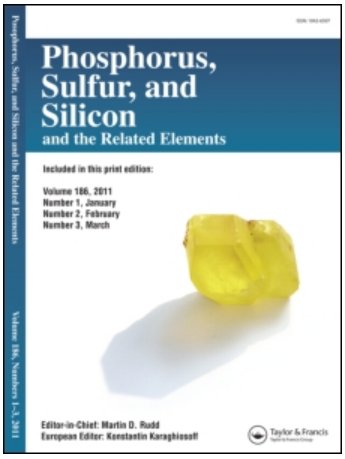

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STEREOSELECTIVE REACTIONS OF CHIRAL AMINES WITH RACEMIC CHLOROPHOSPHINES

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Online publication date: 16 August 2010

To cite this Article Gryshkun, Evgenyi V. , Andrushko, Natalia V. and Kolodiazhnyi, Oleg I.(2004) 'STEREOSELECTIVE REACTIONS OF CHIRAL AMINES WITH RACEMIC CHLOROPHOSPHINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 6, 1027 — 1046
To link to this Article: DOI: 10.1080/10426500490459650
URL: http://dx.doi.org/10.1080/10426500490459650

Phosphorus, Sulfur, and Silicon, 179:1027–1046, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490459650

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STEREOSELECTIVE REACTIONS OF CHIRAL AMINES WITH RACEMIC CHLOROPHOSPHINES

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(Received July 16, 2003; accepted September 30, 2003)

*Racemic chlorophosphines react stereoselectively with chiral l-phenylethylamines or amino acid esters to give diastereomerically enriched aminophosphines **3**, which were isolated as diastereomerically pure crystalline borane complexes. Oxidation, thionation, the reaction with methyl iodide provide optically active derivatives of aminophosphines. (R,S)- and (S,S)-stereomers of phosphinic acid amides were separated by crystallization and a flash-chromatography. The stereochemical properties of phosphorus acid amides were investigated. The mechanism of asymmetric induction at the trivalent phosphorus atom was rationalized.*

Keywords: Asymmetric induction; chiral aminophosphines; stereoselectivity

Chiral trivalent organophosphorus compounds having a stereogenic phosphorus center are important subjects of investigation due to the widespread use of these compounds as ligands for transition metal catalysis.[1,2] The numerous patented chiral phosphines and aminophosphines are proof of the interest in such catalytic reactions from the industrial world.[3,4] Therefore the preparation of enantiomerically pure organophosphorus compounds is an important and challenging area of contemporary synthetic organic chemistry.

Earlier we described the asymmetric synthesis of chiral organophosphorus compounds by the reaction of chiral secondary alcohols[1,5–10] with chlorophosphines, resulting in the formation of optically active phosphinites. In general case it is possibly to suggest that reactions of chiral chlorophosphines with chiral nucleophiles will proceed with

Financial support of this work from the State Foundation of Basic Research of the Ukraine (Project 03.07/00047) is gratefully acknowledged.

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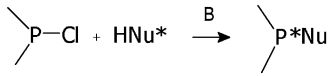


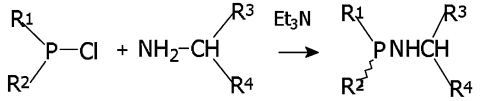
$HNu^* =$ chiral nucleophile, B = base

asymmetric induction at the phosphorus atom. Therefore we have examined the reaction of the chlorophosphines with chiral amines resulting in the formation of diastereomerically enriched aminophosphines.

The present reaction provides an easy access to optically active aminophosphines, used as precursor compounds in the synthesis of chiral organophosphorus compounds. Moreover, this reaction is convenient for studies of the mechanism and stereochemistry of nucleophilic substitution at trivalent phosphorus.

RESULTS AND DISCUSSION

The reaction of optically active amines **2** with racemic chlorophosphines **1** in the presence of triethylamine, or other organic base, proceeds with asymmetric induction at the phosphorus atom to give diastereomerically enriched aminophosphines **3**. The stereoselective substitution of chlorine at phosphorus by an amino group is achieved by reaction of two equivalents of optically active 1-phenylethylamine or amino acid esters **2** with one equivalent of chlorophosphine **1** or by reaction with an equimolar mixture of chiral amines and the triethylamine. The reaction proceeds in hexane, diethyl ether, THF, benzene or toluene to give *N*-substituted aminophosphines **3** in good yield (Scheme 1).



1 **2** **3a-d**

Compd	R^1	R^2	R^3	R^4	Yield, %	*de*, %[c]
3a	*t*-Bu	Ph	Ph	Me	85[a]	84
3b	Ph	Mes	Ph	Me	95[b]	50
3c	*t*-Bu	Ph	i-Bu	CO_2Me	85[a]	50
3d	*t*-Bu	Ph	i-Pr	CO_2Me	85[a]	70

[a] after purification; [b] not purified; [c] ratio of **1**:**2**:Et_3N=1:1:1, in benzene at +20°C

SCHEME 1

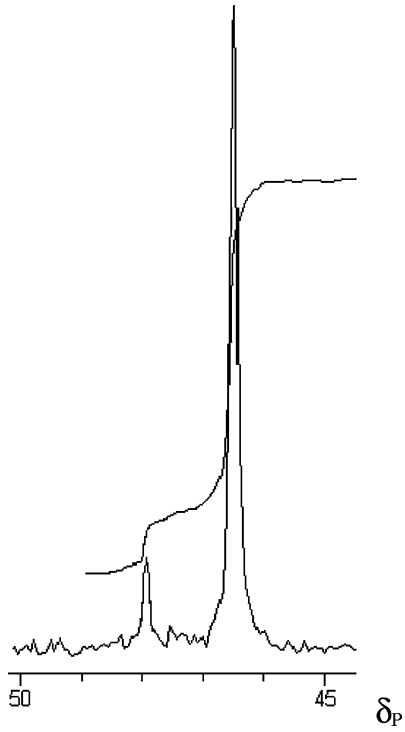


FIGURE 1 ^{31}P NMR spectrum of crude reaction mixture of the *N*-(1-phenylethyl)amino-*tert*-butylphenylphosphine **3a**.

