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Regio- and stereochemistry of nucleophilic attack at the P-chiral center of a dioxaphospholane-borane complex: A model of study for the P–O bond cleavage

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Summary — The diastereomerically pure dioxaphospholane-borane complex **4** derived from *S*-(−)-1,1-diphenylpropane-1,2-diol **3**, reacts regiospecifically at low temperature with organolithium reagents, to yield β-hydroxyphosphinite-boranes **7**, **8** with a major retention of configuration at the phosphorus atom. The reaction of phosphinite-borane **7** (or **8**) in THF with an organolithium reagent leads to its decomposition into the optically active phosphinous acid-borane (+)-**10** (or (+)-**11**), and a mixture of *S*-(−)-diol **3** and its *R*-(+)-epoxide **12**. In contrast, methyllithium reacts in ether with *o*-anisylphenylphosphinite-borane **8a,b** (dr 4:1), to afford the *o*-anisylmethylphenylphosphine (PAMP)-borane **13** in 43% yield and 70% ee. On the other hand, the saponification of the phosphinite-borane **8** occurs with inversion of configuration at the phosphorus atom and gives the optically pure diol *S*-(−)-**3**. The regio- and stereoselectivity involving the P–C bond formation and P–O bond cleavage are explained by an addition–elimination mechanism via the competitive formation of two initial pentacoordinate intermediates evolving in different stereochemical pathways. The definition of the pentacoordinate intermediates, based on the relative stereoapicophilicity of the phosphorus substituents and the use of their topological representation, provides an explanation for the stereochemistry and the asymmetric induction observed at the phosphorus center. The above results show that organophosphorus-borane complexes are interesting models for the study of the regio- and stereochemistry of reactions in phosphorus chemistry.

chiral phosphine / borane complexe / phosphorus stereochemistry / relative stereoapicophilicity

Résumé — Régio- et stéréochimie d'une attaque nucléophile sur le centre chiral P d'un complexe de dioxaphospholane-borane : modèle pour étudier la rupture des liaisons P–O. Le complexe de dioxaphospholane-borane **4** qui est préparé diastéréomériquement pur à partir du *S*-(−)-1,1-diphénylpropane-1,2-diol **3**, réagit régiospécifiquement à basse température avec un organolithien, pour donner les β-hydroxyphosphinites-borane **7**, **8** avec rétention de configuration au niveau de l'atome de phosphore. La réaction du phosphinite-borane **7** (ou **8**) dans le THF avec un organolithien conduit à sa décomposition en acide phosphineux-borane optiquement actif (+)-**10** (ou (+)-**11**) et à un mélange de *S*-(−)diol **3** et de *R*-(+)-époxyde **12**. En revanche, le méthyllithium réagit dans l'éther avec l'*o*-anisylphénylphosphinite-borane **8a,b** (rd 4:1), pour donner l'*o*-anisylméthylphénylphosphine (PAMP)-borane **13** avec 43 % de rendement et 70 % d'ee. Par ailleurs, la saponification du phosphinite-borane **8** se fait avec inversion de configuration au niveau de l'atome de phosphore pour donner le diol optiquement pur *S*-(−)-**3**. La régio- et la stéréosélectivité de formation et de rupture des liaisons P–C et P–O sont expliquées par un mécanisme d'addition–élimination via la formation compétitive de deux intermédiaires pentacoordinés précoces, qui se transforment selon des parcours stéréochimiques différents. L'identification des intermédiaires pentacoordinés en fonction de la stéréoapicophilie relative des substituants du phosphore, et l'utilisation d'une représentation topologique, fournit une explication pour la stéréochimie et l'induction asymétrique observées au niveau de l'atome de phosphore. Ces résultats montrent que les complexes de phosphine-borane sont des modèles très intéressants pour l'étude de la régio- et de la stéréosélectivité des réactions en chimie du phosphore.

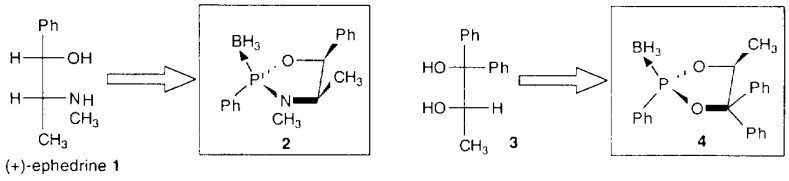
phosphine chirale / complexe de borane / stéréochimie des organophosphorés / stéréoapicophilie relative

Introduction

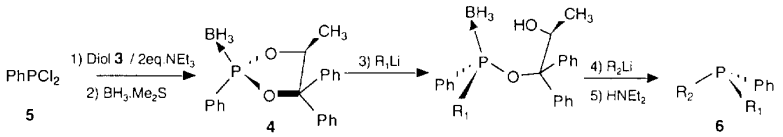
The study of the stereochemistry of reactions at a P-chiral center is important for the understanding of the regioselectivity of hydrolysis of nucleotides [1], for the synthesis of valuable therapeutic [2] or agrochemical [3] targets, and for the preparation of potent ligands for the asymmetric catalysis [4].

In the last years, significant strides were achieved in the asymmetric synthesis of organophosphorus compounds due to the use of the protecting borane group (BH_3), allowing nucleophilic or electrophilic attacks at the phosphorus center, and the recovery of the

* Correspondence and reprints



Scheme 1



Scheme 2

final compound under a non-racemizing decomplexation step [5]. Moreover, borane adducts of phosphorus are interesting in organophosphorus compound synthesis, as they possess an excellent reactivity and do not present any purification or storage problems. In addition, some preliminary results [6] have shown that a decomplexation step is not always required for the use of organophosphorus-boranes in synthesis or in homogeneous catalysis.

A few years ago, we have described a highly stereospecific synthesis [5a, b, d] allowing the access to a broad spectrum of compounds with P–N, P–O, or P–C bonds. The strategy is based on the diastereoselective preparation of an oxazaphospholidine-borane complex **2** derived from (+)-ephedrine **1** (or its enantiomer from (−)-ephedrine), followed by the regio- and stereoselective P–O bond rupture of the ring with organolithium reagents (scheme 1).

In continuation of our study of organophosphorus compound asymmetric synthesis via heterocyclic phosphorus-borane complexes, we present herein the results obtained with *S*-(−)-1,1-diphenylpropane-1,2-diol **3** as chiral auxiliary [5b]. The advantage of this approach resides in the preparation of tertiary phosphines **6** in three key steps only (scheme 2).

As the nucleophilic attack of an organolithium reagent on the oxazaphospholidine-borane **2** leads to a P–O bond rupture with retention of configuration [5a,d,g], it was interesting to investigate this reaction in the case of the dioxaphospholane-borane **4** [7], which bears two non equivalent P–O bonds. In addition, the borane group affords compounds with stable chirality, allowing the organophosphorus-borane complexes to be considered as suitable models for the study of the stereochemistry reaction involving analogous tetracoordinate phosphonates or phosphates.

