Pergamon

Tetrahedron, Vol. 53, No. 12, pp. 4363-4370, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00132-4

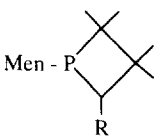
Synthesis and α-Alkylation of 1-Menthylphosphetane Sulfide

Angela Marinetti*, François-Xavier Buzin and Louis Ricard

Laboratoire Hétéroéléments et Coordination, CNRS URA 1499
DCPH, Ecole Polytechnique, 91128 Palaiseau, France.

Abstract. 1-Menthylphosphetane sulfide, **5**, has been prepared from menthylphosphine and 1-bromo-3-chloropropane via the corresponding phosphetane-borane complex. The metalation-substitution reactions of both intracyclic α carbon atoms of **5** with benzyl and / or trimethylsilyl groups have been examined with regard to stereochemistry. The diastereoselectivity of these reactions is high enough to allow a preparative access to new chiral phosphetane sulfides. © 1997 Elsevier Science Ltd.

Recently, we have been developing phosphetanes as a new class of electron-rich chiral phosphines for use in asymmetric catalysis[1]. These ligands have been found to show acceptable reactivity and enantioselectivity in palladium catalyzed hydrosilylations of olefins and allylic alkylations. The structural features common to all of the chiral phosphetanes **1** prepared to date are the *l*-menthyl group (Men) bound to phosphorus and the four methyl substituents of the ring carbons, while the R substituent varies in controlled manner. Phosphetanes bearing R substituents having diverse steric requirements and electronic effects give widely differing levels of chiral induction in the catalytic reactions above. Consequently, a highly variable substitution scheme for the four membered ring is desirable to optimize the properties of these ligands.



1

The presence of the four methyl groups in **1** is dictated by the synthetic approach[2], but the α substituent is introduced through simple metalation-alkylation reactions of the preformed phosphetane oxides. Additional possibilities for modifying the phosphorus environment and optimizing enantioselectivity would appear if both α-carbon atoms were available for functionalization. This requires an alternative access to the four membered ring.

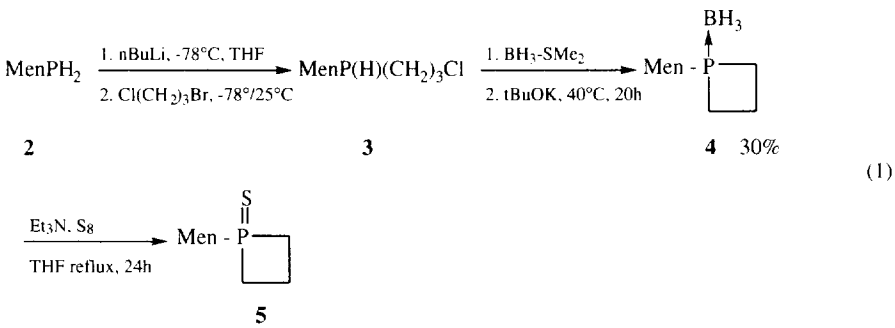
Thus, we describe here the application of a more general and flexible synthesis of the phosphetane moiety to the preparation of 1-menthylphosphetane sulfide. The efficiency and the stereochemistry of α-metalation reactions of this compound have also been examined.

* Fax number: 33 01 69 33 39 90

Results and discussion

The most straightforward and general preparation of saturated cyclic phosphines involves the reaction between the dianion $RPLi_2$, or its synthetic equivalent, and a difunctional electrophile. This approach has been applied most notably to the synthesis of chiral phospholanes from bis-mesylates of optically active 1,4-diols[3]. 1-Phenylphosphetane[4a,b] and its cationic iron complex, $[(1,2\text{-}C_6H_4(PMePh_2)FeCp(phenylphosphetane)]^+ PF_6^-$ [4c,d], have also been prepared in this fashion from phenylphosphine and 1,3-dichloropropane. Here, we employ *l*-menthylphosphine for the synthesis of chiral phosphetanes.

