New Chiral Dichlorophosphines and Their Use in the Synthesis of Phosphetane Oxides and Phosphinic Chlorides

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Myrtanyl-, bornyl- and isopinocampheyldichlorophosphines have been prepared from the corresponding alkyl chlorides via diastereospecific reactions of the Grignard reagents with PCl_3 or $(Et_2N)_2$-PCl. Two applications of these compounds to synthetic asymmetric organophosphorus chemistry have been examined: their reactions with 2,3,3-trimethylbutene and $AlCl_3$ afford either P-chiral phosphetane oxides or, in the presence of gaseous HCl, P-chiral phosphinic chlorides with moderate to high diastereoselectivity.

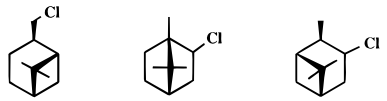
Dichlorophosphines are extremely versatile starting materials for the synthesis of a wide range of organophosphorus compounds. Therefore, the asymmetric version of a number of synthetic procedures could be envisaged, provided that chiral dichlorophosphines are readily accessible. Surprisingly, as far as we know, the only such chiral compound which is readily available is *l*-menthyldichlorophosphine. It is obtained from *l*-menthol in a diastereoselective two step synthesis.[1]

In this report we propose simple routes to optically active dichlorophosphines from α- and *β*-pinene derivatives. We also evaluate their use in the synthesis of phosphetane oxides as part of our ongoing program to develop phosphetanes as chiral ligands in enantioselective catalysis.[2] To date, this subject has been limited to P-menthyl substituted species; the use of other chiral auxiliaries is desirable in order to optimize the catalytic behavior and the chiral inductions. Finally, a preparative scale, diastereoselective approach to chiral phosphinic chlorides from the same dichlorophosphines is depicted.

Results and Discussion

Synthesis of Chiral Dichlorophosphines. Substrates from the chiral pool, which are available on a large scale, are convenient starting materials for extending the range of chiral dichlorophosphines. Pinenes and their derivatives have been selected for this purpose.

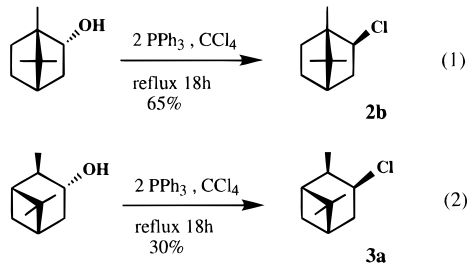
The classical route to dichlorophosphines involves the reaction of Grignard reagents with phosphorus trichloride, so three alkyl chlorides derived from pinene, myrtanyl chloride **1**, bornyl chloride **2a**, and 3-chloro-*cis*-pinane **3**, were targeted as starting compounds.



1 **2** **3**

(1*S*)-Myrtanyl chloride, **1**, was prepared in 67% yield from (1*S*)-myrtanol[3ab] by reaction with triphenylphosphine in carbon tetrachloride using a slight modification of a published procedure.[3c] The competitive generation of *β*-pinene is minimized by performing the reaction in refluxing CCl_4.

Scheme 1



The synthesis of *endo*-2-chlorobornane (bornyl chloride) **2a** through hydrochlorination−rearrangement of α- or *β*-pinene has been known since 1957.[4a] Unfortunately, the literature procedures[4] afford bornyl chloride contaminated with about 10−20% of the isomeric fenchyl chloride. This impurity cannot be totally removed either by subsequent recrystallization from methanol or sublimation. In view of the inadequate purity and low synthetic yield of the bornyl chloride product, an alternative approach to 2-chlorobornane from borneol was envisaged.

exo-2-chlorobornane (isobornyl chloride) **2b** was obtained from commercial (1*S*)(−)-borneol by treatment with 2 equiv of triphenylphosphine in refluxing carbon tetrachloride, according to eq 1 (Scheme 1). The only competitive reaction is the generation of bornylene in about 20% yield, as shown by the ^{1}H NMR spectrum of the crude reaction mixture. As expected,[5] the conversion takes place with total inversion of the carbon configuration. For our purpose, the synthesis of dichlorophosphines, it is immaterial whether bornyl (**2a**) or isobornyl (**2b**) chlorides are used, because the corresponding Grignard reagent is known to equilibrate between its *exo* and *endo* forms.[6]

The only reported synthesis of 3-chloro-*cis*-pinane **3** is, to our knowledge, the chlorination of *cis*-pinane under

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) Krause, H. W.; Kinting, A. *J. Prakt. Chem.* **1980**, *322*, 485.