Results and discussion

Regioselectivity of the dioxaphospholane-borane **4** *ring opening with an organolithium reagent*

The dioxaphospholane-borane **4**, has been prepared diastereoselectively pure by condensation of $PhPCl_2$ **5** and *S*-(−)-1,1-diphenylpropane-1,2-diol **3** [8]. X-ray crystal diffraction analysis [9] yielded the absolute configuration at the phosphorus center as well as the lengths of the P–O(1) (1.604 Å) and P–O(3) (1.592 Å) bonds.

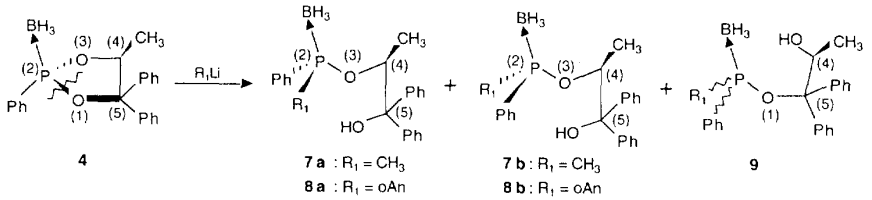
The reaction at low temperature of the dioxaphospholane-borane **4** with an organolithium reagent, leads to phosphinite-boranes **7**, **8** with cleavage of one P–O bond. ^{1}H- and ^{13}C-NMR analyses show the presence of two diastereomers **a** and **b** (table I) with very close chemical shifts for the CH group. The coupling constants $^3J_{POCH}$ = 5 Hz, $^2J_{POC(4)}$ = 3.2–3.5 Hz and $^3J_{POCC(5)}$ = 6–8.3 Hz [10] are in agreement with the formation of two epimers resulting from a P–O(1) bond cleavage (scheme 3).

Table I. Reactions of organolithium reagents with the dioxaphospholane borane complex **4**.

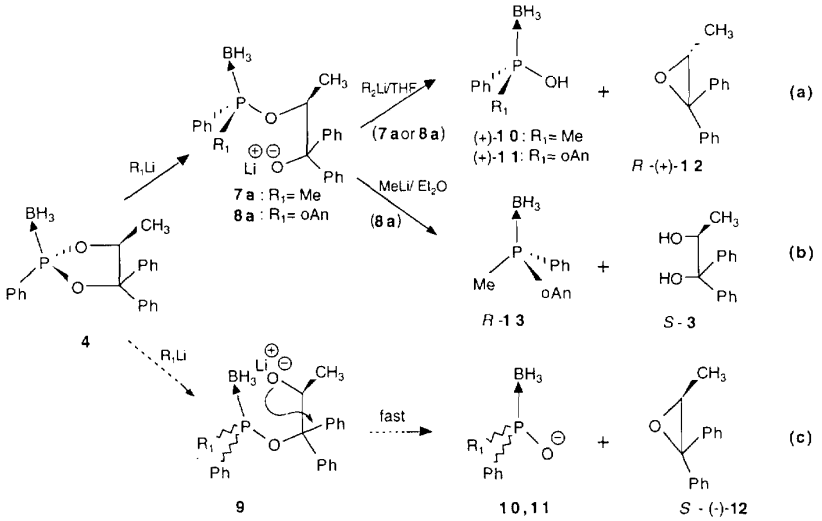
Entry	*T* (°C)	*R_1Li*	*Ring-opened product*	*Diastereomeric ratio*[a]	*Yield*[b] *(%)*
1	−78	MeLi	**7a,b**	4:1	82
2	−100	MeLi	**7a,b**	9:1	85
3	−120	MeLi	**7a,b**	13:1	75
4	−78	*o*-AnLi	**8a,b**	4:1	80
5	−100	*o*-AnLi	**8a,b**	4:1	73

[a] Determined by ^{1}H NMR; [b] isolated yield.

The regioisomer **9** which could arise from a P–O(3) bond rupture was not detected, with coupling constants $^4J_{POCCH}$ = 0 Hz, $^2J_{POC(5)}$ = 3 Hz and $^3J_{POCC(4)}$ = 6–8 Hz. Thus, the reaction at −78 °C with methyllithium (entry 1) gives **7a/7b** in a 4:1 ratio, but at −100 °C and −120 °C ratios of 9:1 and 13:1 are obtained, respectively (entries 2 and 3). The phosphinite-borane **7a** was obtained pure by recrystallization of the crude mixture, while isomer **7b** was obtained as an enriched mixture after flash chromatography. With *o*-anisyllithium, an influence of the temperature on the diastereoselectivity was not observed as a constant ratio of **8a/8b** = 4:1 was obtained at −78 and −100 °C (entries 4 and 5).



Scheme 3



Scheme 4

Table II. Reaction of organolithium reagents with the phosphinite-boranes **7**, **8**.

Entries	*R_1Li*	*Substrates*	*Conditions*		*PhRPOH·BH_3*[c]		*Epoxide* **12**	*Diol* **3**	*PAMP·BH_3* **13**
			T (°C)[b]	*Solvent*		*yield (%)*	*yield (%)*[d]	*yield (%)*[d]	*yield (%)*[d]
1	*o*-AnLi	**7a**	−78 to 0	THF	(+)-**10**	78	50	31	–
2	MeLi	**8a,b**[a]	−78 to 0	THF	(+)-**11**	30	30	–	–
3	MeLi	**8a,b**[a]	−78 to 0	Ether	**11**	–[e]	30	60	43
4	MeLi	**4**	−78 to +20	THF	(+)-**10**	62	59	10[f]	–
5	*o*-AnLi	**4**	−78 to +20	THF	(+)-**11**	84	80	–	–

[a] Diastereomeric ratio 4:1; [b] final temperature corresponds to H_2O quenching; [c] yield of crude product; [d] isolated yield; [e] not isolated; [f] determined by ^1H NMR.

Solvent effect on the chemoselectivity of the reaction of organolithium reagents with the phosphinite-boranes **7**, **8**

The reaction in THF at low temperature of two equiv of an organolithium reagent with the phosphinite-borane **7** (or **8**) leads to a mixture of optically active phosphinous acid-borane (+)-**10** (or (+)-**11**) [11] and *R*-(+)-epoxide **12** (scheme 4a, table II, entries 1 and 2).

A similar product distribution is obtained when complex **4** reacts with an excess of methyllithium (or *o*-AnLi) at −78 °C, and the reaction is quenched with water at room temperature (table II, entries 4, 5).

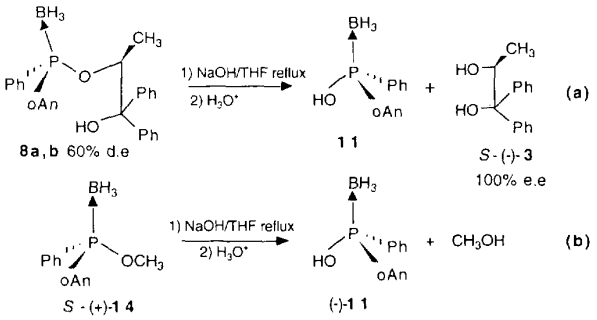
The formation of *R*-(+)-epoxide **12** proves the inversion of configuration of the asymmetric carbon atom compared to the *S*-(−)-diol **3**, and arises from the intramolecular collapse of the phosphinite-borane **7**, **8** alcoholates (scheme 4a). However, the optical activity ($[\alpha]_D = +17.4$) of the (+)-epoxide **12** indicates a partial loss of chirality during its formation [13]. This could be interpreted by a nonstereospecific decomposition of **7** or **8** alcoholates (scheme 4a), or by the formation of (*S*)-(−)-epoxide **12**, which could arise from a rapid collapse of the undetected regioisomer **9** if formed (scheme 4c).

