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Stereoselective Synthesis of New Functionalized Bisphosphines

Yann Gourdel, Pascal Pellon, Loïc Toupet§ and Maurice Le Corre*

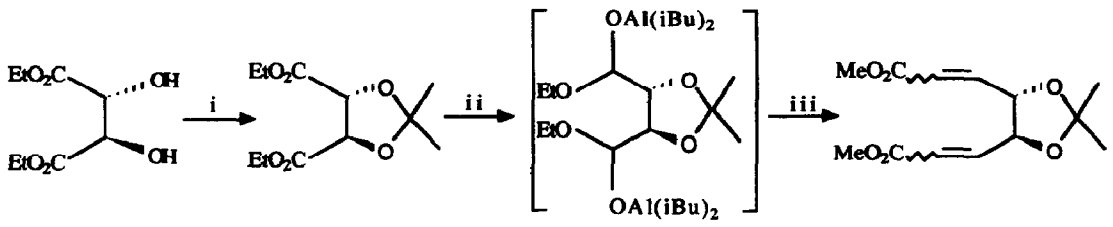
Laboratoire de Synthèse Organique, Associé au CNRS.
Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes Cedex, France.
§ Groupe Matière Condensée et Matériaux, associé au CNRS, Université de Rennes I, 35042 Rennes Cedex, France.

Abstract: Chiral functionalized bisdiphenylphosphines have been prepared and isolated from natural tartaric acid via the dihydrophosphorylation of dimethyl 4,5-O-isopropylidene-2,6-octanedienedioate, 4,5-O-isopropylidene-2,6-octanedienedinitrile and bis 5 (H)-2-furanone.

Chiral bisphosphines became important in asymmetric synthesis since the DIOP was first prepared by Kagan in 1971[1 a-b]. The presence of a functional group in the phosphine and the proximity of a chiral center with respect to the phosphorus atom has been reported to achieve an highly enantioselective reaction in asymmetric transition-metal catalysts[2a-b], but many difficulties were encountered in alkylation of the DIOP[3] in creation of two asymmetric centers close to the phosphorus atoms.

Phosphine-borane complexes have an unexpected stability[4a] and were easily used in synthesis[4b-c]. So, we decided to use them in synthesis of chiral functional bisphosphine.

Krief[5] has proposed an original synthesis of the chiral diene 3 from (2R, 3R)-diethyl tartrate **1**. In the last step, the Wittig reaction can be directly performed to produce, after chromatography purification, the (2Z, 6Z) - (4S, 5S) stereomer **3a** and the mixture of (2E, 6Z) - (4S, 5S) and (2E, 6E) - (4S, 5S) stereomers **3b** and **3c**.



1 **2** **3**

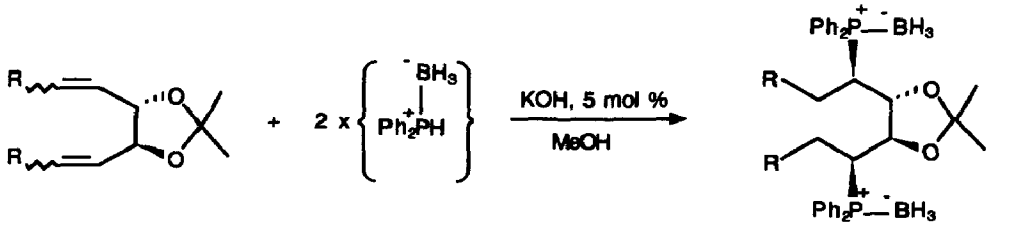
(i): $Me_2C(OMe)_2$ / p-toluenesulfonic acid.
(ii): $AlH(iBu)_2$ / -78°C / toluene.
(iii): $Ph_3P{=}CH\text{-}CO_2Me$ / MeOH / -78°C to 20°C.

R= MeO_2C

3 a : Z,Z.
3 b : E,Z.
3 c : E,E.

Imamoto has carried out the addition reaction of the diphenylphosphine-borane complex with activated olefins[6]. Also, we decided to synthetize the chiral bisphophine-borane complexes 5[7]and 6[8] using the dienes 3 and 4 as precursor.

