

SELECTIVE FORMATION OF KETONES FROM PROPENE, CO AND H₂O : COBALT
BASED CATALYTIC HYDROCARBONYLATION

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A complex prepared in situ from Co₂(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 H₂O³⁾, we have found that the Co₂(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 Co₂(CO)₈ (2 mmol), diphos (2 mmol) and H₂O (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/cm² 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 Co₂(CO)₈) when the reaction was carried out in dioxane under initial CO pressure of 100 Kg/cm² at 165 °C.⁴⁾ (Run 7) However, the yield of ketone was remarkably dependent on reaction conditions: As propene : Co₂(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 Co₂(CO)₈ being completely decomposed during the reaction.⁵⁾ (Run 10) The use of H₂ as hydrogen donor instead of H₂O resulted in the decrease in the yield and n- or iso-butyraldehydes were predominantly produced. (Run 11)

As already reported, Co₂(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 H₂PtCl₆-SnCl₂-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 H₂O(mmol) or H₂(mmol) (Run 11) d) Using

30 mmol of propene. e) The diphos : Co₂(CO)₈ ratio was 1 : 2. f) Using 60 mmol of H₂O. g) Without adding diphos. h) Using H₂(35 mmol) in place of H₂O(30 mmol).

i) Using cobaltcarbonyl cluster(CH₃CCo₃(CO)₉, 1.33 mmol). j) Using RhCl₃·3H₂O(0.5 mmol) and triethylamine(10 mmol) instead of Co₂(CO)₈-diphos. k) Using RuCl₃·H₂O(0.5 mmol) and triethylamine(10 mmol). l) For 24 h -reaction.

References and Notes

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- 2) G. Natta, P. Pino, and R. Ercoli, J. Am. Chem. Soc., 74, 4496(1952).
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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 C₄-aldehydes and C₄-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.
- 6) K. Bando, A. Matsuda, S. Shin, and Y. Sugi, Jap. Kokai, 77-56094; Jap. P. 78-15999 (Chem. Abs., 1977, 87, P74127q).
- 7) No hydrogen was detected in the gas above the catalyst solution after this hydrocarbonylation.
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