In contrast, when methyllithium reacts in ether with the phosphinite-borane **8a,b** (dr 4:1), (*R*)-*o*-anisylmethylphenylphosphine (PAMP)-borane **13** is obtained in 43% yield, along with the optically pure *S*-(−)-diol **3** [12] and the *R*-(+)-epoxide **12** (scheme 4b, table II, entry 3). HPLC analysis on a chiral column of the PAMP-borane **13** shows an *R* absolute configuration and 70% ee instead of the expected 60%, indicating an enantiomeric enrichment resulting from a kinetic resolution of the starting phosphinite-borane **8a,b** (dr 4:1).

The different results obtained from the reaction of methyllithium with the phosphinite-borane **8** in THF or in ether (table II, entries 2 and 3) are explained by the difference in the alcoholate stability depending on the medium. In fact, the Li^+ cation is strongly solvated in THF, leading to a rapid collapse of the alcoholate (scheme 4a), whereas in ether this solvation is less pronounced, stabilizing the alcoholate. Thus in ether this alcoholate can react with methyllithium, giving rise to the PAMP-borane **13** (scheme 4b).

Stereochemistry of the P–O bond cleavage

As the reaction of an organolithium reagent with an acyclic phosphinite-borane occurs with inversion of configuration at the phosphorus atom [5c, e, h], the formation of *R*-PAMP-borane **13** permits the attribution of the S_P configuration to the major isomer **8a** (and R_P to **8b**). Consequently, the ring opening of the dioxaphospholane-borane **4** took place with a predominant retention of configuration at the phosphorus atom (scheme 4), as in the case of oxazaphospholidine-borane **2** [5a,d,g,h]. It appears also that the configuration of the phosphinite-borane **7a** is R_P (and **7b** is S_P), and the (+)-phosphinous acid-borane **10** is R_P whereas (+)-**11** is S_p (scheme 4a). The absolute configurations at the phosphorus atom are corroborated by the saponification of the phosphinite-boranes **8a,b** (dr 4:1) and the S_P-(+)-methyl phosphinite-borane **14** (prepared from the complex **2**) [5d], yielding the (−)-phosphinous acid-borane **11** and the optically pure *S*-(−)-diol **3** in the case of **8** (scheme 5). These results prove an inversion of chirality at the phosphorus atom during saponification.



Scheme 5

Interpretation of the regio- and stereoselectivity in the ring opening of 4

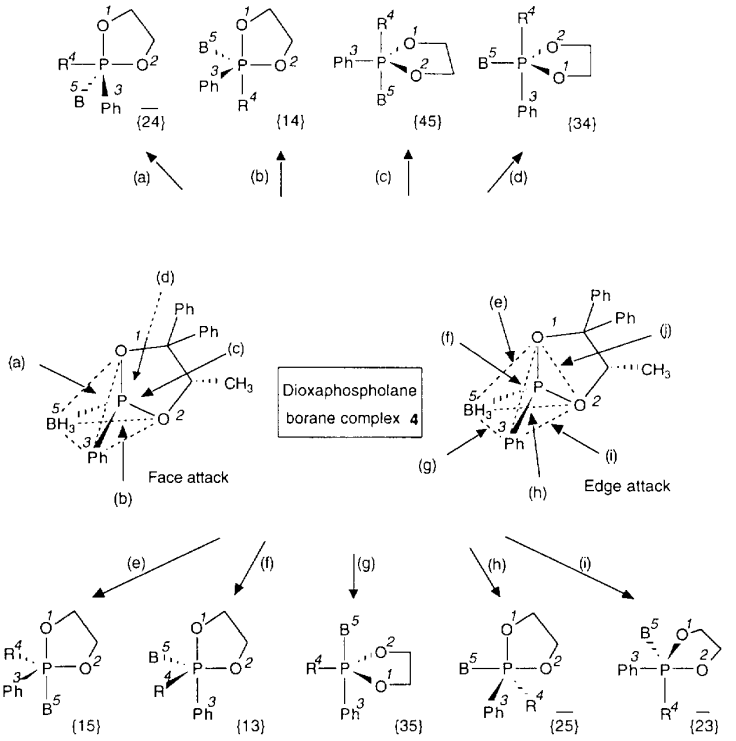
The nucleophilic attack on a P-chiral center proceeds with either a retention or an inversion of the configuration [15], involving an addition–elimination mechanism [16].

In the case of the dioxaphospholane-borane complex **4**, the nucleophilic attack results in P-chiral pentacoordinate intermediates, which stereochemical evolution is responsible for the regio- and stereoselectivity. As the presence of 5 different groups on an atom gives rise to 20 stereoisomers, the stereochemical control observed could be explained by a minimum number of stereopermutations, bringing the initial intermediate to the last one with the P–O(1) bond in an axial position.

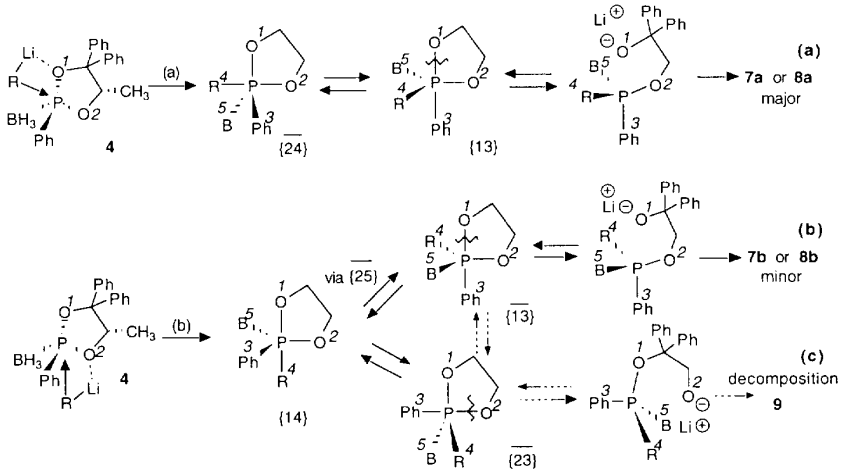
In order to interpret the stereochemical outcome of our synthesis, we have to define the possible pentacoordinate intermediates by the substituents in apical position following the classical convention [17]. Usually the substituents are numbered arbitrarily or by taking into account their electronegativity [18b] or the existence of a ring [18a]. Here the substituents of the phosphorus atom are ranked from *1* to *5* following their 'relative stereoapicophilicity' [19]. This ranking considers their apicophilicity [20] and steric hindrance, thus leading to the increasing order of the series: $OCPh_2$, $OCHCH_3$, Ph, Me or *o*-An, BH_3. Consequently, this corresponds to the relative aptitude of the P-chiral atom substituents to occupy an apical position, and leads to a decreasing stability of the following pentacoordinate intermediates: $\{13\} > \{14\} \approx \{\overline{23}\} > \{\overline{24}\} \approx \{15\} > \{\overline{24}\} \approx \{34\} > \{35\} > \{45\}$ (scheme 6). The existence of two oxygenated substituents $OCPh_2$ and $OCHCH_3$ (ranked *1* and *2* respectively), leads to a similar stability of the following intermediates $\{14\} \approx \{\overline{23}\}$, $\{\overline{23}\} \approx \{15\}$, and $\{\overline{25}\} \approx \{34\}$. Although it is known that the facial nucleophilic attack on a tetrahedral phosphorus atom requires less energy than on an edge [21], we have represented here all the initial pentacoordinate intermediates that could arise from the attack of a nucleophile 'R' (ranked *4*) on the dioxaphospholane-borane **4** (scheme 6).