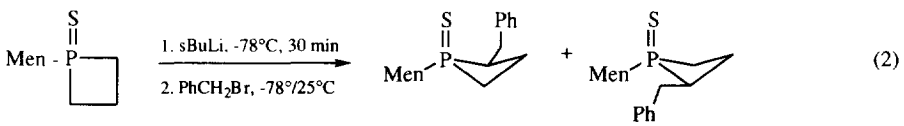
Menthylphosphine was obtained in 70% yield by $LiAlH_4$ reduction of menthyldichlorophosphine[5]. Investigations of its reactivity towards 1,3-dihalopropanes in the presence of bases under various conditions finally led to the experimental protocol shown in eq. 1.



According to ^{31}P NMR monitoring of the reaction, deprotonation of menthylphosphine with nBuLi at -78°C followed by addition of 1-bromo-3-chloropropane affords the secondary phosphine **3** quantitatively, as a mixture of two diastereoisomers (^{31}P NMR (THF) δ -53.2 (J_{HP} = 194 Hz) and -63.5 (J_{HP} = 196 Hz) respectively). The use of bromochloropropane prevents the formation of $(MenP(H)CH_2)_2CH_2$ which was produced in about 20% yield in the analogous reaction with 1,3-dibromopropane. Addition of one equivalent of borane-dimethylsulfide affords the borane complex of **3** (^{31}P NMR (THF) δ -1.8 (J_{BP} = 51 Hz) and -6.1 (J_{BP} = 45 Hz), J_{HP} of about 360 Hz for both isomers) which can be either isolated and purified by column chromatography, or reacted *in situ*, in dilute solution, with potassium tert-butoxide to afford the expected cyclization product **4**. tBuOK was inefficient for the cyclization of uncomplexed **3** and stronger bases such as nBuLi gave samples of the desired phosphetane (^{31}P NMR δ 6.3 ppm) which were contaminated with variable amounts of side products, in reactions which were poorly reproducible. Thus, complexation with BH_3 offers the double advantage of improving the acidity of the PH bond and protecting and stabilizing the final product. The phosphetane-borane complex was obtained in moderate yield, 30% with respect to the starting $MenPH_2$, and fully characterized.

The carbon-unsubstituted phosphetane **4** should be a viable substrate for introducing various substituents on both sides of the phosphorus atom via α-metalation-alkylation reactions[6]. The major question concerns the diastereoselectivity of such reactions or, at least, the chances of obtaining pure single epimers if selectivity is low.

After making a few preliminary metalations with the borane complex **4**, we decided to use the corresponding phosphetane sulfide **5** as starting material, because the multiplicity of NMR signals for the borane complexes precluded an accurate analysis of the reaction mixtures by ^{31}P NMR spectroscopy. Sulfide **5** was obtained quantitatively by refluxing **4** with triethylamine and sulfur for 20 hours, according to the well established amine-phosphine exchange procedure[6a]. The 1-menthylphosphetane sulfide was then subjected to the metalation reaction shown in eq. 2.



(2)

5 **6a** P(R)C(S) **6b** P(S)C(R) 77%

Deprotonation with sBuLi followed by trapping of the intermediate carbanion with benzyl bromide affords the α-benzylphosphetane sulfide **6** as a 1:1 mixture of two isomers (^{31}P NMR δ 77.3 and 76.8 ppm respectively) along with small amount (10%) of an unidentified side product. The benzylation reaction (2), in which two new chiral centers are formed, shows considerable diastereoselectivity: only two of the four possible epimers are observed. Samples of pure **6a** and **6b** were obtained by column chromatography on alumina with hexane-ether as eluent and fully characterized. It should be possible to separate these two isomers quantitatively, but this was not attempted at this stage.

The stereochemistry of **6a** has been established by an X-ray diffraction study (figure 1) which indicates that the phosphorus and the α carbon atom have R and S configurations respectively. The menthyl and benzyl substituents lie *anti* to each other.