Aminophosphines **3a–d** are colorless liquids, configurationally stable at room temperature. They can be distilled under vacuum, without any decomposition or racemization. Compounds **3a–d** 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 **3** contain an asymmetric phosphorus atom, and are obtained as a mixture of two diastereomers. The (R_p,*S*)- and (S_p,*S*)-diastereomers of compounds **3** are easily observed by NMR spectroscopy and high performance liquid chromatography (HPLC) (Figure 1).

The stereoselectivity of the reaction of the chlorophosphines with chiral amines depends to a great degree on the reaction conditions, especially on the nature of organic bases, solvents, and temperature. The effect of the reaction conditions on the stereoselectivity of the reaction of *t*-butylphenylchlorophosphine with 1-methylbenzylamine is shown in Table I. The analysis of these data allowed us to optimize

TABLE I Stereoselectivity of the Reaction of *t*-Bu(Ph)PCl with (*S*)-$NH_2CH(Me)Ph$

Entry	Solvent	Base	Temp.	Ratio of 1:2: Base (mole ratio)	dr^a
1	Benzene	Et_3N	20°C	1:1:1	8:92
2	Benzene	Et_3N	20	1:1:2	13:87
3	Benzene	Et_3N	20	1:1:10	21:79
4	Benzene	Et_3N	20	1:2:1	17.5:82.5
5	Benzene	Et_3N	20	1:1:1	20.5:79.5
6	Toluene	Et_3N	70	1:1:1	16:84
7	Toluene	Et_3N	20	1:1:1	16:84
8	Toluene	Et_3N	0	1:1:1	20:80
9	Toluene	Et_3N	−20	1:1:1	26:74
10	Toluene	Et_3N	20	2:1:1	15:85
11	Toluene	Et_3N	20	4:1:1	14:86
12	Benzene	Et_3N	20	1:1:4	18:82
13	Toluene	DABCO	20	1:1:1	25:75
14	Toluene	PEA	20	1:1:1	17.5:82.5
15	Toluene	DBU	20	1:1:1	42:58
16	Ether	Et_3N	20	1:1:1	12:88
17	Ether	Et_3N	−20	1:1:1	19:81
18	Hexane	Et_3N	20	1:1:1	20:80
19	THF	Et_3N	20	1:1:1	38:62
20	Ether	Et_3N	20	1:1:1	36:64
21	Benzene	Et_3N	20	1:1:1	75:25

[a]The diastereomeric ratio was obtained by the ^{31}P NMR method as average value of 2–3 measurements; PEA = 1-methylbenzylamine; DBU = diazabicycloundecene, DABCO = diazabicyclooctane.

the reaction conditions, ensuring the highest stereoselectivity. The reaction should be carried out at 20°C, with a very slow addition rate of 1-methylbenzylamine and triethylamine in benzene solution to a solution of the chlorophosphine in benzene. Then, the mixture should be allowed to stand for 8–12 h at room temperature to complete the reaction.

Special interest attaches to the question of asymmetric induction at trivalent phosphorus in the reaction of chlorophosphines with chiral amines in the presence of organic bases. Literature data on this question are insufficient though the mechanism and stereochemistry of nucleophilic substitution at pentavalent phosphorus were investigated.[1,4,11–17]

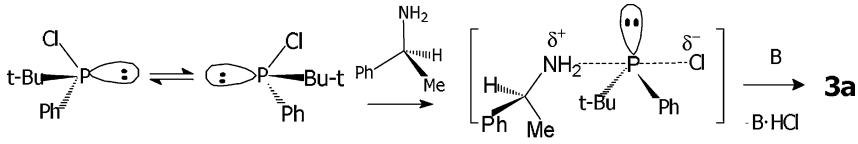
Examples of asymmetric induction in reactions of chlorides of trivalent phosphorus with alcohols and amines were described earlier. For example Mislow obtained menthyl esters of phosphinic acids in low stereochemical yield by reaction of chlorophosphines with menthol in

the presence of pyridine.[12] In our previous work we have observed a high degree of asymmetric induction in the reaction of chlorophosphines with 1,2:5,6-diisopropylidene glucofuranose, together with some other optically active secondary alcohols in the presence of triethylamine which proceeded under kinetic control.[1,5–7]

The stereochemistry of the reaction compounds of trivalent phosphorus with nucleophiles was investigated insufficiently, while the mechanism and stereochemistry of the reaction of chlorophosphines with nucleophiles in the presence of tertiary organic bases was not studied.

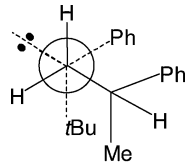
Basically, asymmetric induction at trivalent phosphorus can be explained, as follows: (a) by the S_N2P mechanism of nucleophilic substitution or (b) by a mechanism involving the formation of trigonal bipyramidal intermediates arising from attack of the nucleophile at an apical position, and the leaving group, departing from an apical position. The leaving group must depart before ligand reorganization (Berry pseudorotation or turnstile mechanism) can operate.

The first mechanism of S_N2P substitution, shown in Scheme 2, is typical for reactions proceeding under kinetic control. Chiral (*S*)-1-methylbenzylamine reacts with (*S*)-chlorophosphine faster than with (*R*)-chlorophosphine to give, preferentially, the (R_P, *S*)−diastereomer of the aminophosphine **3**. It is well known that chiral chlorophosphines are configurationally labile compounds existing as an equilibrium racemic mixture of (*R*)- and (*S*)-enantiomers.[4,11,17] For example, tert-butylphenylchlorophosphine, prepared by Omelanczuk,[17b] lost readily its optical activity even in the polarimeter cell. Wild and coworkers[17c] reported that isopropylphenylchlorophosphine in palladium (II) complex can be resolved; however liberation of epimeric chlorophosphines from the complex led to complete racemization of the free phosphine within 5 min. Lambert described mechanisms of the pyramidal atomic inversion in chlorophosphines.[17d]



SCHEME 2

The first mechanism explains the formation of (*R*,*S*)-aminophosphine as the diastereomer of the lowest energy of formation, as proved by MOPAC calculations. MOPAC calculations of the free energy of the

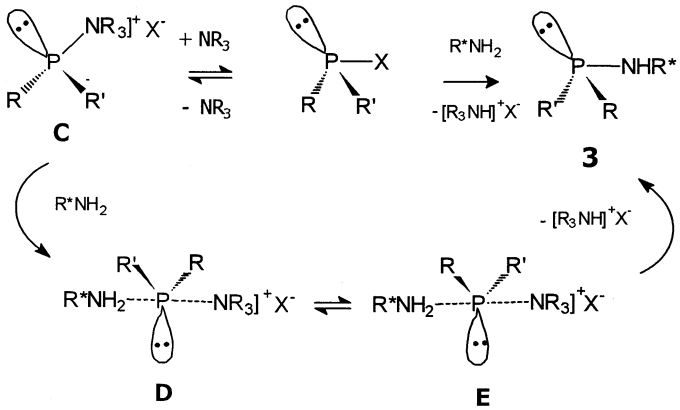


B

FIGURE 2 Thermodynamically stable conformation B.

diastereomers show that in the case of (*S*)-1-methylbenzylamine and *t*-Bu(Ph)PCl the reaction results in the formation of the most thermodynamically stable conformation B leading to the diastereomer (R_P,*S*)-**3a** (Figure 2).