However, the structure of these different pentacoordinate intermediates does not take into account either their relative kinetics of formation or their interconversion or the axial P–O bond energies, making it difficult to identify the initial intermediates. On the contrary, it is easy to determine the last intermediate, as it leads to the major diastereoisomer **a** of the phosphinite-boranes **7**, **8** resulting from an axial $P–O^1$ bond rupture with retention of configuration at the phosphorus atom (scheme 7a). Among the three possible stereoisomeric intermediates {13}, {14} and {15} having an axial $P–O^1$ bond and the appropriate configuration (scheme 6), {13} is the most stable due to the phenyl group in the apical position and the borane in the equatorial one, thus respecting their relative stereoapicophilicities [21b] (scheme 7a). Moreover, it is most likely that the intermediate {13} favours a low energy transition state level to give the end compound, in agreement with Hammond's postulate. On the other hand, the stereoisomer $\{\overline{13}\}$ corresponds to the last intermediate, which leads to the minor diastereoisomer **b** of the phosphinite-boranes **7** (or **8**) (scheme 7b).

In order to understand the stereochemical pathway of the reaction leading to stereoisomer {13} and to identify the initial intermediates, we have indicated the nine pentacoordinate intermediates, derived from the possible directions of nucleophilic attack, in the topological representation proposed by De Bruin et al [18a] (fig 1). These intermediates occupy the top of the figure in bold, while the lines represent the stereopermutations of M1 type (Berry or TR) [22], allowing the passage from one stereoisomer to another. Nine other pentacoordinate stereoisomers could be formed as well and are mentioned on the dotted part of the figure. The remain-



Scheme 6

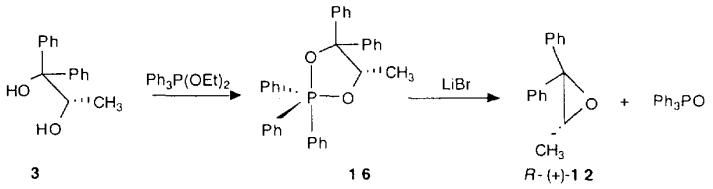


Scheme 7

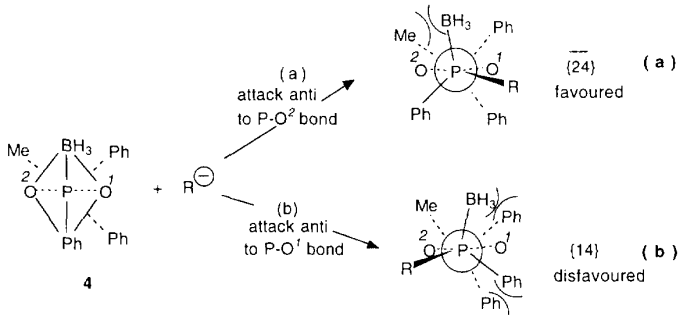
ing two theoretically possible stereoisomers {12} and $\{\overline{12}\}$, are not represented as the existence of a linkage between the two groups $OCPh_2$ and $OCHCH_3$ does not allow them to occupy simultaneously apical positions.

If we examine figure 1, we notice that the stereoisomers $\{\overline{24}\}$ and {15} occupy the same side as the last intermediate {13}, whereas {14}, $\{\overline{23}\}$ and $\{\overline{25}\}$ occupy another side including $\{\overline{13}\}$. However, this last intermediate cannot be obtained directly from a nucleophilic attack on complex **4** (scheme 6). The two series of stereoisomers $\{\overline{24}\}$, {15}, {13} and {14}, $\{\overline{23}\}$, $\{\overline{25}\}$ derive from the nucleophilic attack directions (a), (e), (f) and (b), (i), (h) respectively (scheme 6), and correspond to the tetrahedron faces opposite to the P–O^2 and P–O^1 bonds, respectively. The interconversion of these two groups of pentacoordinate intermediates could not occur under the reaction conditions, as this requires passage through {34}, {35}, or {45} (fig 1), which are energetically unfavourable due to the presence of two intracyclic equatorial P–O bonds [20a].

Despite the possibility of an organolithium edge attack ((e), (f), (i), (h) directions), it is most likely that the stereoselectivity obtained is derived from the two facial attacks (a) and (b) on complex **4**, lead-



Scheme 8



Scheme 9

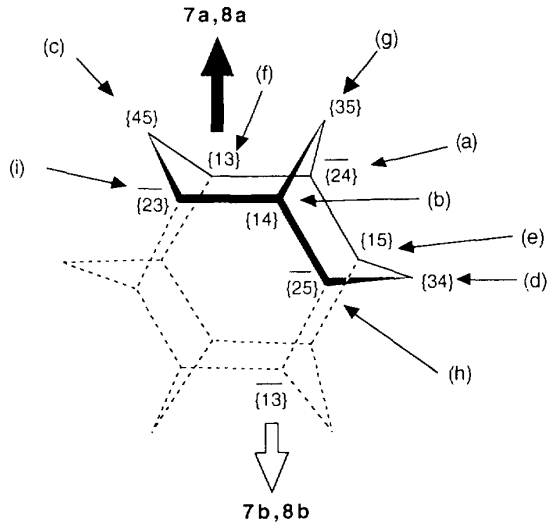


Fig 1. Topological representation of the stereochemical pathways of the pentacoordinate intermediates, evolving towards the last one {13} (or {$\overline{13}$}) precursor of the diastereoisomer **a** (or **b**).

ing to the initial intermediates {$\overline{24}$} and {14}, respectively (scheme 7a,b). The stereoisomer {$\overline{24}$} would easily evolve to the most stable last intermediate {13} by a simple stereopermutation, whereas {14} leads to {$\overline{13}$} following two stereopermutations through the high-energy intermediate {$\overline{25}$} (figure 1, scheme 7b). In contrast, {14} gives, after a single stereopermutation, the intermediate {$\overline{23}$} leading to the regioisomer **9** after a P–O^2 bond rupture (scheme 7c). The formation of this benzylic phosphinite-borane **9** could not be made evident, but this could be explained by its rapid collapse to the phosphinous acid-borane **10** (or **11**) and the *S*-epoxide **12**, explaining the partial loss of chirality for this last compound obtained with a major *R* configuration (scheme 4). Lastly, the regioselectivity in the heterocycle **4** ring opening should be amplified by the P–O^1 bond, slightly longer than P–O^2 ((ie, P–O(3)) [9], and by the Li^+-cation assistance of which the influence has been demonstrated by Murray et al [23] for the dehydration of *S*-(−)-diol **3** via the phosphorane **16** (scheme 8).