(2) (a) Marinetti, A.; Ricard, L. *Tetrahedron* **1993**, *49*, 10291. (b) Marinetti, A. *Tetrahedron Lett.* **1994**, *35*, 5861. (c) Marinetti, A. Ricard, L. *Organometallics* **1994**, *13*, 3956. (d) Marinetti, A.; Le Menn, C.; Ricard, L. *Organometallics* **1995**, *14*, 4983. (e) Marinetti, A.; Kruger, V.; Le Menn, C.; Ricard, L. *J. Organomet. Chem.* **1996**, in press.

(3) (a) Brown, H. C.; Mandal, A. K. *Synthesis* **1980**, 153. (b) Giacomelli, G.; Lardicci, L.; Palla, F. *J. Org. Chem.* **1984**, *49*, 310. (c) Falorni, M.; Lardicci, L. ; Giacomelli, G. *J. Org. Chem.* **1986**, *51*, 5291.

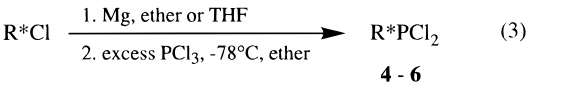
(4) (a) Zeiss, H. H.; Zwanzig, F. R. *J. Am. Chem. Soc.* **1957**, *79*, 1733. (b) Erickson, G. W.; Fry, J. L. *J. Org. Chem.* **1987**, *52*, 462.

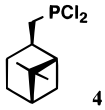
(5) For a review on the hydroxyl group/halogen replacements via organophosphorus reagents see: Castro, B. R. *Org. React.* **1983**, *29*, 1.

(6) Hill, E. A. *J. Chem. Soc.* **1966**, *31*, 20 and references therein.

S0022-3263(96)01708-2 CCC: $14.00

Scheme 2



R*Cl	R*PCl_2	yield
(1S)-*cis*-myrtanyl chloride **1**	 **4**	48%
(1S)-bornyl chloride **2a** or (1S)-isobornyl chloride **2b**	 **5a + 5b**	–
(1R)-*exo*-3-chloro-*cis*-pinane **3a**	 **6**	79%

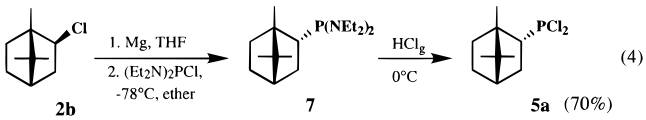
photochemical conditions, which leads to a mixture of isomeric mono- and polychloropinanes.[7a] A more recent attempt to prepare **3** from isopinocampheol failed to give a pure sample of the desired product.[7b] The *endo*-3-chloro-*cis*-pinane **3a** was synthesized as shown in eq 2 from (1R)-isopinocampheol, which was obtained from (1*R*)(+)-α-pinene of 91% enantiomeric excess according to ref 8. The synthesis of **3a** gave only moderate yields, but was quite reproducible. The chloride, which seemed rather heat sensitive, was purified by distillation under mild conditions (30 °C/0.1 mmHg). Substitution of the hydroxyl group proceeds with inversion of the carbon configuration.

The chiral alkyl chlorides **1**, **2**, and **3a** were converted into the corresponding Grignard reagents, which were subsequently used in the synthesis of dichlorophosphines (Scheme 2).

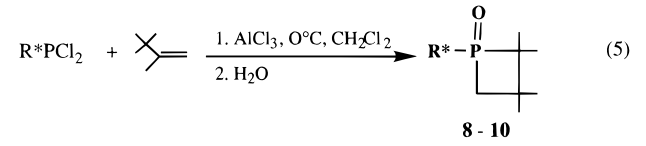
The alkylmagnesium chlorides reacted with excess PCl_3 to afford the expected dichlorophosphines **4**, **5**, and **6**, respectively. The synthesis of **4** does not deserve special comments, but the stereochemical outcome of the two last assays, where phosphorus−carbon bond formation involves a chiral carbon atom, are noteworthy. A single isomer of the isopinocampheyldichlorophosphine **6** is obtained from **3a**, and a 1:1 mixture of **5a** and **5b** (^{31}P NMR ($CDCl_3$) δ 197.7 and 198.7, respectively) is obtained from **2**. The *exo* stereochemistry of **6** was initially deduced from NMR data and was confirmed by the X-ray crystal structure of the phosphinic chloride reported hereafter. The diastereospecific synthesis of **6** could be explained by a configurational preference of the Grignard reagent, but more probably reflects a kinetically favored reaction pathway. To date, no information is available on the stereochemistry of the isopinocampheylmagnesium chloride.

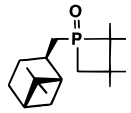
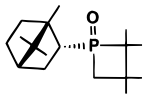
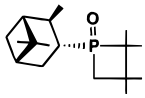
The lack of selectivity in the synthesis of **5** is not unexpected, given the synthesis of (2-norbornyl)dichlorophosphine, where a 2:1 mixture of *exo* and *endo* isomers was obtained.[9] Nevertheless, it represents a major drawback because the mixture of **5a** and **5b** cannot be appreciably separated by fractional distillation. This problem can be eliminated by reacting the bornylmagnesium chloride with bis(diethylamino)chlorophosphine.[10] The single isomer of the bornylphosphinamide **7** which is formed is subsequently treated *in situ* with gaseous HCl to generate the corresponding dichlorophosphine (Scheme 3).

