Phosphorus, Sulfur, and Silicon, 180:2335–2346, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/1042650909210001

Taylor & Francis
Taylor & Francis Group

Diasteroselective Addition of Mono- and Bis-Silylphosphines to Chiral Aldehydes

Anastasia O. Kolodiazhna
Irina V. Guliaiko
Oleg I. Kolodiazhnyi

National Academy of Sciences of Ukraine, Kiev, Ukraine

The addition of silylphosphines to chiral aldehydes proceeds with high diastereoselectivity to give optically pure tertiary α-trimethylsiloxyalkylphosphines. The diastereomeric excesses of the addition products were achieved to 90–100%. The reaction of bis(trimethylsilyl)phenylphosphine with the acetonide of (R)-glyceraldehyde provides diastereomerically enriched tertiary bis(glyceryl)phosphines.

Keywords Asymmetric induction; chiral aldehydes; chiral tertiary phosphines; silylphosphines; stereoselectivity

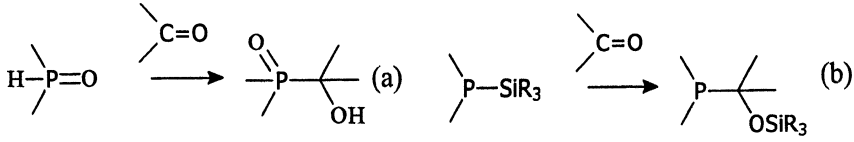
INTRODUCTION

Chiral organophosphorus compounds are an important subject of investigation due to the widespread use of these compounds as ligands for transition metal catalysis, biologically active substances, or drugs.[1–3] The numerous patented chiral phosphines are proof of the interest in such catalytic reactions from the industrial world.[3,4] The preparation of enantiomerically pure organophosphorus compounds is an important and challenging area of contemporary synthetic organic chemistry. Therefore the development of stereoselective methods for the synthesis of organophosphorus compounds represents an important scientific and applied problem.

Earlier we described a number of stereoselective methods for the synthesis of chiral organophosphorus compounds.[5–11] As part of our

Received July 29, 2004; accepted October 22, 2004.
Financial support for this work from the State Foundation of Basic Researches of Ukraine (Project 03.07/00047) is gratefully acknowledged.
Address correspondence to Oleg I. Kolodiazhnyi, Institute of Bioorganic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Street, 1, Kiev 02094, Ukraine. E-mail: oikol123@bpci.kiev.ua

ongoing program directed towards developing new stereoselective reactions, we report the reaction of silylphosphines with chiral aldehydes leading to the formation of optically active tertiary phosphines.



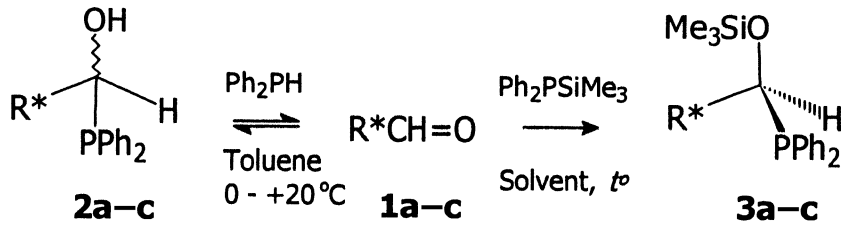
SCHEME 1

In contrast to the reaction of dialkylphosphites with aldehydes (Abramov reaction, Scheme 1, eq. (a)), which was extensively studied, the diastereoselective addition of silylphosphines to aldehydes was up to now not reported (Scheme 1, eq. (b))[1–4] although an achiral variant of this reaction was formerly described.[12–16]

RESULTS AND DISCUSSION

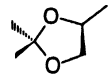
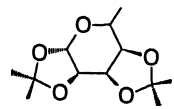
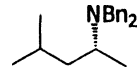
The reaction of diphenyl(trimethylsilyl)phosphine with chiral aldehydes **1a–c** resulted in the formation of products **3a–c** in good yield and high stereoselectivity (Scheme 2). The optical purity of a newly formed α-carbon atom achieved 90–99% *ee* (Table I). The phosphines **3a–c** are colorless liquids and configurationally stable at room temperature. The compounds **3a–c** are hydrolytically stable, but are easily oxidized by oxygen; therefore, all manipulations with these compounds have to be performed in an inert atmosphere.