Model of asymmetric induction

The comprehension of the stereochemical pathway of this reaction leads to the proposition of a model for the interpretation of the asymmetric induction at a phosphorus atom (scheme 9). In fact, examination of the projection of complex **4** along an axis passing through the middle of the sides BH_3/Ph and $CHCH_3$/CPh_2 (scheme 9) shows the phenyl and methyl substituents of the cycle in staggered position with the substituents of the phosphorus atom. The organolithium attack direction according to (a) gives the pentacoordinate intermediate {$\overline{24}$} with the methyl group eclipsed by the borane (scheme 9a). In the case of a (b) direction attack, the two phenyls of the ring are eclipsed by the borane and phenyl substituents of the phosphorus atom, thus disfavoring the formation of intermediate {14} compared to {$\overline{24}$} (scheme 9b).

In summary, we suggest that the facial nucleophilic attack on complex **4** opposite to the P–O^2 bond initially gives the pentacoordinate intermediate {$\overline{24}$} which after one stereopermutation is transformed into {13}, responsible for the major diastereoisomer **a** of the phosphinite-boranes **7, 8** (scheme 7a; fig 1). In contrast, the facial nucleophilic attack opposite to the P–O^1 bond gives the sterically hindered intermediate {14} whose stereopermutation into {$\overline{13}$} is unfavorable, and leads to the minor diastereoisomer **b** (scheme 7b, fig 1).

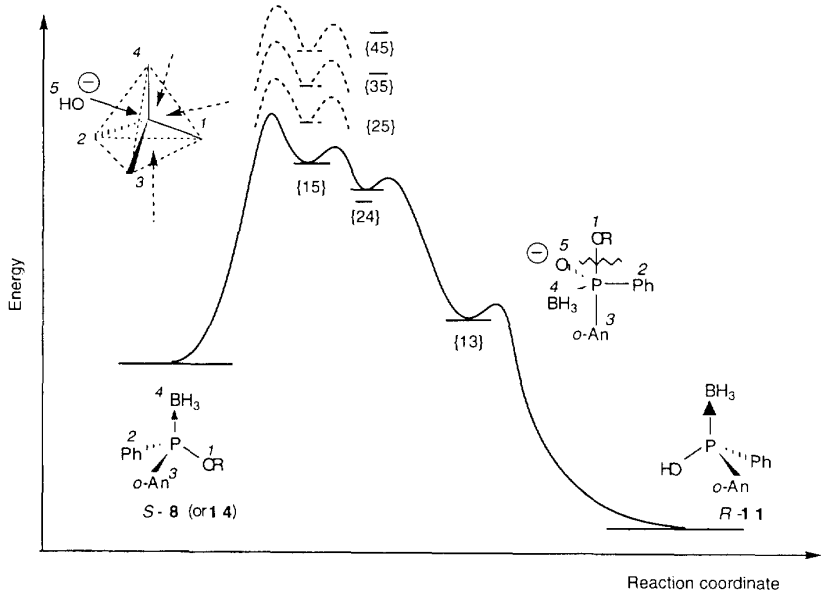


Fig 2. Kinetic control and thermodynamic route of the initial pentacoordinate intermediate {15} on the stereochemistry of the P–O bond cleavage, in acyclic phosphinite-borane **8** (or **14**).

Interpretation of the saponification stereochemistry of the acyclic phosphinite-boranes 8 and 14

The above reasoning will be applied to the interpretation of the stereochemistry with inversion of configuration, occurring during saponification of the phosphinite-boranes **8** and **14** (scheme 5). In this case, the classification of the five phosphorus substituents according to their stereoapicophilicity is established as: OR^1, Ph^2, $o\text{-}An^3$, $BH_3{}^4$, $O(H)^5$, because the fast transformation of the P–OH group into $P\text{–}O^-$ forces the latter to occupy an equatorial position in the pentacoordinate intermediate. Among the four possible intermediates {15}, {$\overline{25}$}, {35} and {$\overline{45}$} resulting from a facial attack, {15} is the most likely initial intermediate due to the difference in the relative stereoapicophilicities between OR and the other substituents (fig 2).

Examination of figure 2 shows that intermediate {15} is transformed into the more stable {13} (via {$\overline{24}$}) occupying the same face of the topological representation of figure 1. The cleavage of the axial $P\text{–}OR^1$ bond of {13} leads to the phosphinous acid-borane **11** with inversion of the configuration.

Conclusion

A novel asymmetric synthesis of organophosphorus compounds was investigated using dioxaphospholane-borane complex **4**, prepared diastereospecifically pure from *S*-1,1-diphenylpropane-1,2-diol **3**, derived from *S*-(−)-ethyl lactate. This complex reacts regiospecifically with organolithium reagents to yield β-hydroxy-phosphinite-boranes **7** or **8**, with a major retention of configuration at the phosphorus atom and $P\text{–}O^1$ bond rupture. The reaction in THF of the phosphinite-borane **7** (or **8**) with an organolithium reagent leads to the enantiomerically enriched phosphinous acid-borane **10** (or **11**). In contrast, methyllithium reacts in ether with *o*-anisylphenylphosphinite-borane **8** (dr 4:1) to afford *R*-PAMP-borane **13** in 43% yield and 70% ee. This demonstrates the validity of our new strategy which offers an alternative route for the asymmetric synthesis of tertiary phosphines.

The stereochemistry is explained by the competitive formation of two initial pentacoordinate intermediates, displayed on two faces of the topological representation of figure 1, evolving in different stereochemical pathways without loss of chirality. The definition of the pentacoordinate intermediates by the 'relative stereoapicophilicity' of the phosphorus substituents, considering their steric hindrance and their relative apicophilicity, affords an explanation for the asymmetric induction observed in the creation of a P–C bond.

The reasoning developed here is applicable to the acyclic phosphinite-boranes **8** and **14** and to the oxazaphospholidine-borane **2**, and also to their reaction with other nucleophiles [24]. This makes the organophosphorus-borane complexes into suitable models for the study of the regio- and stereochemistry of reactions at a phosphorus center.

