Tetrahedron Vol 45, No. 14, pp 4403 to 4414, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00

OPTICALLY ACTIVE SILYL ESTERS OF PHOSPHORUS. II. STEREOCHEMISTRY OF REACTIONS WITH NUCLEOPHILES

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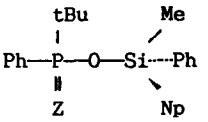
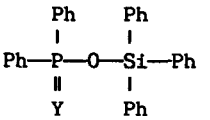
(*Received in Belgium* 24 *April* 1989)

Abstract : We report the stereochemistry of reactions of various nucleophiles with optically active silyl esters of phosphorus of general formula : tBuPhP(X)OSiMePhNp (X = -(1), Oxygen (2), Sulfur (3), Selenium (4). The list of nucleophiles includes O,S,N,C nucleophiles as well as halides. The nucleophilic attack is essentially directed towards silicon. The phosphinous and phosphonic acid esters react with predominant retention of configuration at silicon atom, whereas the thiono and seleno phosphinic analogues give inversion at silicon centre. The stereochemical crossover is explained in terms of possible interaction of the electrophilic part of the nucleophile with the oxyphosphoryl group or tricoordinate phosphorus.

Introduction

Recently, we reported the synthesis of new optically active silyl esters of phosphorus, of general formula t-BuPhP(Z)OSiMePhNp in which both the phosphorus and silicon atoms are chiral centres.[1] The absolute configurations of these esters were assigned. In continuation of that work, we now report results on the stereochemistry of some substitution reactions at the silicon centre of these esters with selected nucleophiles. Silyl esters of phosphorus have been widely used as reactive intermediates in organic reactions, as well as in bioorganic chemistry.[2,3] For example, silyl phosphates and phosphonates undergo facile hydrolysis or alcoholysis.[4,5] They have found wide application as precursors of phosphorus derivatives.[6,10] Their high reactivity towards nucleophiles might be an indication that phosphorus plays some specific role in the substitution at silicon.





Z = :(1) O(2) S(3) Se(4) Y = O(5) S(6)

We hoped that stereochemical studies would give information for the elucidation of this role, and would contribute to a better understanding of processes involving silyl esters of phosphorus.

Reaction of silyl esters of phosphorus acids with nucleophiles

Silyl esters have several potential centers for nucleophilic attack and, a priori, could give a number of products when subjected to the action of nucleophiles. Besides the esters used for stereochemical studies, triphenylsilyl esters of diphenylphosphonic acid 5 and diphenylthiophosphinic acid 6 were used. Nucleophilic reagents include simple oxygen nucleophiles (H_2O, alcohols), sulfur nucleophiles (thiols, thiolates), nitrogen nucleophiles (amines, silazanes) carbon nucleophiles (BuLi and RMgX), halides, and some acid anions.
Reactions in various solvents were followed by ^{31}P n.m.r.spectroscopy (Table 1). The following general observations were made :

Table 1 : Result of reactions of 5 and 6 with nucleophiles[a]

Nuc./solv.	Products of 5 (yield[b])	products of 6 (yield[b])
H_2O/acetone	$Ph_2P(O)OH$ (100%) δ=29 ppm	$Ph_2P(S)OH$ (40%) δ=69 ppm
EtOH/CH_2Cl_2	$Ph_2P(O)OH$ (50%) δ=29 ppm	no reaction
EtSH/CH_2Cl_2	$Ph_2P(O)OH$ (50%)	no reaction
EtSNa/THF	$Ph_2P(O)ONa$ (70%) δ=24.5 ppm	$Ph_2(S)ONa$ (50%) after 5 hrs δ=57 ppm
Et_3SiSH/C_6H_6	$Ph_2P(O)OSiEt_3$ (40% after 24 hrs) δ=20.4 ppm	no reaction
	$Ph_2P(O)OH$ (10%)	
Ph_3SiSH/C_6H_6	$Ph_2P(O)OH$ (30% after 24 hrs) δ=20 ppm	no reaction after 24 hrs
$(Me_3Si)_2NH/C_6H_6$	$Ph_2(O)OSiMe_3$ (40% after 24 hrs) δ=30 ppm	no reaction after 24 hrs
BuLi/THF[c]	$Ph_2P(O)OLi$ (80% after 10 mn) δ=30 ppm	
	unidentified product (20%) δ+30 ppm	$Ph_2P(S)OLi$
BuLi/toluene[c]	$Ph_2P(O)OLi$ (8% after 30 mn)	
	unidentified products resulting from attack on P or lithiation of Ph δ = 33 ppm (54%) δ = 41 ppm (23%) δ = 46 ppm (15%)	

