

Asymmetric Hydroformylation of Styrene by Chiral Platinum Catalysts: A Re-evaluation of the Optical Yields

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Previously estimated optical yields in the asymmetric hydroformylation of styrene (up to 95%) have been found to be considerably lower (up to 73%).

In a previous communication on styrene hydroformylation with the chiral $[(-)-2,2\text{-dimethyl-4,5-bis}(5H\text{-dibenzophosphol-5-ylmethyl})\text{-1,3-dioxolane}]\text{-platinum(II) chloride-tin(II) chloride } [(-)\text{-DBP-DIOP-PtCl}_2]$ catalytic system, a maximum optical yield of *ca.* 95% was estimated by comparing the specific rotatory power of the purified product, 2-phenylpropanal, measured in benzene solution (1.5–20 g in 100 ml) at 21 °C with the maximum specific rotatory power determined for neat (*S*)-2-phenylpropanal at 25 °C ($[\alpha]_{\text{D}}^{25} = +238$).² Since in some cases, $[\alpha]$ in dilute solution can be remarkably different from α neat, we have prepared a sample of 2-phenylpropanal having $\alpha_{\text{D}}^{25} +161.8$ (neat) and we have measured $[\alpha]_{\text{D}}^{25}$ in benzene at different concentrations. The results reported in Table 1 show that $[\alpha]_{\text{D}}^{25}$ in benzene increases substantially with decreasing concentration and it is in all cases larger than α_{D}^{25} (neat). Therefore, to establish the optical purity of the synthesized 2-phenylpropanal without isolating it, the $[\alpha]_{\text{D}}$ measured must be compared with the $[\alpha]_{\text{D}}$ measured using a sample of aldehyde of known optical purity in the same solvent and at the same concentration.

Using this procedure the maximum optical yield obtained in a new series of experiments carried out under the previously

published conditions¹ was *ca.* 73%. For these same samples using α_{D}^{25} (neat) of 2-phenylpropanal as referenced, erroneously higher optical purities between 87 and 95% are obtained by varying the concentration of 2-phenylpropanal in benzene solution between 20 and 1.5 g per 100 ml. These results duplicated the previously published data.¹

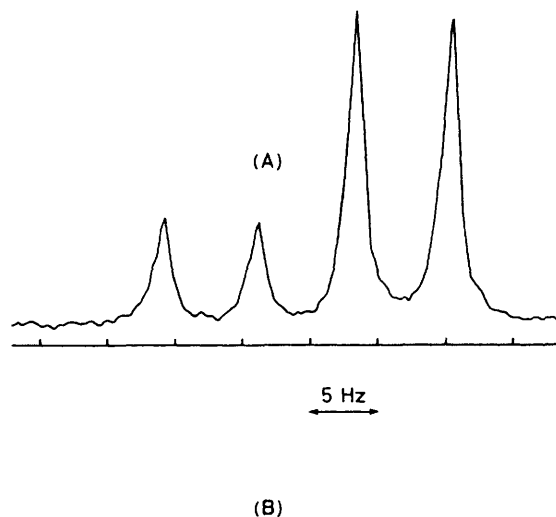


Figure 1. ¹H N.m.r. spectrum (Bruker WH90) of (+)-(S)-2-phenylpropanal [α_{D}^{25} (neat) + 137.6] (10 mg) in [²H₁₂]cyclohexane in the presence of Eu(dmc)₃ (17 mg): (A) methyl proton region; (B) formyl proton region.

Table 1. Influence of the dilution on the specific rotatory power of (*S*)-2-phenylpropanal (o.p. 68%) in benzene solution.

Conc./ (g per 100 ml)	$[\alpha]_{\text{D}}^{25}$	$[\alpha]_{\text{D}}^{21}$
neat	161.8°	166.6°
46.43	177.9	182.2
18.57	190.5	195.4
9.29	196.6	201.9
7.43	202.7	207.9
3.72	205.8	211.3
1.49	209.1	214.7

Table 2. Asymmetric hydroformylation of styrene catalysed by^a homogeneous (–)-DBP–DIOP–PtCl₂

Pressure/ kg cm ⁻²	H ₂ :CO	Time/h	T/°C	Aldehyde ^b selectivity	b:n ^c	[α] _D ²¹	Optical yield/% ^d
225	2.4	40	40	69	4.0	+241.1°	76.3
220	2.6	40	40	65	4.1	+232.5	73.6
314	2.9	55	36	64	4.4	+252.1	79.8

^a Carried out in 50 ml glass-lined autoclaves (steel type 316ss): preformed (–)-DBP–DIOP–PtCl₂, 8 × 10⁻⁶ mol (except run 3 which employed 4 × 10⁻⁵ mol); styrene 0.5 ml, benzene 10 ml. Tin added as SnCl₂–H₂O, Sn:Pt = 2.5. Styrene conversions >90% in each case. The amount of each isomer was determined by g.l.c. (SE 30 on Anakrom, 110–200 °C at 8 °C min⁻¹) with decane as the internal standard. ^b Aldehyde selectivity was based on amount of styrene consumed; ethylbenzene was the other product. ^c b:n is the branched:normal isomer ratio; the overall chemical yield of 2-phenylpropanal is ca. 50% in the experiments reported. ^d Specific rotation based on [α]_D²¹ = 315.8° for 100% optically pure 2-phenylpropanal (ca. 1.5 g in 100 ml of benzene) as determined in this paper.

Since the optical yield does not always reflect exactly the enantiomeric excess, we have confirmed by n.m.r. spectroscopy the maximum value of 238° for α_D²⁵ (neat) of the optically pure (*S*)-2-phenylpropanal previously obtained by extrapolation from samples having a lower optical purity.² Indeed a chemically pure sample of the aldehyde (b.p. 65–66 °C at 5 mmHg; n_D²⁰ 1.5181) having α_D²⁵ +137.6 (neat) shows an enantiomeric excess of 58 ± 2% {determined by n.m.r. spectroscopy in the presence of tris[di-(+)-camphoryl-methanato]europium(III) [Eu(dmc)₃] and based on the integration of the signals corresponding to the methyl and to the formyl protons} (Figure 1).

The corrected values of the optical yield obtained in the hydroformylation of styrene (ca. 73%) still represent the

highest enantiomeric excess reported in asymmetric hydroformylation.³ In fact, we have now achieved even higher optical yields (ca. 80%) by slight modifications of the previously reported conditions¹ (see Table 2).

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