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ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO ARYLALDEHYDES CATALYZED BY CHIRAL COBALT(II) AND PALLADIUM(II) COMPLEXES

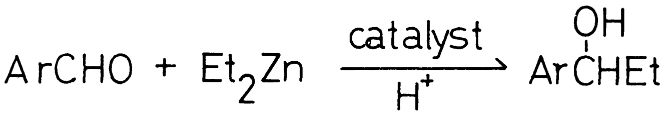
Nobuki OGUNI*, Takao OMI, Yoshihiro YAMAMOTO[†], and Akira NAKAMURA[†]
Department of chemistry, Faculty of Science, Yamaguchi University
Yoshida, Yamaguchi 753

[†]Department of Macromolecular Science, Faculty of Science,
Osaka University, Toyonaka, Osaka 560

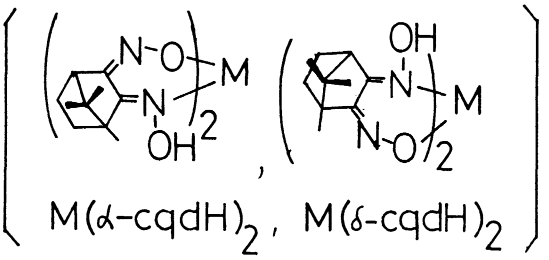
The reaction of diethylzinc with arylaldehydes catalyzed by $\mathrm{Co}(\alpha\text{-cqdH})_2$ and $\mathrm{Pd}(\alpha\text{-cqdH})_2$ in toluene at room temperature gave optically active alcohols almost quantitatively in 40~60% ee.

Recently the preparative methods of optically active alcohols by the reaction of main group organometallics with some aldehydes have been reported by employing chiral organic reagents such as chiral aminoalcohols[1)] and diamines.[2)] In order to attain high optical yield in the reported system, the use of a stoichiometric amount of chiral reagents and to run the reaction at very low temperature of -110~ -120°C are essential. A few attempts have been made in the area of asymmetric alkylation of carbonyl compounds which is catalyzed by chiral transition metal complexes.

We wish to report here that chiral catalysis of bis((-)-camphorquinone-α-dioximato)cobalt(II)[3)] and palladium(II)[4)] (abbreviated $\mathrm{Co}(\alpha\text{-cqdH})_2$ and $\mathrm{Pd}(\alpha\text{-cqdH})_2$, respectively) in reaction of diethylzinc with arylaldehydes gave optically active alcohols almost quantitatively in 40~60% ee at room temperature. It is known that that no reaction occurs between dialkylzinc and arylaldehydes in nonpolar solvents[5)]. Table lists the results obtained by the reaction of several arylaldehydes with diethylzinc.



$$\mathrm{ArCHO} + \mathrm{Et_2Zn} \xrightarrow[\mathrm{H^+}]{\text{catalyst}} \mathrm{Ar}\overset{\mathrm{OH}}{\mathrm{CH}}\mathrm{Et}$$



The general procedure for the reaction is given as follows: to a stirred solution of arylaldehyde(18 mmol) and catalyst(0.18 mmol) in toluene(20 ml) was added diethylzinc(18 mmol), and whole mixture was stirred at 20~30°C for 24~36 h under an argon atmosphere. Then dil HCl was added dropwise to the reaction mixture at 0°C and the organic layer was separated, dried over Na_2SO_4, and concentrated uner reduced pressure. The resulting alcohol was distilled under reduced pressure or purified by sublimation. The optical purity of the alcohols was determined, after acetylation, by 100 MHz NMR analysis using tris(3-heptafluorobutyryl-d-camphorato)europium(III), $\mathrm{Eu(hfbc)_3}$. The palladium(II) complex

Table. Enantioselective Addition of Diethylzinc to Arylaldehydes[a)]

Arylaldehyde	Catalyst[b)]	Time(h)	Yield(%)	$[\alpha]_D^{20}$ in C_6H_6	ee(%)[c)]
benzaldehyde	α-cqdH$_2$	24	96	- 1.50°	3.8
	Co(α-cqdH)$_2$·H$_2$O	24	88	-17.35°	43.3
	Co(δ-cqdH)$_2$·H$_2$O	24	74	- 0.77°	1.9
	Pd(α-cqdH)$_2$	48	98	-23.10°	57.7
	Pd(δ-cqdH)$_2$	48	98	-18.22°	45.5
p-tolualdehyde	Co(α-cqdH)$_2$·H$_2$O	24	91	-16.14°	39.3
	Pd(α-cqdH)$_2$	48	98	-23.20°	56.5
β-naphthaldehyde	Co(α-cqdH)$_2$·H$_2$O	24	98	-13.64°	34.2
	Pd(α-cqdH)$_2$	72	97	-18.81°	44.7

a) The molar ratio of aldehyde:diethylzinc:catalyst was 1.0:1.0:0.01. The reaction temperature was 20°C for cobalt complexes and 30°C for palladium ones. b) All catalysts were prepared by the method reported by Nakamura[3a)] and Angelici.[3b)] c) The absolute configuration of products is S.[7)]

catalysts brought about higher enantioselectivity than any cobalt(II) complex catalyst. α-CqdH itself showed very low enantioselectivity for this reaction. Among four types of cqdH$_2$(α~δ), the metal complex bearing α-type ligand attained the highest enantioselectivity for ethylation of arylaldehydes. It was reported that the highest ee values were attained in asymmetric cyclopropanation catalyzed by the metal complex of α-type camphorquinone dioxime.[6)] Results of a mechanistic study of the reaction is now in progress and will be published elsewhere.

References

1) T. Mukaiyama, K. Soai, T. Sato, H. Shimizu, and K. Suzuki, J. Am. Chem. Soc., 101, 1455(1979).

2) J-P. Mazaleyrat and D. J. Cram, J. Am. Chem. Soc., 103, 4585(1981).

3) (a) A. Nakamura, A. Konishi, and S. Otsuka, J. Chem. Soc., Dalton Trans., 1979, 488. (b) M. S. Ma and R. J. Angelici, Inorg. Chem., 19, 363(1980).

4) Since Pd(α-cqdH)$_2$ obtained by the method reported[3)] was a mixture of two stereoisomers, the main component was separated by the preparative thin-layer chromatography(silica gel). Found:C,48.57;H,6.30;N,11.75%. Calcd for Pd($C_{10}H_{15}N_2O_2$)$_2$:C,48.34;H,6.10;N,11.28%. ^{1}H-NMR in CDCl$_3$(ppm):methyl-H, 0.83(s), 0.93(s), 1.43(s); C^4-H, 2.70(m).

5) N. I. Sheverdina and K. A. Kocheshkov, "The organic compounds of zinc and cadmium," the series of "Methods of elemento-organic chemistry," vol.3, North-Holland Publishing Co. Amsterdam (1967), p. 51.

6) A. Nakamura, A. Konishi, R. Tsujitani, M. Kudo, and S. Otsuka, J. Am. Chem. Soc., 100, 3449(1978).

7) H. Kwart and D. P. Hoster, J. Org. Chem., 32, 1896(1967).

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