Tetrahedron Letters No. 19, pp 1635 - 1636, 1978. 0040-4039/78/0501-1635. $02.00/0.

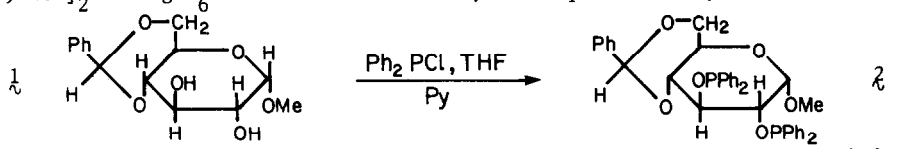
ASYMMETRIC HYDROGENATION CATALYZED BY DIPHOSPHINITE RHODIUM COMPLEXES DERIVED FROM A SUGAR

William R. Cullen* and Yoshihiro Sugi
Department of Chemistry
University of British Columbia
Vancouver, B.C., Canada V6T 1W5

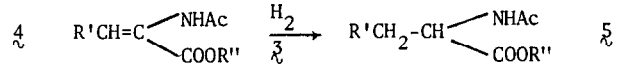
(Received in USA 20 December 1977; received in UK for publication 23 March 1978)

Recently, several chelating chiral ligands have been developed for use in the preparation of transition metal complexes which are catalysts for asymmetric reactions.[1-10] There is considerable interest in utilizing naturally occurring chiral compounds for this purpose and to date, phosphines from tartaric acid,[1] menthol,[3] camphor[3] and 4-hydroxyprolin[4] have been developed for use in asymmetric catalysis. We now wish to describe the first example of a diphosphinite synthesized from a sugar, D-glucose, and its application in the rhodium(I) catalyzed asymmetric hydrogenation of prochiral α-acetamidoacrylic acids and their esters.

Methyl 4,6-O-benzylidene-α-D-glucopyranoside (1) was converted into methyl 2,3-bis-O-diphenylphosphino-4,6-O-benzylidene-α-D-glucopyranoside (2) by chlorodiphenylphosphine in the presence of pyridine. 2 was purified by reprecipitation from chloroform - petroleum ether (b.p. 30-60°), mp. 130-131°, $[\alpha]_D^{25}$ - 9.0° (c 8.8, chloroform).[11] 2 is stable in absolute ethanol and in air. A cationic complex, 3, [(PO-OP)Rh(NBD)]PF_6 was prepared by the reaction of 2, $[(NBD)RhCl]_2$ and $AgPF_6$ in acetone for 24 h by known procedures (NBD=norbornadiene).[12]



Hydrogenation of the α-acetamidoacrylic acids and their esters, 4, was carried out in the presence of 3 in absolute ethanol at -20 to 30°C and 1 atm of hydrogen. Table 1 shows typical results. The reaction is quantitative and rapid at low temperatures. High enantiomeric



4a, 5a R'=H R"=H; 4b, 5b R'=Ph, R"=H; 4c, 5c R'=H R"=Me; 4d, 5d R'=Ph, R"=Me.

excess, up to 80%, can be achieved, probably because of the conformational rigidity of the ligand.[5] The product amino acid derivatives have the natural, S, configuration. Lowering the temperature results in improved enantiomeric excess, but the substrate-to-rhodium ratio has little effect on selectivity. On the other hand, a substrate which has no acetamido group e.g. styrene, atropic acid, and α- and β-methylcinnamic acids, is not hydrogenated in this system. This suggests that the acetamido-group is essential for hydrogenation and that the high optical yields are due to a strong coordination of both the olefin bond and acetamido group to the rhodium.[9c,13,14]

Table 1. Asymmetric Hydrogenation of α-Acetamidoacrylic Acids and their Esters[a]

Substrate	Substrate Rh Ratio	Temperature (°C)	Time (min)	Conversion[b]	Enantiomeric excess (%) (configuration)
4a	40	30	20	100	67 (S)
4a	100	30	20	100	68 (S)
4a	100	0	30	100	74 (S)
4a	100	-20	60	100	80 (S)
4b	100	30	60	100	61 (S)
4b	100	0	90	100	75 (S)
4c	100	30	10	100	53 (S)
4c	100	0	30	100	78 (S)
4d	100	30	30	100	60 (S)
4d	100	0	180	100	65 (S)

