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Preparation of Cyclamenaldehyde by Selective Hydrogenation in Some Cobalt Carbonyl Complex Catalysts under Oxo Conditions[1]

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Selective hydrogenation of *p*-isopropyl-α-methylcinnamaldehyde to cyclamenaldehyde in some cobalt carbonyl complex catalyst systems has been investigated under several oxo conditions. The yield of the aimed aldehyde was improved as much as 84 to 86.3% under controlled conditions. Selectivity of the hydrogen increased with the decrease of temperature and the increase of partial pressure of hydrogenation in a water gas. A maximum yield (84%) was obtained with solvents such as isopropyl ether and hexane when used in 2-fold volume for the cinnamaldehyde. A tris(2-bromoethyl) phosphite-substituted cobalt carbonyl complex catalyst gave the best yield (86.3%) as compared with catalysts unsubstituted and substituted with PR_3, $P(OR)_3$, and $PO(OR)_3$ (R=alkyl, aryl).

Cyclamenaldehyde, one of the principal aromatic chemicals, has been prepared industrially by two well known superior processes, *viz.*, dehydrogenation of the corresponding alcohol using a Cu-Zn catalyst[2] and hydrogenation of *p*-isopropyl-α-methylcinnamaldehyde over 5% Pd on a charcoal catalyst.[3-5]

Recently the hydrogenation of α,β-unsaturated carbonyl compounds to give saturated carbonyl compounds was reported on the following catalyst system; tri(triphenylphosphine)chlororhodium by Jardine and Wilkinson,[6] palladium boride by Kawai *et al*,[7] and cobalt hydrocarbonyl by Goetz and Orchin, who found that the saturated carbonyl compounds were produced at 25°C under one atmosphere of carbon monoxide, while the saturated carbonyl compounds formed were reduced very slowly into the corresponding alcohols.[8]

We found that dicobalt octacarbonyl and its complex substituted with tris(2-bromoethyl) phosphite were useful catalysts for selective hydrogenation to the double bond of *p*-isopropyl-α-methylcinnamaldehyde under oxo conditions.

Experimental

Materials. *p*-Isopropyl-α-methylcinnamaldehyde was prepared according to the Knorr method:[9] bp 117—120°C/2 mmHg, d_{20}^{20} 0.9986, n_D^{20} 1.4343.

The dicobalt octacarbonyl (mp 51°C) was prepared in a 51.4% yield according to the method in literature,[11] which involved the reaction between cobalt-hydroxide and a 150 kg/cm² water gas (H_2 : CO, 1 : 1, purchased from the Takachiho Commercial Co., Ltd.).

The complex of dicobalt octacarbonyl substituted with the following ligands in molar ratio of 1 : 2 were prepared in isopropyl ether under a purified nitrogen flow;[10] tiphenylphosphine, triphenyl phsphite, tributylphosphine, tributyl phosphite, tris(2-bromoethyl) phosphite, triphenyl phosphate, and tricresyl phosphate. They were of chemically pure grade and purchased from the Tokyo Kasei Co., Ltd.

Procedure. After *p*-isopropyl-α-methylcinnamaldehyde (18.8 g, 0.1 mol) and a solution of dicobalt octacarbonyl (0.56 g, 0.0016 mol) in 40 *ml* of isopropyl ether had been put into a 300 *ml* stainless steel autoclave equipped with an outlet tube for sampling, the air in the autoclave was flushed with nitrogen several times. The water gas was then charged at pressure from 60 to 80 kg/cm² at room temperature.

The autoclave was then heated up to the desired temperature with stirring. Aliquots of the reaction mixture were withdrawn from the autoclave at the prescribed time interval during the reaction, and submitted to glc.

Hydrogenation was continued until the peak of *p*-isopropyl-α-methylcinnamaldehyde disappeared, and the end point was detected from the gauge pressure-time relation. After the hydrogenation, the autoclave was cooled, purged, and then a solution of triphenylphosphine (1.7 g) in isopropyl ether (300 *ml*) was added. The insoluble precipitates (phosphine complex) were then filtered off. The resulting filtrate was neutralized with 200 *ml* of an aqueous solution of 5% sodium carbonate, and dried over sodium sulfate. After the removal of ether from the solution, an oily product obtained as a residue was distilled *in vacuo* to separate volatile products.