Scheme 3



Scheme 4



R*PCl_2	Phosphetane oxides (isomers ratio)	^{31}P NMR*	yield
4	 **8a + 8b** (50:50)	56.7; 56.8	61%
5a	 **9a + 9b** (60:40)	66.5; 59.8	50%
6	 **10a + 10b** (80:20)	66.3; 62.0	42%

* in the reaction mixture, in CH_2Cl_2

The *endo* stereochemistry of **5a** is tentatively proposed on the basis of a comparison of its ^{13}C NMR spectrum with those of the analogous *exo* and *endo* (2-norbornyl)-dichlorophosphines[9] of known geometries. The large coupling constants (29.0 and 21.6 Hz) between phosphorus and the C-3 or C-6 atoms are particularly indicative of *endo* substitution.

Thus, using pinene derivatives has allowed a general diastereoselective synthetic approach to the three chiral dichlorophosphines **4**, **5a**, and **6**, which represent new tools for the asymmetric phosphorus chemistry. As a first application they have been used for the synthesis of P-chiral phosphetane oxides as shown hereafter.

Synthesis of Phosphetane Oxides. The above study on chiral dichlorophosphines was initially motivated by a need for new chiral starting materials for use in the Mc Bride phosphetane synthesis.[11] Our recent work[2] on P-menthyl substituted phosphetanes underlines that a variety of such species are easily accessible and that they have a significant potential as chiral ligands in asymmetric catalysis. In this context, the variation of the chiral auxiliaries bound to the phosphetane phosphorus atom should allow a comparison of their respective properties and a chance to optimize the enantioselectivities of the catalytic reactions.

The use of the dichlorophosphines **4**, **5a**, and **6** in the phosphetane synthesis was examined as follows.

(7) (a) Tatibouët, M. F. *Bull. Soc. Chim. Fr.* **1951**, 871. (b) Nelson, D. J.; Soundararajan, R. *J. Org. Chem.* **1988**, *53*, 5664.

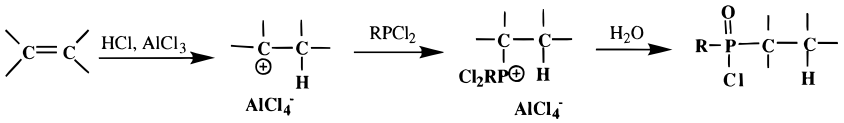
(8) Lane, C. F.; Daniels, J. J. *Organic Syntheses*; Wiley: New York, 1988; Coll. Vol. VI, p 719.

(9) Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chesnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136.

(10) Block, H. D. in *Houben-Weyl Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1982; E1, 389.

(11) McBride, J. J.; Jungermann, E.; Killheffer, J. V.; Clutter, R. J. *J. Org. Chem.* **1962**, *27*, 1833.

Scheme 5



Compounds **4**, **5a**, and **6** were reacted with 2,3,3-trimethylbutene in dichloromethane at 0 °C, in the presence of aluminum chloride. After hydrolysis, the phosphetane oxides **8**, **9**, and **10** were obtained as mixtures of two isomers which differ in their respective configurations at phosphorus (Scheme 4).

Samples of the pure P-myrtanyl phosphetane oxide **8a**, and of the P-isopinocampheyl phosphetane oxide **10a** (major isomer) have been obtained by column chromatography and crystallization, respectively. Both isomers **9a** and **9b** of the P-bornyl phosphetane have been characterized separately as pure and enriched samples, respectively. The stereochemistries of the phosphorus atoms in the various phosphetane oxides have yet to be assigned. Preparative scale separation of each isomeric mixture and stereochemical assignments are currently under investigation.

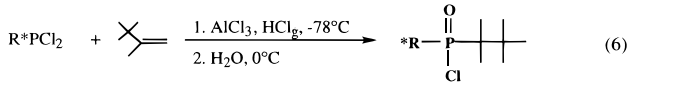
The levels of diastereoselectivity of reactions 5 are highly dependent on the chiral auxiliary used: no or moderate selectivities are afforded by the myrtanyl and bornyl substituents while the isopinocampheyl moiety induces a significant chiral discrimination at phosphorus (80:20 ratio of isomers). For comparison, we recall that the analogous P-menthyl substituted phosphetane oxides are formed as a 1:1 mixture of isomers.[2a] The diastereoselection takes place at the hydrolysis step according to different isomer ratios in the intermediate phosphetanium salts and in the final oxides (see Experimental Section). Previous studies on the hydrolysis of phosphetanium salts indicate that the stereochemical consequences of the reaction are variable and strongly dependent upon the precise experimental mode of water addition.[12] Hopefully, optimized hydrolysis conditions could improve the diastereoselectivity of the above phosphetane synthesis.