Surprisingly, a single diastereomer of 5 is obtained (79 % yield) from a mixture of the stereomers 3a, 3b and 3c ; the same process give 6 (58 % yield) from a mixture of stereomers of 4 .



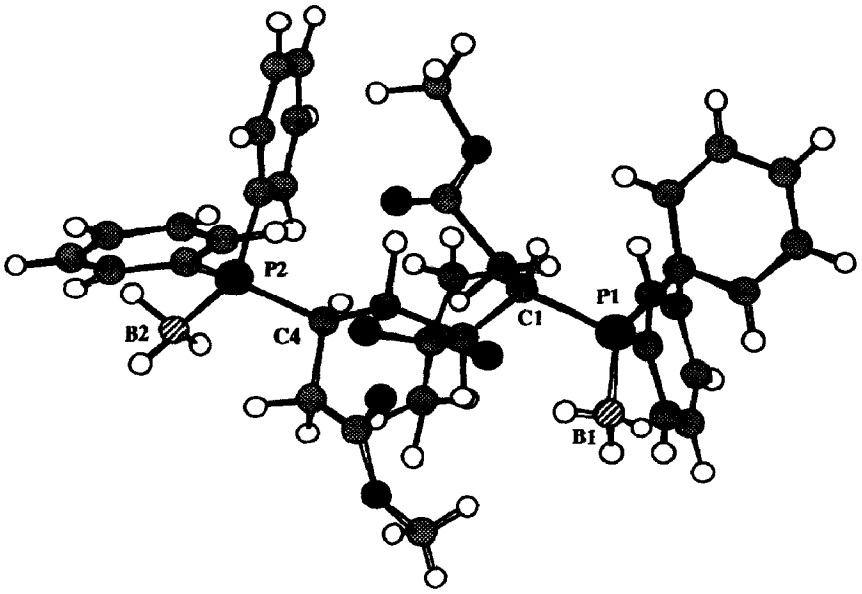
3 R = MeO_2C

4 R = NC

5 R = MeO_2C

6 R = NC

The stereochemistry of 5 was established by an X-ray crystal structure[9]:



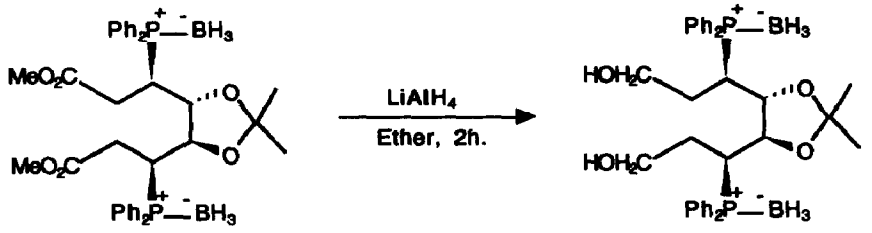
Perspective drawing of the molecule in the crystal structure of 5 with some atom numbering

Selected bonds distances (Å) and angles (°):

P1-C1 1.87; P1-B1 1.88; B-H1($_{B1}$) 1.08; B1-H2($_{B1}$) 1.03; B1-H3($_{B1}$) 1.19; P2-B2 1.90; P2-C4 1.86; B2-H1($_{B2}$) 0.98; B2-H2($_{B2}$) 0.99; B2-H3($_{B2}$) 0.94;

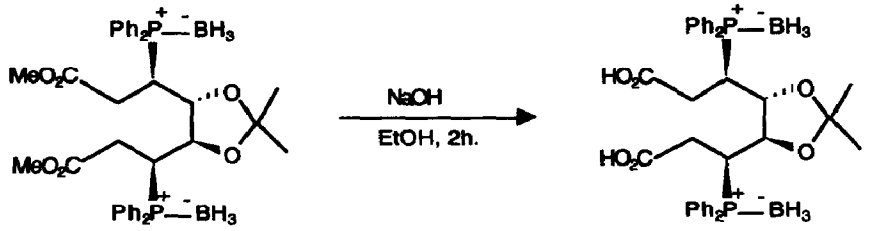
B1-P1-C1 115.0; B2-P2-C4 110.2.

The bidentate ligand **5** could be reduced with $LiAlH_4$ to give the dihydroxy-bisphosphine-borane complex **7**[10] in 67 % yield.