However, the first mechanism does not explain the important role of the tertiary base that follows from experimental studies. Therefore, we suggest that the second mechanism shown in Scheme 3 is more probable. This mechanism includes the formation of a pentacoordinate transition state, pseudorotation and an exchange of ligands at pentacoordinate phosphorus as a result of which the thermodynamically most stable diastereomer is formed. The stability of the intermediate **3**, the apicophilicity of ligands, and also the asymmetric induction under the effect of the optically active 1-methylbenzylamine determine the stereochemical outcome of the reaction.



SCHEME 3

The analysis of the results of various factors describing the influence on the stereochemical outcome of the reaction of *tert*-butylphenylchlorophosphine with 1-methylbenzylamine in the presence of organic bases presented in Table I leads to the following conclusions:

1) the stereoselectivity of the reaction depends on the nature of the solvent, decreasing in the sequence, THF > hexane > toluene > benzene > diethyl ether;
2) the stereoselectivity of the reaction depends on the nature of the organic bases, increasing strength and concentration of organic bases reduces the stereoselectivity, thus Et_3N > DABCO > DBU;
3) an increase of the amount of chlorophosphine increases the stereoselectivity, while an increase of the amount of methylbenzylamine reduces the stereoselectivity;
4) a decrease of the reaction temperature reduces the stereoselectivity;
5) (*S*)-1-methylbenzylamine generates the (*R*)-configuration at phosphorus while, in contrast, (*R*)-1-methylbenzylamine gives rise to the (*S*)-configuration.

In the overwhelming majority of cases S_N2 nucleophilic substitution at chiral tricoordinate trivalent phosphorus results in the inversion of configuration that assumes the formation of a pentacoordinate anionic species (S_N2 type), containing attacking and leaving groups in apical positions.

The results obtained show a significant role of the tertiary organic base in the process of nucleophilic substitution at trivalent phosphorus. Thus, the reaction of chlorophosphine with the sodium derivative of 1-methylbenzylamine proceeds with low stereoselectivity to give the diastereomers (*R*, *S*)-**3a** and **(***S*, *S*)-**3a** in the ratio 2:1, unlike the reaction of chlorophosphine with 1-methylbenzylamine in the presence of triethylamine:

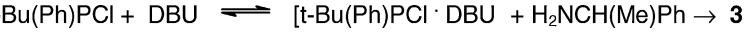
$$\mathbf{1} + (S)\text{-LiNHCH(Me)Ph} \rightarrow (R,S)\text{-}\mathbf{3a} + (S, S)\text{-}\mathbf{3a}.$$

The depending of the stereoselectivity on the temperature shows that the reaction is not kinetically controlled because in case of kinetically controlled reactions the decreasing of the temperature raises the stereoselectivity.

It is possible to suggest the formation of complexes of phosphorus chlorides with organic base of type **C**, having an ammonium structure.[18] Complexes of this type are formed, in particular, with chlorides of carboxylic acids and also phosgene with pyridine or triethylamine.[18a,b] The role and influence of these complexes on kinetics and mechanism of nucleophilic substitution reactions at the carbonyl sp^2-carbon atom have been investigated.[18a]

Complex **C** reacts with amine to give the intermediate **D**. Pseudorotation of the latter, **C** $\rightleftharpoons$ **E**, and subsequent deprotonation determine the diastereomeric ratio of reaction product **3**.

We have observed the formation of the complex having **probably** the structure of the type **C** by ^{31}P NMR during the reaction of *tert*-butylphenylchlorophosphine with DBU. Mixing of *tert*-butylphenylchlorophosphine with DBU in diethyl ether at low temperature led to the formation of a colorless, salt-like product precipitating from the solution as a voluminous solid (Scheme 4). The formation of the adduct was followed by ^{31}P NMR. The $\delta(^{31}P)$ value of *tert*-butylphenylchlorophosphine (108 ppm) changed to lower field (165.86 ppm). In one spectrum both signals were seen, δ_P 108 ppm, and 165.86 ppm, when an equimolar quantity of DBU was added. Further treatment of the reaction mixture with 1-methylphenylamine furnished the aminophosphine **3a**.



SCHEME 4

The effect of various factors on the stereochemical course of the reaction suggests an equilibrium competition between the formation of a pentacoordinate intermediate and its deprotonation. Therefore, an increase of the strength and concentration of the organic bases results in deprotonation before an equilibrium is established. This explains the decrease in stereoselectivity at low temperature (Entries 9 and 17; Table I). A decrease in temperature slows down the ligand pseudorotation, therefore the pentacoordinate intermediate is deprotonated before equilibrium is attained. It is quite possible that some degree of asymmetric induction is achieved in the first step of the reaction during the nucleophilic attack of the amine on the chlorophosphine, because a small but distinct increase of asymmetric induction is observed when the amount of chlorophosphine in the reaction mixture increases (Entries 1–3, 9–11; Table I).

Diastereomeric mixtures of the aminophosphine **3** were obtained and then purified via their borane complexes.[17–20] The diastereomerically pure phosphine-borane complex **4** was prepared in one step from the aminophosphine **3** and the borane-tetrahydrofuran complex. The reaction of aminophosphines **3** with borane proceeded readily in tetrahydrofuran to give, in almost quantitative yield, stable crystalline complexes **4**. The complexes **4** were then additionally purified by crystallization from hexane. The ^{1}H and ^{31}P NMR investigation of the borane complexes **4** indicated the formation of only one diastereomer.