According to ^{31}P NMR spectra, the compounds **3a–c** containing two asymmetric centers (α- carbon atom and R*) were obtained as a mixture of two diastereomers (Figure 1a). The chemical shifts δ_P–10– −4 ppm of **3a–c** agree with the nature of the trivalent phosphorus atom. The big differences between chemical shifts of two diastereomers attract special attention.



SCHEME 2 Reaction of chiral aldehydes **1a–c** with Ph_2PH and Ph_2PSiMe_3.

TABLE I Stereoselectivity of Reaction Between Ph_2PSiMe_3 and Aldehydes 1a–c

Entry	Compound	R	Solvent	t^o(°C)	Yield, %	dr^a
1	**3a**		THF	−20	85	95:5
2	**3b**		Toluene	−20–0	90	∼100:0
3	**3c**		Toluene	−20–+20	60	90:10

[a]Diastereomeric ratio (*dr*) was determined by NMR spectra.

To elucidate the effect of the Me_3Si group, we have examined the reaction of diphenylphosphine with chiral aldehydes **1a–c** and found that this reaction is reversible and proceeds with low stereoselectivity to give a mixture of the initial compounds and the addition product **2a** with *dr* 45:55 (Schme 2). The ^{31}P NMR spectra of this reaction mixture show the signals −8.30 and −10.09 ppm (diastereomers of **2a**) and the signal −40.7 ppm (diphenylphosphine) (Figure 1b).

We concluded that the reaction of silylphosphines with aldehydes is kinetically controlled, unlike the reaction of diphenylphosphine with aldehydes **1a–c** which is probably thermodynamically controlled,

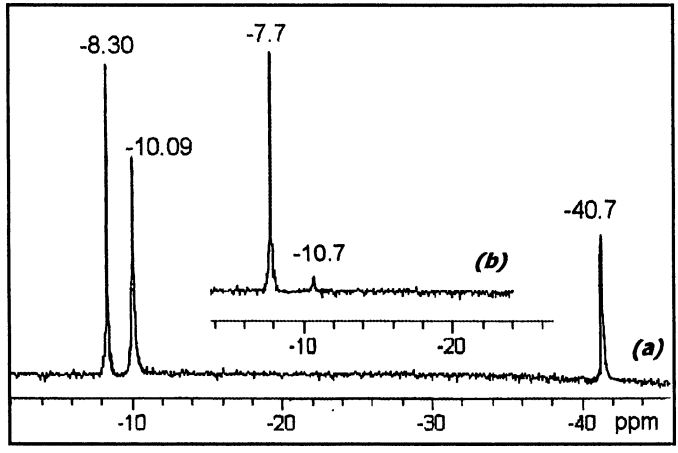


FIGURE 1 ^{31}P NMR spectrum of crude reaction mixtures of **2a** (*a*) and **3a** (*b*).

because the adducts **2a–c** dissociate with the formation of initial compounds and easily racemize.

Compounds **3a–c** react with borane in THF solution and were transformed into borane complexes **4a–c,** which were purified by column chromatography on silica gel. Structure and purity of the borane complexes **4a–c** were confirmed by nuclear magnetic resonance and elemental analysis.

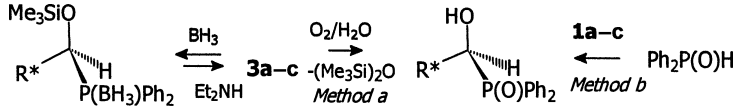
The ^{31}P NMR signals of the borane complexes are observed at +20–+30 ppm and have the typical shape of broad multiplets resulting from phosphorus-boron coupling that enable easy monitoring of these compounds.[17–20] The ^{1}H NMR spectra show the signals of all hydrogen atoms in the molecule, without any doubling caused through the presence of diastereomers.

Borane-phosphine complexes **4a–c** are configurationally stable at room temperature. They are also hydrolytically stable and are not oxidized by oxygen of the air.

Decomplexation of the compounds **4a–c** with a large excess of an amine such as diethylamine led to the formation of chemically and stereochemically pure tertiary phosphines **3a–c** (Table II). The reaction proceeds slowly and is completed at room temperature over a period of 16 h. The BH_3-part of the phosphine-borane complex was removed on treatment with a large excess of an amine such as diethylamine. The identity of the purified (*R*,*S*)-diastereomer **3a**, and the major diastereomer of the initial diastereomeric mixture of the tertiary phosphine (*R*,*S*)-**3a** and (*S*,*S*)-**3a**, was confirmed by ^{31}P NMR spectra of the mixture of these two products.

