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MOLECULAR ASYMMETRY INDUCED BY UNSATURATED ADDITIVES IN THE ENANTIOSELECTIVE DEHYDROGENATION OF RACEMIC 1-PHENYLETHANOL BY $RuCl_2(PPh_3)_3$ AND (+)-NEOMENTHYLDIPHENYLPHOSPHINE

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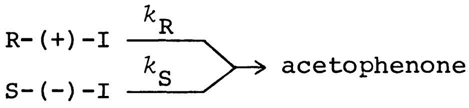
Several unsaturated additives enhanced the enantioselective ability of a catalytic system of $RuCl_2(PPh_3)_3$ and (+)-neomenthyldiphenylphosphine in dehydrogenation of racemic 1-phenylethanol through the chirality induced by their coordination to the complex.

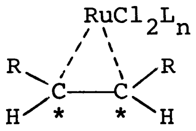
Although the hydrogen transfer from alcohols to unsaturated compounds catalyzed by Ru(II) triphenylphosphine complexes has recently been documented,$^{1)}$ there are no reports on the enantioselective dehydrogenation of racemic alcohols with Ru(II) chiral phosphine complexes except our short communication$^{2)}$ on the catalytic enantioselection of 1-phenylethanol, I, by $RuCl_2(PPh_3)_3$ and (+)-neomenthyldiphenylphosphine (NMDP). It has recently been observed that unsaturated compounds such as benzalacetone enhance the catalytic enantioselection of I with the predominant formation of acetophenone (more than 95 mol% in the products):

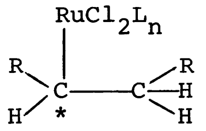


(k_R and k_S=pseudo-first-order rate constants)

The selectivity defined by k_R/k_S was also found to be kept constant during the transfer hydrogenation from I to an unsaturated species.

The present authors report, here, on the effect of unsaturated additives on the catalytic enantioselection of I by $RuCl_2(PPh_3)_3$ and NMDP at 180° C. The results of a representative series of the experiments are shown in Table 1. The enhancement of the enantioselectivity by the unsaturated additives suggests the importance of the chirality induced by coordination of the unsaturated species to the complex:





(L=PPh_3 and/or NMDP;n=2 or 3$^{3)}$)

It is also notable from Table 1 that there is no direct correlationship between the dehydrogenation rate and the enantioselectivity.

Among the unsaturated additives tested, two unsaturated ketones, PhCH=CHCOPh and PhCH=CHCOMe, were the most effective, and PhCH=CHPh was markedly less effective than the above ketones. Hence, one could suppose that with the particular additives (the ketones) there is some phosphobetaine formation with the chiral ligand$^{4)}$ and the phosphobetaine $(R'_3\overset{+}{P}CH(Ph)CH{=}C(R)\overset{-}{O})$ formed is then bound in a new catalytically active species. Secobarbital having an asymmetric center

Table 1. Catalytic Enantioselection of I by $RuCl_2(PPh_3)_3$ (8 mM) and (+)-NMDP ($[NMDP]_0/[RuCl_2(PPh_3)_3]_0=6$) at 180° C for 8 hr ($[\text{unsaturated additive}]_0/[I]_0=0.84$)

Unsaturated additives	Conversion (%)	$[\alpha]_D^{23}$ a)	Optical purity (%)	$10^5 k_R$ (s^{-1})	$10^5 k_S$ (s^{-1})	k_R/k_S
Benzalacetone b)	38.2	-1.199°	2.284	2.802	2.548	1.100
Benzalacetophenone	17.3	-1.055°	2.010	0.7289	0.5892	1.273
trans-Stilbene	26.2	-0.053°	0.100	1.089	1.051	1.036
Secobarbital b)	22.6	-0.376°	0.715	1.464	1.385	1.057
2-Ethylhexyl methacrylate	11.0	-0.289°	0.570	0.4158	0.3958	1.051
n-Hexyl methacrylate	13.7	-0.073°	0.138	0.5161	0.5064	1.019
n-Dodecyl methacrylate	34.2	-0.065°	0.124	2.333	2.319	1.006
Ethyl cinnamate	36.1	-0.050°	0.095	1.558	1.552	1.003
None b)	19.4	-0.023°	0.044	1.199	1.194	1.004

a) $[\alpha]_D^{23}$ -52.5°, c 2.27 in CH_2Cl_2 (from Ref.6). b) Reaction time=5 hr.

in its stereochemically bulky fragment was next to the unsaturated ketones in terms of the enhancement of the enantioselectivity of I.

In regard to methacrylate esters ($CH_2=C(Me)CO_2R$), 2-ethylhexyl methacrylate involving an asymmetric carbon in the R group resulted in the distinctive high selection. The importance of such an asymmetric center in the R group is now under investigation. Anyhow, $CH_2=C(Me)CO_2R$ *per se* was observed to be less effective than PhCH=CHCOR-type olefins. This may be in harmony with the fact that, in the asymmetric hydrogenation of $CH_2=C(Ph)COPh$ and $CH_2=C(Ph)CO_2Me$ with a chiral Co(II) complex, the optical yield of the hydrogenation product of the latter is very low in comparison with that of the former.5)

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