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The Selective Hydrogenation of α-Methylcinnamaldehydes Catalyzed by Cobalt Carbonyl in the Presence of Amines

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The selective hydrogenation of α-methylcinnamaldehydes to the hydrocinnamaldehydes, catalyzed by cobalt carbonyl and a limited amount of amines, has been investigated. The addition of such amines as diisopropylamine, diethanolamine, tributylamine, triethylamine, and pyridine showed a remarkable selectivity and gave the desired α-methylhydrocinnamaldehydes in 96.4—91.5% theoretical yields. Especially, diisopropylamine gave the best selectivity, in it the yields of *p*-*t*-butyl-α-methylhydrocinnamaldehyde and cyclamenaldehyde amounted to 96%. The optimum amount was found to be 1.0—1.3 equivalents of cobalt carbonyl.

p-*t*-Butyl-α-methylhydrocinnamaldehyde (lilyal) and *p*-isopropyl-α-methylhydrocinnamaldehyde (cyclamenaldehyde), the most appreciated synthetic perfumes, are prepared industrially by two well-known processes, *viz.*, the dehydrogenation of the corresponding alcohol using a Cu–Zn catalyst[1] and the selective hydrogenation of the cinnamaldehyde using a palladium-alumina catalyst containing potassium acetate.[2]

Previously we have reported a selective hydrogena-

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[1] S. Abe and T. Yasukawa, *Yuki Gosei Kagaku Kyokai Shi*, **22**, 144, 209 (1964).

[2] D. Morris, E. Daniel J, and S. Alfred, U.S. 3520934 (1970).

tion of *p*-isopropyl-α-methylcinnamaldehyde to cyclamenaldehyde with a cobalt carbonyl catalyst or its ligand-substituted complex under oxo conditions.[3] It was found that a tris(2-bromoethyl) phosphite-substituted cobalt carbonyl gave the best yield (86.3%) among those substances unsubstituted and substituted with PR_3, $P(OR)_3$, and $PO(OR)_3$ (R=alkyl, aryl).

Wender *et al.*[4] have reported on the behavior of amines in the hydroformylation of cyclohexene as follows: 1) The rate of hydroformylation is increased by the addition of a small amount of organic amines, but decreased with a larger amount of them. 2) Both the basicity and the steric factor of the amines affect the rate of the reaction. Matsuda and Uchida[5] have proved that the addition of an appropriate amount of pyridine improves not only the selectivity for the hydroesterification of propylene with carbon monoxide and methanol, but also the rate of conversion. These findings urged us to study more closely the effect of organic amines upon the rate and the selectivity of the hydrogenation of the cinnamaldehyde under controlled oxo conditions.

The present paper will describe the selective hydrogenations of *p*-*t*-butyl-α-methylcinnamaldehyde and *p*-isopropyl-α-methylcinnamaldehyde using a cobalt carbonyl catalyst in the presence of various organic amines. Diisopropylamine was found to be the best and gave the highest yields, 96.4 and 96.2%, for lilyal and cyclamenaldehyde respectively.

Experimental

Materials. *p*-*t*-Butyl-α-methylcinnamaldehyde (I) was prepared according to the Knorr method[6] in the same manner as *p*-isopropyl-α-methylcinnamaldehyde (II).[3] I; bp 114—116 °C/l mmHg, mp 69 °C, purity by gas liquid chromatography (glc) 100%. The dicobalt octacarbonyl (mp 51 °C) was the same as has been described in previous papers.[3,7] It was used with one of the following organic amines in an equimolar ratio or a little more in relation to dicobalt octacarbonyl in isopropyl ether:[5] Triphenylamine, 3-aminopropionitrile, quinoline, pyridine, dimethylaniline, diethanolamine, isopropylamine, cyclohexylamine, triethylamine, tributylamine, diisopropylamine, and piperidine. They were all chemically pure-grade reagents, purchased from the Tokyo Kasei Co., Ltd.

Procedure. I or II (0.3 mol, 60.6 or 56.4 g respectively) and a solution of dicobalt octacarbonyl (5.2 mmol, 1.8 g) in isopropyl ether (150 ml) containing a small amount of an amine were put into a 500 ml stainless steel autoclave equipped with an outlet for sampling. The air in the autoclave was flushed with nitrogen several times. Then the autoclave was filled with water gas (65 kg/cm^2, H_2: CO=12: 1) at room temperature, heated to 107 °C in 30 min, and stirred. The temperature was kept within a range of ±1 °C during the reaction. During the reaction, small amounts of the reaction mixture were withdrawn at prescribed time intervals for glc analysis. Hydrogenation was continued until the peak of I or II disappeared. The end point was checked from the gauge-time relation as well. The rate of hydrogenation was then estimated from the depression in the pressure. The rate constant (k) of hydrogenation was obtained according to the following equation:

$$k = 2.303 \log (P_o - P_f)/(P_t - P_f)/t$$

where P_o is the initial pressure at the beginning of stirring, where P_f is the final one at the end of the reaction, and where P_t is the one at time t.