From an experimental standpoint it must be emphasized that the phosphetane synthesis requires high quality aluminum chloride. Sublimation of the $AlCl_3$ is strongly recommended in order to eliminate the hydrochloric acid usually formed on storage. The presence of HCl is responsible for the major side-reaction generally observed in phosphetane synthesis: the formation of acyclic phosphinic chlorides discussed hereafter.

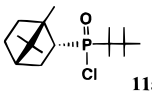
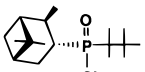
Among the phosphetane oxides prepared here, compound **10a** seems to be the most promising because of the high diastereoselectivity of its synthesis. Besides its desirable practical consequences, the observed selectivity suggests a better chiral induction of the isopinocampheyl group with respect to other chiral auxiliaries and, notably, to the menthyl moiety. Trivalent phosphetanes derived from **10a** will be particularly targeted for their use in asymmetric catalysis.

Synthesis of Phosphinic Chlorides. A number of reports concerning phosphetane synthesis using the McBride method have mentioned the competitive formation of phosphinic chlorides.[13] This has been observed more generally in various reactions involving $RPCl_2$ derivatives, olefins, and $AlCl_3$.[14] The mechanism has been the subject of debate, but the reaction is now assumed to occur via H^+ addition to the olefinic double bond followed by an electrophilic addition of the intermediate carbocation to the phosphorus derivative[14d,13b] (Scheme 5).

Scheme 6



11, **12**

R^*PCl_2	Phosphinic chlorides (isomers ratio)	^{31}P NMR*	yield
5a	 **11a** + **11b** (>90:10)	95.9	42%
6	 **12a** + **12b** (75:25)	94.7; 95.1	80%

*$CDCl_3$

This has generally been viewed as an undesirable side reaction and apparently has not yet been developed as a preparative approach, unlike the closely related Kinnear and Perren synthesis of organic phosphorus compounds from alkyl chlorides.[15] We show hereafter its application to the synthesis of chiral phosphinic chlorides.

In the presence of gaseous HCl, the reactions between **5a** or **6** and 2,3,3-trimethylbutene led exclusively to the phosphinic chlorides **11** and **12**, respectively (Scheme 6).

Significant diastereoselectivity was observed in both cases, but especially for bornyldichlorophosphine: a single isomer of **11** was isolated after chromatography. The second isomer was possibly formed in yields of less than 10%, but it could not be unequivocally identified from the crude mixture.

Starting from the (isopinocampheyl)dichlorophosphine **6**, the reaction is quantitative according to ^{31}P NMR of the reaction mixture. The major isomer **12a** was obtained in the pure state after crystallization from hexane and fully characterized. An X-ray diffraction study[19] was also performed to establish the phosphorus configuration and to confirm the assumed *exo* stereochemistry of the phosphorus substituent with respect to the pinane framework. The X-ray structure shows that phosphorus has the *S* configuration.

Albeit not yet fully optimized, reactions 6 afford P-chiral phosphinic chlorides in moderate to excellent yields with high diastereoselectivity. Pure **11a** and **12a** are easily obtained on a useful preparative scale and their use as chiral synthons is envisaged. The scope of this

(12) (a) Cremer, S. E.; Weitl, F. L.; Farr, F. R.; Kremer, P. W.; Gray, G. A.; Hwang, H. *J. Org. Chem.* **1973**, *38*, 3199. (b) Cremer, S. E.; Cowles, J. M.; Farr, F. R.; Hwang, H.; Kremer, P. W.; Peterson, A. C.; Gray, G. A. *J. Org. Chem.* **1992**, *57*, 511.

(13) (a) Rotem, M.; Kashman, Y. *Tetrahedron Lett.* **1978**, *1*, 63. (b) Vilkas, E.; Vilkas, M. Sainton, J.; Meunier, B.; Pascard, C. *J. Chem. Soc., Perkin Trans 1*, **1980**, 2136.

(14) (a) Rudi, A.; Kashman, Y. *Tetrahedron Lett.* **1978**, *25*, 2209. (b) Kashman, Y.; Menachem, Y.; Benary, E. *Tetrahedron*, **1973**, *29*, 4279. (c) Crews, P. *J. Org. Chem.* **1975**, *40*, 1170. (d) Symmes, C.; Quin, L. D. *J. Org. Chem.* **1978**, *43*, 1250.

(15) Kinnear, A. M.; Perren, E. A. *J. Chem. Soc.* **1952**, 3437.

highly diastereoselective reaction and its potential in asymmetric synthesis are under investigation.

