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ASYMMETRIC REDUCTION OF KETONES VIA HYDROSILYLATION CATALYZED BY A RHODIUM(I) COMPLEX WITH CHIRAL PHOSPHINE LIGANDS

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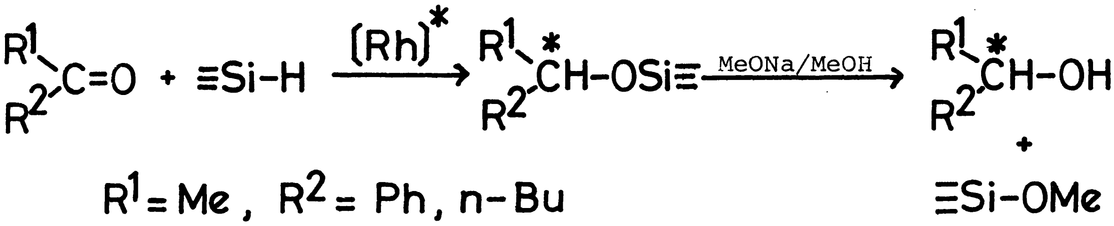
Asymmetric reduction of ketones has been achieved via catalytic hydrosilylation using rhodium(I) complex with an optically active phosphine ligand as a catalyst.

Homogeneous hydrogenation catalyzed by rhodium complex is attracting much interest,1) and recently, asymmetric hydrogenation of ketones by the use of a cationic rhodium(I) catalyst with a chiral phosphine ligand was reported to be achieved with a low optical yield.2) However, non-cationic rhodium complexes such as tris(triphenylphosphine)chlororhodium can effect only the reduction of the unsaturated carbon-carbon bonds but not of the carbonyl functions, because of the lack of activity for the latter system.3) This limitation can be overcome, since we already reported the effective reduction of various carbonyl compounds via hydrosilylation catalyzed by tris(triphenylphosphine)chlororhodium.4) We now report our preliminary results on the new asymmetric reduction of prochiral ketones with this method to optically active alcohols.5)

We prepared an optically active catalyst using as the ligand (-)-(S)-benzylmethylphenylphosphine6) (optical purity7) 62%) by the reaction of $[Rh(1,5\text{-hexadiene})Cl]_2$ or $[Rh(\text{cyclooctadiene})Cl]_2$ with two equivalents of the chiral ligand.1)



Scheme 1.