The structure and stereochemical purity of the borane complexes was confirmed by ^{1}H, ^{13}C NMR, and ^{31}P spectroscopy. The δ_P value of the borane complex is observed at +70 ppm as a broad doublet, due to

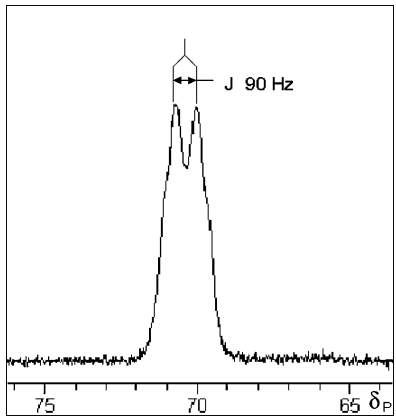
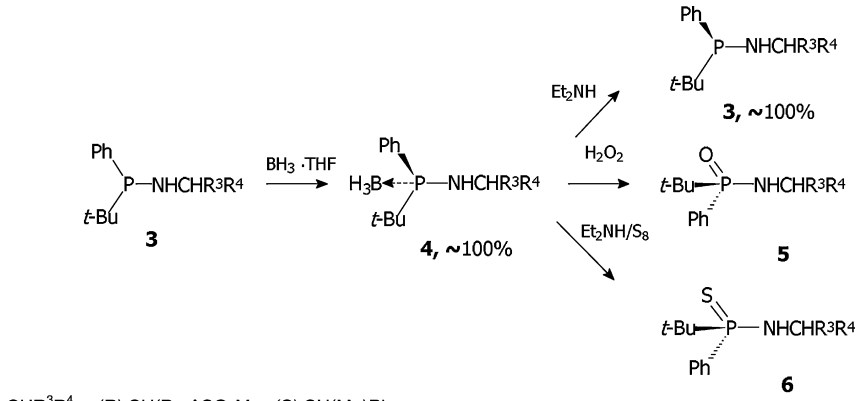


FIGURE 3 The ^{31}P NMR spectra of the borane complex **4a**.

spin-spin coupling, ^{31}P-{^{9}B} (Figure 3). The ^{1}H and ^{13}C spectra show the signals of all hydrogen and carbon atoms in the molecule, without any doubling caused through the presence of diastereomers.

Borane complexes of aminophosphines **4** are useful initial compounds for preparation of stereochemically pure chiral reagents (Scheme 5).

The treatment of **4** with diethylamine furnished the initial aminophosphine **2** in 100% stereochemical purity. The BH_3-part of the phosphine-borane complex was removed on treatment with a large excess of an amine such as diethylamine. This reaction has been proved to proceed in a stereospecific manner with retention of configuration.[9]



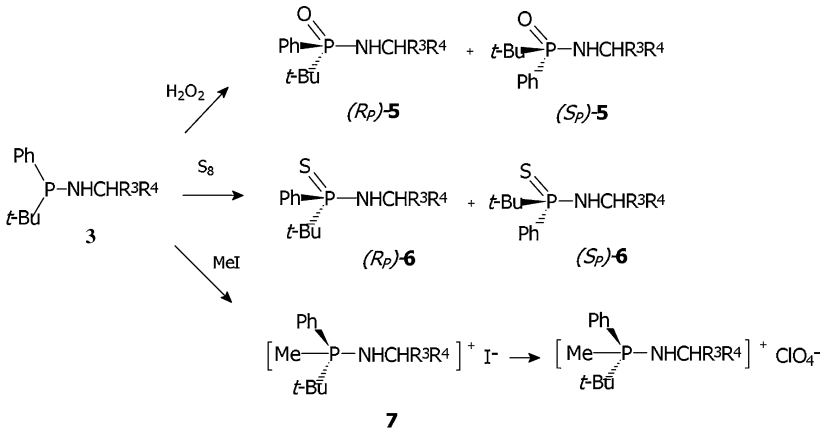
CHR^3R^4 = *(R)*-CH(Bu-*i*)CO_2Me, *(S)*-CH(Me)Ph

SCHEME 5

The identity of the purified (R_P,S)-diastereomer **3a**, and the major diastereomer of the initial diastereomeric mixture of the aminophosphine (R_P,S)-**3a** and (S_P,S)-**3a** was confirmed by ^{31}P NMR spectra of the mixture of these two products. The reaction proceeds slowly, and is completed only on heating of the complex in a solution of diethylamine at 50°C over a period of 16 h.

The oxidation of compounds **4** with hydrogen peroxide in a dioxane proceeds stereospecifically and gives aminophosphine oxides **5** with very good yields and purity. The treatment of **4** with diethylamine and sulfur in a toluene gives aminophosphine sulfides **5** with very good yields and 100% stereochemical purity.

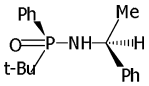
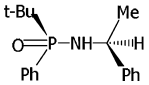
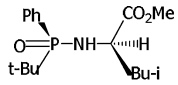
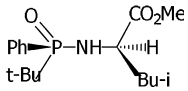
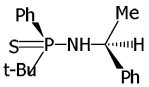
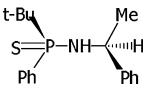
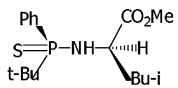
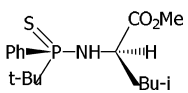
At the same time the analogous reaction of diastereomeric mixtures of aminophosphines **3** provide the compounds **5** and **6** as diastereomeric mixtures (Scheme 6). The (S_P,S)- and (R_P,S)-diastereomers of the aminophosphine oxides **5** are easily identified through their ^{31}P NMR spectra and HPLC.



SCHEME 6

The major (S_PS)-aminophosphine oxides have a longer retention time than the (R_P,S)-isomers presented to a smaller proportion. No significant difference between the diastereomeric ratio of the compounds, as estimated by ^{31}P NMR and HPLC, was noted. The diastereomers of compound **5** were separated by flash-chromatography. A 50 cm column filled with silica gel was used; a mixture of isopropanol-hexane in a 92:8 ratio served as an eluent. The chromatographic fractions were analyzed by HPLC. Under these conditions we were able to completely separate

TABLE II Diastereomeric Pairs of Aminophosphine Derivatives **5,6**

Compd.	Formule	Mp	$[\alpha]_D^{20}$	δ_P
(*S,S*)-**5a**		171–172°C	−82.5 (ethanol)	41.32
(*R,S*)-**5a**		142–144	−125.5 (ethanol)	42.86
(+)-**5c**		140–141	+6	46.91
(−)-**5c**		128	−68.2	46.90
(*S,S*)-**6a**		106–06	−66	78.10
(*R,S*)-**6a**		Oil	—	80.74
(+)-**6c**		62–62.5	+81	80.82
(−)-**6c**		Oil	—	81.4

the diastereomers and obtain them in a pure state. Some physical and chemical data of the diastereomerically pure compounds **5,6** are shown in the Table II.