[a] All hydrogenations were carried out with substrate (2 mmole) and 3 (0.4 ∿ 5)x10^{-2} mmole in 15 ml of absolute ethanol under 1 atm of hydrogen.
[b] Estimated by proton NMR spectra.
[c] Calculated on the basis of reported value for the optically pure compounds (R)-5a $[\alpha]_D^{25}$ + 66.5° (c 2, water) (S.M. Birbaum, L. Levitow, R.B. Kingley, and J.P. Greenstein, J. Biol. Chem., 194, 1022 (1952)); (S)-5b $[\alpha]_D^{25}$ -91.7° (c 2, water) (D.P. Wolf and C. Niemann, Biochemistry, 2, 493 (1963)); (S)-5c $[\alpha]_D^{25}$ + 46.0° (c 1, ethanol) (Ref. 1b); S-5d $[\alpha]_D^{25}$ + 101.5 (c 1, chloroform) (R. Glaser and B. Vainas, J. Organomet. Chem., 121, 249 (1976)).

A neutral rhodium catalyst formed in situ from 2 and $[RhCl(C_8H_{14})_2]_2$ is less active than the cationic one described above. It required a low substrate-to-rhodium ratio (∿40), high pressure (∿50 atm) and long reaction times (1-2 days). The enantiomeric excess results were also low; 30% (4a), 14% (4b), and 19% (4d). In contrast the related ligand (+)-trans-1,2-bis(diphenylphosphinoxy)cyclohexane does form a neutral rhodium(I) derivative which catalyzes the hydrogenation of α-acylaminoacrylic acids in high optical yields.[7]

Acknowledgments. We thank the National Research Council of Canada for financial support and Dr. G.G.S. Dutton for discussions.

References

1. (a) H.B. Kagan and J.P. Dang, J. Am. Chem. Soc., 94, 6429 (1972); (b) H.B. Kagan, J.P. Dang, and J.C. Poulin, J. Organomet. Chem., 91, 105 (1974).
2. B.D. Vineyard, W.S. Knowles, M.J. Sabacky, G.L. Bachman, and D.J. Weinkauff, J. Am. Chem. Soc., 97, 2567 (1976); 99, 5946 (1977).
3. J.D. Morrison, W.F. Masler, and M.K. Neuberg, Adv. Catal., 25, 81 (1976).
4. (a) K. Achiwa, J. Am. Chem. Soc., 98, 8265 (1976); (b) Chem. Lett., 777 (1977); (c) Tetrahedron Lett., 3735 (1977).
5. M.D. Fryzuk and B. Bosnich, J. Am. Chem. Soc., 99, 6262 (1977).
6. K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi, and M. Kumada, Tetrahedron Lett., 1389 (1977).
7. (a) M. Tanaka and J. Ogata, J. Chem. Soc., Chem. Comm., 735 (1975); (b) T. Hayashi, M. Tanaka, and I. Ogata, Tetrahedron Lett., 295 (1977).
8. R.H. Grubbs and R.A. DeVies, Tetrahedron Lett., 1879 (1977).
9. (a) T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 4405 (1974); (b) T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 1133 (1976); (c) W.R. Cullen and E.-S. Yeh, J. Organomet. Chem., 139, C13 (1977).
10. (a) M. Fiorini, G.M. Giongo, F. Marcati, and W. Marconi, J. Molecular Catal., 1, 451 (1974/76); (b) G. Pracejus and H. Pracejus, Tetrahedron Lett., 3497 (1977).
11. Satisfactory spectral and analytical data were obtained for this compound.
12. R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93, 3089 (1971).
13. D. Sinou and H.B. Kagan, J. Organomet. Chem., 114, 325 (1976).
14. J. Halpern, D.P. Riley, A.S.C. Chan, and J.J. Pluth, J. Am. Chem. Soc., 99, 8055 (1977).