a) Reactions were carried out as described in the experimental part. N.M.R. spectra were taken after 2 hrs unless stated otherwise. δ is ^{31}P N.M.R.chemical shift in ppm relative to H_3PO_4.
b) The remaining part is unreacted substrate.
c) Reaction was carried out at -40°C.

1. In most cases, nucleophilic attack only occurs at the silicon atom. Only the reaction of BuLi with 5 carried out in THF at -40°C showed some contribution from substitution at phosphorus. However the same reaction with 2, having the bulky t-butyl group attached to phosphorus, led to exclusive substitution at silicon. The reaction of 5 with BuLi in hydrocarbons leads to considerable amounts of products substituted in the phenyl group.
2. In almost all cases, oxyphosphoryl derivatives react much faster than the corresponding thiophosphoryl compounds. Reactions of 6 at ambient temperature in benzene with several nucleophiles, including EtOH, EtSH, EtSNa and $(Me_3Si)_2NH$ do not proceed at detectable rate.
3. Selenophosphoryl ester 4 reacts in a similar way to its thiophosphoryl analogue 3.
4. In all cases studied, the corresponding ester of tricoordinate phosphorus 1, reacted via attack at the silicon atom; however, fast consecutive reactions were very often observed leading to other products including those of substitution at phosphorus.

Stereochemical results

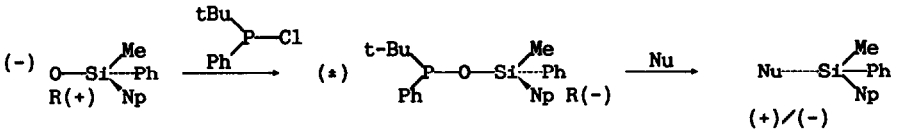
Stereochemical studies of the reactions of the silyl esters were performed with compounds of known absolute configuration at the silicon atom in both the reactant [1] and the product[11]. In all the reactions studied, a 50/50 mixture of diastereoisomers with regard to the phosphorus centre was used. That means that the optical activity was due only to the silicon part of the molecule. All our models showed distinct diastereomeric shifts in the ^{31}P n.m.r spectra for the RS-SR and RR-SS isomer pairs, and it was thus possible to determine the relative rate of reaction of an R_PS_{Si} diastereomer compared to that of an S_PS_{Si} diastereomer (and similarly the relative rate for the S_PR_{Si}/R_PR_{Si} pair). In no case did we find a significant difference in rate as a consequence of the chirality at phosphorus.

Nucleophiles were selected to study the stereochemistry of the following processes : hydrolysis, alcoholysis, reduction, and alkyl substitution with organometallic reagents. All nucleophiles exclusively reacted via nucleophilic attack at silicon. The stereochemical outcome of the process was usually established by several independent experiments, performed in our two laboratories. Since most of the substrates are optically unstable, the optically active esters 1-4 were prepared shortly before the stereochemical studies. The results clearly show the general stereochemical trend, but the reported enantiomeric excesses (e.e) are only approximate.

Reactions of tBuPhPOSiMePhNp (1)

Reactions of both optically active isomers of 1 with nucleophiles are presented in the Table 2. In all cases but two, reactions are stereoselective leading to predominant retention of configuration at silicon. We made the reasonable expectation that for a given reaction, both diastereoisomers (+)P(+)Si/(-)P(+)Si on one hand and (+)P(-)Si/(-)P(-)Si on the other hand react at similar rates.