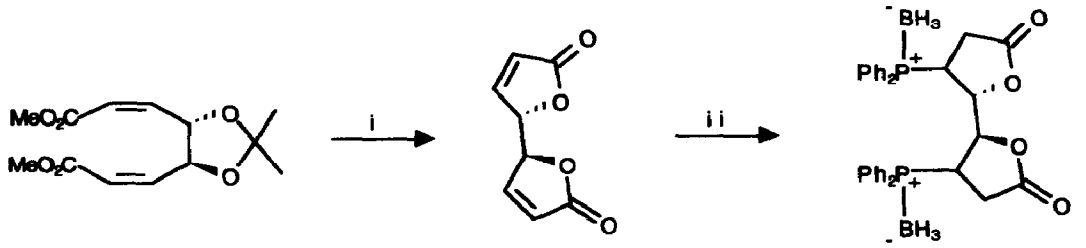
5 **7**

Basic hydrolysis of **6** leads to the diacid bisphosphine-borane complex **8**[11] in 60 % yield.



5 **8**

In the other hand, the compound **3a** was easily transformed by deprotection and cyclisation procedure into the new compound: the 5(H)2-bisfuranone **9**[12].This diene reacts with $Ph_2P(H)BH_3$ to give the new chiral bisphosphine-borane complex **10**[13] (^1H, ^{31}P and ^{13}C NMR showed only one diastereomer).



3a **9** **10**

(i): $MeSO_3H$, 2 mol %, EtOH ,78 °C, 3h, 75% yield.
(ii): $Ph_2P^+(H)BH_3^-$, NaH, THF, 0°C to 20°C, 61% yield.

The decomplexation of chiral phosphine-borane complexes and the direct use of these complexes in an asymmetric catalytic reaction were described[4c]. In summary, the chiral dienes **3** and **4** may provide a route to obtain functionalized bisphosphine-borane complexes **5, 6, 7, 8** and **10**. The use of these chiral products in asymmetric transition-metal catalyzis is presently under investigation.

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7 - Compound **3** was treated with 2 eq of $Ph_2PH(BH_3)$ and KOH 5% mol in MeOH at 20°C during 3 h to give the compound **5** : mp = 162-163°C ; $[\alpha]_D$ = - 10.75 (c = 1, $CHCl_3$) ;
^{1}H-NMR (300MHz, $CDCl_3$) δ : 0.8 (s,3H), 1.0 (s,3H), 2.5 (m,2H), 2.7 (m,2H), 3.4 (m,2H), 3.5 (s,3H), 3.7 (s,3H), 3.9 (m,1H), 4.2 (m,1H), 7.3-7.9 (m,20H) ;
^{31}P-NMR (121.496MHz, $CDCl_3$) δ : 25.2 and 30.5 ;
^{13}C-NMR (75.469MHz, $CDCl_3$) δ : 25.6 and 26.3 (2 CH_3), 29.2 and 31.6 (2 CH_2), 31.7 (d,$^1J_{P-C}$ = 43.2 Hz, CH), 34.1 (d,$^1J_{P-C}$ = 36.3 Hz, CH), 52.4 and 52.6 (2 OCH_3), 77.9 and 77.8 (2 CHO), 108.5 (Cq), 128-133 (C aromatics), 172.1 and 172.9 (2 C=O).

8 - Compound **4** was treated with 2 eq of $Ph_2PH(BH_3)$ and NaH 10% mol in THF at 0°C during 3 h to give the compound **6** : mp = 94 95 °C ; $[\alpha]_D$ = - 51.8 (c = 1, $CHCl_3$) ;
^{1}H-NMR (300MHz, $CDCl_3$) δ : 0.9 (s,3H), 1.3 (s,3H), 2.4 (m,2H), 2.8 (m,2H), 3.0 (m,1H) and 3.65 (m,1H), 4.5(m,1H), 4.2 (m,1H), 7.3-7.9 (m,20H) ;
^{31}P-NMR (121.496MHz, $CDCl_3$) δ : 23.8 and 28.3 .
^{13}C-NMR (75.469MHz, $CDCl_3$) δ : 25.8 and 26.3 (2 CH_3), 29.7 and 30.1 (2 CH_2), 31.1 (d,$^1J_{P-C}$ = 39.1 Hz, CH), 34.5 (d,$^1J_{P-C}$ = 36.3 Hz, CH), 77.4 and 77.5 (2 CHO), 109.7 (Cq), 118 (2 CN), 128-133 (C aromatics).