The oxidation of the compounds **3a–c** by oxygen of the air provides the phosphine oxides **5a–c** in high yield (~90%) (method *a*, Table II). The

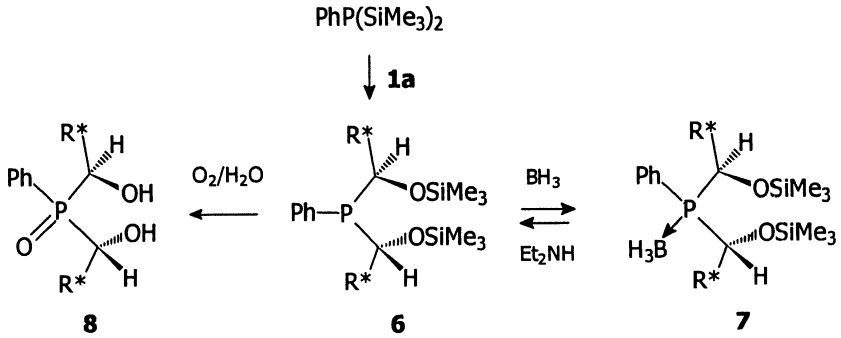
TABLE II Synthesis of Tertiary Phosphine Oxides 5a–c



4a–c **5a–c**

Entry	Compound	Yield (%) (Method *a*)	*de*[a] (%) (Method *a*)	Yield (%) (Method *b*)	*de*[a] (%) (Method *b*)
1	**5a**	90	95	60	75
2	**5b**	50	98	70	80
3	**5c**	40	98	40	70

[a]*de* = diastereomeric excess.



SCHEME 3 Reaction of the aldehyde **1a** with the phenyl-*bis*(trimethylsilyl)-phosphine.

compounds **5a–c** were isolated as colorless crystalline substances; the structure and purity were confirmed by elemental analysis and spectroscopic studies. To additionally confirm the structure of compounds **5a–c** we have prepared them also by an alternative reaction between diphenylphosphine oxide and aldehydes **1a–c** (method *b*, Table II). We have found that this reaction proceeds with moderate stereoselectivity (∼75% *de)*; however, the crystallization of additional products in toluene provides the optically pure compounds **5a–c**, which are identical to compounds **5a–c** prepared by method *a*.

The reaction of *bis*(trimethylsilyl)phenylphosphine with aldehyde **1a** proceeds as well with good stereoselectivity. The product **6** contains four chiral atoms and can exist as a mixture of several diastereomers, but the reaction led to the formation of one predominantly diastereomer. The subsequent treatment of the compound **6** with borane resulted in the optically pure borane complex **7,** which constitutes a new chiral ligand.[21] The compound **7** is stable to oxidation and hydrolysis by air, can be kept without racemisation, and can be purified by column chromatography on Silica Gel. The BH_3-part of the phosphine-borane complex **7** was removed on treatment with diethylamine to give the diastereomerically pure tertiary phosphine **6**. The compound **6** was oxidized to the corresponding tertiary phosphine oxide **8,** which was isolated as a crystalline product. The structure, chemical, and optical purity of compounds **6–8** have been confirmed by elemental analysis, NMR spectra, and HPLC. We have also used derivatization with dimenthylchlorophosphite and Mosher acid.[22]

The newly formed asymmetric center of the compounds **3–5**, evidently, is of the (*S*)-configuration, as was found on the basis of NMR spectra: The big value of the $^3J_{HH}$ constant and small value of the $^2J_{HP}$ constant of compounds **3–5** show the *anti*-conformation of H—C^1—C^2—H