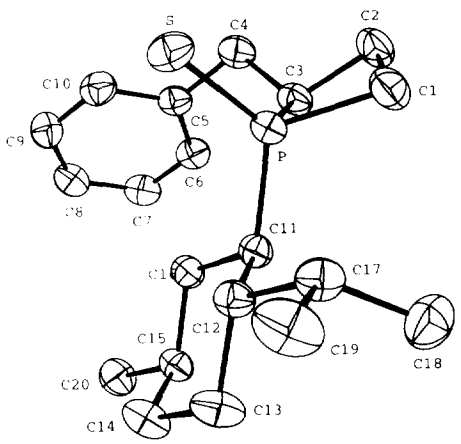
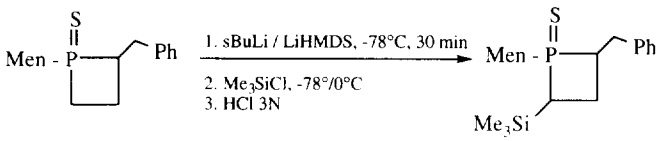


Figure 1. ORTEP drawing of the phosphetane sulfide **6a**. Selected bond distances (Å) and angles (degrees): P-C1, 1.841(2); P-C3, 1.848(2); P-C11, 1.840(2); C1-C2, 1.553(4); C2-C3, 1.567(3); C3-C4, 1.527(3). C1-P-C3, 79.1(1); C1-P-C11, 113.2(1); C3-P-C11, 110.18(9); P-C3-C2, 88.6(1); P-C1-C2, 89.3(1); P-C3-C4, 119.7(2).

The stereochemistry of **6b**, P(S)C(R), was tentatively assigned on the basis that the menthyl and benzyl substituents strongly prefer mutually *anti* positions and that chiral induction from the menthyl group on the phosphorus atom is usually not very effective[1]. Both factors favour the P(S)C(R) configuration.

Starting from **6**, a second metalation reaction should allow substitution of the remaining α-CH_2 group by either a second benzyl or a different group. As an example, the reaction of **6** with chlorotrimethylsilane was examined (eq. 3).



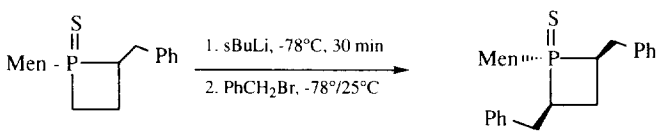
(3)

6a,b **7a,b,c,d** (ratio 8:8:2:1) 75%

The anion of **6** was formed using sBuLi - lithium hexamethyldisilazane (LiHMDS) at -78°C and subsequently quenched with excess chlorotrimethylsilane. Analogous reaction conditions have been used previously in the diastereospecific synthesis of 2-silyl-3,3,4,4,-tetramethylphosphetane oxides[7]. ^{31}P NMR analysis of the crude reaction mixture of eq. 3 showed the formation of four compounds in 8:8:2:1 ratios (δ 81.4, 78.8, 84.4, 80.4 ppm respectively). Three of them have been separated in pure form by column chromatography and identified as different epimers of the expected silyl substituted phosphetane sulfide **7**. The minor product was not isolated in the pure state, but it is assumed to be the fourth isomer of the same sulfide. The two major epimers are presumed to have an *anti* stereochemistry for the menthyl and trimethylsilyl substituents, which implies a mutually *syn* position of the benzyl and TMS groups.

The stereochemical control of the second substitution reaction is clearly less efficient than the first. This phenomenon has already been observed in analogous alkylation reactions of phospholanate esters with benzyl bromide, where the diastereomeric excess fall from 40% to 10% in the second step[8]. We presume that the carbanionic center of the lithiated phosphetane sulfide is not configurationally stable[9], hence, the stereoselection depends upon the diastereoface of the carbanion which is approached by the electrophile. The lack of diastereoselectivity in the second alkylation may reflect the fact that the menthyl and benzyl substituents in **6** hinder opposite faces and have opposite directing effects, while addition *anti* to the menthyl group is largely favored in the first step. From a practical standpoint, the level of diastereoselectivity for the double substitution reaction is sufficient to envisage preparative synthetic applications, particularly since the epimers are easily separated by column chromatography.

In an additional experiment, the double alkylation with benzyl bromide has been performed: the phosphetane sulfide **8a** was obtained in 48% isolated yield (eq. 4). Formation of the other epimers of **8** has not yet been firmly established, although two minor products have been observed in the reaction mixture (^{31}P NMR δ 75.4 and 80.1 ppm) in about 25% and 10% amounts respectively. The epimer **8a** represents about 65% of the crude product, according to ^{31}P NMR analysis.



