Solvent	Initial rate of formation (mmol/min)	
	Methyl 2-pentenoate	Methyl 4-pentenoate
Benzene	2.0	0.42
Acetonitrile	1.4	0.07
THF	2.4	0.49

The fact that the selectivity to total formylesters increased by the use of such a solvent as THF, dioxane, methyl acetate, and acetonitrile instead of benzene, or by the addition of pyridine to the benzene solvent, suggests that the polymerization of formylester slows down in the presence of those above-mentioned solvents or pyridine. The fact that the 5F/(4F+3F) ratio increased in the order of acetonitrile<methyl acetate<benzene, dioxane<THF may have a bearing upon the ease of the isomerization of methyl 3-pentenoate in these solvents.

The Initial Rate of the Isomerization of Methyl 3-Pentenoate. For the measurement of the initial rate of the isomerization of methyl 3-pentenoate, the reactions were carried out in a 100-ml autoclave with 0.02 mol of methyl 3-pentenoate diluted with a solvent to 50 ml(room temp.) and with 0.2 mmol of $Co_2(CO)_8$, at 140°C under a constant pressure (70 kg/cm²) of carbon monoxide containing 2% hydrogen; under these conditions (a very low hydrogen partial pressure), only the isomerization of methyl 3-pentenoate occurred measurably without the hydroformylation. A small portion of the reaction mixture was withdrawn from the autoclave 10 minutes after the stirring began; this portion was analyzed. The results are summarized in Table 9. Clearly, the isomerization of methyl

3-pentenoate into methyl 2-pentenoate and methyl 4-pentenoate proceeds more rapidly in THF than in benzene, and this isomerization proceeds most slowly in acetonitrile.

Discussion

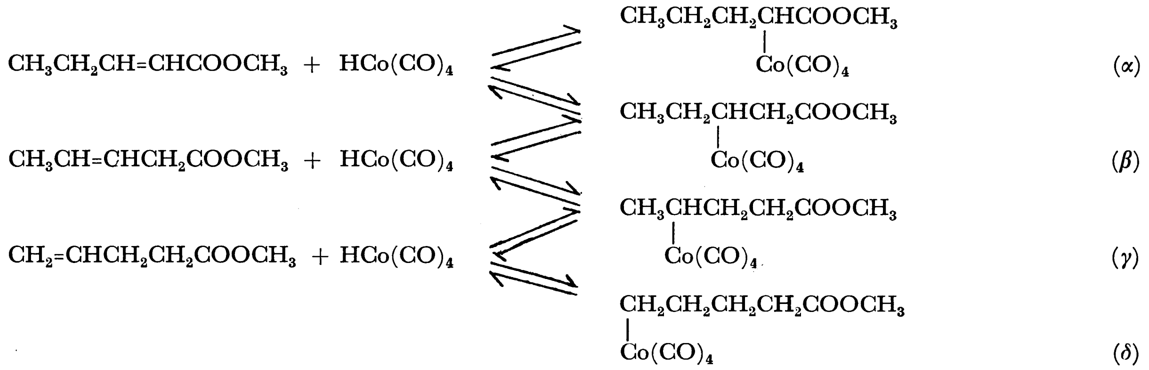
The cobalt carbonyl-catalyzed oxo reaction of butadiene is known to yield a mixture of mono aldehydes and ketones, without any formation of dialdehydes. It is believed that butadiene is hydrogenated by $HCo(CO)_4$ into butenes, which then undergo hydroformylation to give monoaldehydes.[7]

In the case of the present hydroesterification of butadiene, however, the reaction was carried out with carbon monoxide containing almost no hydrogen, and it was observed that the reaction started in the presence of $Co_2(CO)_8$ without any induction time, and that the reaction rate did not increase upon the addition of hydrogen (Table 5). Presumably, $HCo(CO)_4$, the active intermediate of the oxo reaction, does not take part in the present reaction. As a matter of fact, the inhibition by pyridine observed in the usual oxo reaction (as a result of salt formation between $HCo(CO)_4$ and pyridine)[8] was not observed here, and the reaction was successfully carried out in pyridine. Dicobalt octacarbonyl undergoes disproportionation in the presence of pyridine (Eq. (1)), as has been stated by Wender *et al.*[9]; that this also occurs during the reaction is evident form the fact that the strong absorption of $Co(CO)_4^-$ at 1890 cm^{-1} and the weak bands at 1960—2100 cm^{-1} (probably the absorption of $Co^+(CO)_4Py$) appeared on the IR spectrum of the pyridine solution of $Co_2(CO)_8$ when it was treated under the present reaction conditions.

$$Co_2(CO)_8 + Py \longrightarrow Co^+(CO)_4Py(+Co(CO)_4^-) \qquad (1)$$

Therefore, the present reaction probably involves the ion-pair, $Co^+(CO)_4Py(+Co(CO)_4^-)$, as the active intermediate; however, the mechanism is still not clear, nor will it be until more detailed studies of the reaction intermediate are performed.