The subsequent recrystallization allowed us to obtain the diastereomers of compound 4 with ca ∼100% stereochemical purity. The purity of these compounds was confirmed by ^{31}P and ^{1}H NMR spectroscopy.

The signals of the *tert*-butyl and methyl groups (of MeOCO) were observed in the spectra without any doubling, confirming the high purity of the compounds.

The synthesis of the 1-phenylethylamide of *tert*-butylphenylphosphinic acid as a mixture of diastereomers was described.[21] However, this compound was not purified, its diastereomers were not separated and the stereochemical properties were not studied. Therefore, the physical and chemical data of 1-phenylethylamino-*tert*-butylphenylphosphine

oxide described in Kolodiazhnyi[24] differ strongly from those of the stereomerically pure compound 4, prepared in the present work.

Since the 1-phenylethylamine used in the synthesis had the (*S*)-configuration, the configuration at phosphorus in this major diastereomer **5** is *S*. Accordingly, the other (minor) diastereomer must have the (S_C,R_P)-configuration.

The thionation of the diastereomeric mixture of **3** proceeds with change of the diastereomeric ratio to give, mainly the (*S*,*S*)-diastereomer **6**. The diastereomers of the phosphine sulfide **6** were observed through HPLC and NMR spectroscopy. The pure major diastereomer **5** was isolated by crystallization from hexane as a colorless stable solid (needles) in ~100% diastereoisomeric purity. The minor diastereomer of (*R*,*S*)-(−)-**5** was isolated as a colorless viscous liquid containing about 20% of (*R*,*S*)-diastereomer which could not be separated either by crystallization or by column chromatography. The aminophophines **3** are easily alkylated by methyl iodide with formation of the phosphonium salts 7.

The absolute configuration of the compounds was established by chemical methods. The amino group of the compound (S_P,*S*)-(+)-**5b** was replaced by a methoxy group at the reflux in methanol containing sulfuric acid for 5 h. In result the methyl ether (*R*)-(−)-phenyl(mesityl)-phosphinic acids (ee 75%) which has been earlier described[15] is formed. The sign of optical rotation allows us to define a configuration of phosphorus atom in the initial amide which, obviously, should be S_P because S_N2 replacement proceeds with the inversion of the configuration.[11] The given reactions proceed stereospecifically according to the S_N2 mechanism with the inversion of the configuration at the phosphorus atom.[11]

The compound (R_P,*S*)-(+)-**3a** was hydrolyzed by formic acid with the formation of (*S*)-(−)-tert-butylphenylphosphine oxide, which has been earlier described.[22,23] The (*S*)-configuration of the hydrolysis product was confirmed by its negative optical rotation.[24]

The compound (S_P,*S*)-(−)-**5a** is stable to hydrolysis and is not hydrolyzed even at reflux during 48 h in aqueous dioxane, containing sulfuric acid. It was not possible to effect the methanolysis of (S_P,*S*)-(−)-**5a**. The compound was unchanged during 48 h reflux in methanol, containing 5% of sulfuric acid.

EXPERIMENTAL

Melting points are uncorrected. The NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 (^{1}H), 60 (^{13}C) and 126.16 MHz (^{31}P). ^{1}H and ^{13}C 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), ethyl acetate (over $CaCl_2$).

HPLC separations were carried out on the instruments Milichrom-1A (Russia) and LKB (Sweden) with Ultrapack TSK ODS 120 T 5 um 250 × 4.6 mm column (65–75% aqueous methanol as eluent); Silasorb DEA column 120 × 2 mm (hexane-isopropanol mixture in a 95:5 ratio as eluent); Silasorb C_{18} 120 × 2 mm column (50% aqueous acetonitrile as eluent); UV detector, λ 260 nm.

Column chromatography was performed using silica gel 60 (Fluka).

Optical rotations of the compounds were determined on a Perkin-Elmer Model 241 spectropolarimeter. Solvents were purified by standard methods. Optically active reagents, (−)-(*S*)- and (+)-(*R*)-1-phenylethylamines, were obtained from Fluka, and were used without special purification.

N-(1-Phenylethyl)amino-*tert*-butylphenylphosphine (3a)

To a solution of 4.5 g (0.025 mmol) of *tert.*-butylphenylchlorophosphine in 10 ml of benzene was added slowly with stirring over 3 h a solution of 0.025 mol of (*S*)-*N*-(1-methylbenzyl)amine and 0.026 mmol of triethylamine in 10 ml of benzene. The solution was stirred for 2–3 h at room temperature. Then, the reaction mixture was allowed to stand at room temperature overnight. The precipitate of triethylamine hydrochloride was filtered off and washed with 50 ml of diethyl ether. The filtrate was evaporated under reduced pressure; the residue was distilled in vacuo. The product was obtained as a colorless liquid. The reaction was performed under different conditions. Depending on the nature of the tertiary base and the solvent different ratios of diastereomers were obtained (see Table I).

b.p. 140°C (0.01 mmHg). Yield: 80%.

Anal. Calcd for $C_{18}H_{24}NP$: N 4.91; P 10.85. Found: N 4.85; P 10.91.

^1H NMR, δ, ppm, ($CDCl_3$): 0.77 d [$^3J_{HP}$ 5.0, $(CH)_3C$]; 0.81 d [$^3J_{HP}$ 7.0, $(CH)_3C'$]; 1.60 m (CH); 1.45 d [$^3J_{HH}$ 14.0, (CH_3)]; 1.51 d [$^3J_{HH}$ 14.0, (CH_3')]; 3.54 m (NH); 7.10–7.33 m (C_6H_5). ^{31}P NMR ($CDCl_3$), δ_P: 49.9; 47.24.