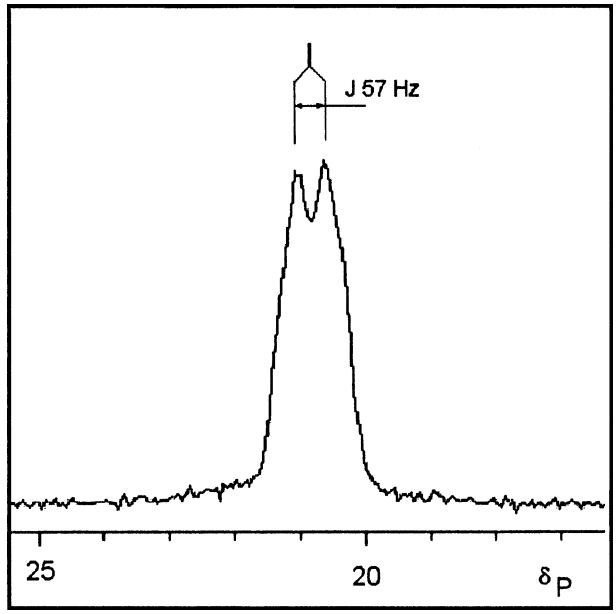


FIGURE 2 The ^{31}P NMR spectra of the borane complex **4a**.

and O=P–C^1–H bonds.[23] The stereochemistry of this reactions probably is kinetically controlled. Therefore the nucleophilic attack of silylphosphines to the less shielded *(Si)* face of the carbonyl group provides preferentially the (*S*)-**3** diastereomer according to the Cram's rule. Consideration of the stereochemical model of the formed products showed that the stereochemistry of the phosphaaldol reaction is in the agreement with Cram's rule (Figure 3).[24]

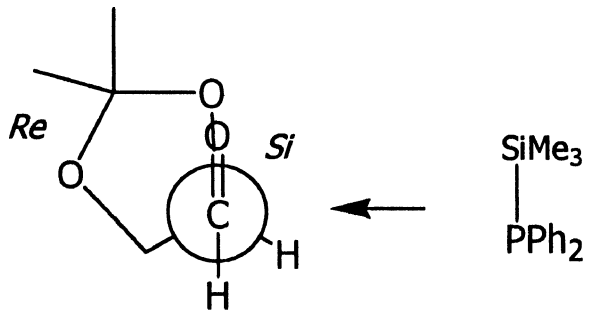


FIGURE 3 Stereochemical Cram model of the reaction between the aldehyde **1a** and Ph_2PSiMe_3.

CONCLUSION

In conclusion, we have found that the reaction between silylphosphines and chiral aldehydes proceeds with good stereoselectivity to give chiral tertiary phosphines in high chemical yields. The reaction can be applied for asymmetric synthesis of new chiral organophosphorus compounds, including organophosphorus ligands or bioactive substances.

EXPERIMENTAL

Melting points are uncorrected. The NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 (^{1}H) and 126.16 MHz (^{31}P). ^{1}H chemical shifts are given in δ (ppm) relative to Me_4Si as internal standard. ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 as an external standard. All manipulations were carried out in an argon atmosphere. The following solvents were distilled in an inert atmosphere: diethyl ether, hexane, heptane, benzene, CCl_4 (over P_4O_{10}), methanol, triethylamine (over sodium), and ethyl acetate (over $CaCl_2$). Column chromatography was performed using silica gel 60 (Fluka). Optical rotations of the compounds were determined on a Polax-2L polarimeter in solvents, which were purified by standard methods. Optically active reagents were obtained from Aldrich and Fluka and were used without special purification. Silylphosphines were prepared according to the procedure which we described earlier.[25]

2,2-Dimethyl-1,3-dioxolan-4-yl-trimethylsiloxymethyl-diphenylphosphine (3a)

To a solution of **1a** (1.1 mmol) 5 mL of toluene was added to Ph_2PSiMe_3 (1.0 mmol) at -20°C. The reaction mixture was allowed to stand at this temperature overnight. The temperature was raised to $+20^\circ$C and in 1 h the solvent was evaporated to give tertiary phosphine **3a**. The product was obtained as a colorless liquid.

To a solution of **3a** in THF (3 mL) a solution of 0.12 mmol of borane in THF (1.1 mmol) was added dropwise with stirring at -20°C and the reaction mixture was allowed to stand at room temperature. After 6 h the solvent was removed in vacuo and the residue was chromatographed on a column with silica gel with hexane-ethyl acetate (6:1) as an eluent to give the borane complex **4a**.

Yield 80%. R_f 0.3 (hexane-ethyl acetate = 3:1). $[\alpha]_D + 41.6$ (c 1.5, ethyl acetate).

