PREPARATION OF PERCYCLOALKYLPHOSPHINES BY CATALYTIC HYDROGENATION USING A Rh/Pt CATALYST OF THE ADAMS TYPE

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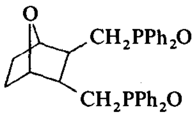
By smooth catalytic hydrogenation phenylated phosphine oxides are reduced to the corresponding cyclohexyl derivatives using a Rh/Pt catalyst. In chiral phosphines the optical activity is restored.

1. Introduction

The catalytic hydrogenation of P-aryl substituted phosphine oxides to the corresponding saturated phosphine oxides and their reduction has been carried out since 1982 [1–4]. Either Ru/C, Rh/Al_2O_3 or PtO_2 catalysts have been applied demanding rather high pressure (70–130 atm) and even sometimes higher temperature to complete the reaction. PtO_2 or 5% Rh/Al_2O_3 proved to be less effective. We found some years ago and are using it since that time, that just the mixture of Rh_2O_3/PtO_2 [5] prepared from $H_2PtCl_6 \cdot 6H_2O$ and $RhCl_3 \cdot 3H_2O$ (g atom Rh/g atom Pt 3 : 1) according to the Adams catalyst [6] resulted in a very suitable catalyst for the smooth hydrogenation of phosphine oxides. It was checked for chiral and achiral phosphine oxides which were obtained by known methods. The oxides DPPON-O and DPPEA-O were prepared by H_2O_2 oxidation in acetone starting from the phosphines DPPON [7] and DPPEA [8] respectively. The results are summarized in the table 1.

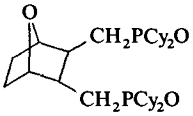
The hydrogenation proceeds at room temperature in EtOH/HOAc at a pressure between 0.5 to 3.0 MPa hydrogen. Of course higher pressure is tolerated (e.g. run 5) but in most cases lower pressure is sufficient and the reaction ran to completeness within 48–72 hours. In case of run 5 the aromatic system of the backbone was hydrogenated simultaneously as occurred also with the double bonds in DPPE-O and NORPHOS-O. The reaction was accomplished without any destruction of the phosphine oxides or with loss of the optical activity as

Abbreviations



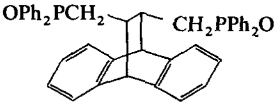
DPPON-O

trans-2,3-bis(diphenylphosphinomethyl)-7-oxanorbornane



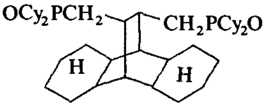
DCYPON-O

trans-2,3-bis(dicyclohexylphosphinylmethyl)-7-oxanorbornane

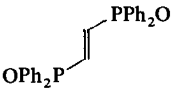


DPPEA-O

trans-11,12-bis(diphenylphosphinylmethyl)-9,10-dihydro-9,10-ethanoanthrancene

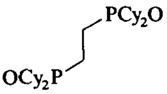


DCYPEA-O



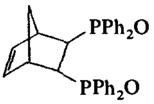
DPPE-O

1,2-bis(diphenylphosphinyl)ethene



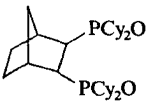
DCYPE-O

1,2-bis(dicyclohexylphosphinyl)ethane



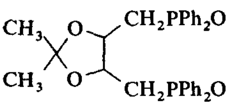
NORPHOS-O

2,3-trans-bis(diphenylphosphinyl-norborn-5-ene



CYNORPHOS-O

2,3-trans-bis(diphenylphosphinyl)-norbornane



DIOP-O

4,5-bis(diphenylphosphinylmethyl)-2,2-dimethyl-1,3-dioxolane

CYDIOP-O

4,5-bis(dicyclohexylphosphinylmethyl)-2,2-dimethyl-1,3-dioxolane

Table 1
Hydrogenation of phosphine oxides catalyzed by Rh/Pt catalyst. Reaction temperature 25 °C, solvens: ethanol/acetic acid = 5/1

run	phosphino oxide	(mmol)	solvens (ml)	catalyst (mg)	time (hrs)	pressure (MPa)	Hydrogenation [a] product	Yield (%)
1	Ph_3PO	5.4	30	100	5	1.0	CY_3PO (acetone/H_2O)	75
2	Ph_3PO	36	180	300	48	2.4	CY_3PO (acetone/H_2O)	85
3	DPPON-O	3.8	30	100	48	3.0	DCYPON-O	80
4	DPPON-O	1.9	24	80	48	0.8	DCYPON-O	75
5	DPPEA-O	4.7	60	150	48	9.8	DCYPEA-O	73
6	DPPEA-O	1.6	24	80	72	0.8	DCYPEA-O	75
7	DPPE-O	3.5	30	100	48	3.0	DCYPE-O (EtOH/H_2O)	75
8	Norphos-O [b]	6.1	100	100	72	0.8	CYNorphos-O [c] (Hexan)	73
9	DIOP-O [d]	0.9	24	30	48	0.8	CYDIOP-O [e]	95

[a] ^{1}H nmr: No resonance in the range of aromatic protons (6.75–7.75 ppm).

[b] (−)-Norphos-O (2 R, 3 R) $[\alpha]_D^{20}$ −62° ($c = 1$, $CHCl_3$) [9].

[c] Double bond reduced, $[\alpha]_D^{23}$ −25.8° ($c = 1$, EtOH).

[d] (−)-DIOP (4 R, 5 R) $[\alpha]_D$ −12° ($c = 2$, toluene) [10].

[e] $[\alpha]_D^{25}$ −4.5° ($c = 4$, benzene) [2].

indicated by run 8 and 9. It was totally inhibited by use of the free phosphines as anticipated due to complexation. The chemical yields are normally in the range of 70–80% (see table 1). Since the oxides are easily reduced by silanes the procedure offers a reasonable route to basic phosphines.

2. Procedure

The phosphine oxide, the catalyst and the solvens are placed in a 100–500 ml autoclave and the hydrogenation was performed in the usual manner with stirring. When the hydrogen uptake was complete the catalyst was filtered off (caution it is now in general pyrophoric) washed two times with ethanol and the filtrate was concentrated in vacuo. The rest containes adherent acetic acid. Addition of water gives the crystalline phosphine oxides which if necessary were recrystallized to obtain the pure products (table 1).

Acknowledgement

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References

[1] K. Tani, K. Suwa, T. Yamagata and S. Otsuka, Chem. Lett. (1982) 265.
[2] K. Yamamoto and S.U. Rehman, Chem. Lett. (1984) 1603.
[3] K. Tani, K. Suwa, E. Tanigawa, T. Ise, T. Yamagata, Y. Tatsuno and S. Otsuka, J. Organometal. Chem. 370 (1989) 203.
[4] K. Tani, T. Ise, Y. Tatsuno and T. Saito, J. Chem. Soc., Chem. Commun. (1984) 1641.
[5] S. Nishimura, Bull. Chem. Soc. Japan 33 (1960) 566.
[6] R. Adams, V. Voorhees and R.L. Shriner, Org. Synth. Coll., Vol. I (1941) 463.
[7] H.-J. Kreuzfeld and Chr. Döbler, Z. Chem. 24 (1984) 405.
[8] Chr. Döbler and H.-J. Kreuzfeld, J. prakt. Chem. 325 (1983) 1021.
[9] H. Brunner and W. Piezonczyk, Angew. Chem. 91 (1979) 655.
[10] H.B. Kagan and T.P. Dang, J. Amer. Chem. Soc. 94 (1972) 6429.