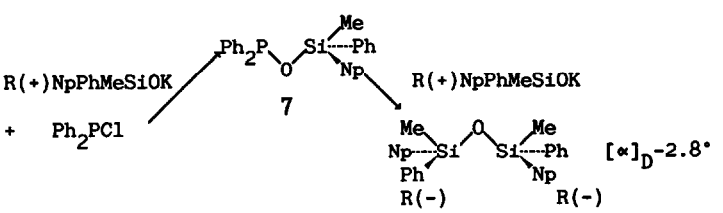
Table 2 : Stereochemistry of the coupling reaction of 1 with nucleophiles.



Substrate	Nucleophile	Product (e.e)[a]	Solvent	Predominant stereochemistry
S(+)≡Si-O-P⟨(±) (+) 1	H_2O(dioxane)	(+) SiOH (23%)	THF-xylene	RETENTION
	MeOH	(+) SiOMe (67%)	THF-xylene	RETENTION
	$LiAlH_4$	(+) SiH (86%)	THF-xylene	RETENTION
R(-)≡Si-O-P⟨(±) (-) 1	MeOH	(-) SiOMe (66%)	THF-Xylene	RETENTION
	PhOH	(-) SiOPh (68%)	THF-xylene	RETENTION
	PhONa	(-) SiOPh (26%)	THF-xylene	RETENTION
	PhONa/crown	(±) SiOPh	THF-xylene	RACEMIZATION
	t-BuOH(1 : 1)	(+) SiO(t-Bu)(58%)	THF-xylene	RETENTION
	t-BuOH excess	(±) SiO(t-Bu)	THF-xylene	RACEMIZATION
	t-BuONa excess	(+) SiO(t-Bu)(17%)	THF-xylene	RETENTION
	DIBAL-H (Et_2O)	(-) SiH (86%)	THF-xylene	RETENTION

a) *enantiomeric excess(e.e) corrected according to the optical purity of the starting silanolate*

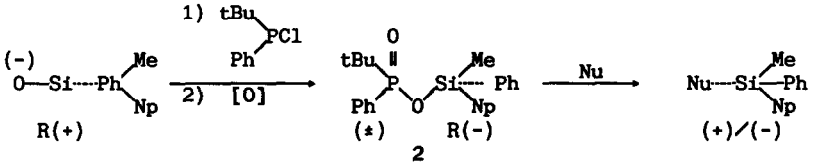
It should be noted that the reaction of silyl esters of phosphinous acid with (+)NpPhMeSiOK also leads to retention of configuration at silicon, as judged from the optical activity of the resulting disiloxane (inversion on 7 would be expected to give the meso disiloxane) : in no case, were we able to isolate 7. The second step is therefore faster than the coupling reaction of the silanolate with the P-Cl derivative.



Reactions of t-BuPhP(O)OSiMePhNp (2)

The ester 2 is the most reactive of the compounds here studied and shows also the least optical stability. For example, an exothermic reaction occurs immediately at room temperature with EtMgBr and $LiAlH_4$ leading to the corresponding substituted compounds. Despite the low optical activity of the products, the stereochemical results (Table 3) are similar to those of the analogous reactions with substrate 1. The racemization of the hydrolysis product is probably the result of the subsequent exchange reaction of the OH groups, catalyzed by the relatively strong t-butylphenylphosphinic acid, present as a product.

Table 3 : Stereochemistry of the coupling reaction of 2 with nucleophiles.