In the case of constant-pressure experiments, hydrogen was continuously introduced from a pressure storage tank through a needle valve in order to keep the total pressure constant throughout the reaction. After the hydrogenation, the autoclave was cooled and the remaining gas was eliminated. An aqueous solution (150 ml) of 0.25 M iodine–potassium iodide and an acetic acid–isopropyl ether solution (1: 100 v/v, 150 ml) were stirred in 1 hr to decompose the cobalt carbonyl catalyst. The upper layer was separated, washed with 300 ml of 5% aqueous hydrosulfite and subsequently with 200 ml of 5% aqueous sodium carbonate, and dried over sodium sulfate. After the removal of the ether, an oily product was distilled *in vacuo*; this separated volatile products and a resinous matter (1—3% by weight) through a packed column-type rectifier.

Identification of the Products. Lilyal and the corresponding alcohol, *p*-*t*-butyl-α-methylhydrocinnamyl alcohol (III), in the products were separated by distillation through the packed column-type rectifier and identified by means of their NMR spectra in $CDCl_3$ with tetramethylsilane as the internal standard, on a JEOL 4H-10 spectrometer. As the NMR spectra and physical constants of cyclamenaldehyde and cyclamenalcohol, were described in a previous paper,[3] they will be omitted here. Lilyal: Bp 96—98 °C/1 mmHg, d^{25}_{25} 0.9385, n^{25}_{D} 1.5056. NMR spectrum: 1.05 ppm (d) doublet (J=2.5 Hz) methyl 3H; 1.30 ppm (s) singlet *t*-butyl 9H; 2.52 ppm (d) methylene 2H; 3.0 ppm (m) multiplet methine H; 7.10 ppm (m) phenyl 4H; 9.6 ppm (s) aldehyde H. III: Bp 106—108 °C/1 mmHg, d^{25}_{25} 0.9360, n^{25}_{D} 1.5068. NMR spectrum: 0.90 ppm (d) (J=3.0 Hz) methyl 3H; 1.30 ppm (s) *t*-butyl 9H; 1.55 ppm (d) methylene 2H; 1.82 ppm (bs) broad singlet hydroxy H; 1.87 ppm (m) methine H; 3.30 ppm (d) hydroxymethylene 2H; 7.10 ppm (m) phenyl 4H.

The composition of the aforementioned oily product and the volatile matter were determined by the normalization method with glc, using a gas chromatograph, Kotaki GU-21, equipped with a 2 m stainless steel column of KF 54 (5% by weight) on Celite 545 sk (60—80 mesh) at 180 °C. They were analyzed within a relative experimental error of ±1.5%. Authentic lilyal was prepared by the dehydrogenation of III with a Cu-Zn catalyst (bp 96—98 °C/1 mmHg, d^{25}_{25} 0.9387, n^{25}_{D} 1.5058) and III by the catalytic hydrogenation of I over a nickel diatomaceous earth catalyst (bp 106—108 °C/1 mmHg, d^{25}_{25} 0.9357, n^{25}_{D} 1.5065).

Results and Discussion

In the preceding paper,[3] we reported that the conversion of cinnamaldehyde into hydrocinnamaldehyde can be increased by both increasing the pressure of hydrogen in water gas and by the use of a 2.0—2.5-fold volume of solvent for the cinnamaldehyde.

On the basis of those results, the foregoing experiments were carried out using dicobalt octacarbonyl

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3) K. Kogami, O. Takahashi, and J. Kumanotani, This Bulletin, **45**, 604 (1972).

4) I. Wender, H. W. Sternberg, and M. Orchin, "Catalysis," **V**, Reinhold Publishing, N.Y. (1957), p. 110.

5) A. Matsuda and H. Uchida, This Bulletin, **38**, 710 (1965).

6) A. Knorr and A. Weissenborn, U.S. 1844013 (1932).

7) S. Usami, T. Kondo, K. Nishimura, and Y. Koga, This Bulletin, **42**, 2961, 2966 (1969).