Experimental section

All reactions were carried out under an argon atmosphere in glassware dried over night. Solvents (THF, ether) were dried and freshly distilled under an argon atmosphere over sodium/benzophenone, and toluene over CaH_2. Ethyl acetate and CH_2Cl_2 were of reagent grade and distilled before use. Hexane and ethanol for HPLC were of chromatography grade and used without further purification. Methyl lithium, *sec*-butyl lithium, BH_3·DMS in toluene were purchased from Aldrich. Commercially available *S*-(−)-ethyl lactate, bromobenzene, 2-bromoanisole and dichlorophenyl phosphine

were distilled before use. The HPLC analyses were performed on a Gilson model 302 UV detector using a Chiracel OK column (Daicel), with a mixture of hexane/EtOH (55:45) as the mobile phase. Flash chromatography was realized on silica gel (230–400 mesh; Merck) and when necessary diastereomeric samples were obtained by preparative TLC on commercially tapered silica gel plates $60F_{254+366}$ (Merck).

All NMR spectra data were obtained on a Bruker AM 80 (^1H), AM 200 (^1H,^{13}C) et AM 250 (^1H,^{13}C,^{31}P) spectrometer with TMS as the internal reference for ^1H and ^{13}C NMR, and 85% phosphoric acid as the external reference for ^{31}P NMR. Infrared spectra were recorded on Perkin-Elmer 297, 251, 1600 FT and a Bruker FT 45.

Melting points were measured on a Büchi melting point apparatus and are uncorrected. Specific rotation values were determined at 20 °C on a Perkin-Elmer 241 polarimeter. Mass spectral analyses were performed on a NERMAG R10-10C and a KRATOS MS-50 for the exact mass at the laboratories of mass spectroscopy of ENSCP and Structural Chemistry of the University Pierre-et-Marie-Curie, Paris, respectively. The major peak m/z is mentioned with the intensity as percentage of the base peak in brackets.

Elemental analyses were measured with a precision superior to 0.3%, at the Laboratories of Microanalysis of the University Pierre-et-Marie-Curie, Paris, and of the CNRS (Vernaison, France).

(2R,5S)-(−)-[5-Methyl-2,4,4-trimethyl-1,3,2-dioxaphospholane]-2-borane **4**

A solution of (−)-1,1-diphenylpropane-1,2-diol **3** (7g, 30.7 mmol) and dichlorophenyl phosphine (4.17 mL, 30.7 mmol) in dry THF (300 mL) was cooled to 0 °C and treated dropwise with triethylamine (8.94 mL, 64 mmol). After stirring for 1 h, the mixture was filtered under argon, then BH_3·Me_2S (2 M in toluene, 18 mL, 36 mmol) was added. The mixture was stirred for 12 h, then the solvent was removed under reduced pressure. The crude product was filtered through a plug of flash silica using toluene/cyclohexane (4:1) as eluent. The complex **4** obtained was recrystallized from hexane/ether (4:1) (5.87 g, 55% yield). White solid: Mp 158 °C (hexane/ether); $[\alpha]_D = -234.5$ (c 1, $CHCl_3$).

IR (KBr) 2 410 (br, m), 1650 (s), 1270 (s), 920–950 (br) cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.2–7.5 (m, 15H), 5.12 (dq, 1H, $^3J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 4 Hz, CH), 1.24 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH_3), 1.9–0.2 (q, 3H, $^1J_{BH}$ = 83 Hz, BH_3).

^{13}C NMR ($CDCl_3$) δ 132.3, 130.7, 130.5, 128.6, 128.5, 128.3, 128.2, 128.1, 127.5, 126.8, 126.7, 80.7 (d, $^2J_{POCH}$ = 5.5 Hz, CH), 18.8 (d, $^1J_{POCC}$ = 8 Hz, CH_3).

^{31}P NMR ($CDCl_3$) δ +154.7 (q, $^1J_{PB}$ = 87 Hz).

MS (EI) m/z (relative intensity) 194 (6), 183 (34), 181 (36), 105 (100), 77 (63).

Anal calc for $C_{21}H_{22}BO_2P$ (348): C, 72.4; H, 6.3. Found: C, 72.3; H, 6.4.

Typical procedure for the reaction of complex **4** *with methyllithium*

A solution of complex **4** (348 mg, 1 mmol) in dry THF (3 mL) was cooled at −78 °C and treated with MeLi (1.6 M, 0.63 mL, 1 mmol). The reaction mixture was stirred for 15 min and then quenched with H_2O (0.1 mL). The solvent was removed in vacuo and the aqueous layer was extracted with CH_2Cl_2. The combined organic solutions were dried over $MgSO_4$, filtered and concentrated, affording the phosphinite-borane **7** (301 mg, 82% yield).

When the hydrolysis of the reaction was realized at room temperature, a mixture of phosphinite-borane **7** (42 mg, 12% yield) phosphinous acid-borane (+)-**10** (97 mg, 62% yield, $[\alpha]_D$ = +11.6 (c 4.2, CH_2Cl_2)), epoxide (+)-**12** (125 mg, 59% yield, $[\alpha]_D$ = +17.4 (c 3, $CHCl_3$)) and diol **3** (23 mg, 10% yield) was obtained.

[(S)-2-Hydroxy-2,2-diphenyl-1-methylethyl]methylphenylphosphinite-borane **7a,b**

The major isomer **7a** was obtained by recrystallization from hexane/EtOH, whereas **7b** was obtained as an enriched mixture (**a**/**b**, 1:4) by flash chromatography on silica gel with toluene as eluent.

*Isomer (R_P)-***7a**

White solid: Mp 143 °C (hexane/EtOH); TLC R_f = 0.46 (benzene); $[\alpha]_D = -2.97$ (c 4.3, $CHCl_3$).

IR (KBr) 3 480 (br, s), 3 060 (w), 2 400 (br, s), 1 450 (m), 1 380 (m), 1 180 (m), 1 060 (s), 1 015 (s), 985 (s), 965 (s), 910 cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.40–7.57 (m, 3H), 7.0–7.4 (m, 12H), 5.48 (dq, 1H, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 8.5 Hz), 2.79 (s, 1H), 1.68 (d, 3H, $^3J_{PH}$ = 8.9 Hz), 1.32 (d, 3H, $^3J_{HH}$ = 6.2 Hz), 1.8–0.2 (q, 3H, $^1J_{BH}$ = 93 Hz).

^{13}C NMR ($CDCl_3$) δ 145.0, 143.0, 131.3, 130.0, 129.8, 128.3, 128.2, 128.1, 126.9, 126.8, 125.8, 125.5, 80.0 (d, $^3J_{POCC}$ = 6.8 Hz, CPh_2), 79.9 (d, $^2J_{POC}$ = 2.7 Hz, CH), 18.6 (d, $^1J_{PC}$ = 44.4 Hz), 17.0; off-resonance δ 80.0 (d), 79.9 (dd).

^{31}P NMR ($CDCl_3$) δ + 112 (m, $^1J_{PB}$ = 85 Hz).

MS (EI) m/z (relative intensity) 217 (100), 183 (34), 165 (20), 140 (33), 125 (37), 105 (82), 77 (70).

Anal calc for $C_{22}H_{26}BO_2P$ (364): C, 72.50; H, 7.14; Found: C, 71.49; H, 7.19.