(4)

6a,b **8a** 48%

The major phospetane sulfide isomer **8** which is obtained from a 1:1 mixture of **6a** and **6b** must be the symmetrically substituted derivative ("*meso*" isomer) shown in eq. 4, since it can be formed from both epimers of **6**. Its formation as the major product is also consistent with the stereochemical outcome of the analogous silylation reactions above. Moreover, the very similar values of the $^{2}J_{C\text{-}P}$ coupling constants for the two $\underline{C}H_2Ph$ carbons of **8a** (see Table 1) also suggest the same arrangement of the benzyl substituents with respect to the P(S) group. The structural assignment for **8a** is based on such observations.

The stereochemical course of both reactions 3 and 4 indicates that the presence of the benzyl substituent in **6** does not override the directing effect of the menthyl moiety, which favors the "*meso*" isomer. The formation of the R,R and S,S epimers of α,α' symmetrically disubtituted phosphetanes (relative *anti* position of the two α substituents) could probably be improved by using more hindered electrophiles in the alkylation reaction.

In summary, the synthetic approach described here seems to be appropriate for the preparation of diastereomerically pure α,α'-disubstituted phosphetane sulfides, chiral on both the phosphorus and carbon atoms, when different electrophiles are used successively in the alkylation reactions.
If the same electrophile, benzyl bromide, is used in both alkylation steps the predominant product is the "*meso* form" of the disubstituted phosphetane sulfide, in which the menthyl group is the only chiral moiety. Probably, the use of more hindered electrophiles could reverse the diastereoselectivity and afford chiral "C_2 symmetric" phosphetanes in significant, preparative quantities.

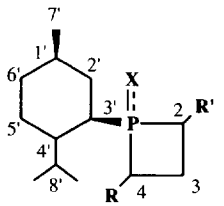
Next, we envisage to broaden the scope of the α-alkylation of **6**, to prepare new and diverse phosphetane sulfides and to check the properties of the corresponding phosphetanes[10] as chiral auxiliaries in transition metal catalyzed reactions.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere. Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone immediately prior to use. Neutral aluminium oxide (50-160 μm - Prolabo) and silica gel (15-40 μm) were used for chromatographic separations. Elemental analyses were performed by the "Service d'Analyse du CNRS", Gif sur Yvette, France. Optical rotations were measured at room temperature with a Perkin-Elmer 241 polarimeter. Mass spectra were obtained with a Hewlett Packard 5989D instrument by the direct inlet method. All commercially available reagents were used as received from the suppliers.

Spectroscopic data. NMR spectra were recorded on a Bruker AC 200 SY spectrometer at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. ^{1}H NMR spectra were poorly resolved, most of the signals being between 0 and 3 ppm. Only the methyl groups of the menthyl moiety are easily identified, their chemical shifts are reported below. Generally, ^{13}C NMR spectra are by far more useful for structural assessments.
^{13}C NMR data and assignments, based on DEPT.135 experiments and literature data for the menthyl moiety[11], are reported in Table 1.

Table 1. Selected ^{13}C NMR data for compounds **4**, **5**, **6a,b**, **7a,b,c** and **8a**. $CDCl_3$, δ in ppm [J_{C-P} in Hz].



4 : X = BH_3 , R = R' = H
5 : X = S , R, R' = H
6a : X =S , R = H, R' = CH_2Ph P(R)C(S)
6b : X =S , R = H, R' = CH_2Ph P(S)C(R)
7a,b,c : X =S , R = $SiMe_3$, R' = CH_2Ph
8a : X =S , R = R' = CH_2Ph