TABLE 1. HYDROGENATION OF CINNAMALDEHYDES IN THE PRESENCE OF PYRIDINE

Run	Cinnamaldehyde[a]	Organic amine (mmol)	Molar ratio Amine/$Co_2(CO)_8$	k_1[b] (min^{-1})	SP[c] (%)
1	I	None		0.0030	79.6
2	II	None		0.0031	81.8
3	I	Pyridine, 2.6	0.5	0.0036	86.5
4	I	Pyridine, 5.2	1.0	0.0042	92.6
5	I	Pyridine, 7.8	1.5	0.0038	88.4
6	II	Pyridine, 2.6	0.5	0.0037	87.2
7	II	Pyridine, 5.2	1.0	0.0042	93.0
8	II	Pyridine, 7.8	1.5	0.0039	89.4

a) I or II (0.3 mol, 60.6 or 56.4 g, respectively) was hydrogenated in 150 ml of isopropyl ether using 5.2 mmol of $Co_2(CO)_8$ as catalyst at 107±1 °C and 65 kg/cm², initial pressure of water gas (H_2: CO=12: 1).

b) $k_1=2.303\log[(P_o-P_f)/(P_t-P_f)]/t$.

c) SP designates Selective Parameter given by the eqation; hydrocinnamaldehyde × 100%/(hydrocinnamaldehyde + hydrocinnamyl alcohol).

with or without pyridine, often used in conventional hydroformylations, under the following favorable conditions:[3] At 107±1 °C and 65 kg/cm² of the initial pressure of water gas (H_2: CO=12: 1). They revealed that the hydrogenation of I or II apparently obeyed a first-order kinetics in the partial pressure of hydrogen and that the addition of pyridine not only increased the rate of hydrogenation, but also improved the selectivity for forming lilyal or cyclamenaldehyde (Table 1). Equimolar pyridine to dicobalt octacarbonyl increased the rate and the selectivity of the hydrogenation; however, greater or lesser amounts had negative effects. The analysis of the hydrogenation products in the presence of pyridine proved the absence of the hydroformylates formed. Plots of the consumed amount of cinnamaldehyde against the reaction time gave a linear relation under a constant pressure of hydrogen, indicating that the hydrogenation was first order in the partial pressure of hydrogen, and zero order in the concentration of cinnamaldehyde, when a small amount of pyridine existed (Fig. 1).

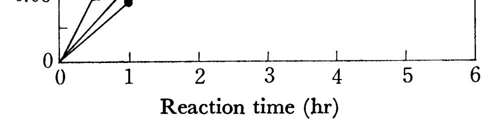


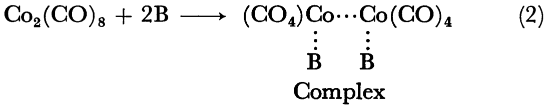
Fig. 1. Plots of the consumed amount of cinnamaldehyde, C_o-C_t, *vs.* reaction time at 107±1 °C and 65 kg/cm² the total pressure of water gas (H_2: CO=12: 1) in the presence of pyridine.

Run	$Co_2(CO)_8$ mmol	Pyridine mmol	*S P* %
□	6.4	6.4	91.3
○	5.2	5.2	93.7
●	2.9	2.9	89.5

C_0; the initial molar concentration of I.
C_t; the molar concentration of I at reaction time *t*.

Iwanaga[8] observed that the rate of the hydroformylation of methyl acrylate in benzene under an oxo condition is nearly doubled with only a small amount of pyridine, and that the pyridine accelerates the rate of the reaction by forming an intermediate complex (Eq. 2), which is then rapidly converted into cobalt hydrocarbonyl by the subsequent hydrogenation (Eq. 3). The amount of free cobalt hydrocarbonyl, however, decreases upon combination with amine (Eq. 4) and increases with the increased basicity of the amine applied. Some amines with low steric requirements, such as pyridine, can replace the free cobalt hydrocarbonyl (Eq. 5):[5]

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4 \qquad (1)$$



$$Co_2(CO)_8 + 2B \longrightarrow \underset{\text{Complex}}{(CO_4)\underset{\vdots\atop B}{Co}\cdots\underset{\vdots\atop B}{Co}(CO)_4} \qquad (2)$$

$$\text{Complex} + H_2 \longrightarrow 2HCo(CO)_4 + 2B \qquad (3)$$

$$HCo(CO)_4 + B \longrightarrow (BH)^+(Co(CO)_4)^- \qquad (4)$$

$$HCo(CO)_4 + B \longrightarrow HCo(CO)_3B + CO \qquad (5)$$

In the hydrogenation of α,β-unsaturated carbonyl compounds catalyzed by cobalt hydrocarbonyl, the saturated carbonyl compounds formed are very slowly transformed into the corresponding alcohols.[3,9] This indicates that the cobalt hydrocarbonyl coordinate more intimately around the carbonyl group of cinnamaldehyde than around that of hydrocinnamaldehyde, resulting in the formation of the π-oxapropenyl intermediate complex.[10] Furthermore, the slow transformation into the hydrocinnamyl alcohol can be interpreted in terms of the difficulty in the formation of the cyclic-transition-state intermediate between the cobalt hydrocarbonyl and the hydrocinnamaldehyde.[11] Consequently, the favorable selectivity in the formation of hydrocinnamaldehyde is considered to occur with the cobalt hydrocarbonyl produced by strong amines with appropriate steric factors. In order to

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[8] R. Iwanaga, This Bulletin, **35**, 865, 869 (1962).