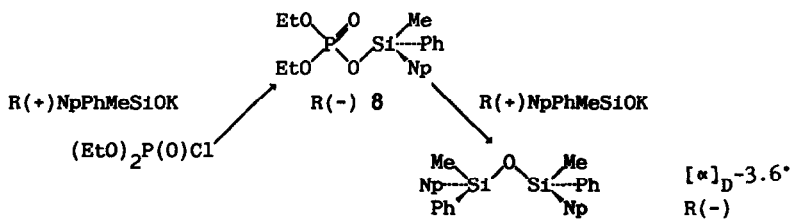
Substrate	Nucleophile	Product (e.e)[a]	Solvent	Predominant Stereochemistry
S(+)≡Si-OP(O)<(±) (+) 2 [b]	MeOH	(+) SiOMe	THF-xylene	RETENTION
	$LiAlH_4$	(+) SiH	cyclohexane - THF	RETENTION
	EtMgBr	(-) SiEt	THF-xylene	RETENTION
R(-)≡Si-O-P(O)<(±) (-) 2	EtMgBr	(+) SiEt (72%)	THF-xylene	RETENTION
	MeOH	(-) SiOMe (76%)	THF-xylene	RETENTION
	H_2O(dioxane)	(±) SiOH	THF-xylene	RACEMIZATION
	$LiAlH_4$	(-) SiH (61%)	THF-xylene	RETENTION

a - enantiomeric excess corrected according to the optical purity of the starting silanolate.

b - substrate (+) 2 was obtained according to the reaction:

$$t\text{-BuPhP(O)OSnMe}_3 + (-)\text{NpPhMeSiCl} \xrightarrow[\text{retention}]{} (+)\text{NpPhMeSiOP(O)t-BuPh}$$

The coupling reaction of the chloroanhydride of O,O diethylorthophosphoric acid with an excess of potassium naphthylphenylmethylsilanolate can be interpreted as resulting from predominant retention in the nucleophilic substitution of the silyl ester intermediate by the silanolate anion.

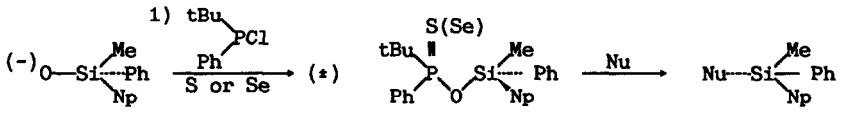


As for compound 7, we were not able to isolate 8 ; again we suppose that the subsequent reaction with the nucleophilic silanolate anion was too fast.

Reactions of t-BuPhP(S)OSiMePhNp (3) and t-BuPhP(Se)OSiMePhNp (4)

The stereochemistry of the nucleophilic substitution reactions at silicon on esters 3 and 4 is essentially different from the stereochemistry of the reactions of their oxygen analogue. Results are presented in Table 4. In all cases in which the process leads to an optically active silicon product, the predominant stereochemistry is inversion. Methanolysis and hydrolysis proceed with nearly complete racemization, but we cannot exclude the possibility of further epimerisation of the silanol and/or methoxysilane, in these experimental conditions. Alkoxyl group exchanges in t-butoxysilanes are known to proceed more slowly than the exchange of methoxy groups : as expected, the reaction of t-butanol with 3 gives better stereoselectivity. Another point is that 3 and 4 show greater optical stability than esters 1 and 2, but as they react with nucleophiles more slowly than their oxygen analogue, racemization of the silyl esters is still extensive.

Table 4 : Stereochemistry of the coupling reaction of 3, 4 with nucleophiles.



R(+) R(-) (+)/(-)

Substrate	Nucleophile	Product (e.e)[a]		Solvent	Predominant stereochemistry
S(+)≡Si-O-P(S)(±) (+) 3	MeOH	(-) Si-OMe	(22%)	benzene	INVERSION
	nBuLi	(+) Si-nBu	(74%)	benzene hexane	INVERSION
	EtMgBr	(-) Si-Et	(54%)	benzene Et_2O	INVERSION
	t-BuOH	(+) Si-O-tBu	(68%)	benzene	INVERSION
R(-)≡Si-O-P(S)(±) (-) 3	H_2O	(±) Si-OH		benzene	RACEMIZATION
	MeOH	(+) Si-OMe	(27%)	benzene	INVERSION
	nBuLi	(-) Si-nBu	(63%)	benzene hexane	INVERSION
R(-)≡Si-O-P(Se)(±) (-) 4	$LiAlH_4$	(+) Si-OH	(78%)	benzene Et_2O	INVERSION
	MeOH	(+) Si-OMe	(43%)	benzene	INVERSION

a) *enantiomeric excess corrected according to the optical purity of the starting silanolate.*