Anal. calcd. for $C_{21}H_{32}BO_3PSi$:P, 7.70; Found: P, 7.55.

^{1}H NMR ($CDCl_3$), δ, ppm (J, Hz): −0.16 s ($SiMe_3$); 0.18–1.4 m (BH_3); 1.25 s; 1.33 s [$(CH_3)_2C$]; 3.23 dd J 8, J 1; 3.43 dd J 7.5, J 1 (CH_2O); 4.53 m (C<u>H</u>CH_2O); 5 dd J 4.5, $J < 1$ (PCH); 7.66 m; 7.93 m (C_6H_5).

^{31}P NMR ($CHCl_3$): δ_P 21.6 ppm, d J_{PB} 57 Hz.

The borane complex **4a** was dissolved in excess diethylamine and kept under argon for 16 h. Excess diethylamine was removed in vacuo, and residue was extracted with hexane, which was filtered under argon to leave the optically pure tertiary phosphine **3a**. The ^{31}P NMR spectrum showed only one signal due to the *(SR)*-diastereomer (confirmed by mixed testing with an authentic diastereomer).

Yield 90%, $[\alpha]_D^{20}$–7 (c 4, toluene).

NMR ^{1}H ($CDCl_3$), δ, ppm (J, Hz): −0.02 s (CH_3Si); 1.33 s (CH_3); 4.33 m; 4.49 (OC<u>H</u>$_2$CH); 4.72 m (CH_2C<u>H</u>O); 4.99 m (PC<u>H</u>); 7.5 m; 7.9 m (C_6H_5).

^{31}P NMR ($CHCl_3$): δ −7.69; −10.62 ppm (ratio ~11:1).

Trimethylsiloxy (2,2,7,7-Tetramethylperhydrodi[1,3]dioxolo-[4,5-*b*:4,5-*d*]pyran-5-yl)methyl-diphenylphosphine (3b)

A solution of aldehyde **1b** (0.01 mol) in toluene was added to a solution of diphenyl trimethylsilylphosphine (0.01 mol) in toluene at 0°C and the reaction mixture was left for 2 h at this temperature. The solvent was removed under pressure and reduced. Yield 80%. ^{31}P NMR (toluene), ppm: δ_P 4.4.

To a solution of phosphine **3b** in 5 mL of THF a solution of borane (0.012 mol) in THF was added dropwise with stirring and the reaction mixture was allowed to stand at room temperature for 12 h. The solvent was removed in vacuo and the residue was chromatographed on a column with silica gel (3:1 hexane-ethyl acetate as eluent). The diastereomeric excesses and yields are collected in Table I.

R_f 0,35. $[\alpha]_D$ −71.8 (c 3, $CHCl_3$).

^{1}H NMR ($CDCl_3$), δ, ppm (J, Hz): −0.18 c (9H, CH_3Si); 0.8–1.6 m (3H, BH_3); 1.13 s (3H, CH_3); 1.18 s (3H. CH_3); 1.27 s (3H. CH_3); 1.48 s (3H. CH_3); 3.99 ddd (1H, PCCH,J_{PH} 7; J_{HH} 7, J_{HH} 9); 4.16 dd (1H, PCH, J_{HH} 3, J_{HH} 5.1); 4.21 dd (1H, CH, J_{HH} 8, J_{HH} 1) 4.53 dd (1H, CH, J_{HH} 9, J_{HH} 1.2); 4.94 dd (1H, PCH, J_{HH} 9, J_{HP} 1.5); 5.29 d (1H, CH, J_{HH} 5.4); 7.4 m; 8.0 m (10H, C_6H_5).

^{31}P NMR ($CDCl_3$): δ 25.3 ppm, m.

The borane complex **4b** was dissolved in 5 mL of diethylamine and left for 12 h. The solvent was removed in vacuo to give the tertiary phosphine **3b** as a diastereoisomerically pure, easily oxidized liquid. The ^{31}P NMR spectrum showed only one signal due to the *(SR)*-diastereomer **3a** (confirmed by mixed testing with an authentic diastereomer).

^{31}P NMR ($CDCl_3$): δ 4.4 ppm.

N,N-Dibenzyl-1-trimethylsiloxy-2-pentanamine-methyl-diphenylphosphine (3c)

The product **3c** and its borane complex **4c** were prepared analogously to compounds **3a**, **4a**. The diastereomeric excesses and yields are collected in Table I. The product was prepared in spectroscopically pure state and used for further conversions without special purification.