[9] L. Marco, *Proc. Chem. Soc.*, 1962, 67.

[10] R. W. Goetz and M. Orchin, *J. Org. Chem.*, **27**, 3698 (1962).

[11] R. W. Goetz and M. Orchin, *J. Amer. Chem. Soc.*, **85**, 2782 (1963).

Table 2. Selective hydrogenation of cinnamaldehydes in the presence of organic amines

Run	Cinnamaldehyde[a] Variety	Amine mmol	React. time min	Rate $k_1 \times 10^8$ (min^{-1})	SP (%)	Hydrocinnamaldehyde[b] %
1	I	None	393	3.0	79.6	78.2
2	I	Triphenylamine, 5.2	786	1.5	80.3	78.5
3	I	3-Aminopropionitrile, 5.2	590	2.0	80.5	78.5
4	I	Quinoline, 5.2	281	4.2	88.5	86.5
5	I	Pyridine, 5.2	281	4.2	92.6	91.5
6	I	Dimethylaniline, 5.2	282	4.2	88.3	86.3
7	I	Diethanolamine, 5.2	262	4.5	93.4	92.5
8	I	Isopropylamine, 5.2	263	4.5	89.8	88.4
9	I	Cyclohexylamine, 5.2	262	4.5	85.6	85.2
10	I	Triethylamine, 5.2	245	4.8	93.2	92.0
11	I	Tributylamine, 5.2	241	4.9	94.2	93.0
12	I	Diisopropylamine, 5.2	190	6.2	96.3	95.1
13	I	Piperidine, 5.2	190	6.2	87.8	86.2
14	I	Diisopropylamine, 6.8	200	5.9	97.5	96.4
15	I	Diisopropylamine, 7.8	210	5.6	95.4	94.1
16	II	Diisopropylamine, 6.8	200	5.9	97.6	96.2

a) I or II (0.3 mol, 60.6 or 56.4 g, respectively) was hydrogenated in 150 ml of isopropyl ether at 107±1 °C and 65 kg/cm² of water gas (H_2: CO, 60: 5) with 5.2 mmol of $Co_2(CO)_8$ as catalyst.

b) Theoretical yield of lilyal or cylcamenaldehyde.

establish the optimum conditions for obtaining the hydrocinnamaldehydes, the hydrogenation was investigated with various organic amines such as diisopropylamine, tributylamine, triethylamine, and pyridine. The results obtained are shown in Table 2.

The applied amines showed increasing effects on the rate of hydrogenation as well as on the selectivity in the formation of the hydrocinnamaldehyde, in accordance with the order of basicity. The rates of hydrogenation were found to be as follows: Triphenylamine ($pK_b=14.0$)<3-aminopropionitrile ($pK_b=11.9$) <quinoline ($pK_b=9.0$), pyridine ($pK_b=8.96$) and dimethylaniline ($pK_b=8.94$)<diethanolamine ($pK_b=5.52$), isopropylamine ($pK_b=3.34$) and cyclohexylamine ($pK_b=3.32$)<triethylamine ($pK_b=3.32$)<tributylamine ($pK_b=3.11$)<diisopropylamine ($pK_b=2.89$), and piperidine ($pK_b=2.79$). Smaller rate constants were observed with triphenylamine and 3-aminopropionitrile, which gave almost the same selectivity in the formation of hydrocinnamaldehyde as in the absence of an amine. Quinoline, dimethylaniline, isopropylamine, cyclohexylamine, and piperidine had only feeble effects on increasing the selectivity, although larger rate constants of hydrogenation were obtained. This can be explained in terms of the persistency of activity for the further conversion of hydrocinnamaldehyde into hydrocinnamyl alcohol in the cases of amines with a relatively stronger basicity and less steric hindrance. Pyridine, diethanolamine, triethylamine, tributylamine, and diisopropylamine showed larger rate constants of hydrogenation, in good argeement with the order of basicity, and showed the best effects in producing hydrocinnamaldehyde. In spite of the weak basicity and small steric effect, pyridine affords good selectivity in the formation of hydrocinnamaldehydes. The knowledge[5] at present available on the catalytic behavior of $HCo(CO)_3Py$ can not make possible a satisfactory interpretation of the effect.

Among the effective amines, diisopropylamine gave the largest rate constants and the best selectivity; the yields of lilyal and cyclamenaldehyde amounted to 96%, suggesting the effectiveness of both the strong basicity and the appropriate bulkiness. The optimum amount of diisopropylamine was found to be 1.0—1.3 equivalents, based on the dicobalt octacarbonyl.

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