Alkoxyl group exchanges in t-butoxysilanes are known to proceed more slowly than the

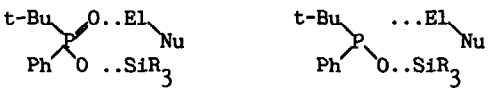
exchange of methoxy groups; as expected, the reaction of t-butanol with 3 gives better stereoselectivity.

In fact, 3 and 4 show greater optical stability than esters 1 and 2, but as they react with nucleophiles more slowly than their oxygen analogue, racemization is still extensive.

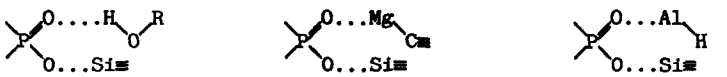
Mechanism of the displacement of the phosphorus group at silicon with nucleophiles

The most interesting feature of the stereochemical course of the reactions of silyl esters of phosphorus with the nucleophiles studied here is the cross-over in stereochemistry in going from phosphinous and phosphinic acid esters to their thiono and selenophosphinic analogues. The former react with predominant *RETENTION* of configuration at silicon, while the latter give *INVERSION*. It should also be mentioned that most of the reactions leading to the formation of these esters, which also proceed via substitution at silicon, occur with *INVERSION*. They include reactions of (+)NpPhMeSiH with t-BuPhP(O)OH and t-BuPhP(S)OH catalysed by Pd/C and reactions of (-)NpPhMeSiCl with t-BuPhP(O)H.NR_3 and t-BuPhP(S)OH.NR_3. The only exception to this stereochemistry is the reaction of t-BuPhP(O)O$SnMe_3$ with (-)NpPhMeSiCl which results in retention of the configuration at silicon. This result is puzzling taking into account the fact that inversion is the usual stereochemical result of the substitution of chlorine at silicon.[12] The mechanism of the substitution of the silyl esters of phosphorus acids must also explain the observation that the esters of oxyphosphoryl acids are much more reactive towards nucleophiles than their thiono analogues. It should also account for the low optical stability of these esters having an optical activity originating from silicon chiral centers.

The most plausible explanation of the above features seems to be a mechanism involving a cooperative interaction of the oxyphosphoryl group or tricoordinate phosphorus with the electrophilic part of the nucleophile. Such interaction decreases the electron density on the silicon, making easier nucleophilic attack at silicon and cleavage of the leaving group. This electrophilic assistance also provides a good explanation of the high reactivity of silyl esters of phosphoric and phosphinous acids.



If the interaction involves the formation of a five or six membered ring, then it explains the observed *RETENTION* at the central atom, since in-line attack would be more difficult for geometrical reasons.

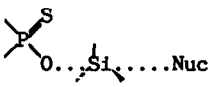


hydrolysis alcoholysis | reaction with organometallics | reduction

The oxyphosphoryl group is known to be an excellent nucleophile. It is able to interact effectively with many electrophiles [13]. On the other hand, the thionophosphoryl and selenophosphoryl

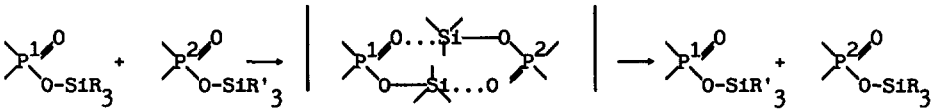
groups are much weaker nucleophiles and they are not able to provide any assistance to the substitution of the silyl groups through interaction with the electrophilic part of the nucleophilic reagent.

