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SHORT COMMUNICATION

Enantioselective Dehydrogenation of Racemic 1-Phenylethanol by Some New Ruthenium(II) Chiral Phosphine Complexes

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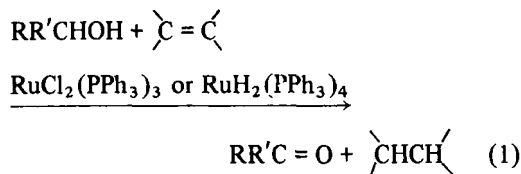
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Key Words: Asymmetric Dehydrogenation of 1-Phenylethanol by Chiral Ruthenium(II) Complexes.

INTRODUCTION

Ruthenium(II) triphenylphosphine complexes are known to catalyze the transfer hydrogenation of olefins by primary or secondary carbinols:¹

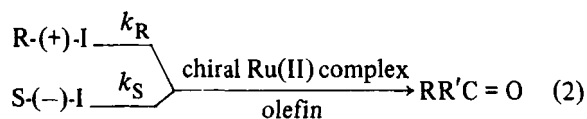


When the above reaction is carried out with Ru(II) chiral phosphine complexes, an enantioselective dehydrogenation of racemic RR'CHOH could be expected.

The present authors report, here, on the enantioselective dehydrogenation of racemic 1-phenylethanol, I, by isolated crystalline Ru(II) chiral phosphine complexes² of RuCl₂((-)-o-ampp)₂(PPh₃), RuCl₂((-)-p-ampp)₂(PPh₃), RuCl₂((+)-bmpp)₃, RuCl₂((-)-pmpp)₃, and Ru₂Cl₄((-)-diop)₃ (note Table I) or by RuCl₂((+)-nmdp)₃ and RuBr₂((+)-nmdp)₃ (nmdp = neomenthylidiphenylphosphine) prepared *in situ* from RuCl₂(PPh₃)₃ (and/or RuBr₂(PPh₃)₃) and nmdp.

The enantioselective dehydrogenation of I by the above chiral Ru(II) complexes at 120–190°C in the presence of benzylideneacetone resulted in the appreciably predominant consumption of one of the enantiomers with an almost quantitative formation of acetophenone. The enantioselectivity was very low but reproducible, and the optical purity (O.P.) of I obtained by fractional distillation without any contaminants possessing the optical rotation

increased with increasing conversion (Conv.), obeying a pseudo-first-order rate law reflected in almost constant k_R/k_S ratio under Conv. 70% (see Table I):



where each rate constant was evaluated by $k_R = (\ln[R]_0/[R])/t = -(\ln(100-\text{Conv.})(100 - \text{O.P.})/10^4)/t$ $k_S = (\ln[S]_0/[S])/t = -(\ln(100-\text{Conv.})(100 + \text{O.P.})/10^4)/t$ (t: reaction time).

The results of a representative series of the experiments are shown in Table I. There was no regularity between the selection of the R or S isomer and the optical rotation (+ or -) of the complex or the chiral phosphine, and the magnitude of the enantioselectivity (defined by k_R/k_S) showed no direct correlation with the dehydrogenation rate and the molecular rotation ($[\alpha]_M$) of the complex or the phosphine.³ These facts may imply that the reaction course and the coordination distance of RR'CHOH toward a complex in Reaction(3c) are not systematically constant. However, it can be said that the unsaturated additive of benzylideneacetone substantially increases the selectivity, in comparison with the results of the dehydrogenation of I without olefins, *via* the induced asymmetry⁴ shown by the intermediate II in Reaction(3b). In this respect, the hydrogenation of benzylideneacetophenone by I with RuCl₂((+)-nmdp)₃ or that of 2-ethylhexylmethacrylate by I with Ru₂Cl₄((-)-diop)₃ at 180°C under the same conditions as in Table I resulted in $k_R/k_S = 1.27$ (O.P. = 2.01% at Conv. = 17.3%) and

TABLE I
Enantioselective dehydrogenation of I by Ru(II) chiral phosphine complexes in the presence of benzylideneacetone^a

