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Phosphine-Borane Complexes; Direct Use in Asymmetric Catalysis

Hugues Brisset, Yann Gourdel, Pascal Pellon and Maurice Le Corre*

Laboratoire de Synthèse Organique, Associé au CNRS.
Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes CEDEX, FRANCE.

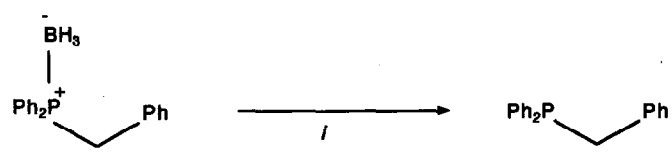
Abstract : An easy and soft method of decomplexation of phosphine-borane complexes, by DABCO, allows its use in situ in asymmetric catalytic hydrogenation of double bonds with metal phosphine complexes.

The use of the phosphine-borane complexes has been widely developed recently[1]. These complexes are very stable, they are not sensitive to the usual oxidizing reagents[2] and very easy to use in organic synthesis[3].

The decomplexation of phosphine-borane complexes with a large excess of amine was described by Imamoto[4]. Nevertheless, the use of a secondary amine in excess is not compatible with all functional groups, particularly with carbonyl functions.

We have thus elaborated a softer method of decomplexation and we have tried to apply this method in the preparation of complexes with transition metals which can be used in asymmetric catalysis.

The choice of the amine and solvent has been determined thanks to the study of the benzyldiphenylphosphine-borane decomplexation.



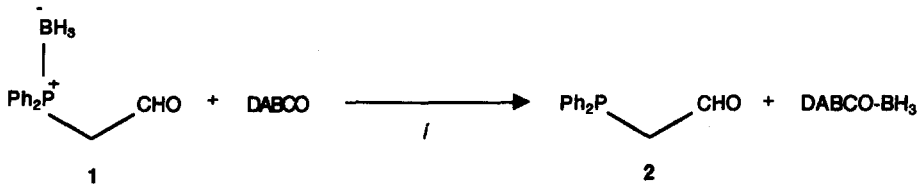
(i) : $R_1R_2R_3N$ / toluene / 40°C / 4h

By using one equivalent of amine the percentages of decomplexation (at 40°C for 4h in toluene) by DABCO, TMEDA and diethylamine are respectively 100, 67 and 20. DABCO seems to be the best decomplexation agent.

Concerning the solvent, toluene gives the best results; indeed the solvent must be able to render phosphine-borane complexes and amine soluble without being too polar. The decomplexation rate decreases rapidly for polar solvents like dichloromethane, acetonitrile or methanol.

The easy use of this decomplexation method is exemplified in two cases: decomplexation of an aldehyde and by direct use of phosphine-borane complex in an asymmetric catalytic reaction.

The preparation of diphenylphosphinoacetaldehyde 2 in quantitative yield shows the good chemioselectivity of this method compared with Imamoto's one; indeed it is not possible to obtain compound 2 in diethylamine.

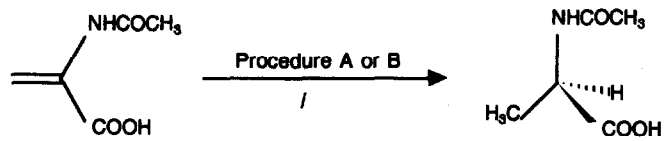


1 2

(i) : toluene / 40°C / 4h

Complex 1 was obtained by oxidation of the corresponding alcohol[2].

Chiral diphosphines are often used in asymmetric catalysis as ligands of transition metals[5]. The preparation and the protection towards oxidation of the functionalized phosphines are sometimes tedious. Phosphine-borane complexes should solve these problems. We have chosen, as a catalytic reaction, the reduction of α-acetamido-acrylic acid 3 with the DIOP-rhodium complex[6].