Moreover, analogous reactions between phosphorus derivatives, electron rich olefins, and strong, non nucleophilic acids, e.g. HBF_4, may provide a rather general and direct synthetic approach to phosphorus−carbon bonds, when suitably developed.

Experimental Section

General Methods. All reaction solvents were distilled immediately prior to use. THF and ether were distilled from sodium/benzophenone. All reactions were carried out under an argon atmosphere. Neutral aluminum oxide (50−160 μm, Prolabo) and Florisil (100−200 mesh, Aldrich) were used for chromatographic separations. NMR spectra were recorded at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. ^{13}C NMR assignments are based on literature data,[16−18] DEPT 135 experiments and, eventually, ^{1}H−^{13}C correlations. Selected NMR data are given below. Elemental analyses were performed by the "Service d'Analyse du CNRS", Gif sur Yvette, France. Optical rotations were measured at room temperature. All commercially available reagents were used as received from the suppliers, unless otherwise stated.

General Procedure for the Synthesis of the Alkyl Chlorides 1, 2b, and 3a. A solution of the appropriate alcohol (12 g, 78 mmol) and triphenylphosphine (40.9 g, 156 mmol) in CCl_4 (220 mL) was refluxed for 16 h. After cooling to rt, about 200 mL of hexane were added, and the white precipitate of triphenylphosphine oxide was removed by filtration. After evaporation of the solvent, the mixture was eventually extracted with hexane and filtered in order to remove the residual Ph_3PO. Fractional distillation afforded the desired chloride.

(1*S*,2*R*)-2-(Chloromethyl)-6,6-dimethylbicyclo[3.1.1]heptane (1). (1*S*)-*cis*-myrtanyl chloride was obtained from (1*S*)-myrtanol (prepared by hydroboration-oxidation of (1*S*)-(−)-*β*-pinene $[\alpha]_D$ −21° (neat) according to ref 3b). Fractional distillation afforded 9.0 g of **1** (67%) (98 °C/15 mm). ^{1}H NMR ($CDCl_3$) δ 0.94 (d, ^2J = 9.7 Hz, H_{endo}, CH_2-7), 0.98 (s, Me), 1.20 (s, Me), 3.47 (*AB*, J_{AB} = 10.5, ^3J = 1.0 Hz, 1H, CH_2Cl), 3.56 (A*B*, ^3J = 0.8 Hz, 1H, CH_2Cl); ^{13}C NMR ($CDCl_3$) δ 50.2 (CH_2Cl). Selected NMR and physical data have been reported.[3a,b]

(1*S*)-*exo*-2-Chloro-1,7,7-trimethylbicyclo[2.2.1]heptane (2b). (1*S*)-*exo*-isobornyl chloride was obtained from (1*S*)-*endo*-borneol (Aldrich, $[\alpha]_D$ −35.3 (c = 5, EtOH). Fractional distillation under vacuum (0.1 mm) afforded the olefinic dehydration byproduct, bornylene (0−25 °C, trapping at −78 °C), containing only very small amounts of the chloride. The desired chloride **2b** was subsequently obtained in 65% yield (8.7 g) by sublimation at 40−50 °C (0.1 mm) as a colorless solid. Selected ^{1}H NMR (CCl_4)[17a] and ^{13}C NMR (CS_2)[17b] data have been reported. ^{1}H NMR ($CDCl_3$) δ 0.85 (s, Me), 1.00 (s, Me), 1.09 (s, Me), 2.01 (*AB*, J_{AB} = 13.8, ^3J = 8.4 Hz, 1H, CH_2-3), 2.2 (A*B*, m, 1H, CH_2-3), 3.95 (dd, ^3J = 8.4, ^3J = 4.7 Hz, 1H, CHCl); ^{13}C NMR ($CDCl_3$) δ 68.3 (CHCl). Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.55, H, 9.92. Found: C, 69.98, H, 9.32, $[\alpha]_D$ + 52° (c = 1, $CHCl_3$).

(1*R*)-*endo*-3-Chloro-2,6,6-trimethylbicyclo[3.1.1]heptane (3a). (1*R*)-neoisopinocampheyl chloride **3a** was obtained from (1*R*)-isopinocampheol (prepared by hydroboration−oxidation of (1*R*)-(+)-α-pinene of 91% ee according to ref 8). The final mixture was separated by fractional distillation: the byproduct, α-pinene, was recovered at 25 °C/0.5 mm, and then **3a** was recovered (30 °C, 0.1 mm) in 30% yield (3.6 g). ^{1}H NMR (400 MHz) ($CDCl_3$) δ 1.08 (s, Me-8), 1.21 (s, Me-9), 1.23 (d, ^3J = 7.8 Hz, Me-10), 1.24 (d, ^2J = 10.4 Hz, H_{endo}, CH_2-7), 1.8−2.0 (m, 2H, CH-1 and CH-5), 2.1−2.3 (m, 2H, CH_2-4 and CH_2-7), 2.5−2.7 (m, 2H), 4.73 (td, ^3J = 10.1, ^3J = 7.5 Hz, 1H, CHCl); ^{13}C NMR ($CDCl_3$) δ 55.8 (CHCl). $[\alpha]_D$ + 25° (neat).