N-(1-Phenylethyl)amino-phenymesitylphosphine (3b)

The product was prepared analogously to compound **3a**. Yield 85%. The product was prepared in spectroscopically pure state and used

for further conversions without special purification. ^{31}P NMR, δ, ppm ($CDCl_3$), δ_P: 29.75; 29.23.

N-(l-carbomethoxy-3-methyl)butylamino-*tert*-butylphenylphosphine (3c)

To a solution of 9 g (0.05 mmol) of *tert*-butyl-phenylchlorophosphine and 10 g (0.1 mmol) of triethylamine in 100 ml of benzene cooled in an ice-bath was added with stirring 7.2 g (0.05 mmol) of L-Leucine methyl ester. The solution was stirred for 30 min at room temperature and then the reaction mixture was left overnight. The precipitate of triethylamine hydrochloride was filtered off and washed with 100 ml of ether. The filtrate was evaporated and the residue was distilled under reduced pressure.

Yield 10.85 g (70%), b.p. 148–150°C (0.04 mm Hg). Colorless oil.
Anal. Calcd. for $C_{17}H_{28}NO_2P$: P 10.01. Found: P 9.81.
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H: 0.78 m [$(CH_3)C$]; 0.85 d [J_{HH} 10 $(CH_3)_3C$]; 0.87 d [J_{HH} 10.0 $(CH_3)_3C'$]; 1.52 m (CH_2); 1.82, spt (CH); 2.21 dd (J_{HH} 11.0, J_{HP} 11.0, NH); 3.34 s (CH_3O); 3.66 s (CH_3O); 3.60 m (CHN); 7.26 m; 7.86 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P: 56.98.

N-(l-carbomethoxy-2-methyl)propylamino-*tert*-butylphenylphosphine (3d)

The product was prepared analogously to compound **3a**. Yield 80%, b.p. 120–125°C (0 04 mm Hg). Colorless oil. ^{1}H NMR, δ, ppm, J, Hz, ($CDCl_3$): δ_H 0.8 dd [$(CH_3)2C$], 0 9 d [J_{HH} 10 $(CH_3)_3C$], 1 52 m (CH_2); 1.9, spt (CH), 3 2 m (NH), 3 15 s (CH_3O); 3 8 m (CHN), 7 26 m; 7 86; m (C_6H_s). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 56.96; 57.69.

Borane Complex of the (S_P)-*N*-(1-phenylethyl) amino-*tert*-butylphenylphosphine (4a)

To an (*S,S*)+(*R,S*)-diastereomeric mixture of *N*-(1-phenylethyl)amino-*tert*-butyl-phenylphosphine **3a** (0.1 mmol) in 5 ml THF a solution of 0.12 mmol of borane in THF was added dropwise with stirring. Then, the reaction mixture was allowed to stand at room temperature. After 6 h the solvent was removed in vacuo and the crystalline complex 3 was obtained in satisfactory purity for further synthetic applications. Complex 3 could be purified additionally by recrystallization from hexane or by filtration through a short column over silica gel with hexane-ethyl acetate as eluent.

m.p.140–141°C (hexane). Yield: 80%; $[\alpha]_D^{20} = +24.5$ (c 1, CH_2Cl_2).
Anal. Calcd. for $C_{18}H_{27}BNP$: P 10.35. Found: P 10.46.
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): 0.2-2, m (BH_3); 1.01 d [$^3J_{HP}$ 14.16, $(CH_3)_3C$]; 1.50 d [$^3J_{HH}$ 6.72, (CH_3)]; 2.07 br.d [$^2J_{HP}$16.0, (NH)]; 4.45 m (CHN); 7.10–7.40 m (C_6H_5). ^{13}C NMR, δ, ppm ($CDCl_3$): 24.57 d [$^2J_{CP}$ 2.76, ($\underline{CH_3}$)$_3$C]; 25.57 d [$^3J_{CP}$ 5.20 ($\underline{CH_3}$)CHN]; 30.69 d [$^1J_{CP}$ 43.40, $(CH_3)_3\underline{C}$]; 52.47 d [$^2J_{CP}$ 2.01, ($\underline{CH}$N)]; 126.10 s; 126.94 s; 127.58 d J_{CP} 9.50; 130.37 d J_{CP} 2.50; 130.75 d J_{CP} 46.80; 131.94 d J_{CP} 9.40 (C_6H_5).^{31}P NMR, δ, ppm ($CDCl_3$): 69.76 br, d [$^1J_{BP}$ 90 Hz].

Borane Complex of the *N*-(l-Carbomethoxy-3-methyl)-butylamino-*tert*-butyl-phenylphosphine (4c)

The product was prepared analogously to compound **4a**.

Yield: 75%; m.p. 93°C (hexane). $[\alpha]_D^{20} = +91$ (c 1, hexane).
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): 0.2–2, m (BH_3); 0.83 d $^3J_{HH}$ 6.6, 0.86, d$^3J_{HH}$ 6.6 [$(CH_3)_2$C]; 0.98 d [$^3J_{HP}$ 14.3, $(CH_3)_3$C]; 1.492 t [$^3J_{HH}$ 6.6, (CH_2)]; 2.6 br.d [$^2J_{HP}$ 10.0, (NH)]; 3.4 s (OCH_3); 3.98 m (NHC$\underline{H}$) 7.20–7.60 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): 71.5 br. d [$^1J_{BP}$ 90 Hz].

Decomplexation of Borane Complex (4a).(*S*$_P$,*S*)-*N*-(1-Phenylethyl)amino-*tert*-butyl-phenylphosphine (3a)

A solution of 3 g (0.01 mmol) of complex **4a** in 10 ml of degassed diethylamine was kept under argon at +50°C for 16 h. Then, excess diethylamine was removed in vacuo to leave the optically pure aminophosphine **3a**. The ^{31}P NMR spectrum showed only one signal, due to the *(SR)*-diastereomer (confirmed by mixed testing with an authentic diastereomer).

Yield: 50%. bp. 160–161°C (0.02 mm Hg). $[\alpha]_D^{20}$ +120 (0.3, toluene).
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): 0.81 d [$^3J_{HP}$ 7.0, CH_3C]; 1.60 m (NH); 1.45 d [$^3J_{HH}$ 14.0, $(CH_3)_3$C]; 3.54 m (CHN); 7.10–7.33 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): 49.00.