^{31}P NMR (toluene): δ −10.5; −11.3 ppm (ratio 9:1).

Borane complex (**4c**): Yield 64%. R_f 0,35, $[\alpha]_D$ −71.8 (*c* 3, $CHCl_3$).

Anal. calcd. for $C_{35}H_{37}BNOPSi$: P, 5.46; Found: 5.30.

^{31}P NMR ($CHCl_3$) δ, ppm (*J*, Hz): δ 25.3, m, $^1J_{PB}$ 57.

2,2-Dimethyl-1,3-dioxolan-4-yl-trimethylsiloxymethyl-diphenylphosphine Oxide (5a)

Method a

The compound **3a** was dissolved in toluene and left for 12 h in the air. As a result a solid product was obtained. This product was dissolved in toluene and was left to crystallize. The crystalline product was filtered to provide the pure diastereomer **5a**.

Mp 167°C, $[\alpha]_D^{20}$+11 ($CHCl_3$, c 2).

Method b

To a solution of diphenylphosphine oxide (0.01 mol) of 5 mL of toluene a solution of aldehyde (**1a**) (0.011 mol) and diazabicycloundecene (0.001 mol) in 3 mL of toluene was added with cooling. The reaction mixture was left for 6 h at 0°C. The solvent was removed in vacuum. The ^{31}P NMR spectrum showed the presence of (1*S*, 2*R*)- and (1*R*, 2*R*)-diastereomers. ^{31}P NMR ($CHCl_3$): δ 30.87 and 29.45 ppm.

The residue was obtained as a viscous liquid to which toluene was added and left to crystallize. The next day the crystalline product was filtered off and was recrystallized from toluene. The mother liquor was evaporated. The residue, enriched in the minor diastereomer, was separated by column chromatography with silica gel ($CHCl_3$-ethylacetate 1:1). The diastereomeric excesses and yields are collected in Table II. *Anti-diastereomer*. M.p. 167°C, $[\alpha]_D^{20} = +11$ (*c* 2, $CHCl_3$).

NMR ^{1}H ($CDCl_3$), δ, ppm (*J*, Hz): 1.17 s (Me_2C^a); 1.20 s (Me_2C^b); 3.88 d *J* 2 (C^aH_2); 3.897 d *J* 1.5 (C^bH_2); 4.39 dt *J* 6.5, *J* 2 ($OC\underline{H}CH_2$); 4.59 dd *J* 5, *J* 0.9 (PCH); 4.4 m (OH); 7.8 m, 4H; 7.49 m (6H).

NMR ^{31}P ($CHCl_3$): δ 30.87 ppm.

Cis- diastereomer. R_f 0.2.

^{1}H NMR ($CDCl_3$) 1.14 s [$(CH_3)_2C^a$]; 1.23 s [$(CH_3)_2C^b$]; 3.992 s; 3.902 s (CH_2); 4.39 dt J 6.5, J 2 (OC<u>H</u>CH_2); 4.4 br (OH); 4.59 dd J 5, J_{HP} 5 Hz (PC<u>H</u>); 7.8 m, 4H; 7.49 m (6H).

NMR ^{31}P ($CHCl_3$): δ 29.45 ppm.

Anal. calcd. for $C_{18}H_{21}O_4P$:P, 9.32; Found: 9.55.

1-Hydroxy-[(2,2,7,7-tetramethylperhydrodi[1,3]dioxolo[4,5-*b*:4,5-*d*]pyran-5-yl]-methyl Diphenylphosphine Oxide (5b)

The compound **5b** was prepared analogously to **5a**. The diastereomeric excess and yield are collected in Table II.

m.p. 156°C, $[\alpha]_D^{20}$ −59 (c 3, $CHCl_3$).[26]

Anal. calcd. for $C_{24}H_{29}O_7P$: P, 6.73; Found: 6.54.