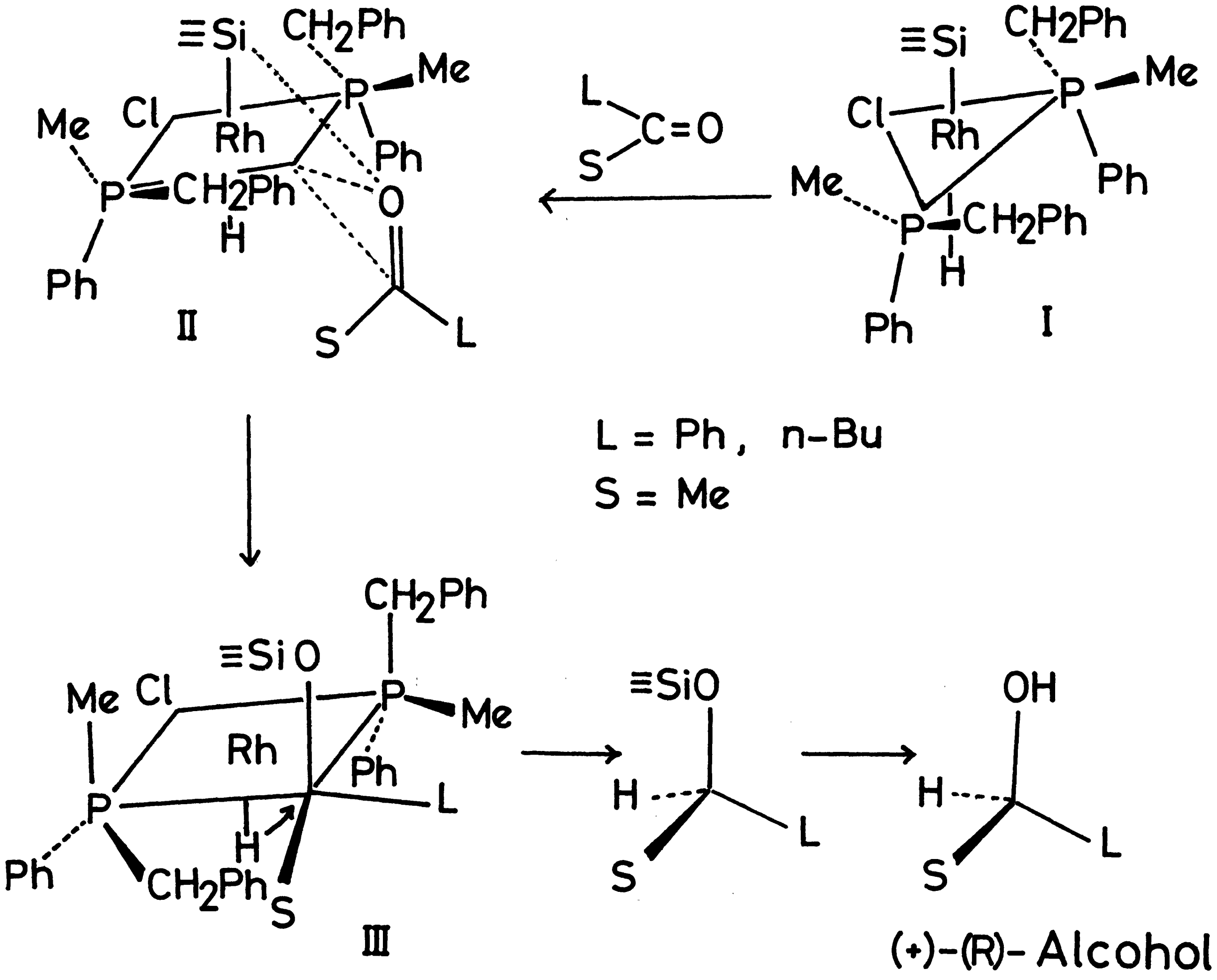
A typical procedure is described for the reduction of phenyl methyl ketone; To a benzene solution (15 ml) of the catalyst (0.2 mmol, 1 Mol%) were added 2.72 g (20 mmol) of dimethylphenylsilane and 2.40 g (20 mmol) of phenyl methyl ketone and heated at 50°C for 8 hr with stirring. The resulting silyl ether,8) PhMe$\overset{*}{\mathrm{C}}$H-OSiMe$_2$Ph, was obtained by distillation of the reaction mixture (92% yield, bp 92°C/0.18 mmHg, $[\alpha]_D^{21}$ + 20.8°, c 10.0, in benzene). The silyl ether was easily solvolyzed by methanol in the presence of sodium methoxide to give (+)-(R)-1-phenylethanol in quantitative yield ($[\alpha]_D^{21.5}$ + 14.3°, c 1.50 in CH_2Cl_2; For the pure (-) isomer lit.,9) $[\alpha]_D^{23}$ - 52.5°, c, 2.27 in CH_2Cl_2) with an optical yield10) of 43.1 %,11) accompanied by phenyldimethylmethoxysilane which was readily separated by a column chromatography on silica gel.

In a similar manner, hexan-2-one was reduced to hexan-2-ol with a significant optical activity corresponding to an enrichment in the (+)-(R)-enantiomer. Thus, (+)-(R)-hexan-2-ol ($[\alpha]_D^{23}$ + 2.24°; for the pure sample, lit.,12) + 12.0°) was obtained with an optical yield of 30% when diethylsilane was used.10) The corresponding silyl ether was obtained in 93% yield (n-BuMe$\overset{*}{\mathrm{C}}$H-OSiHEt$_2$8); bp 65°C/10 mmHg, $[\alpha]_D^{20}$ + 3.20, c, 3.99). However, the optical yield was rather low (3.1%) when phenyldimethylsilane was employed.

The optical yield appears to depend on the structure of the substrate and is also affected by that of the hydrosilane employed, as seen above. Since we can use various hydrosilanes as reducing agent,4) and this is a characteristic point of this reduction method, optimum optical yield will be attained with a hydrosilane of proper character.