N-(1-Phenylethyl)amino-*tert*-butylphenylphosphine Oxide (5a)

(a) To a solution of the borane complex **4a** in dioxane an equimolar quantity of hydrogen peroxide was added with cooling. After the temperature was raised to room temperature, the reaction mixture was allowed to stand for 6 h. The solvent was evaporated, and the residue was obtained as a solid to which heptane was added, and which was left

to crystallize. Then the crystalline product was filtered off to provide the pure diastereomer *(Sp,S)*-**5a**.

(Sp,S)-diastereomer. m.p. 171–172°C (heptane). Yield 80%. $[\alpha]_D^{20}$-82.5 (c 0.5, ethanol).

(b) To a solution of the aminophosphine **3a** in dioxane an equimolar quantity of hydrogen peroxide was added with cooling. After the temperature was raised to room temperature, the reaction mixture was allowed to stand for 0.5 h. The solvent was evaporated, and the residue was obtained as a viscous liquid to which hexane was added, and which was left to crystallize. The next day the crystalline product was filtered off and was recrystallized from ethyl acetate. The mother liquor was evaporated. The residue, enriched in the minor diastereomer, was separated by column chromatography (SiO_2; 92: 8 hexane-isopropanol as eluent).

(Sp,S)-diastereomer. m.p.171–172°C (from ethyl acetate). Yield 75%. $[\alpha]_D^{20}$-82.5 (c 0.5, ethanol).

Anal. Calcd. for $C_{18}H_{24}NOP$. N 4.65; **P** 10.28. Found: %: N 4.67; P 10.42.
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H 1.01, d J_{HH} 14.8 [$(CH_3)_3C$]; 1.33 d, J_{HP} 7.0 (CH_3); 2.80 br (NH); 4.44 br J_{HH} 8 (CH); 7.19–7.4 m; 7.87 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 41.32.

(Rp,S)-diastereomer. M.p. 142–144°C (heptane). $[\alpha]_D$ −125.5 (c 0.5, ethanol). Yield 5%.

Anal. Calcd. for $C_{18}H_{24}NOP$: N 4.65; P 10.28. Found: N 4.65; P 10.32.
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H 1.04 d J_{HP} 14.4 [$(CH_3)_3C$]; 1.48 d J_{HH} 7.4 (CH_3C); 2.76 dd J 7 (NH); 4.17 m (CH); 7.13–7.57 (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 42.86.

(*S,S*$_P$)-1-Phenylethylamino-mesitylphenylphosphine Oxide (5b)

The product was prepared analogously to compound **5a**.

Yield 50%. $[\alpha]_D^{20}$ +10 (c 1, ethanol), m.p. 157°C (ethyl acetate). ^{1}H NMR ($CDCl_3$), δ, ppm (J, Hz): 1.67 d, (3H, PhCHMe, J_{HH} 7); 2.29 c (3H, 4-Me); 2.38 s (6H, 2- ;4-Me), 3.00 m (1H, NH,J_{HH} 9.0, J_{PH} 9.0); 4.5 m (1H, PhCHMe); 6.9 d (2H, 3-,5-H, J_{PH} 4.0); 7.2–7.4 m (5H, C_6H_5); 7.35 m (5H, C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 28.0.[14]

N-(l-Carbomethoxy-3-methyl)butylamino-*tert*-butylphenylphosphine Oxide (5c)

The product was prepared analogously to compound **5a**. The column chromatography (silica gel L 100/160) of crude product using

hexane-isopropanol (95:5) as eluent yielded two fractions of two diastereoisomers in the following order:

(+)-Diastereomer. Yield 0.3 g (10%), m.p. 140–141.5°C (heptane), colorless needles, $[\alpha]_D^{20}$+ 6° (c = 2.5, C_2H_5OH).
Anal. calcd. for $C_{17}H_{28}NO_3P$: N 4.30; P 9.52. Found N 4.38; P 9.61.
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H: 0.70 d [J_{HH} 6.5, $(CH_3)_2C$]; 0.79 d [J_{HH} 6.5, $(CH_3)_2C$]; 1.10 d [J_{HH} 15.0, $(CH_3)_3C$]; 1.47 m (J_{HH} 6.3, CHO; 1.64 m (CH); 3.24 dd (J_{HH} 11, J_{HP} 11, NH); 3.71 s (CH_3O); 3.8 m (CHN); 7.46 m; 7.79 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 46.91.
(−)-Diastereomer. Yield 2.0 g (61%), m.p. 128°C (hexane), colorless prismatic crystals, $[\alpha]_D^{20}$ −68.42° (c = 1, C_2H_5OH). IR (liquid, ν,cm^{-1}): 1180 (P=O); 1720 (C=O); 3400 (NH).
Anal. calcd. for $C_{17}H_{28}NO_3P$: N 4.30; P 9.52. Found N 4.35; P 9.58.
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H: 0.87 d [J_{HH} 6.3, $(CH_3)_2C$]; 0.89 d [J_{HH} 6.3, $(CH_3)_2C'$]; 1.09 d [J_{HH} 15.0, $(CH_3)_3C$]; 1.58 m (CH,); 1.806 spt (CH); 3.19 dd (J_{HH} 11, J_{HP} 11, NH); 3.558 s (CH_3O); 3.79 m (CHN); 7.247 m; 7.696 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 46.9.

Alcoholysis of (+)-(S_P,S)-*N*-(1-Phenylethyl)amino (phenyl)mesitylphosphine Oxide (5b)

The mixture of 18.2 mmol (+)-(S_P,S)-*N*-(1-phenylethyl)amino(phenyl)-mesitylphosphine oxide (**5b**) ethanol and 1.6 ml of 98% sulfuric acid was refluxed for 5 h. The reaction mixture was cooled, and 200 ml of chloroform was added. The mixture was washed with 10% solution of sodium bicarbonate (3 × 50 ml) and water (2 × 50 ml). The organic part was treated with magnesium sulfate and concentrated under vacuum. The residue was purified by flesh-chromatography. The methyl (*R*)-(−)-methyl-(2,4,6-trimethylmethyl)phosphinate was obtained as a colorless liquid.