Identification and Analysis of Products. Cyclamenaldehyde and cyclamen alcohol were separated by the distillation of the products of Run 9 in Table 2 with a packed type rectifier, and identified by NMR spectra in carbon deuterium trichloride with tetramethylsilane as an internal standard on a JEOL 4H-100 spectrometer. Cyclamenaldehyde: bp 98—100°C/1 mmHg, d_{20}^{20} 0.9486, n_D^{20} 1.5080. NMR spectrum: 1.05 ppm (d) doublet (J=2.5) methyl 3H; 1.20 ppm (d) doublet (J=2.5) isopropyl methyl 6H; 2.64 ppm (m) multiplet methine H; 2.85 ppm (m) multiplet isopropyl methine H; 7.08 ppm (m) multiplet phenyl 4H; 9.26 ppm (s) singlet aldehyde H.

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Cyclamen alcohol: bp 120—122°C/1 mmHg, d_{20}^{20} 0.9492, n_D^{20} 1.5080. NMR spectrum: 0.90 ppm (d) (J=3.0) methyl 3H; 1.21 ppm (d) (J=2.0) isopropyl methyl 6H; 1.80 ppm (bs) broad singlet hydroxy H; 1.91 ppm (m) methine H; 2.87 ppm (m) isopropyl methine H; 3.47 ppm (d) hydroxy methylene 2H; 7.09 ppm (m) phenyl 4H.

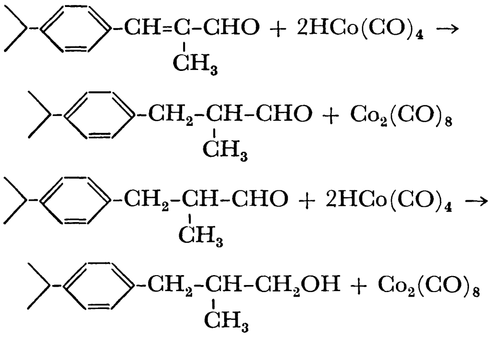
The composition of the products was determined by glc using a gas chromatograph (Kotaki GU-21) with a 2 m stainless steel column of KF 54 (5% by weight) on cellite 545 sk (60—80 mesh) at 180°C. Both of the above products were analyzed within a relative experimental error of ±1.5%. The standard materials cyclamenaldehyde and cyclamen alcohol were prepared by the following procedures.[2] Cyclamenaldehyde was prepared by dehydrogenation of cyclamen alcohol with a Cu-Zn catalyst (bp 110—112°C/4 mmHg, d_{20}^{20} 0.9498, n_D^{20} 1.5083), and cyclamen alcohol by the catalytic hydrogenation of *p*-isopropyl-α-methylcinnamaldehyde over a nickel-diatomaceous earth catalyst (bp 130—132°C/4 mmHg, d_{20}^{20} 0.9490, n_D^{20} 1.5076).

Results and Discussion

Hydrogenation of p-*Isopropyl-α-methylcinnamaldehyde Using Dicobalt Octacarbonyl Catalyst.* It is well known that cobalt hydrocarbonyl is formed by the reaction with dicobalt octacarbonyl and a water gas (H_2 : CO, 1 : 1) at 100°C under a pressure greater than 45 kg/cm².

From the results it is suggested that the hydrogenation of *p*-isopropyl-α-methylcinnamaldehyde into cyclamenaldehyde with a minor amount of $Co_2(CO)_8$ under oxo conditions proceeds by the repetition of the process given by the following equations.

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



(2)

However, it should be noticed that cyclamenalcohol may be formed simultaneously by the reaction of cyclamenaldehyde with $HCo(CO)_4$ at such a high temperature.

Increase in the partial pressure of carbon monoxide in the water gas would decrease the concentration of the cobalt hydrocarbonyl in the system (Eq. (1)), resulting in either a slower or a higher-temperature hydrogenation. The effect of solvents such as isopropyl ether and *n*-hexane upon the product distribution should also be examined under various conditions. The results obtained are summarized in Table 1.

1) Effect of the Amount of Catalyst Complex and Reaction Temperature. Increase in $Co_2(CO)_8$ from 5 to 18% (by weight) for the cinnam aldehyde served to shorten the reaction time, but the undesired cyclamen alcohol and resinous matter tended to increase it (Runs 1—3, Table 1).

A decrease in the catalyst from 5 to 1% (Run 5 and 6) was necessary to raise the reaction temperature, resulting in an increase in the above two compounds.

It was found that the increase of the partial pressure of hydrogen in a water gas at 55 kg/cm² lowered the reaction temperature, resulting in an increase in the yield of cyclamenaldehyde to 80.3% of the theoretical (Run 7, Table 1).