*Isomer (S_P)-***7b**

White solid: Mp 163 °C; TLC R_f = 0.54 (benzene); $[\alpha]_D = -53.9$ (c 1.5, $CHCl_3$); (mixture of epimers **7a**/**7b** in 1:4 ratio).

IR (KBr) 3 500 (br, s), 3 060 (m), 2 400 (br, s), 1 455 (m), 1440 (m), 1 385 (m), 1 180 (m), 1 080 (s), 1 060 (s), 1 015 (s), 980 (s), 965 (s), 910 (s) cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.67–7.76 (m, 2H); 7.05–7.51 (m, 13H), 5.51 (dq, 1H, $^3J_{HH}$ = 6.3 Hz, $^3J_{PH}$ = 7.7 Hz, CH), 2.76 (1H, OH), 1.22 (d, 3H, $^3J_{PH}$ = 9.2 Hz, PCH_3), 1.05 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3), 1.8–0.2 (q, 3H, $^1J_{BH}$ = 100 Hz, BH_3).

^{13}C NMR ($CDCl_3$) δ 145.5, 143.0, 131.8, 130.0, 128.7, 128.2, 127.1, 126.3, 125.7, 79.9 (s, CH), 80 (d, $^3J_{POCC}$ = 6.8 Hz, CPh_2), 17.1 (d, $^1J_{PC}$ = 47.85 Hz, PCH_3), 16.5.

^{13}C NMR (DEPT) δ 79.9 (d, CH).

^{31}P NMR ($CDCl_3$) δ + 112 (m, $^1J_{PB}$ = 85 Hz).

MS (EI) m/z (relative intensity) 217 (100), 183 (34), 165 (16), 140 (28), 123 (32), 105 (85), 77 (86), 51 (34).

Anal calc for $C_{22}H_{26}BO_2P$ (364): C, 72.50; H, 7.14. Found: C, 71.27; H, 7.39.

Methylphenylphosphinous acid-borane **10** *[25]*

Uncrystallized; IR (KBr) 3 600–2 500 (br, s), 2 370 (s), 1 440 (s), 1 150(br, s), 935(s) cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, 5H), 1.60 (d, 3H, J_{PH} = 9 Hz, CH_3P), 1.5–0.0 (q, 3H, $^1J_{BH}$ = 83 Hz, BH_3).

^{13}C NMR ($CDCl_3$) δ 132.6, 130.6, 130.0, 128.8, 128.3, 18 (d, $^1J_{PC}$ = 46.3 Hz, PCH_3).

^{31}P NMR ($CDCl_3$) δ + 95 (m).

MS (EI) m/z (relative intensity) 153 (10), 140 (100), 125 (60), 123 (50), 109 (15), 91 (10), 77 (20).

HRMS (EI) calc for $C_7H_{11}BOP$ [M - 1] 153.0641, found $[M - 1]^+$ 153.0644.

*Typical reaction of complex **4** with o-anisyllithium*

A solution of 2-bromoanisole (748 mg, 4 mmol) in dry ether (4 mL) was cooled to 0 °C and treated dropwise with *s*-BuLi (1.4 M, 2.7 mL, 4 mmol). After stirring for 0.5 h, the mixture was added dropwise to a solution of complex **4** (696 mg, 2 mmol) in dry THF (3 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, then quenched with H_2O. The solvent was removed in vacuo and the aqueous layer was extracted with CH_2Cl_2. The combined organic solutions were dried over $MgSO_4$, filtered and concentrated. Flash chromatography with toluene/AcOEt (9:1) as eluent gave phosphinite-borane **8** as a mixture of epimers **a, b** (4:1) (730 mg, 80% yield).

When the hydrolysis of the reaction was realized at room temperature, a mixture of phosphinous acid-borane (+)-**11** (414 mg, 84% yield, $[\alpha]_D$ = + 15.3 (*c* 1.3, $CHCl_3$)) and epoxide (+)-**12** (336 mg, 80% yield, $[\alpha]_D$ = + 17 (*c* 4.5, $CHCl_3$)) was obtained.

*[(S)-2-Hydroxy-2,2-diphenyl-1-methylethyl]-o-anisylphenylphosphinite-borane **8a,b***

White solid: Mp 115–116 °C; (TLC R_f = 0.40 toluene); $[\alpha]_D$ = −67.9 (*c* 1.9, $CHCl_3$); (mixture of epimers **8a/8b** in 4:1 ratio).

IR (KBr) 3 550 (br, m), 3 057 (m), 2 386 (s), 1 590 (m), 1 477 (s), 1 064 (s), 954 (s) cm^{-1}.

^1H NMR ($CDCl_3$) major isomer δ 8.0–6.45 (m, 19H), 5.69 (m, 1H, $^3J_{HH}$ = 6.2 Hz, $^3J_{POCH}$ = 5 Hz, CH), 3.09 (s, 1H, OH), 3.55 (s, 3H, CH_3O), 1.08 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3), 1.9–0.2 (q, 3H, BH_3); minor isomer δ 5.69 (m, 1H, $^3J_{HH}$ = 6.2 Hz, CH), 3.38 (s, 3H, CH_3O), 3.15 (s, 1H, OH), 1.21 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3).

^{13}C NMR ($CDCl_3$) major isomer δ 161.2, 145.6, 143.1, 134.4, 130.4, 130.1, 129.9, 128.2, 127.8, 127.6, 126.9, 126.3, 125.6, 120.8, 111.8, 80.4 (d, $^3J_{POCC}$ = 8.3 Hz, CPh_2), 79.5 (d, $^2J_{POC}$ = 3.5 Hz, CH), 55.5 (CH_3O), 16.1 (CH_3), minor isomer δ 80.0 (d, $^3J_{POCC}$ = 6 Hz, CPh_2), 79.7 (d, $^2J_{POC}$ = 3.2 Hz, CH), 55.0 (CH_3O), 17.1 (CH_3).

^{31}P NMR ($CDCl_3$) δ + 103.5 (m).

MS (CI, NH_3) 474 $[M + NH_4]^+$, 455 $[M - H]^+$, 439 $[M - H_2O + H]^+$; 425; 309.

Anal calc for $C_{28}H_{30}BO_3P$ (456): C, 73.68; H, 6.53; Found: C, 73.70; H, 6.59.

*o-Anisylphenylphosphinous acid-borane **11** [25]*

White solid: Mp < 50 °C.

IR (KBr) 3 228 (br, s), 2 377 (s), 1 590 (s), 1478, 1 436, 1 162 (br, m), 921(s) cm^{-1}.

^1H NMR ($CDCl_3$) δ 8.0–6.7 (m, 9H), 3.7 (s, 3H, CH_3O), 1.9–0.0 (q, 3H, $^1J_{BH}$ = 85 Hz, BH_3).

^{13}C NMR ($CDCl_3$) δ 160.7, 134.9, 133.4, 130.8, 130.6, 130.4, 127.7, 111.1 (d, $^2J_{PCC}$ = 33 Hz), 55.6 (OCH_3).

^{31}P NMR ($CDCl_3$) δ + 93.9 (q, $^1J_{PB}$ = 64 Hz).

