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SELECTIVE FORMATION OF KETONES FROM PROPENE,CO AND H_2O : COBALT BASED CATALYTIC HYDROCARBONYLATION

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A complex prepared in situ from $Co_2(CO)_8$ and 1,2-bis(diphenylphosphino)ethane (diphos) was found to be an effective catalyst for selective hydrocarbonylation of propene to give dipropyl ketones.

Hydrocarbonylation,by which dialkyl ketones are produced from olefins, can proceed under oxo conditions by means of a transition metal catalyst.1) The yield of ketone, however, depends strongly on the olefin structure; only ethylene gives rise to a ketone(diethyl ketone) in substantial yield.2)

During the course of our study on the cobalt-catalyzed hydroformylation of propene with CO and H_2O3), we have found that the $Co_2(CO)_8$-diphos-polar ether solvent system is greatly effective for the selective hydrocarbonylation of the olefin to give dipropyl ketones.

Representative reaction procedure was as follows. A catalyst solution containing $Co_2(CO)_8$(2 mmol), diphos(2 mmol) and H_2O(30 mmol) in a polar ether solvent (50 ml) was placed in a stainless-steel autoclave(300 ml), which was subsequently charged with both propene(400 mmol) and CO(70 Kg/cm^2 at room temp.). After reaction at 165 °C for 17 h, the reaction vessel was cooled to room temperature and the solution was analyzed by GLC.

As shown in Table, dipropyl ketones were formed in 87 % yield (ca. 1300 % based on $Co_2(CO)_8$) when the reaction was carried out in dioxane under initial CO pressure of 100 Kg/cm^2 at 165 °C.4)(Run 7) However, the yield of ketone was remarkably dependent on reaction conditions: As propene : $Co_2(CO)_8$ ratio was decreased, for example, the yield drastically decreased.(compare Run 1 and 2) In the absence of diphos, the ketones were obtained in 29 % yield with $Co_2(CO)_8$ being completely decomposed during the reaction.5)(Run 10) The use of H_2 as hydrogen donor instead of H_2O resulted in the decrease in the yield and n- or iso-butyraldehydes were predominantly produced.(Run 11)

As already reported, $Co_2(CO)_8$-diphos system has been also effective for homogeneous water gas shift reaction when it was used in an organic tertiary amine solvent.6,7) However, the yields of ketones were low with other transition metal catalysts active for the shift reaction.(Run 13,14)8) Further four systems($Cr(CO)_6$-KOH9), $Mo(CO)_6$-KOH9), $Fe(CO)_5$-triethylamine9), and H_2PtCl_6-$SnCl_2$-HCl10)) gave no carbonylation products. Conclusively, under the conditions employed, cobalt system appears to be desirable for the selective formation of dipropyl ketones from propene.

Table. Formation of dipropyl ketones[a] from propene[b]

Run	Solvent	CO Pressure (Kg/cm^2)	Temp. (°C)	Total yield of ketones (%)[c]
1	THF	50	150	61
2[l]	THF	50	150	6[d]
3[l]	THF	50	150	43[e]
4	dioxane	50	150	71
5	dioxane	100	150	83
6	dioxane	140	150	80
7	dioxane	100	165	87
8	dioxane	100	180	76
9	dioxane	100	165	81[f]
10	dioxane	100	165	29[g]
11	dioxane	100	165	31[h]
12	dioxane	100	165	53[i]
13	THF	50	150	29[j]
14[l]	THF	50	150	3[k]

a) hepta-4-one + 2-methyl hexa-3-one + 2,4-dimethyl penta-3-one Satisfactory spectral data were obtained for these three products.

b) Conditions are as in the text. c) Based on H_2O(mmol) or H_2(mmol)(Run 11) d) Using 30 mmol of propene. e) The diphos : $Co_2(CO)_8$ ratio was 1 : 2. f) Using 60 mmol of H_2O. g) Without adding diphos. h) Using H_2(35 mmol) in place of H_2O(30 mmol). i) Using cobaltcarbonyl cluster($CH_3CCo_3(CO)_9$, 1.33 mmol). j) Using $RhCl_3.3H_2O$(0.5 mmol) and triethylamine(10 mmol) instead of $Co_2(CO)_8$-diphos. k) Using $RuCl_3.H_2O$(0.5 mmol) and triethylamine(10 mmol). l) For 24 h -reaction.

References and Notes

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4) In this run,the product molar ratio of hepta-4-one : 2-methyl hexa-3-one : 2,4-dimethyl penta-3-one was ca. 1 : 2 : 1.1 . Also C_4-aldehydes and C_4-alcohols were obtained in 11 % and 0.9 % yields,respectively, as detectable amounts of by-products.

5) The decomposition was confirmed by the determination of dissolved cobalt in the reaction solution by means of EDTA-titration.

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7) No hydrogen was detected in the gas above the catalyst solution after this hydrocarbonylation.

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