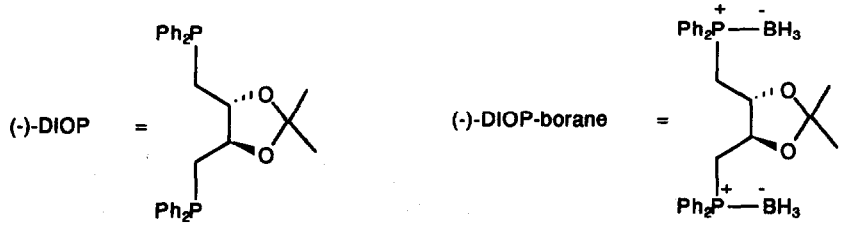


3 4

(i) : H_2 / 25°C / Catalyst

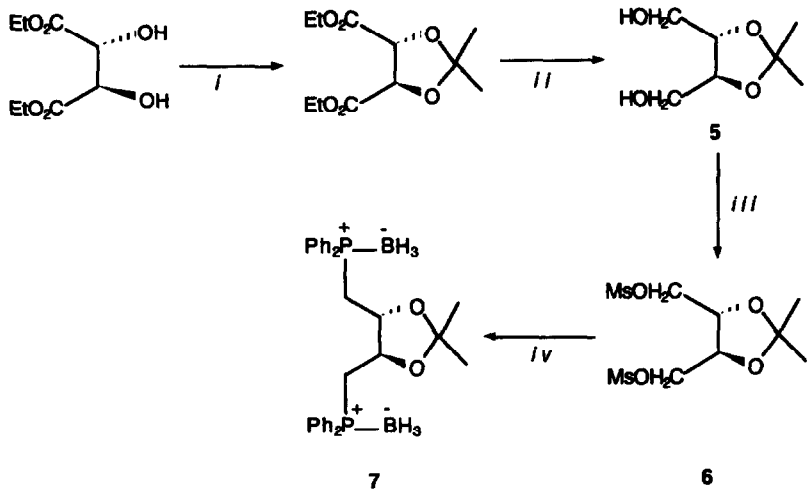
(A). In the usual procedure[6], the catalyst was prepared in toluene by the reaction of DIOP on $(ClRhCOD)_2$ in 15 min at room temperature. The former catalyst can be employed directly.

(B). From DIOP-Borane, the DIOP-borane decomplexation is realized during catalyst formation. $(ClRhCOD)_2$ is shaken for 45 min with DIOP-borane and one equivalent of DABCO at 40°C in toluene. The catalyst, which is obtained in this way, is used directly for α-acetamido-acrylic acid reduction.



The results can be compared to Kagan's ones. In the same conditions the reaction time and the enantiomeric excess are similar. $[\alpha]_D$ = +43.2 (c = 1, H_2O) by procedure A or B for the N-acetyl-(R)-alanine 4.

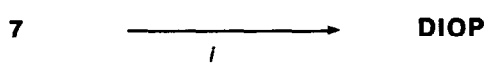
We can obtain the DIOP-borane complex by addition of $Ph_2P(Li)BH_3$ to the bismethanesulfonate 6[7]. $Ph_2P(Li)BH_3$ was prepared from commercially available triphenylphosphine-borane and lithium[8]. The bishydroxy-compound 5 was obtained in two steps from diethyl L-tartrate[9,10]. The DIOP-borane complex 7 is an air-stable crystallized product[7].



(i) : $Me_2C(OMe)_2$ / p-toluenesulfonic acid / 83% yield
(ii) : $LiAlH_4$ / ether / 36°C, 3h / 84% yield
(iii) : $MeSO_2Cl$ / Et_3N / 25°C,1h / 78% yield
(iv) : $Ph_2P(BH_3)Li$ / THF / 20°C,12h / 80% yield

The use of $Ph_2P(Li)BH_3$ instead of Ph_2PLi in the last step enables us to increase the reaction yield. The least basic $Ph_2P(Li)BH_3$ prevents an elimination reaction on the last compound.

For the procedure A, the same results have been obtained with commercially DIOP or with DIOP coming from quantitative decomplexation of DIOP-Borane complex in the conditions already mentioned for the diphenylphosphinoacetaldehyde-borane complex 1.



(i) : DABCO / toluene / 40°C / 4h

The preparation and the use of new chiral diphosphines by means of phosphine-borane complexes are actually under investigation.

References and Notes

1. For recent works dealing with phosphine-borane complexes and related compounds :
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7. Compound 10 : mp : 83-84°C ;
   ^{1}H-NMR (300MHz, $CDCl_3$): δ : 1.4 (s, 6H) ; 3.1 (s, 6H) ; 4.2 (m, 2H) ; 4.4 (m, 4H) ;
   ^{13}C-NMR (75.469MHz, $CDCl_3$): δ : 26.8 (CH_3) ; 37.7 (O-CH_3) ; 67.9 (CH_2) ; 75.1 (CH) ; 111 (Cq).
   Compound 11 : mp : 163-164°C , $[\alpha]_D$ = + 4 (c = 3, $CHCl_3$) ;
   ^{1}H-NMR (300MHz, $CDCl_3$): δ : 1.1 (s, 6H) ; 2.2 (m, 2H) ; 2.5 (m, 2H) ; 4.1 (m, 2H) ; 7.5 (m, 20 H) ;
   ^{31}P-NMR (121.496MHz, $CDCl_3$) : δ : + 15.1;
   ^{13}C-NMR (75.469MHz, $CDCl_3$): δ : 26.8 (CH_3) ; 29.3 (CH_2, $^{1}J_{P-C}$ = 36.7 Hz) ; 77.3 (CH-O, $^{2}J_{P-C}$ = 10.9 Hz) ; 109.2 (Cq) ; 128.4 - 132.6 (C aromatics).
8. To a magnetically stirred suspension of the triphenylphosphine-borane complex (0,02 mol) in dry tetrahydrofuran (15 ml) at 25 °C were added thin, finely cut strips of lithium (0,04 mol). The mixture was stirred for 4 h during which time the colourless suspension turned into a red solution, and the lithium was consumed. Tert-butyl chloride (0,02 mol) was then added dropwise to the reaction and the solution was stirred for 30 min at 25 °C.
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