Yield 4.0 g (80%); $[\alpha]_D^{20}$ -20 (c 1, ethanol).[15]
^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): 2.3 c (3H, 4-CH_3), 2.50 d (6 H, 2-, 6-CH_3, J_{PH} 1.2), 3.70 d (3 H, OCH_3, J_{PH} 11.1), 6.90 d (2 H, 3-, 5-H, J_{PH} 4.2), 7.5 m (3 H, C_6H_5), 7.60 m (2 H, C_6H_5); ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 37.0 ppm.

1-Phenylethylamino-*tert*-butylphenylphosphine Sulphide (6a)

(a) A solution of the borane complex **4a** in diethylamine was kept under argon at +50°C for 16 h. Then, excess diethylamine was removed in vacuo, the rest was dissolved in benzene and an equimolar quantity of

sulfur was added. The reaction mixture was allowed to stand for 6 h. The residue was diluted with hexane and left to crystallize. Next day a crystalline product was filtered off, and was recrystallized from ethyl acetate to provide the pure diastereomer (S_P,S)-**6a**.

(S_P,S)-*Diastereomer*. Yield 70%, m.p. 105–106°C (hexane). $[\alpha]_D^{20}$-66 (c = 2.5, ethanol).

(b) To a solution of the aminophosphine **3a** in benzene cooled to 0 to +5°C was added a 10% excess of sulfur, dissolved in benzene. The temperature was raised to room temperature, and the reaction mixture was allowed to stand for 1 h. The residue was obtained as a viscous liquid which was diluted with hexane and left to crystallize. Next day a crystalline product was filtered off, and was recrystallized from ethyl acetate. The mother liquor was evaporated and then chromatographed on a silica gel column, using a mixture of hexane-isopropanol (92 : 8 ratio) as eluent.

(S_P,S)-*Diastereomer*. Yield 50%, m.p. 105–106°C (hexane). $[\alpha]_D^{20}$-66 (c = 2.5, ethanol).

^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H 1.15, d J_{HP} 16.2 [$(CH_3)_3C$]; 1.5 d J_{HH} 6, 6 (CH_3); 2.3 br (NH); 4.4 dq J_{HH} 6.6 J_{HP} 8 (CHN); 7.2 m; 7.93 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 78.10.

(R_P,S)-*Diastereomer*. Yield 8%. Anal. calcd. for $C_{18}H_{24}NPS$: N 4.41; P 9.76. Found: N 4.45; P 9.62.

^{1}H NMR, δ, ppm; J, Hz ($CDCl_3$): δ_H: 0.98 d [J_{HP} 16.6 $(CH_3)_3C$]; 1.21 d [J_{HH} 6.0 CH_3]; 2.21 m (NH); 4.41 dd.[J_{HH} 6.0, J_{HP} 6.0 (CH); 7.2 m; 7.93 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 80.74.

N-(l-Carbomethoxy-l-methyl)butylamid-*tert*-butylphenylphosphine Sulphide (6c)

To a solution of 3.1 g (0.01 mmol) of aminophosphine **3c** in 5 ml of benzene was added 0.5 g (0.0155 mmol) of sulfur. The reaction mixture was allowed to stand for 12 h at room temperature, then the solvent was evaporated and the residue dissolved in hexane. The excess of sulfur was filtered off and the hexane was evaporated. The ^{31}P NMR spectrum indicated that the product was a 75:25 mixture of diastereomers. The crude product was then chromatographed over a column of a silica gel L 100/160 with hexane-ethylacetate (3:1) as eluent yielding two fractions of two diastereomers. The first fraction after the evaporation of a solvent was dissolved in hexane and kept in a refrigerator for 48 h at −20°C. A colorless crystalline solid of the major diastereomer was separated and dried in vacuum.

Yield 2.0 (59%), m.p. 62–62.5°C, $[\alpha]_D^{20}$ +8.1 (C = 1, CH_3OH).
^{1}H NMR, δ, ppm; *J*, Hz ($CDCl_3$): δ_H: 0.83 d [J_{HH} 6.3 $(CH_3)_2C$]; 0.92 d [J_{HH} 6.3 $(CH_3)_2C'$]; 1.08 d [J_{HH} 16.8, $(CH_3)_3C$]; 1.61 m (CH,); 1.70 spt (CH); 3.0 dd (J_{HH} 11.0, J_{HP} 11.0, NH); 3.48 s (CH_3O); 4.12 m (CHN); 7.37 m; 7.78 m (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P: 80.82.

The minor diastereomer was obtained as colorless oil, containing trace of the first diastereoisomer: Yield 0.4 g (12%).

Anal. Calcd. for the $C_{17}H_{28}NO_2PS$: N 4.10; P 9.07; S 9.37. Found N 4.12; P 9.29; S 9.55.
^{1}H NMR, δ, ppm; *J*, Hz ($CDCl_3$): δ_H: 0.69 d [/$_{HH}$ 6.3, $(CH_3)_2C$]; 0.76 d [J_{HH} 6.3 $(CH_3)_2C''$]; 1.09 d [J_{HH} 17.0, $(CH_3)_3C$]; 1.45 m (CH,); 1.70 spt (CH); 3.01 dd (J_{HH} 11. J_{HP} 11, NH); 3.48 s (CH_3O); 4.12 m (CHN); 7.37 m; 7.92 m (C_6H,). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P: 81.4.

(*R*$_P$,*S*)-(1-Phenylethyl)amino-*tert*-butyl-phenyl-methylphosphonium Iodide (7)

To a solution of (1-phenylethyl)amino-*tert*-butyl-phenylphosphine **3a** (2.8 g; 0.01 mmol) in toluene (10 ml) excess methyl iodide (1.8 g; 0.0125 mmol) was added, and the reaction mixture was allowed to stand overnight. After 20 h the precipitate was separated and purified by crystallization.

Yield: 84%, m.p. 220–221°C; $[\alpha]_D^{20}$ -57.3 (c 2.5, C_2H_5OH).
Anal. Calcd. for $C_{19}H_{27}INP$: N 3.28; P 7.25. Found: N 3.29; P 7.45.
^{1}H NMR, δ, ppm; *J*, Hz ($CDCl_3$): δ_H: 1.21 d $(CH_3)_3C$, J_{HH} 16); 1.51d *J* 6.5 (CH_3); 2.45 d *J* 11.5 (CH_3P); 4.11 br (CH); 6.14 br (NH), 7.30 (C_6H_5). ^{31}P NMR, δ, ppm; ($CDCl_3$): δ_P 55.8.

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