A higher molar ratio of carbon monoxide in a water gas at 45 kg/cm² (H_2 : CO, 1 : 2) raised the reaction temperature from 100—130°C to 140—145°C, giving greater amounts of cyclamen alcohol and resinous matter (Run 3 and 4, Table 1).

2) Solvent Effect. When isopropyl ether or *n*-hexane was used in 5—2-fold volume for the cinnam aldehyde, the reaction temperature was lowered from 100—130°C to 90—125°C, giving rise to an increase in the amount of cyclamenaldehyde as well as a decrease in that of the alcohol and resinous matter (compare Runs 10—12 with Run 8 in Table 1).

The higher molar ratio of hydrogen in the water gas, *e.g.* 65 kg/cm² water gas (H_2 : CO, 12 : 1) used instead of the 100 kg/cm² gas (H_2 : CO, 1 : 1) much lowered the reaction temperature from 90—125°C to 90—96°C and increased the yield of cyclamenaldehyde as much as 84.0% (Runs 11 and 12, Table 1).

By employing an 1.5-fold volume of isopropyl ether, the yield of the cyclamenaldehyde was lowered from 83.2 to 77.8%, accompanied by an increase of distillation residue from 8.9 to 13.6% (Runs 9 and 10, Table 1). From the results, the optimum conditions for yielding cyclamenaldehyde can be given as follows. *p*-Isopropyl-α-methylcinnam aldehyde is reduced at 90—96°C for 6.5 hr under stirring with a 65 kg/cm² water gas (H_2 : CO, 12 : 1) in a 2-fold volume of isopropyl ether with 3% (by weight) $Co_2(CO)_8$ for the cinnamaldehyde.

3) Effect of Ligand Substitution upon Selective Hydrogenation In order to improve the yield of cyclamenaldehyde, hydrogenation was carried out with ligand-substituted cobalt carbonyl complex catalysts. The ligand substitution (Table 2) was performed with the following compounds.

Tributylphosphine, triphenylphosphine, tributyl phosphite, tris(2-bromoethyl) phosphite, triphenyl phosphite, triphenyl phosphate, and tricresyl phosphate.[10] Hydrogenation with these complex catalysts was carried out in a 5-fold volume of isopropyl ether for the cinnamaldehyde at 122—180°C with a 100 kg/cm² water gas (H_2 : CO, 1 : 1). In the case of the tributylphosphine, tributyl phosphite, or triphenylphosphine complex, the reaction proceeded at higher temperature and the yield of cyclamenaldehyde was lowered, while the cyclamenalcohol increased in quantity as compared with the other cases.

The triphenyl phosphite complex catalyst, and triphenyl phosphate- or tricresyl phosphate-$Co_2(CO)_8$ catalyst gave a comparable yield of cyclamenadehyde and a product distribution similar to that given in

TABLE 1. SELECTIVE HYDROGENATION USING DICOBALT OCTACARBONYL CATALYST UNDER OXO CONDITIONS

Run	*p*-Isopropyl-α-methylcinnam-aldehyde (g)	(mol)	Catalyst wt% for cinnam-aldehyde $Co_2(CO)_8$	Solvent (m*l*)	Partial pressure (kg/cm²) H_2	CO	Reaction temperature (°C)	Reaction time (hr)	Composition of reaction product (wt%) Cyclamen-aldehyde	Cyclamen alcohol	Distillation residue (%)	Yield of cyclamen-aldehyde (%)
1	18.8	0.1	18	*n*-Hexane 100 m*l*	50	50	110—130	2.5	52.2	29.4	18.4	51.6
2	18.8	0.1	9	*n*-Hexane 100 m*l*	50	50	110—133	2.5	65.7	20.3	14.0	65.4
3	18.8	0.1	5	*n*-Hexane 100 m*l*	50	50	100—130	4.5	76.4	10.4	13.2	76.1
4	18.8	0.1	5	*n*-Hexane 100 m*l*	15	30	140—145	3.0	78.6	10.6	10.8	78.0
5	18.8	0.1	3	*n*-Hexane 100 m*l*	50	50	120—140	4.0	68.5	17.7	13.8	68.1
6	18.8	0.1	1	*n*-Hexane 100 m*l*	50	50	120—145	6.5	66.8	17.9	15.3	66.0
7	18.8	0.1	5	*n*-Hexane 100 ml	50	5	90— 96	6.5	81.2	9.6	9.2	80.3
8	18.8	0.1	5	Isopropyl ether (5 folds) 100 m*l*	50	50	100—130	3.0	79.8	9.7	10.5	78.8
9	18.8	0.1	3	Isopropyl ether (1.5 folds) 30 m*l*	50	50	90—125	6.5	77.8	8.6	13.6	77.0
10	18.8	0.1	3	Isopropyl ether (2 folds) 40 m*l*	50	50	90—125	6.5	83.2	7.9	8.9	83.0
11	18.8	0.1	3	Isopropyl ether 40 m*l*	60	5	90— 96	6.5	83.3	8.2	8.5	82.6
12	18.8	0.1	3	*n*-Hexane 40 m*l*	60	5	90— 94	6.5	84.0	8.0	8.0	84.0

