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HYDROFORMYLATION OF OLEFINS WITH PARAFORMALDEHYDE CATALYZED BY RHODIUM COMPLEXES

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Abstract The addition of formaldehyde to olefins is efficiently catalyzed by $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ and gives the corresponding aldehydes in neutral solution

Transition metal complexes exhibit high reactivities toward aldehydes under neutral condition The decarbonylation[1] of aldehydes and the hydroacylation[2] of olefins with aldehydes are established as valuable synthetic methods. On the other hand, formaldehyde has been rarely employed as a raw material for metal-catalyzed organic syntheses[3] in spite of its wide uses as carbonylating or reducing agent for metal complexes Formaldehyde is one of the so-called C_1-compounds Hence it is important to investigate the new reactivities of formaldehyde In this paper we describe a novel carbon-carbon bond-forming reaction between formaldehyde and olefins

When a mixture of paraformaldehyde[4] (CH_2O , 50 mmol), 1-hexene (50 mmol), and $RhH_2(O_2COH)$-$[P(i\text{-}Pr)_3]_2$[5] (**1**) (0 05 mmol) in THF (10 ml) was heated in a 65 ml stainless steel autoclave with stirring at 120°C for 20 h, linear and branched C_7-aldehydes were obtained in 384 turnovers per rhodium atom as determined on the basis of GC analysis The conversion of 1-hexene was 59 3 %. Small amounts of C_7-alcohols, C_7-carboxylates, and hexane were also formed in the following turnover number

$$C_4H_9CH{=}CH_2 \;+\; (CH_2O)_n \xrightarrow{\text{Complex } \mathbf{1}} C_6H_{13}CHO \;+\; C_6H_{13}CH_2OH \;+\; C_6H_{13}COOCH_3 \;+\; C_6H_{14}$$

Turnover Number (% linear product) 384 (44) 36 (57) 36 (84) 23

When $RhH(CO)(PPh_3)_3$ was used under the same condition, the conversion was only 6 % and the turnover number for the C_7-aldenydes was 31 The catalysts such as $RhCl(PPh_3)_3$ and $Ru(CO)_3(PPh_3)$ were virtually inactive, and a small amount of hexane alone was obtained

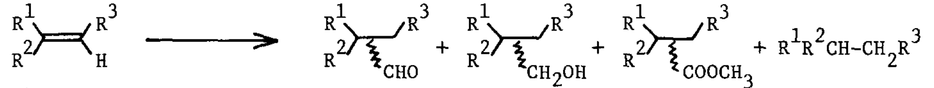
In the reaction catalyzed by **1**, raising temperature (150°C) resulted in a decrease in the yield of aldehydes and in an increase in the formation of alcohols and esters A reaction using 1-heptanal (20 mmol) instead of 1-hexene afforded heptanol, and methyl and heptyl heptanoate at

$$C_6H_{13}CHO \;+\; (CH_2O)_n \xrightarrow{\text{Complex } \mathbf{1}} C_6H_{13}CH_2OH \;+\; C_6H_{13}COOCH_3 \;+\; C_6H_{13}COOCH_2C_6H_{13}$$

Yield 42 % 28 % 5 %

150°C These facts suggest that in the reaction of 1-hexene the alcohols and the methyl esters are produced by disproportionation between the pre-formed C_7-aldehydes and formaldehyde Analogous disproportionation reactions of aldehydes to give alcohols and carboxylic acids[6], or esters[7] are known to be catalyzed by rhodium complexes.

Table Hydroformylation of Olefins with Paraformaldehyde Catalyzed by $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ a)



Substrate				Yield of Products (%) b),c)				Selectivity to
R^1	R^2	R^3	Conversion(%) b)	A	B	C	D	Carbonylation (%) d)
C_4H_9	H	H	100	67 (41)	4 (61)	13 (80)	3	97
C_6H_5	CH_3	H	73	54 (97)	12 (95)	28 (95)	5	95
$-(CH_2)_6-$			64	59	12	11	5	94
C_6H_5	H	H	100	26 (63)	14 (75)	12 (83)	23	69
H	CH_3	$COOCH_3$	100	19 (48)	5	17 (43)	49	46
H	C_6H_5	$COOCH_3$	88	11	2	10	77	23

a) Reaction conditions $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (0 05 mmol), olefin (20 mmol), paraformaldehyde (CH_2O, 50 mmol), THF (10 ml), 120°C, 20 h b) Determined by GC c) The ratios (%) of $R^1R^2CH\text{-}CHXR^3$ (X= CHO, CH_2OH, $COOCH_3$) are shown in parentheses d) (A+B+C)/(A+B+C+D) × 100

The application to several olefins was examined (see Table) Olefins having aliphatic and/or arylic substituents underwent the carbon-carbon bond-forming reaction exclusively, and gave mainly the corresponding aldehydes The reaction has an advantage of occurring under low pressures (< 10 atm) compared with the hydroformylation with CO and H_2. However, α,β-unsaturated esters were subjected to reduction

References and Notes

1) For example, see J. Tsuji, in 'Organic Syntheses Via Metal Carbonyls', Vol 2, eds. I. Wender and P. Pino, Wiley, New York, **1977**, p. 595.

2) For example, see R E campbell, Jr., C. F Lochow, K P Vora, and R C Miller, *J. Am Chem. Soc*, **102**, 5824 (1980), R. C. Larock, K. Oertle, and G F Potter, *ibid*, **102**, 190 (1980)

3) Under basic conditions, α-methylation of ketones and N-methylation of amines are known to be catalyzed by rhodium complexes Y Watanabe, Y. Shimizu, K. Takatsuki, and Y Takegami, *Chem Lett*, **1978**, 215, Y Watanabe, M Yamamoto, T Mitsudo, and Y. Takegami, *Tetrahedron Lett.*, **1978**, 1289, Y. Sugi, A Matsuda, K Bando, and K. Murata, *Chem. Lett.*, **1979**, 346.

4) Paraformaldehyde was dried in a desicator containing $CaCl_2$ for several months before use As the melting point was about 150-180°C, the CH_2O content is estimated to be at least 95 %

5) The complex can readily be prepared according to the literature method T. Yoshida, D L Thorn, T Okano, J A Ibers, and S Otsuka, *J Am Chem Soc*, **101**, 4212 (1978).

6) J Cook, J. E. Hamlin, A Nutton, and P M Maitlis, *J Chem Soc., Dalton.*, **1981**, 2342

7) T Ito, H Horino, Y Koshiro, and A Yamamoto, *Bull Chem Soc. Jpn*, **55**, 504 (1982), S Murahashi, K. Ito, T. Naota, and Y Maeda, *Tetrahedron Lett*, **1981**, 5327.

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