Synthesis of the Dichlorophosphines 4 and 6. Magnesium (1.0 g, 45 mmol) and ethyl bromide (0.1 mL) were stirred for 15 min in 10 mL of refluxing ether (for the synthesis of **4**) or at 50 °C in 10 mL of THF (for the synthesis of **6**). A solution of the chloride (6.0 g, 35 mmol) in 15 mL of dry solvent (ether for **1** and THF for **3a**) was then added slowly. During the addition of **1**, the reaction temperature was maintained at about 40 °C. With **3a** a slightly exothermic reaction was observed. Formation of the Grignard reagent was completed by heating the mixture at 50−60 °C for about 30 min. After cooling to rt, the solution was decanted into a pressure-equalizing dropping funnel and added dropwise to a stirred solution of PCl_3 (3.3 mL, 38 mmol) in 50 mL of dry ether at −78 °C. The mixture was allowed to rise to rt and filtered under argon. (In the case of **6**, the solvents ether-THF were evaporated under vacuum, ether was added, and the mixture was filtered). The solvent and the excess PCl_3 were removed under vacuum to give the crude product which was distilled in a kugelrohr apparatus at about 110 °C/0.1 mm.

(1*S*)-*cis*-Myrtanyldichlorophosphine (4): was obtained in 48% yield (4.0 g); bp 84 °C/0.1 mm. It contains less than 5% of a second dichlorophosphine observed in the ^{31}P NMR spectrum. **4**: colorless, air sensitive liquid; ^{31}P NMR ($CDCl_3$) δ 197.5; ^{1}H NMR ($CDCl_3$) δ 0.97 (d, ^2J = 9.8 Hz, H_{endo}, CH_2-7), 1.07 (s, Me), 1.22 (s, Me), 1.5−2.6 (m); ^{13}C NMR ($CDCl_3$) δ 52.9 (J_{C-P} = 44.9 Hz, CH_2P). Mass spectrum (^{35}Cl) m/z 238 (M, 4%), 223 (M − Me, 16%), 81 (100%).

(1*R*)-*exo*-Isopinocampheyldichlorophosphine (6): obtained in 79% yield (6.6 g) as a colorless liquid; ^{31}P NMR ($CDCl_3$) δ 185.0; ^{1}H NMR ($CDCl_3$) δ 0.92 (dd, ^2J = 10.1 Hz, J = 2.4 Hz, H_{endo}, CH_2-7), 1.07 (s, Me-8), 1.23 (s, Me-9), 1.25 (d, ^3J = 8 Hz, Me-10), 1.8−2.6 (m); ^{13}C NMR ($CDCl_3$) δ 45.5 (J_{C-P} = 47.3 Hz, CHP). Mass spectrum (^{35}Cl) m/z 238 (M, 2%), 137 (M − PCl_2, 22%), 81 (100%). $[\alpha]_D$ −54° (c = 1, $CHCl_3$).

Synthesis of the (1*S*)-*endo*-Bornyldichlorophosphine (5a). $(Et_2N)_2PCl$ was prepared from PCl_3 and diethylamine according to ref 10 and distilled at 62−66 °C/1 mm. The Grignard reagent prepared from *exo*-isobornyl chloride **2b** (6.0 g, 35 mmol) and magnesium (1.0 g, 45 mmol) in THF (25 mL) was decanted and added dropwise to a stirred solution of $(Et_2N)_2PCl$ (7.4 g, 35 mmol) in diethyl ether (50 mL) at −78 °C. The temperature was allowed to rise and the formation of **7** was checked by ^{31}P NMR: δ = 93. The reaction mixture was cooled to 0 °C, and gaseous HCl was bubbled through the solution for about 5 min. The oily-solid insolubles were decanted or filtrated, and the solvent was removed under vacuum. The crude product was distilled on a kugelrohr apparatus at about 110 °C/0.1 mm. **5a** was obtained in 70% yield (5.9 g) after distillation. The isomeric **5b** was not detected by ^{31}P NMR spectroscopy. **5a**: ^{31}P NMR ($CDCl_3$) δ 197.3; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, $^4J_{H-P}$ =1.0 Hz, Me-10), 0.93 (s, Me), 1.07 (s, Me), 2.17 (m, 1H), 2.65 (m, PCH); ^{13}C NMR ($CDCl_3$) δ 28.3 (CH_2), 31.6 (J_{C-P} = 29.0 Hz, CH_2), 33.8 (J_{C-P} = 21.6 Hz, CH_2), 56.6 (J_{C-P} = 49.9 Hz, CHP). Mass spectrum (^{35}Cl) m/z 239 (M + 1, 26%), 137 (M − PCl_2, 100%), 95 (26%), 81 (37%). $[\alpha]_D$ −22° (c = 1.6, $CHCl_3$).

