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ASYMMETRIC HYDROFORMYLATION OF STYRENE BY OPTICALLY ACTIVE PHOSPHINE-RHODIUM COMPLEX CATALYST

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Styrene was hydroformylated by a rhodium catalyst in the presence of excess (+)-benzylmethylphenylphosphine (10 moles per 1 atom Rh) at 120°c under 100 atm(initial) of synthesis gas ($CO/H_2=1$) to give an optically active product ($[\alpha]_D^{25}$ +38.5°, content of hydratropaaldehyde 90%).

Attempt to synthesize optically active compounds using asymmetric catalyst is a current trend in the field of metal complex chemistry, and fairly good results have so far been obtained in the hydrogenation of substituted olefins1).

Very recently, Tanaka et al2) have briefly reported the formation of optically active hydratropaaldehyde (α-phenylpropionaldehyde) in the hydroformylation of styrene using an optically active phosphine-rhodium complex catalyst, i.e., $RhCl(CO)(PPh_2R^*)_2$ (R*= Neomenthyl), but the optical yields were very low.

On the basis of the facts described in our preceding paper3), we are of the opinion that the number of the phosphine ligands attached to the proposed active catalyst species, $HRh(CO)_{4-n}(PR_3)_n$, may be smaller than two under the usual "Oxo-reaction" conditions, i.e., at high temperature and under high carbon monoxide pressure. Therefore, we tried the titled reaction under the conditions which would be favorable for the co-ordination of phosphine to rhodium and could really obtain significant results as shown in Table I. Thus, the chirality of phosphine ligand could be effectively transfered to the products through applying more than two moles of (+)-benzylmethylphenylphosphine4) per one atom of rhodium and at preferably lower reaction temperature, namely, in the conditions which are favorable for the formation of α-isomer as described previously3).

Table I. Hydroformylation[a] of Styrene (8 g) in Toluene (16 ml) by [RhCl(1,5-hexadiene)]$_2$ (8 mg) and (+)-Benzyl·Me·Ph·Phosphine[b]

Exp. No.	1	2	3	4	5	6	7
P/Rh (atom/atom)	1.5	2	3	4	10	10	10
Reaction temperature (°C)	140	140	140	140	120	140	160
Reaction time (min)	60	65	95	180	400[c]	200	120
Analyses of "Oxo-product"							
Yield (wt%)[d]	93	91	97	93	88	85	90
Content of α-isomer (%)[e]	48.5	47.1	78.3	84.3	90.2	85.6	80.1
$[\alpha]^{25}_{D}$ of mixture[f]	+2.6	+1.8	+14.9	+22.0	+38.5	+22.1	+11.5
$[\alpha]^{25}_{D}$ of α-isomer[g] (calcd.)	+5.4	+3.8	+19.0	+26.1	+42.7	+25.8	+14.4

a) Carried out in a 100 ml autoclave(SUS-27) under 100 atm(initial) of synthesis gas (1:1). b) Added as a toluene solution to make up desired phosphine-rhodium ratio in the reactor. c) Reaction was discontinued at ca 85% conversion. d) Obtained by vacuum distillation (bp 85～100°C/10 mmHg), and containing only α- and β-phenylpropionaldehydes. e) Analyzed by g.l.c. at 160°C using a 3 mmØ × 3 m column of DEGS 15% on NEOPAK-AS(60～80 mesh). f) Measured by a RUDOLPH 80 spectropolarimeter in toluene (c=2～3, ℓ=1.0). g) Value of the optically pure (+)-hydratropaaldehyde is unknown. Its reduction by $LiAlH_4$ seems to result significant racemization. (+)-α-Phenylpropanol[5] and (+)-hydratropic acid[6] are known to have $[\alpha]^{25}_{D}$-value of +16.7° and +92.5°, respectively.

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