Asymmetric Hydrogenation at a Rhodium Complex using (+)- or (-)-PhCHMe·NHCHO or (-)-MeCH(OH)·CONMe₂ as Ligands

By Peter Abley and F. J. McQuillin*

(School of Chemistry, The University, Newcastle upon Tyne NE1 7RU)

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 observation¹ 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 py3RhCl3 with sodium borohydride in (+)- or (-)-PhCHMe·NHCHO as solvent was found to catalyse the hydrogenation of methyl 3-phenyl-butenoate (I):

$$\begin{array}{ccc} \text{PhCMe}: \text{CH} \cdot \text{CO}_2 \text{Me} & \rightarrow & \text{PhCHMe} \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Me} \\ & & \text{(I)} & \text{(II)} \end{array}$$

with the following results:

PhCHMe·CH₂·CO₂Me^a PhCHMe·NHCHO (ref. 2) $[\alpha]_D + 180^\circ$ (i) $+33^{\circ}$ (ii) $+31^{\circ}$ $[\alpha]_{D}$ -172° (i) -28° (ii) -27.2°

^a Pure PhCHMe·CH₂·CO₂Me,[α]_D + or - 58° (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 acid⁴ with (S)-(-)-1-phenylethylamine,5 and the induced asymmetry observed leads to (III) as a reasonable representation of the half-hydrogenated state; the complementary steric arrangement of the ligands

These observations extend earlier results in heterogeneous⁴ and homogeneous⁶ 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 phenylbutenoate (I) using (S)-(-)-lactdimethylamide 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.

We thank Unilever for financial support.

(Received, March 19th, 1969; Com. 391.)

¹ I. Jardine and F. J. McQuillin, preceding Communication.

 I. Jardine and F. J. McGuinin, preceding Communication.
R. Huisgen and C. Rüchardt, Annalen, 1956, 601, 1.
D. J. Cram, J. Amer. Chem. Soc., 1952, 74, 2137.
V. Prelog and H. Scherrer, Helv. Chim. Acta, 1959, 42, 2227.
H. I. Bernstein and F. C. Whitmore, J. Amer. Chem. Soc., 1939, 61, 1324; C. L. Arcus and J. Kenyon, J. Chem. Soc., 1939, 916.
L. Horner, H. Siegel, and H. Büthe, Angew. Chem. Internat. Edn., 1968, 7, 942; W. S. Knowles and M. J. Sabacky, Chem. Comm., 1920, 1445. 1968, 1445.