9 - The X-ray analysis of the compound **5** is : $P_2O_6C_{37}B_2H_{46}$: Mr = 670.35. orthorhombic, $P2_12_12_1$, a = 10.530(4), b = 17.441(3), c = 20.093(4) Å, V = 3690(2)Å^{-3}, Z = 4, D_x = 1.206 Mg.m^{-3}, (MoKa) = 0.70926 Å, m = 1.55 cm^{-1}; F(000) = 1424, T = 294 K, final R = 0.073 for 2233 observations.
The sample (0.30*0,45*0;45 mm) is studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized MoKa radiation.

10 - Compound **7** : mp = 98 - 99 °C; $[\alpha]_D$ = + 18.5 (c = 1, $CHCl_3$)
^{1}H-NMR (300MHz, $CDCl_3$) δ = 0.8 (s,3H), 1.1 (s,3H), 2.6 (sl,2OH) , 2.9 (m,1H), 3.1 (m,1H), 3.5 (m,4H), 4.1 (m,1H), 4.2 (m,1H), 7.2-7.9 (m,20H);
^{31}P-NMR (121.496MHz, $CDCl_3$) δ : 23.4 and 28.1.
^{13}C-NMR (75.469MHz, $CDCl_3$) δ : 25.8 and 26.6 (2 CH_3), 29.6 and 30.1 (2 CH_2), 31.5 (d,$^1J_{P-C}$ = 32.75 Hz, CH), 33.5 (d,$^1J_{P-C}$ = 33.4, CH), 60.2 and 60.7 (2 CH_2), 77.7 and 77.9 (2 CHO), 108.3 (Cq), 127.8-133.8 (C aromatics).

11 - Compound **8** : mp = 94 - 95°C; $[\alpha]_D$ = + 11.1 (c = 0.66, $CHCl_3$) ;
^{1}H-NMR (300MHz, $CDCl_3$) δ = 0.7 (s,3H), 1.2 (s,3H), 2.8 (m,2H), 3.0 (m,2H), 3.3 (m,2H), 3.7 (m,1H), 4.0 (m,1H), 4.1 (sl,2OH), 7.2-7.9 (m,20H);
^{31}P-NMR (121.496MHz, $CDCl_3$) δ : 24.0 and 28.6.
^{13}C-NMR (75.469MHz, $CDCl_3$) δ : 25.6 and 26.5 (2 CH_3), 29.1 and 30.3 (2 CH_2), 31.6 (d,$^1J_{P-C}$ = 36 Hz, CH), 33,5 (d, $^1J_{P-C}$ = 32.0 Hz, CH), 76.7 and 77.3 (2 CHO), 109.3 (Cq), 128.0-133.0 (C aromatics), 177.1 and 178.1 (2 C=O).

12 - Compound **9** mp =183-184 °C; $[\alpha]_D$ = - 1.8 (c = 1, CH_3COOEt) ;
^{1}H-NMR (300MHz, DMSO) δ : 5.5 (s,2H), 5.9 (d,$^3J_{H-H}$ = 5.4 Hz, 2H), 7.9 (d,2H);
^{13}C-NMR (75.469MHz, DMSO) δ : 81.5 (CHO),122.8 (CHβ),155.6(CHα), 173.3 (C=O).

13 - Compound **10** mp = 123-125 °C; $[\alpha]_D$= - 3.1 (c = 1, $CHCl_3$) ;
^{1}H-NMR (300MHz, $CDCl_3$) δ : 2.7 (m,4H), 3.7 (m,2H), 4.1 (m,2H), 7.3-8.1 (m,20H) ;
^{31}P NMR (121.496MHz, $CDCl_3$) δ : 19.7 ;
^{13}C NMR (75.469MHz, $CDCl_3$) δ = 30.5 (CH_2), 31.9 (d,$^1J_{P-C}$ = 39.1Hz), 78.9 and 79.0 (2CHO), 128.2-133.0 (C aromatics), 172,7 (2 C=O).

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