TABLE 2. THE EFFECT OF LIGAND SUBSTITUTION

Run	*p*-Isopropyl-α-methyl-cinnam-aldehyde (g)	(mol)	Catalyst for the cinnam-aldehyde (wt%)	Ligand (g)	Solvent (Isopro-pyl ether) (m*l*)	Partial pressure (kg/cm²) H_2	CO	Reaction temperature (°C)	Reaction time (hr)	Composition of Product by glc (wt%) Cyclamen-aldehyde	Cyclamen alcohol	Distilla-tion residue (%)	Yield (theor.) of aldehyde (%)
1	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(CH_3(CH_2)_3)_3$ 1.2	100	50	50	145—160	1.5	65.7	24.3	10.0	65.1
2	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(C_6H_5)_3$ 1.7	100	50	50	178—180	1.5	70.6	18.4	11.0	70.0
3	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(CH_3(CH_2)_3O)_3$ 1.5	100	50	50	132—145	3.7	68.5	19.5	12.0	68.1
4	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(C_6H_5O)_3$ 1.8	100	50	50	126—132	3.2	76.5	11.5	12.0	76.2
5	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(C_6H_5O)_3$ 1.8	40	50	50	122—144	6.0	79.2	8.8	12.0	79.0
6	18.8	0.1	$Co_2(CO)_8$ 1.0	$PO(C_6H_5O)_3$ 1.9	100	50	50	125—128	4.0	76.5	10.5	13.0	75.9
7	18.8	0.1	$Co_2(CO)_8$ 1.0	$PO(CH_3C_6H_4O)_3$ 2.2	100	50	50	126—128	4.0	76.5	10.5	13.0	76.0
8	18.0	0.1	$Co_2(CO)_8$ 1.0	$P(BrCH_2CH_2O)_3$ 1.6	100	50	5	120—132	2.0	85.0	6.0	9.0	84.5
9	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(BrCH_2CH_2O)_3$ 2.5	100	50	50	130—136	2.0	85.6	5.4	9.0	85.1
10	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(BrCH_2CH_2O)_3$ 2.5	40	50	50	128—134	3.0	86.5	4.5	9.0	86.3
11	18.8	0.1	$Co_2(CO)_8$ 1.0	$P(BrCH_2CH_2O)_3$ 1.6	50	50	50	128—134	3.0	86.5	4.3	9.2	86.3

the $Co_2(CO)_8$ system unsubstituted (Run 4—7, Table 2).

Use of the tris(2-bromoethyl) phosphite afforded a maximum yield of cyclamenaldehyde (86.3%) (Runs 8—11, Table 2).

The increase in cyclamen alcohol can reasonably be interpreted in terms of the stability of the cobalt carbonyl phosphine and phosphite complexes, in which the scission of cobalt–carbon coordination in the π-oxapropenyl intermediate complex occurred at a relatively higher temperature. Hydridic character of the cobalt hydrocarbonyl complex persisted even at the higher temperature, and resulted in facilitating the hydrogenation of cyclamenaldehyde to cyclamen alcohol.

The increase in cyclamenaldehyde can be interpreted in terms of the fallen electron density of cobalt atom in the complex, which was caused by an electron-attracting effect of the 2-bromoethyl group and which favored the enhancement of the back donation of π-oxapropenyl intermediate as well as the transformation from σ- to π-intermediates of the complex.

The smaller yield in cyclamen alcohol may result from the difficulty in the formation of the cyclic transition state intermediate between the tris(2-bromoethyl) phosphite-substituted cobalt hydrocarbonyl complex and cyclamenaldehyde based on the steric effect of the complex.

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