NMR ^{1}H ($CDCl_3$), δ, ppm (J, Hz): 1.11 s (3H, CH_3); 1.18 s (3H, CH_3); 1.31 s (3H, CH_3); 1.32 s (3H, CH_3); 4.02 dd (1H, CH, J_{HH} 2.1; J_{PH} 5); 4.22 ddd (1H, PCCH, J_{HH} 2.0, J_{HH} 7, J_{HH} 8); 4.43 dd (1H, CH, J_{HH} 8, J_{HH} 1.5); 4.58 dd (1H, CH, J_{HH} 8, J_{HH} 1); 4.63 dd (1H, PCH, J_{HP} 3, J_{HH} 8); 5.07 d (1H, CH, J_{HH} 5); 6.14 br (1H, OH); 7.3 m; 7.8 m (10H, C_6H_5).
^{31}P NMR ($CHCl_3$): δ 32.2 ppm.

N,N-Dibenzyl-1-hydroxy-2-pentanamine-methyl-diphenylphosphine Oxide (5c)

The compound **5c** was prepared analogously to **5a**. The diastereomeric excess and yield are collected in Table II.

m.p. 121°C, $[\alpha]_D^{20} = -30$ ($CHCl_3$, c 2).

Anal. calcd. for $C_{35}H_{44}NO_2PSi$: P, 5.44; Found: 5.41.

^{1}H NMR ($CDCl_3$): 0.11, d J 6.6 [$(CH_3)_2CH$]; 0.84, d J 6.6 [$(CH_3)_2CH$]; 1.23 m (CH_2); 1.83 m (CH_2); 2.84 m (CH); 3.35 s; 4.0 s; 3.88 s; 3.93 s (CH_2N); 4.42 m (OH); 4.82 dd J 1, J 1 (PCH); 7–7.8 m (C_6H_5).

NMR ^{31}P ($CHCl_3$): δ 29.4 ppm.

Bis[2,2-Dimethyl-1,3-dioxolan-4-yl(trimethylsiloxy)-methyl]phenylphosphine (6)

(a) Preparation of Borane Complex (7)

To a solution of **1a** (2.2 mmol) 5 mL of toluene was added slowly to $PhP(SiMe_3)_2$ (1.0 mmol) while cooling. The solution was left at this temperature overnight. The temperature was raised to +20°C and in 1 h the solvent was evaporated to give tertiary phosphine **6**.

NMR ^{31}P ($CHCl_3$): δ −10.68 ppm.

Then to a solution of **6** in THF (3 mL) a solution of borane (1.1 mmol) in THF was added dropwise with stirring at −20°C. The reaction

mixture was allowed to stand at room temperature. After 6 h the solvent was removed in vacuo to give tertiary phosphine **6** and the residue was chromatographed on column with silica gel, using a mixture of hexane-ethyl acetate (6:1) as eluent.

Yield 70%. R_f 0.37 (hexane-ethyl acetate 6:1). $[\alpha]_D^{20} = +23.6$ (*c* 3, $CHCl_3$).

Anal. calcd. for $C_{24}H_{46}BO_6PSi_2$: P, 5.86; Found: P, 5.66.

NMR ^1H ($CDCl_3$), δ, ppm: −0.17 s ($SiMe_3$); −0.20 s ($SiMe_3$); 0.6–1.3 m (BH_3); 1.11 s; 1.20 s; 1.33 s; 1.36 s [$(CH_3)_2C$]; 4.59 m; 4.53 m ($CHC\underline{H}CH_2$); 3.64 dt; 3.77 dt; 3.9 dt; 4.11 dt (OCH_2); 5.16 dd *J* 9, *J* <1 (PCH); 7.2 m; 7.8 m (C_6H_5).

NMR ^{31}P ($CHCl_3$): δ 27.4 ppm.

(b) Decomplexation of Borane Complex (7)

The borane complex **7** was dissolved in excess diethylamine and the mixture was kept under argon for 12 h. Then volatile matter was evaporated in vacuum and the residue was extracted with hexane, which was filtered under argon to give spectroscopically pure tertiary phosphine **6**.

Yield 90%, colorless easily oxidable liquid, $[\alpha]_D^{20} = -12.5$ (*c* 3, ethyl acetate). NMR ^{31}P ($CHCl_3$): δ −10.68 ppm.

Bis(2,2-Dimethyl-1,3-dioxolan-4-yl-hydroxymethyl)-phenylphosphine Oxide (8)

The compound **8** was prepared analogously to **5a**. R_f 0.25 (hexane-ethyl acetate 2:1). Anal. calcd. for $C_{18}H_{27}O_7P$: P, 8.02; Found: P, 7.86.