*Reaction of phosphinite-borane **7a** with o-anisyllithium*

A solution of phosphinite-borane **7a** (500 mg, 1.37 mmol) in dry THF (3 mL) was cooled to −78 °C and treated dropwise with *o*-anisyllithium (4.2 mmol). After stirring for 0.5 h, the mixture was then warmed to room temperature and quenched with H_2O. The solvent was removed in vacuo and the aqueous layer was extracted with CH_2Cl_2. The combined organic solutions were dried over $MgSO_4$, filtered and concentrated affording a mixture of epoxide (+)-**12** (144 mg, 50% yield, $[\alpha]_D$ = + 15 (*c* 5, $CHCl_3$)) and diol (−)-**3** (96 mg, 31% yield) [12] separated by flash chromatography. The phosphinous acid-borane **10** was obtained by extracting the acidified aqueous layer (120 mg, 78% yield).

*(R)-(+)-3-Methyl-2,2-diphenyloxizane **12** [13]*

White solid: Mp 64 °C (hexane; literature: 64 °C) [14]; $[\alpha]_D$ + 22.1 (*c* 1.5, $CHCl_3$) or $[\alpha]_D$ + 23.3 (*c* 1.5, C_6H_6).

IR (KBr) 3 526 (br, m), 1 716 (s), 1 602 (m), 1 493 (s), 1448(s) cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.42–7.18 (m, 10H), 3.47 (q, 1H, $^3J_{HH}$ = 5.3 Hz, CH), 1.16 (d, 3H, $^3J_{HH}$ = 5.4 Hz, CH_3).

^{13}C NMR ($CDCl_3$) δ 141.1, 137.4, 129.2, 128.1, 127.5, 126.8, 65.9 (CPh_2), 62.3 (CH), 15.4 (CH_3).

MS (EI) m/z (relative intensity) 210, 181 (19), 167 (100), 152 (19).

Anal calc for $C_{15}H_{14}O$ (210): C, 85.8; H, 6.7; O, 7.6. Found: C, 85.5; H, 6.7; O, 8.0.

*Reaction of phosphinite-borane **8a,b** with methyllithium*

A solution of phosphinite-borane **8a,b** (dr 4:1; 228 mg, 0.5 mmol) in dry ether (4 mL) was cooled at −78 °C and treated dropwise with MeLi (1.6 M, 1.25 mL, 2 mmol). After being stirred for 0.5 h, the mixture was then warmed to 0 °C and quenched with H_2O. The aqueous layer was extracted with CH_2Cl_2 and the combined organic solutions were dried over $MgSO_4$, filtered and concentrated. Flash chromatography with toluene/AcOEt (90:10) as eluent gave PAMP·BH_3 **13** (52 mg, 43% yield, $[\alpha]_D$ = −21.5 (*c* 2.4, MeOH)), epoxide **12** (32 mg, 30% yield) and diol **3** (69 mg, 60% yield).

When the reaction was carried out in THF and warmed to room temperature for a night, a mixture of the starting phosphinite-borane **8**, phosphinous acid borane **11** (30% yield) and epoxide **12** (30% yield) was obtained.

*o-Anisylmethylphenylphosphine-borane **13***

The enantiomeric excess (70% ee) was determined by HPLC on a Chiracel OK Daicel column with hexane/EtOH (55:45) as eluent.

White solid: Mp 55 °C.

IR (KBr) 3 060 (w), 2 380 (br, s), 1 590 (m), 1 460 (m), 1 250 (s), 1 060 (s), 910 (s) cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.9–6.9 (9H, Ar), 3.67 (s, 3H, CH_3O), 1.94 (d, 3H, $^2J_{PH}$ = 10.6 Hz, CH_3P), 1.5–0.4 (q, 3H, $^1J_{BH}$ = 88 Hz, BH_3).

^{13}C NMR ($CDCl_3$) δ 161.5, 135.6 (d, ^2J = 15 Hz), 133.7, 131.1 (d, ^3J = 4.5 Hz), 130.3, 128.3 (d, ^3J = 10 Hz), 121.1 (d, ^3J = 13 Hz), 111.3 (d, ^3J = 4.5 Hz), 55.4, 10.7 (d, $^1J_{PC}$ = 42 Hz).

^{31}P NMR ($CDCl_3$) δ 9.2 (q, $^1J_{PB}$ = 72 Hz).

MS (EI) m/z 230 (100), 119 (43), 183 (35), 91 (57).

Anal calc for $C_{14}H_{19}BOP$ (245): C, 68.8; H, 7.4. Found: C, 69.0; H, 7.6.

Hydrolysis of phosphinite-borane ***8a,b***

A mixture of phosphinite-borane **8a,b** (dr 4:1; 120 mg, 0.26 mmol) in THF (1 mL) and NaOH (2 M, 0.5 mL) was refluxed for 2 days. The mixture was then cooled and the aqueous layer was extracted with CH_2Cl_2, affording the phosphinous acid borane (−)-**11** and the diol (*S*)-(−)-**3** (30 mg, 50% yield, $[\alpha]_D = -114$ (*c* 1.5, EtOH), literature [8b]: $[\alpha]_D = -114$).

Hydrolysis of phosphinite-borane ***14***

The hydrolysis of phosphinite-borane (*S*)-(+)-**14** (130 mg, 0.5 mmol) was realized in THF (1.5 mL) and NaOH (2 M, 0.5 mL) via the same procedure as described above. The aqueous layer was acidified and extracted with CH_2Cl_2, affording *o*-anisylmethylphenylphosphinous acid-borane (−)-**11** (70 mg, 57% yield, $[\alpha]_D = -7.1$ (*c* 1.2, $CHCl_3$).

Acknowledgments

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c) For a review concerning the structures and geometries associated with pentacoordinated phosphorus

compounds, see: Burgada R, Setton R, In: *The Chemistry of Organophosphorus Compounds* (Hartley FR, Ed) Wiley, 1994, Vol 3, pp 185-272

21 a) Luckenbach, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*, Thieme, 1973
b) Determined by ab initio calculation in the case of oxazaphospholidine-borane **2**: Sini G, Grimbert D, Jugé S, to be published

22 The modes describe all the basic stereochemical modifications of a trigonal bipyramid (TBP), so that every TBP rearrangement can be classified according to which one or more of these modes is attained by the rearrangement mechanism involved: Musher JI, *J Am Chem Soc* (1972) 94, 5662-5665

23 a) Murray TM, Evans Jr SA, *J Org Chem* (1989) 54(10), 2440-2446
b) Murray TM, Evans Jr SA, *New J Chem* (1989) 13, 329-334

24 Sodium methanolate stereospecifically reacts with the complex **2**, leading to ring opening by P–O bond cleavage.

25 The phosphinous acid-boranes **10**, **11** are of moderate stability, giving (after decomplexation) the corresponding phosphinites MePhP(O)H [^{1}H NMR ($CDCl_3$) δ 7.7 (d, $^1J_{PH}$ = 480 Hz, PH); ^{31}P NMR ($CDCl_3$) δ 25] and *o*-AnPhP(O)H (^{31}P NMR ($CDCl_3$) δ 15).