Synthesis of the Phosphetane Oxides 8−10. $AlCl_3$ was sublimed under argon at 170 °C immediately prior to use. To 0.32 g (2.4 mmol) of aluminum chloride in 2 mL of CH_2Cl_2 was added at 0 °C a solution of 0.50 g (2.1 mmol) of dichlorophosphine and 0.32 mL (2.3 mmol) of 2,3,3-trimethylbutene in 1 mL of methylene chloride. The reaction mixture was stirred at 0 °C for about 20 min, warmed to rt (^{31}P NMR of the intermediate phosphetanium salts $R_3PCl_2^+AlCl_4^-$: **8′** δ = 113.0, 112.6 (ratio 1.4:1); **9′** δ = 120.1, 117.3 (ratio 5:1); **10′** δ = 123.6, 119.0 (ratio 1:1)), and then hydrolyzed slowly at 0 °C with distilled water. The organic layer was separated, washed with water, and finally dried over $MgSO_4$. The final product was purified by column chromatography on neutral alumina with hexane−ethyl acetate 60:40 as eluent (R_f = 0.3).

1-Myrtanyl-2,2,3,3-tetramethylphosphetane Oxide (8a,b): obtained from myrtanyldichlorophosphine in 61% yield

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as a 1:1 mixture of two isomers. A sample of pure **8a**, the first eluting isomer, has been recovered by chromatography and fully characterized. **8a**: ^{31}P NMR ($CDCl_3$) δ 55.5. ^{1}H NMR ($CDCl_3$), tentative assignments, δ 0.96 (d, ^2J = 9.8 Hz, H_{endo}, CH_2-7), 1.06 (s, 2Me), 1.11 (d, $^3J_{H-P}$ = 19 Hz, Me-5′), 1.16 (s, Me), 1.19 (s, Me), 1.24 (d, $^3J_{H-P}$ = 16.6 Hz, Me-6′), 1.4−2.7 (m); ^{13}C NMR ($CDCl_3$) δ 37.0 (J_{C-P} = 42.8 Hz, CH_2P), 44.7 (J_{C-P} = 50.0 Hz, CH_2P), 48.9 (J_{C-P} = 59.6 Hz, *C*P). Mass spectrum: *m*/*z* 282 (M, 34%), 267 (M − Me, 24%), 146 (M − $C_{10}H_{17}$, 82%), 55 (100%).

1-Bornyl-2,2,3,3-tetramethylphosphetane Oxide (9a,b): obtained from bornyldichlorophosphine in 50% yield after chromatography, as a 4:6 mixture of two isomers. A pure sample of the first isomer **9a** was obtained by chromatography; **9b** was characterized by NMR spectroscopy from an enriched mixture (90:10). **9a**: colorless oil; ^{31}P NMR ($CDCl_3$) δ 66.4; ^{1}H NMR ($CDCl_3$) δ 0.81 (s, Me), 0.84 (s, Me), 1.00 (s, Me), 1.06 (s, Me), 1.11 (d, $^3J_{H-P}$ = 19.7 Hz, Me-5′), 1.17 (d, $^3J_{H-P}$ = 16.9 Hz, Me-6′), 1.25 (s, Me), 1.3−2.4 (m); ^{13}C NMR ($CDCl_3$) δ 42.0 (J_{C-P} = 49.9 Hz, CH_2P), 42.1 (J_{C-P} = 45.5 Hz, CHP), 48.9 (J_{C-P} = 58.4 Hz, *C*P). Mass spectrum: *m*/*z* 282 (M, 70%), 267 (M − Me, 50%), 198 (M − C_2Me_4, 100%). $[\alpha]_D$ −57° (*c* = 0.5, $CHCl_3$).

9b: ^{31}P NMR ($CDCl_3$) δ 59.2; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, Me), 0.89 (s, Me), 1.02 (s, Me), 1.09 (s, Me), 1.09 (d, $^3J_{H-P}$ = 18.0 Hz, Me-5′), 1.21 (d, $^3J_{H-P}$ = 16.4 Hz, Me-6′), 1.22 (s, Me), 1.3−2.6 (m); ^{13}C NMR ($CDCl_3$) δ 43.4 (J_{C-P} = 47.3 Hz, CHP), 43.9 (J_{C-P} = 48.7 Hz, CH_2P), 49.3 (J_{C-P} = 54 Hz, *C*P).