	C-2	CH_2-3	C-4	CH-1'	CH_2-2'	CH-3'	CH-4'	CH_2-5'	CH_2-6'	CH-8'	CH_2Ph	$SiMe_3$
4	21.3 [41.4]	18.8 [17.9]	24.4 [39.3]	33.0 [12.1]	34.4	39.5 [19.1]	43.7	24.3 [10.5]	33.5	29.5 [5.8]		
5	33.9 [48.1]	15.2 [19.9]	36.6 [45.7]	33.0 [14.0]	34.4	41.6 [36.0]	42.7	24.1 [12.1]	33.5	28.6 [5.1]		
6a	45.1* [47.2]	24.0 [18.1]	33.1 [45.7]	32.5 [12.2]	34.0	45.6* [31.9]	42.4 [3.0]	23.8 [12.3]	32.6	28.7 [5.1]	35.8 [4.3]	
6b	45.6* [44.4]	22.9 [17.5]	29.9 [48.6]	33.0 [13.6]	34.2	46.0* [32.2]	42.2	23.8 [12.2]	33.4	29.3 [5.5]	35.7 [4.6]	
7a	43.6 [48.8]	25.0 [18.0]	31.5 [34.1]	32.7 [12.2]	34.1	47.8 [32.1]	42.3 [2.7]	24.1 [12.0]	32.6	28.5 [5.3]	36.0 [4.4]	-1.3 [2.9]
7b	45.0* [43.3]	25.2 [18.6]	34.7 [36.7]	32.9 [13.4]	34.8	45.1* [32.6]	43.1 [2.5]	24.2 [12.1]	34.3	28.8 [5.0]	35.6 [3.3]	-1.1 [2.6]
7c	44.0* [47.8]	26.6 [18.8]	38.1 [30.9]	32.9 [13.8]	34.5	45.7* [27.4]	42.0 [2.8]	24.8 [12.1]	33.7	30.2 [4.4]	35.7 [4.7]	-1.1
8a	41.4 [46.9]	31.5 [15.2]	42.3 [42.5]	32.6 [13.7]	33.9	47.6 [29.9]	41.9	23.7 [12.1]	33.0	29.4 [4.5]	35.1; 35.6 [3.4] [4.5]	

The methyl signals of the menthyl moiety are omitted. CH_2-2' and CH_2-6' may be reversed. * CH-2 and CH-3' may be reversed

Menthylphosphine (2): An ether solution of menthyldichlorophosphine[5] (20g, 83 mmol) was added slowly to excess $LiAlH_4$ (4.7g, 124 mmol) in ether (50 mL) at -78°C. The mixture was allowed to warm to room temperature and stirred for about 30 min. It was then hydrolyzed at 0°C by careful addition of saturated aqueous NH_4Cl. The organic phase was decanted and dried over $MgSO_4$. After evaporation of the solvent, the crude product was distilled under reduced pressure (b.p. 98-100°C, 20 mm Hg). Yield: 10g, 70%. ^{31}P NMR (C_6D_6) δ -122 ($^1J_{PH}$ = 190 Hz); ^1H NMR (C_6D_6) δ 0.71 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHMe_2$), 0.80 (d, $^3J_{HH}$ = 6.3 Hz, CHMe), 0.85 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHMe_2$), 2.54 (m, AB, $^1J_{HP}$ = 190.3 Hz, $^2J_{AB}$ = 12.2 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, PH_2), 2.75 (m, AB, $^1J_{HP}$ = 190.7 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, PH_2); ^{13}C NMR (C_6D_6) δ 15.3 (Me), 21.9 (Me), 22.8 (Me), 25.5 (d, J_{CP} = 7.5 Hz, CH_2), 29.7 (d, J_{CP} = 10.9 Hz, CH), 30.5 (d, J_{CP} = 7.4 Hz, CH), 34.2 (d, J_{CP} = 7.2 Hz, CH), 35.6 (CH_2), 46.7 (CH_2), 49.1 (d, J_{CP} = 9.0 Hz, CH) ppm.