Consequently, reactions with thionophosphoryl and selenophosphoryl esters proceed much more slowly than those of the corresponding oxyphosphoryl and tricoordinate phosphorus esters. The stereochemical outcome of their reactions is *INVERSION* of configuration at silicon according to the scheme :



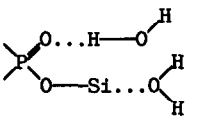
It should be mentioned that if the cooperative interaction with the oxyphosphoryl group is made difficult as in the case of DIBAL-H associated in n-hexane, then, the reaction proceeds slowly. Unfortunately its stereochemistry cannot be determined since other reactions leading to racemization are relatively too fast.

The unusually high ability of the optically active oxyphosphoryl silyl esters to racemize can also be explained by the cooperative action of the oxyphosphoryl group. The spontaneous racemization of these esters could be due to intermolecular exchange[14] of the silyl group according to the following scheme :



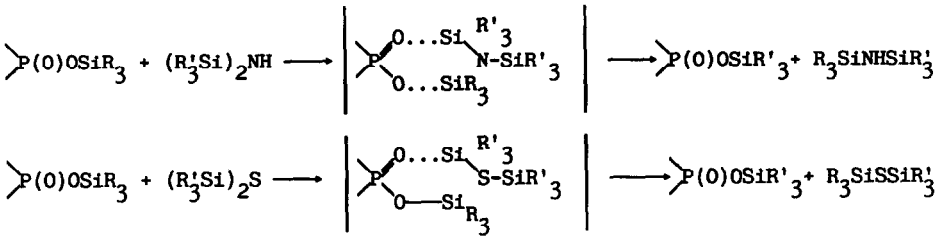
This multicentre reaction involves an eight membered ring transition state structure, which makes possible an in-line arrangement of incoming group, silicon atom and leaving group leading to overall inversion at silicon.

The rather low stereoselectivity of some reactions, particularly those with ROH and H_2O has been explained by product or susbtrate partial racemization. However, it cannot be excluded that the observation may be also the result of a competitive substitution with inversion, within a larger ring involving hydrogen-bonded dimer of water or alcohol to be formed in the transition state



The unusual stereochemistry of the reaction of the trimethylstannyl ester of t-butylphenylphosphinic acid with optically active naphthylphenylmethylsilyl chloride[15] is also well explained by the cooperative mechanism, a six-membered ring-containing transition state feasible for this process, favouring retention at silicon. The excess of the tin ester would cause the partial racemization as the result of subsequent exchange reaction which, involving an eight membered ring, occurs with inversion;

In the light of this proposed cooperative phosphorus group interaction mechanism, it is also easier to understand some reactions of the silyl esters of phosphinic and phosphinous acids. For example the exchange of silyl groups as a result of the interaction of the esters with disilathianes and disilazanes can be explained in a similar way.



Experimental

All experiments have been carried out under an inert atmosphere of argon or nitrogen additionally dried by passing through a column filled with P_2O_5. All solvents were purified and dried according to [16]. THF was distilled from $LiAlH_4$ under nitrogen, just prior to use. ^{31}P NMR spectra were recorded on a Jeol JNMFX-60 FT spectrometer using sample tubes of 10 mm outside diameter. Chemical shifts are reported relative to external 85% H_3PO_4. Optical rotations were determined with a Perkin-Elmer 291 MC polarimeter at λ = 589 nm. Gas chromatography analysis were made on a Jeol 1100 GC spectrometer.

Preparation of starting materials

Racemic silyl esters 1 - 6 were prepared by known methods[14]. Optically active silyl esters 1 - 4 were already described[1]. Chemical purity was checked by ^{31}P N.M.R spectroscopy. Enantiomeric excess at silicon in the organosilicon esters of phosphorus (e.e%) was uniformly corrected except when specified, according to the optical purity[11] of the starting silanolate, $[\alpha]_{D\ max}$-84°. They were reacted further with nucleophiles, without additional purification except for 3, recrystallized from pentane-benzene solution. Optically active organosilicon products have been described, also with their higher optical activity values [11].