In connection with the mechanism of the asymmetric induction, it is of interest that (+)-(R)-alcohols were obtained from (-)-(S)-chiral ligand. The phenomenon can be well explained by taking into account the intermediacy of the organorhodium complex III as shown in the Scheme 2, and its stereochemistry: It is appropriate to assume the intervention of the complex I and II since the first step of the reaction may be the oxidative addition of a hydrosilane to the rhodium(I) complex,4a) considering also the established structures of a dihydrido complex and a silyl hydrido complex of tris(triphenylphosphine)chlororhodium.13) The formation of the organorhodium complex III is also reasonable on account of large bond energies of silicon-oxygen bond and rhodium-carbon bond.4c) A hydride transfer in this conformation from the rhodium complex to the carbon atom may lead to the silylated (+)-(R)-1-phenylethanol or (+)-(R)-hexan-2-ol.

A further investigation on the details of this asymmetric reduction is now undergoing.



Scheme 2.

References

1) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, J. Amer. Chem. Soc., 93, 1301 (1971); T. P. Dang and H. B. Kagan, Chem. Commun., 1971, 481; P. Abley and F. J. McQuillin, ibid., 1969, 477; P. Abley and F. J. McQuillin, J. Chem. Soc. (C), 1971, 844; W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, J. C. S. Chem. Commun., 1972, 10; L. Horner, H. Siegel, and H. Buthe, Angew. Chem. Internat. Ed., 7, 942 (1968); W. S. Knowles and M. J. Sabacky, Chem. Commun., 1968, 1445.

2) P. Bonvicini, A. Levi, G. Modena, and G. Scorrano, J. C. S. Chem. Commun., 1972, 1188.

3) R. R. Schrock and J. A. Osborn, Chem. Commun., 1970, 567; A. J. Birch and K. A. M. Walker, J. Chem. Soc. (C), 1966, 1894.

4) (a) I. Ojima, M. Nihonyanagi, and Y. Nagai, Chem. Commun., 1972, 938; (b) I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, Bull. Chem. Soc. Japan, 45, 3232 (1972); (c) I. Ojima, M. Nihonyanagi, and Y. Nagai, ibid., 45, 3722 (1972); (d) I. Ojima, T. Kogure, and Y. Nagai, Tetrahedron Lett., 1972, 5035.

5) During our investigation on the asymmetric reduction via hydrosilylation, Yamamoto, Hayashi, and Kumada reported on the same subject using a platinum catalyst although the optical yields were low. [K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 46, C65 (1972).]

6) K. Naumann, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 91, 7012 (1969).

7) An optical purity was determined by quarternization[6] using n-propyl bromide: $(-)$-PhMe(PhCH$_2$)P$^+$Pr^{n}Br$^-$, $[\alpha]_D^{28}$ -22.68°; the value for the pure sample calculated from that in the literature[6]: $[\alpha]_D$ -36.58°.

8) The nmr spectra and elemental analyses of the silyl ethers were consistent with the assigned structures.

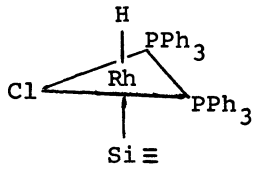
9) U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, Tetrahedron, 21, 1701 (1965).

10) Optical yields are calibrated for the optical purity of the chiral phosphine employed.

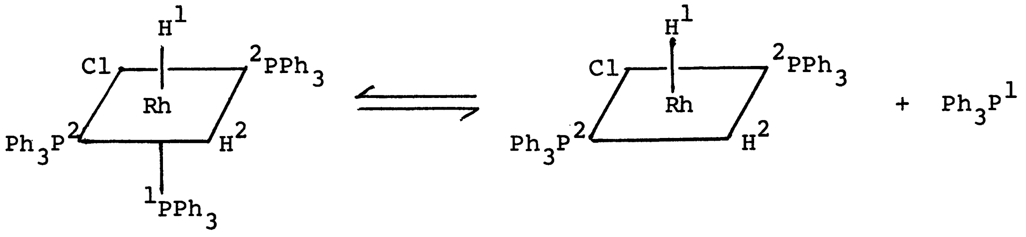
11) The optical yield obtained by us is the highest one ever known for the asymmetric reduction of simple ketones by homogeneous catalytic reactions.

12) P. G. Stevens, J. Amer. Chem. Soc., 55, 4237 (1933).

13) Haszeldine et al. established the trigonal bipyramidal configuration for the structure of the silyl hydrido complex on the basis of X-ray analyses [R. N. Haszeldine, R. V. Parish, and D. J. Parry, J. Chem. Soc. (A), 1969, 683],



and as for the dihydrido complex, the following structure was confirmed by Meakin et al. [P. Meakin, J. P. Jesson, and C. A. Tolman, J. Amer. Chem. Soc., 94, 3240 (1972)]



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