The hydroesterification of methyl 3-penteonate, on the other hand, evidently involves $HCo(CO)_4$ as the active intermediate, since the reaction was retarded by a high concentration of pyridine and since the hydrogenation took place simultaneously(Table 6). The isomerization of olefins can proceed by the cycle of the addition and elimination of $HCo(CO)_4$.[10] Thus, four types of alkylcobalt tetracarbonyls can be produced from methyl 3-pentenoate in the following equilibrium:



$$CH_3CH_2CH{=}CHCOOCH_3 + HCo(CO)_4 \rightleftharpoons \underset{\textstyle Co(CO)_4}{CH_3CH_2CH_2CHCOOCH_3} \qquad (\alpha)$$

$$CH_3CH{=}CHCH_2COOCH_3 + HCo(CO)_4 \rightleftharpoons \underset{\textstyle Co(CO)_4}{CH_3CH_2CHCH_2COOCH_3} \qquad (\beta)$$

$$CH_2{=}CHCH_2CH_2COOCH_3 + HCo(CO)_4 \rightleftharpoons \underset{\textstyle Co(CO)_4}{CH_3CHCH_2CH_2COOCH_3} \qquad (\gamma)$$

$$\underset{\textstyle Co(CO)_4}{CH_2CH_2CH_2CH_2COOCH_3} \qquad (\delta)$$

The mechanism of the formation of ester in the presence of pyridine *via* an alkylcobalt tetracarbonyl intermediate have already been discussed in a previous paper;[2] dimethyl adipate should result *via* δ, dimethyl α-methylglutarate from γ, dimethyl ethylsuccinate from β, and dimethyl propylmalonate from α. The facts that the selectivity to esters decreased in the order of dimethyl adipate>dimethyl α-methylglutarate>dimethyl ethylsuccinate, and that dimethyl propylmalonate was not detected in the products, suggest that the hydroesterification rates *via* these intermediates decrease in the order of $\delta>\gamma>\beta$, and that the α-intermediate is extraordinarily unreactive in this reaction.

The hydroformylation of methyl 3-pentenoate may also proceed *via* these intermediates, *i. e.*, by the formation of acylcobalt tricarbonyls from these intermediates, followed by its hydrogenation to give formylesters according to the mechanism proposed by Heck;[11] 5-formyl-(5F), 4-formyl-(4F), 3-formyl-(3F), and 2-formyl-(2F) esters should result from the δ, γ, β, and α intermediates respectively. The fact that the effectiveness of solvents in increasing the 5F/(4F+3F) ratio decreased in the order of THF>benzene, dioxane>methyl acetate>acetonitrile may be explained in connection with the fact that the effect of solvents in increasing the rate of the isomerization of methyl 3-pentenoate decreased in a similar order; THF>benzene>acetonitrile (Table 8), since the 5F/(4F+3F) ratio will increase as the rate of the isomerization of γ into the δ intermediate increases. However, another possibility exists that the equilibrium toward the straight-chain acylcobalt carbonyl may be particularly favored in THF, as has been mentioned by Takegami *et al.*,[12] who studied the isomerization of acyl-

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cobalt carbonyls in various solvents. In a previous paper concerning the intramolecular hydroesterification of allylalcohol,[13] it has already been mentioned that the double-bond isomerization of allylalcohol is reduced by the use of acetonitrile as a solvent.

In conclusion, it can be said that THF is effective in increasing the ratio of the straight-chain formylester, because it accelerates the isomerization of γ- into the δ-intermediate, or because the equilibrium toward the straight-chain acylcobalt carbonyl is particularly favored in THF, or because of a combination of the above two factors. Also, it may be said that acetonitrile decreases the ratio of the straight-chain formylester because it retards the isomerization of γ- into the δ-intermediate.

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