1-Isopinocampheyl-2,2,3,3-tetramethylphosphetane oxide (10a,b): obtained from isopinocampheyldichlorophosphine in 42% yield after chromatography, as a 8:2 mixture of isomers. A sample of pure **10a** was obtained from an enriched chromatographic fraction, after separation of the residual **10b** by crystallization from hexane. **10a**: ^{31}P NMR ($CDCl_3$) δ 65.6; ^{1}H NMR ($CDCl_3$) tentative assignement δ 0.97 (s, Me), 1.00 (s, Me), 1.06 (d, ^3J = 7.2 Hz, Me-10), 1.14 (s, Me), 1.15 (d, $^3J_{H-P}$ = 18.8 Hz, Me-5′), 1.17 (d, $^3J_{H-P}$ = 14.5 Hz, Me-6′), 1.20 (s, Me), 1.6−2.7 (m); ^{13}C NMR ($CDCl_3$) δ 34.2 (J_{C-P} = 41.0 Hz, CHP), 41.8 (J_{C-P} = 50.7 Hz, CH_2P), 49.2 (J_{C-P} = 55.3 Hz, *C*P). Mass spectrum: *m*/*z* 282 (M, 2%), 267 (M − Me, 3%), 213 (10), 146 (24%), 90 (88%), 55 (100%). Anal. Calcd for $C_{17}H_{31}OP$: C, 72.30; H, 11.06. Found: C, 72.54; H, 11.01. $[\alpha]_D$ −28° (*c* = 0.5, $CHCl_3$).

Synthesis of the Phosphinic Chlorides 11 and 12. To 0.32 g (2.4 mmol) of aluminum chloride in 2 mL of CH_2Cl_2, saturated with gaseous HCl, was added at −78 °C a solution of 0.50 g (2.1 mmol) of dichlorophosphine and 0.32 mL (2.3 mmol) of 2,3,3-trimethylbutene in 1 mL of methylene chloride. The reaction mixture was stirred at −78 °C for about 1 h, warmed to rt (^{31}P NMR of the intermediate phosphetanium salts $R_2PCl_3^+AlCl_4^-$: **11′** δ = 152.4; **12′** δ = 155.2) and then hydrolyzed slowly at 0 °C with distilled water. The organic layer was separated, washed with water, and finally dried over $MgSO_4$. The final product was purified either by chromatography on a short Florisil column with hexane−ether 60:40 as eluent (**11**) or by direct crystallization from the reaction mixture (**12**). Chromatographic purification causes partial loss of the product. Only the major isomers **11a** and **12b** have been characterized. **11a**: colorless solid, ^{31}P NMR ($CDCl_3$) δ 95.9; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 2Me), 1.07 (d, $^3J_{H-P}$ = 20.2 Hz, PCMe), 1.14 (s, CMe_3), 1.19 (s, Me), 1.24 (d, $^3J_{H-P}$ = 18.2 Hz, PCMe), 1.3−2.3 (m), 2.73 (m, *J* = 11.4, 5.2, 2.6 Hz, 1H, PCH); ^{13}C NMR ($CDCl_3$) δ 19.8 (d, Me), 20.4 (Me), 27.5 (J_{C-P} = 4.6 Hz, C*Me*$_3$), 37.5 (*C*Me$_3$), 47.0 (J_{C-P} = 63.9 Hz, CHMe), 48.5 (J_{C-P} = 62.6 Hz, P*C*Me$_2$). Mass spectrum (^{35}Cl): *m*/*z* 318 (M, 21%), 220 (M − C_2Me_5, 35%), 137 ($C_{10}H_{17}$, 65%), 57 (100%). Anal. Calcd for $C_{17}H_{32}ClOP$: C, 64.04; H, 10.12. Found: C, 64.16; H, 10.05. $[\alpha]_D$ −21° (*c* = 1, $CHCl_3$)

12a: colorless solid; ^{31}P NMR ($CDCl_3$) δ 94.7; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, Me), 1.17 (s, CMe_3), 1.22 (s, Me), 1.26 (d, $^3J_{H-P}$ = 19.8 Hz, PCMe), 1.28 (d, ^3J = 6.4 Hz, Me-10), 1.31 (d, $^3J_{H-P}$ = 17.8 Hz, PCMe), 1.8−2.0 (m, 3H), 2.1−2.3 (m, 3H), 2.5−2.8 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.3 (J_{C-P} = 2.8 Hz, Me), 21.3 (Me), 27.5 (J_{C-P} = 5.3 Hz, C*Me*$_3$), 37.5 (*C*Me$_3$), 43.3 (J_{C-P} = 56.2 Hz, PCH), 49.2 (J_{C-P} = 58.3 Hz, *C*Me$_2$). Anal. Calcd for $C_{17}H_{32}ClOP$: C, 64.04; H, 10.12. Found: C, 63.87; H, 9.89. $[\alpha]_D$ −63° (*c* = 1, $CHCl_3$).

Supporting Information Available: Additional ^{13}C NMR data for all compounds (Tables 1−4), ORTEP drawing, and X-ray acquisition data for **12a** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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