Reactions of α-naphthylphenylmethylsilyl t-butylphenylphosphinite (1)

The optically active (+) 1 was prepared by reaction of (-)silanolate[11] with t-butylphenylchlorophosphine ($[\alpha]_D$ max. for (+) 1 is 14°).

Hydrolysis : The solution of 0.038g (0.1 mmol) of t-BuPhPOSiMePhNp ($[\alpha]^{25}_D$ = 3°, e.e. 22%) in 1 ml THF-xylene (1 : 1) was mixed 2 mn with 0.01g (0.56 mmol) of H_2O in 0.4 ml of dioxane. NpPhMeSiOH $[\alpha]^{25}_D$ = 1.34°, (e.e. corrected 23%), was the only organosilicon product as confirmed by GC.

Reductions : To a suspension of 0.05g $LiAlH_4$ in 2 ml of Et_2O, 0.057g (0.17 mmol) of 1 ($[\alpha]^{25}_D$ + 3°) in 1.5 ml of benzene was carefully added. The optical rotation after 1 hour was α^{25}_D + 0.06°. t-BuPhP(O)H was the primary phosphoro organic product (^{31}P NMR), but it was reduced to t-BuPhPH (δ =-6.1 ppm). Calcd. specific rotation of (+)NpPhMeSiH was $[\alpha]^{25}_D$ = + 6.3° corrected to optical purity of starting silanolate 1 it was $[\alpha]^{25}_{Dcorr}$ + 29.4°, e.e. 86%.

The solution. of 0.2g (0.46mmol) of-1 ($[\alpha]^{25}_D$ -7.4°, e.e. 53%) in 2 ml of THF-xylene (1 : 1) was carefully added at room temp. to 0.45 ml 20% soln. of DIBAL-H in Et_2O. After the reaction was completed the solvents were distilled off, the salt was filtered. Optical activity $[\alpha]^{25}_D$ - 15.5° (e.e. corrected 86%).

The reduction of 1 by hexane soln. of DIBAL-H was performed in an analogous way. After 48 hours, almost all the 1 was recovered. Partial racemization of 1 had occurred ($[\alpha]^{25}_D$ = -0.38°).

Alcoholysis

1. To a solution of 0.095g (0.2 mmol) of-1 ($[\alpha]^{25}_D$ - 7.4°), in 2 ml of THF-xylene (1:1), soln. of 0.03g (0.3 mmol) of PhOH in 1 ml THF was added. After the reaction was completed (^{31}P NMR), the optical rotation of NpPhMeSiOPh was measured : $[\alpha]^{25}_D$-3.2° (e.e. corrected 68%).
2. 0.095g (0.2 mmol) of 1 ($[\alpha]^{25}_D$-7.4°) in 2 ml of THF-xylene (1:1) was added to 0.054g (0.5mmol) of PhONa in 1 ml of THF. After filtering the suspension, the optical rotation of the solution was measured, $[\alpha]^{25}_D$-1.2° (e.e. corrected 26%). After removing the solvents and dissolving the products in CCl_4, NpPhMeSiOPh was found to be racemic.

3. 0.095g (0.2 mmol) of 1 ($[\alpha]^{25}_D$ - 7.4°) in 0.2 ml THF-xylene was added to a solution of 0.07g PhONa (30% excess) and 0.1g 12-crown-6 in 1 ml THF. After the reaction rotation, was very low α =-0.005°. NpPhMeSiOPh was analyzed by GC.
4. 2 ml of the same-1 was stirred 10 mn with 0.1g MeOH, giving NpPhMeSiOMe, ($[\alpha]^{25}_D$=- 5.9° (e.e. corrected 66%).
5. A solution of 0.158g (0.37 mmol) of -1 ($[\alpha]_D$-4.8°, e.e. 34%) in 1.5 ml THF-xylene (1 : 1) was added dropwise to :
   a. 0.028g t-BuOH in 1 ml THF (0.37 mmol)
   b. 0.2g t-BuOH in 0.5 ml THF (2.7 mmol)
   c. 1 ml of solution of t-BuONa in t-BuOH (0.38 M)
   After the reactions were complete (from GC and ^{31}P NMR spectra), the optical rotation of NpPhMeSiOtBu was measured.
   a. α =+ 0.369, $[\alpha]^{25}_D$+5.75° (e.e. corrected 58%).
   b. $[\alpha]^{25}_D$= 0°
   c. α =+ 0.07° $[\alpha]^{25}_D$+ 1.7° (e.e. corrected 17%).