1-Menthylphosphetane-borane (4): nBuLi (12.0 mL, 19.2 mmol, 1.6 M solution in hexane) was added to a solution of menthylphosphine (3.0 g, 17.4 mmol) in THF (50 mL) at -78°C. After a few minutes 1-bromo-3-chloropropane (1.7 mL, 17.4 mmol) was added and the mixture was allowed to warm to room temperature. Quantitative formation of the secondary phosphine **3** was monitored by ^{31}P NMR: δ -53.2 (J_{HP} = 194 Hz) and -63.5 (J_{HP} = 196 Hz). The reaction mixture was then cooled to 0°C and the BH_3-SMe_2 complex (2.0 mL, 20.9 mmol) was added dropwise to afford the borane complex of **3** (^{31}P NMR (THF) δ -1.8 (J_{BP} = 51 Hz) and -6.1 (J_{BP} = 45 Hz), J_{HP} = 360 Hz. This compound can be isolated and purified by chromatography on a short column of

neutral aluminium oxide with hexane-ether 95:5 as eluent). The solvent and the excess borane were removed in vacuo and the residue was dissolved in 300 mL of dry THF. Potassium *tert*-butoxide (3.9 g, 35 mmol) was then added and the mixture was stirred at 40°C overnight. After hydrolysis, the organic phase was recovered, dried over $MgSO_4$, the solvent was removed and the residue was chromatographed on alumina with an hexane-ether 95:5 mixture to afford the desired complex **4** in 30% yield (1.2g). ^{31}P NMR ($CDCl_3$) δ 51.5 ($^1J_{PB}$ = 46 Hz); ^1H NMR ($CDCl_3$) δ 0.79 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHMe_2$), 0.91 (d, $^3J_{HH}$ = 6.4 Hz, CHMe), 0.93 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHMe_2$), 0.7-2.6 (m) ppm. Mass spectrum, m/e (relative intensity): 212 (M-BH_3, 18%), 169 (212 - $CHMe_2$, 39%), 55 (100). Anal. Calcd. for $C_{13}H_{28}BP$: C, 69.04; H, 12.48. Found: C, 68.94, H, 12.34.

1-Menthylphosphetane sulfide (5): The borane complex **4** (1.2 g, 5.3 mmol) and sulfur (0.25g, 8 mmol) were heated overnight in refluxing triethylamine (5 mL). The excess of triethylamine was removed and the final product was purified by column chromatography on aluminium oxide with hexane-ether 95:5 as eluent (R_f = 0.3). 5 was obtained as a colorless solid in 93% yield (1.2 g). ^{31}P NMR ($CDCl_3$) δ 70.7; ^1H NMR (400 MHz) ($CDCl_3$) δ 0.83 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHMe_2$), 0.93 (d, $^3J_{HH}$ = 6.4 Hz, CHMe), 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHMe_2$), ...1.93 (m, $^3J_{HH}$ = 6.8 Hz, 1H, C<u>H</u>Me_2), ... ppm. Mass spectrum, m/e (relative intensity): 244 (M, 5%), 106 (M-$C_{10}H_{18}$, 36%), 55 (70%), 43 (100%). $[\alpha]_D$= + 53 (c = 0.5, $CHCl_3$) Anal. Calcd. for $C_{13}H_{25}PS$: C, 63.89; H, 10.31. Found: C, 63.34, H, 10.26.

2-Benzyl-1-menthylphosphetane sulfides (6a,b): A solution of 1-menthylphosphetane sulfide **5** (0.45g, 1.8 mmol) in THF was cooled to -78°C, then 1.6 mL of sBuLi (2.0 mmol, 1.3M solution in cyclohexane) were added dropwise. After about 30 min, benzyl bromide (0.24 mL, 2 mmol) was added and the reaction mixture was allowed to warm slowly to room temperature. ^{31}P NMR analysis of the reaction mixture shows the formation of **6** together with a small amount of a side product (^{31}P NMR δ 70.5 ppm, non benzylated derivative which probably results from a ring opening reaction after sBuLi addition to the starting phosphetane sulfide). After hydrolysis with distilled water, THF was removed on a rotary evaporator and the residue wasextracted with ether, dried ($MgSO_4$) and concentrated. The resultant solid was purified by column chromatography on silica gel with hexane-ethyl acetate 96:6 as eluent. A mixture of **6a** and **6b** was obtained in 77% yield (0.47 g). Mass spectrum, m/e (relative intensity): 334 (M, 10%), 196 (M-$C_{10}H_{18}$, 100%). Anal. Calcd. for $C_{20}H_{31}PS$: C, 71.81; H, 9.34. Found: C, 69.64, H, 9.06. Samples of pure **6a** and **6b** were obtained separately by chromatography on alumina with hexane-ether 95:5 as eluent (**6a** eluted first) and crystallization from hexane. **6a** P(R)C(S): ^{31}P NMR (THF) δ 77.3; ^1H NMR ($CDCl_3$) δ 0.72 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CHMe), 0.81 (d, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 0.96 (d, $^3J_{HH}$ = 6.7 Hz, 3H, $CHMe_2$) ppm. $[\alpha]_D$= - 109 (c = 0.5, $CHCl_3$). The stereochemistry of **6a** has been established by X-ray crystallography. **6b**: ^{31}P NMR (THF) δ 76.8; ^1H NMR ($CDCl_3$) δ 0.79 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHMe_2$), 0.92 (d, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 0.93 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CHMe) ppm. $[\alpha]_D$= - 24 (c = 0.5, $CHCl_3$).