Complex ^b ([α] M)	Temp. (°C)	Time (hr)	Conv. (%)	[α] _D ²⁵ (deg.)	O.P. (%)	10 ⁶ k _S (sec ⁻¹)	10 ⁶ k _S (sec ⁻¹)	k _R /k _S	ΔH^\ddagger ΔH^\ddagger (kcal/mol)	$-\Delta S^\ddagger$ $-\Delta S^\ddagger$ (e.u.)
RuCl ₂ ((+)- nmdp) ₃	165 (165)	5.0 (5.0)	18.7 (11.3)	-0.616 (-0.035)	1.17 (0.07)	12.1 (6.73)	10.8 (6.65)	1.12 (1.01)	21.1 ± 0.6 22.5 ± 0.7 7.4	32.7 ± 1.3 30.6 ± 1.4 2.1
	180	2.5	22.8	-0.910	1.73	30.7	26.9	1.14		
	180	5.0	38.2	-1.199	2.28	28.0	25.5	1.10		
	180 (180)	5.0 (5.0)	19.4 (19.4)	-0.023 (-0.023)	0.044 (0.044)	12.0 (12.0)	11.9 (11.9)	1.01 (1.01)	(14.3) (14.5)	(50.3) (49.9)
	180	7.5	54.1	-1.613	3.07	30.0	27.7	1.08		
	190	5.0	60.3	-1.106	2.11	52.4	50.1	1.05		
	170	5.0	23.5	-0.899	1.71	15.8	13.9	1.14	34.3 ± 0.1	3.81 ± 0.1
	180	2.0	28.6	-0.293	0.56	47.6	46.1	1.03	36.1 ± 0.1	-0.01 ± 0.1
	190	1.0	27.1	-0.321	0.61	89.4	86.4	1.03	7.8	3.82
	160	30.0	8.56	0.088	0.17	0.85	0.88	0.96	41.6 ± 0.1	-8.88 ± 0.1
RuCl ₂ ((-)- ampp) ₂ (PPh ₃) (-260°)	170	24.0	21.29	0.170	0.32	2.69	2.76	0.97	39.8 ± 0.1	-4.97 ± 0.2
	180	10.0	51.58	-1.645	3.13	21.0	19.3	1.09	7.8	3.97
	160	7.0	36.63	0.100	0.19	18.3	18.4	0.99	20.69 ± 0.0 ₃	-33.31
	170	6.0	45.31	0.136	0.26	27.6	27.8	0.99	20.67 ± 0.0 ₃	-33.34
	180	5.0	63.47	0.192	0.37	55.0	55.4	0.99	0.02	0.03
	160	24.0	54.73	-0.335	0.64	9.25	9.10	1.02	16.5 ± 0.5	44.3 ± 1.1
	170	17.0	61.82	-0.518	0.99	15.9	15.6	1.02	16.3 ± 0.5	44.6 ± 1.1
	180	9.0	49.31	-0.469	0.89	21.3	20.7	1.03	0.2	0.3
	190	8.0	63.89	-0.726	1.38	35.9	34.9	1.03		
	160	14.5	34.24	0.379	0.72	7.89	8.17	0.99	4.18	73.0
RuCl ₂ ((-)- pmpp) ₃ (+260°)	170	12.0	32.36	0.096	0.18	9.01	9.09	0.99	3.22	75.2
									0.96	2.2
									0.1	0.2
Ru ₂ Cl ₄ ((-)- diop) ₂ (+6938°)	120	34.0	18.51	-0.152	0.09	2.35	2.28	1.03	20.4 ± 0.1	33.1 ± 0.3
	130	24.0	35.94	-0.324	0.62	5.23	5.09	1.03	20.3 ± 0.2	33.3 ± 0.4
	150	6.0	27.10	-0.303	0.58	14.9	14.4	1.03	0.1	0.2

^a [benzylideneacetone]₀/[I]₀ = 0.84.

^b [complex]₀ = 8.0 mM except [Ru₂Cl₄((-)-diop)]₀ = 4.0 mM. ampp = anisylmethylphenylphosphine; bmpp = benzylmethylphenylphosphine; pmpp = propylmethylphenylphosphine; diop = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane.

^c [α]_D²⁵ -52.5° (c 2.27, CH₂Cl₂).^d Italic values are parameter difference between the isomers, and values in parentheses are those for the reaction without olefins.

The detailed investigation of these circumstances of the temperature effect is now in progress in connection with the enhancement of the enantioselectivity by the use of more bulky carbinols and effective Ru(II) chiral phosphine complexes.

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