NMR ^{31}P ($CHCl_3$): δ 43 ppm.

REFERENCES

[1] O. I. Kolodiazhnyi, *Tetrahedron: Asymmetry*, **9,** 1279 (1998).

[2] O. I. Kolodiazhnyi, *Advances in Asymmetric Synthesis*, vol. 3, p. 273. A. Hassner (Ed.), London: JAI Press.

[3] (a) R. A. Sheldon, *Chirotechnology*. New York: Marcel Dekker (1993); (b) A. N. Collins, G. N. Sheldrake, and J. Grosby, *Chirality in Industry*. New York: John Wiley & Sons (1992); (c) S. Stinson, *Chem. Eng. News* **76,** 83 (1998); (d) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*. New York: John Wiley & Sons (1994).

[4] O. I. Kolodiazhnyi, *Tetrahedron*, **59,** 5923 (2003).

[5] O. I. Kolodiazhnyi, N. V. Andrushko, and E. V. Grishkun, *Zh. Obshch. Khim.*, **74,** 515 (2004).

[6] O. I. Kolodiazhnyi, E. V. Grishkun, O. R. Golovatyi, and S. N. Ustenko, *Phosphorus, Sulfur, and Silicon*, **109/110,** 485 (1996).

[7] O. I. Kolodiazhnyi and E. V. Grishkun, *Tetrahedron: Asymmetry*, **7,** 967 (1996).

[8] O. I. Kolodiazhnyi and E. V. Grishkun, *Phosphorus, Sulfur, and Silicon*, **115,** 115 (1996).
[9] O. I. Kolodiazhnyi and N. Prynada, *Tetrahedron Lett.*, **41,** 7997 (2000).
[10] O. I. Kolodiazhnyi, E. V. Grishkun, and N. V. Andrushko, et al., *Tetrahedron: Asymmetry*, **14,** 181 (2003).
[11] O. I. Kolodiazhnyi, *Tetrahedron Lett.*, **36,** 3921 (1995).
[12] M. Epstein and S. A. Buckler, *Tetrahedron*, **18,** 1231 (1962).
[13] O. I. Kolodiazhnyi, *Tetrahedron Lett.*, **23,** 4933 (1982).
[14] O. I. Kolodiazhnyi, In *Synthetic methods of organometallic chemistry (Hermann-Brauer)*. vol. 3, p. 36. W. A. Herrmann (Ed.), New York: Thieme, Stuttgart (1996).
[15] K. A. Petrov and V. A. Parshina, *Zh. Obshch. Khim*., **31,** 3417 (1961).
[16] G. Becker and O. Mundt, *Z. Anorg. Allgem. Chem*., **462,** 130 (1980).
[17] T. Imamoto, *Pure Appl. Chem*., **65**, 655 (1993).
[18] S. Juge, M. Stephan, J. A. Laffitte, and J. P. Genet, *Tetrahedron Lett*., **31,** 6357 (1990).
[19] J. Uziel, C. Darcel, D. Moulin, C. Bauduin, and S. Juge, *Tetrahedron: Asymmetry*, **12,** 1441 (2001).
[20] T. Imamoto, T. Oshiki, T. Onazawa, T. Kusumoto, and K. Sato, *J. Am. Chem. Soc*., **112,** 5244 (1990).
[21] Studies of compounds **6–8** as ligands in transition metal complexes are currently in progress.
[22] O. I. Kolodiazhnyi, O. M. Demchuk, and A. A. Gerschkovich, *Tetrahedron: Asymmetry*, **10,** 1729 (1999).
[23] Y. Hanaya, A. Miyoshi, A. Nogushi, H. Kawamoto, M.-A. Armour, A. M. Hogg, et al. *Bull. Chem. Soc. Jpn*., **63,** 3590 (1990).
[24] R. S. Ward, *Selectivity in organic reactions*, 12–29 Chichester: John Wiley & Sons, (1999).
[25] O. I. Kolodiazhnyi, In *Synthetic methods of organometallic chemistry*/ *(Hermann-Brauer)*. vol. 3, p. 70. W. A. Herrmann (Ed.), New York: Thieme, Stuttgart (1996).
[26] I. V. Guliaiko and O I. Kolodiazhnyi, *Zh. Obshch. Khim.*, in press.