4-Benzyl-1-menthyl-4-trimethylsilylphosphetane sulfides (7a-d): A mixture of 2-benzyl-1-menthylphosphetane sulfide **6a,b** (400 mg, 1.2 mmol) and hexamethyldisilazane (0.25 mL, 1.2 mmol) in THF (5 mL) were cooled to -78°C. sBuLi (2.0 mL, 2.6 mmol) was then added dropwise. After stirring the colorless solution for 30 min, Me_3SiCl (0.19 mL, 1.5 mmol) was added dropwise, the reaction mixture was allowed to warm slowly to 0°C and hydrolyzed with aqueous HCl (3N). Ether was added and the organic phase was separated and dried over $MgSO_4$. The solvent was removed and the residue chromatographed on a short silica gel column with hexane ethyl acetate 98:2 as eluent. The mixture of isomers **7a-d** was obtained in 75% yield (0.36g): Mass spectrum, m/e (relative intensity): 406 (M, 5%), 268 (M-$C_{10}H_{18}$, 100%), 177 (268-CH_2Ph, 24%), 162 (38%), 73 ($SiMe_3$, 53%). The three major isomers **7a-c** were obtained separately after column chromatography on alumina with an hexane-

ether gradient (from 96:4 to 80:20) as eluent: **7a** was eluted first, together with a small amount of the fourth isomer **7d,** and was purified by crystallization in hexane. Then **7c** and finally **7b** were eluted.

7a: colorless solid. ^{31}P NMR ($CDCl_3$) δ 78.9; ^{1}H NMR ($CDCl_3$) (400 MHz) δ 0.20 (s, $SiMe_3$), 0.77 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CHMe), 0.81 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $CHMe_2$), 0.94 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, $CHMe_2$), 0.9-1.0 (m, 3H), 1.28 (m, 2H), 1.6-2.0 (m, 6H), 2.23 (dt, J = 12.6, 10.5, CHSi), 2.49 (m, 1H), 2.8-2.9 (m, 1H, CH_2Ph), 3.0 (m, 1H, PCH), 3.1-3.2 (m, 1H, CH_2Ph), 7.2 (m, Ph) ppm. $[\alpha]_D$= - 47 (c = 0.5, $CHCl_3$). Anal. Calcd. for $C_{23}H_{39}PSSi$: C, 67.93; H, 9.67. Found: C, 67.69, H, 9.65. **7b**: colorless solid. ^{31}P NMR ($CDCl_3$) δ 82.5; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, $SiMe_3$), 0.84 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, $CHMe_2$), 0.93 (d, $^{3}J_{HH}$ = 6.5 Hz, 6H, CHMe + $CHMe_2$) ppm. **7c**: colorless solid. ^{31}P NMR ($CDCl_3$) δ 85.3; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, $SiMe_3$), 0.72 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, CHMe), 0.79 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, $CHMe_2$), 1.02 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, $CHMe_2$) ppm.

