

**Asymmetric Hydrogenation at a Rhodium Complex using (+)- or (-)-PhCHMe·NHCHO or (-)-MeCH(OH)·CONMe<sub>2</sub> as Ligands**

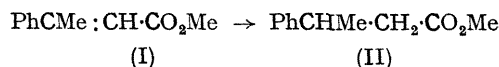
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**Summary** Methyl 3-phenylbut-2-en-oate is homogeneously hydrogenated at a rhodium complex formed in (+)- or (-)-1-phenylethylformamide to give (+)- or (-)-methyl 3-phenylbutanoate in better than 50% optical yield.

FOLLOWING our observation<sup>1</sup> of homogeneous hydrogenation by a rhodium complex formed in dimethylformamide solution and bearing dmf as a ligand, we examined the possibility of asymmetric hydrogenation in a system of this

kind. A complex prepared by reducing  $\text{py}_3\text{RhCl}_3$  with sodium borohydride in (+)- or (-)- $\text{PhCHMe}\cdot\text{NHCHO}$  as solvent was found to catalyse the hydrogenation of methyl 3-phenyl-butanoate (I):



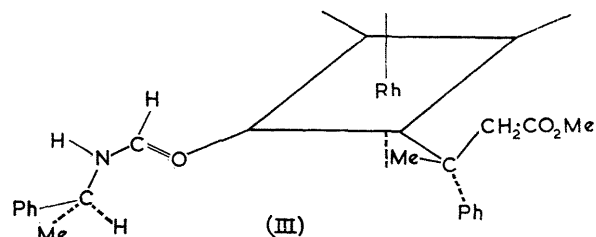
with the following results:

$\text{PhCHMe}\cdot\text{NHCHO}$ (ref. 2)	$\text{PhCHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}^a$
$[\alpha]_D +180^\circ$	(i) $+33^\circ$ (ii) $+31^\circ$
$[\alpha]_D -172^\circ$	(i) $-28^\circ$ (ii) $-27.2^\circ$

<sup>a</sup> Pure  $\text{PhCHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ ,  $[\alpha]_D +$  or  $-58^\circ$  (ref. 3).

The values of  $[\alpha]_D$  under (i) refer to distilled methyl 3-phenyl-butanoate (II) from the reaction. To avoid the possibility of contamination with the optically active amide this product was hydrolysed and the crystalline 3-phenylbutanoic acid was re-esterified; the ester gave the data under (ii). (*R*)-(-)-3-Phenylbutanoic acid correlates *via* (*S*)-(+)-hydratropic acid<sup>4</sup> with (*S*)-(-)-1-phenylethylamine,<sup>5</sup> and the induced asymmetry observed leads to (III) as a reasonable representation of the half-hydrogenated

state; the complementary steric arrangement of the ligands is apparent.



These observations extend earlier results in heterogeneous<sup>4</sup> and homogeneous<sup>6</sup> systems. However, the degree of induced asymmetry represents an appreciable advance. Also, in this catalyst system, the asymmetric ligand may easily be varied. For example, hydrogenation of methyl phenylbutanoate (I) using (*S*)-(-)-lactidimethylamide as solvent gave methyl 3-phenylbutanoate (II) of  $[\alpha]_D -9^\circ$ . The correlation is again between the (*S*)-amide and the (*R*)-phenyl butanoate, but the hydroxy-group being much smaller than phenyl, the effective asymmetry of the ligand and the induced asymmetry is smaller in this case.

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