2,4-dibenzyl-1-menthylphosphetane sulfide (8a): sBuLi (1.0 mL, 1.3 mmol) was added to a solution of 2-benzyl-1-menthylphosphetane sulfide **6** (400 mg, 1.2 mmol, 1:1 mixture of **6a** and **6b**) in THF at -78°C. After 30 min, benzyl bromide (0.16 mL, 1.3 mmol) was added, the mixture was stirred for 15 min at -78°C then allowed to warm slowly to room temperature and hydrolyzed with distilled water. After extraction with ether, drying with $MgSO_4$ and evaporation of the solvent, the residue was chromatographed on an alumina column with hexane-ether 95:5 as eluent to afford **8a** in 48% yield (0.24 g). Crystallization of **8a** from hexane may be necessary in order to remove residual small amounts of the other isomers. **8a**: colorless solid. ^{31}P NMR ($CDCl_3$) δ 85.6; ^{1}H NMR ($CDCl_3$) δ 0.71 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, CHMe), 0.82 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $CHMe_2$), 0.96 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, $CHMe_2$) ppm. Mass spectrum, m/e (relative intensity): 424 (M, 5%), 286 (M-$C_{10}H_{18}$, 100%).$[\alpha]_D$= - 77 (c = 0.5, $CHCl_3$). Anal. Calcd. for $C_{27}H_{37}PS$: C, 76.37; H, 8.78. Found: C, 76.28, H, 8.87.

References

1. (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.; Kruger, V.; Ricard, L. *J. Organomet. Chem.* **1996** in press.
2. Mc Bride, J.J.; Jungermann, E.; Kilheffer, J.V.; Clutter, R.J. *J. Org. Chem.* **1962**, 27, 1833.
3. (a) Burk, M.J.; Feaster, J.E.; Harlow, R.L. *Organometallics* **1990**, 9, 2653. (b) Burk, M.J.; Feaster, J.E.; Harlow, R.L. *Tetrahedron : Asymmetry* **1991**, 2, 569.
4. (a) Kang, Y.B.; Pabel, M.; Willis, A.C.; Wild, S.B. *J. Chem. Soc. Chem. Commun.* **1994**, 475. (b) Hockless, D.C.R.; Kang, Y.B.; Mc Donald, M.A.; Pabel, M.; Willis, A.C.; Wild, S.B. *Organometallics* **1996**, 15, 1301. (c) Bader, A.; Pathak, D.D.; Wild, S.B.; Willis, A.C. *J. Chem. Soc. Dalton Trans.* **1992**, 1751. (d) Bader, A.; Kang, Y.B.; Pabel, M.; Pathak, D.D.; Willis, A.C.; Wild, S.B. *Organometallics* **1995**, 14, 1434.
5. Krause, H.W.; Kinting, A. *J. Prackt. Chem.* **1980**, 322, 485.
6. Several C-alkylations of phosphine-borane stabilized carbanions have been reported. See for example: (a) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, 112, 5244. (b) Imamoto, T.; Tsuruta, H.; Wada, Y.; Masuda, H.; Yamaguchi, K. *Tetrahedron Lett.* **1995**, 36, 8271. (c) Muci, A.R.; Campos, K.R.; Evans, D.A. *J. Am. Chem. Soc.* **1995**, 117, 9075.
7. Marinetti, A.; Kruger, V.; Le Menn, C.; Ricard, L. *J. Organomet. Chem.* **1996**, 522, 223.
8. Polniaszek, R.P.; Foster, A.L. *J. Org. Chem.* **1991**, 56, 3137.
9. (a) O'Brien, P.; Warren, S. *Tetrahedron Lett.* **1995**, 36, 8473. (b) O'Brien, P.; Warren, S. *Tetrahedron Lett.* **1996**, 37, 4271. (c) Vedejs, E.; Garcia-Rivas, J.A. *J. Org. Chem.* **1994**, 59, 6517.
10. Stereospecific reductions of chiral phosphine sulfides to the corresponding trivalent phosphine have been reported: Corey, E.J.; Chen, Z.; Tanoury, G.J. *J. Am. Chem. Soc.* **1993**, 115, 11000.
11. Aguiar, A.M.; Morrow, C.J.; Morrison, J.D.; Burnett, R.E., Masler, W.F.; Bhacca, N.S. *J. Org. Chem.* **1976**, 41, 1545.

(*Received in Belgium* 23 *October* 1996; *accepted* 3 *February* 1997)