Reactions of α-naphthylphenylmethylsilyl t-butylphenylphosphinate (2)

The preparation of (+)2 from (-) NpPhMeSiCl and (±) tBuPhP(O)OSnMe$_3$, and that of (-) 2 by oxidation of phosphinite (-) 1 have been described previously[1], ($[\alpha]_D$ max 10°. Enantiomeric excess at silicon in (-) 2 as calculated, like above, according to optical purity of starting silanolate. In the case of (+) 2, obtained by exchange reaction of chlorosilane with stannyl ester, optical stability was so poor (t1/2 20mn) that further coupling reaction with nucleophiles needed to be performed immediately. Enantiomeric excess at silicon was roughly estimated from optical activity to be 33%.

Hydrolysis

0.119g (0.28 mmol) of 2 ($[\alpha]^{25}_D$=-1.93° d.e. 19%) in 1 ml of THF-xylene was added to 0.1g H_2O in 1 ml of dioxane. The optical rotation after 5 mn was zero. Other attempts to obtain optically active NpPhMeSiOH in this reaction failed.

Reduction

0.238g (0.56 mmol) of 2 ($[\alpha]^{25}_D$- 1.93°,) in 1 ml of THF-xylene was carefully added to the slurry of 0.05g $LiAlH_4$ in 2 ml THF at room temp. After decomposition of the excess of $LiAlH_4$ and extraction with Et_2O, the optical rotation of the solution of NpPhMeSiH was measured. $[\alpha]^{25}_D$= - 4°, (e.e. corrected 61%).

A second experiment was performed with (+) 2, $[\alpha]_D$ + 3.4°. Optical activity of NpPhMeSiH was $[\alpha]_D$ + 5.1° (e.e. corrected 44%).

Reaction with Grignard reagent

0.238g (0.56 mmol) of 2 ($[\alpha]^{25}_D$ -1.93°) in 2 ml of THF-xylene was added to 2 ml of 0.5 M Et_2O solution of EtMgBr; the reaction proceeded exothermically. After decomposition of excess EtMgBr, NpPhMeSiEt was extracted with Et_2O; $[\alpha]^{25}_D$= -0.85°, e.e. corrected 72%).

Another reaction with 2, $[\alpha]_D$+3.4° (e.e. 33%) gave NpPhMeSiEt $[\alpha]_D$ + 1.7°, (e.e. corrected 82%).

Methanolysis

To a solution of 0.238g of 2 ($[\alpha]^{25}_D$= -1.93°) in 2 ml of THF-xylene, 0.02g (0.62 mmol) MeOH in 0.5 ml THF was added. After 20 mn NMR spectrum and optical rotation of NpPhMeSiOMe was measured. $[\alpha]^{25}_D$= -2.57° (e.e. corrected 76%); (^{31}P NMR: tBuPhP(O)H, 86%, tBuPhP(O)OSiMePhNp, 5%,[tBuPhP(O)]$_2$, 9%.

A second experiment was performed with 2 $[\alpha]_D$ + 3.4°. The product, NpPhMeSiOMe, had $[\alpha]_D$ + 3.8° (e.e. corrected 64%).

Reactions of α-naphthylphenylmethylsilyl t-butylphenylthiophosphate (3)

Optically active silyl ester 3, $[\alpha]_D$ max 32.7°, was prepared by addition[1] of sulfur to 1. Enantiomeric excess at silicon was calculated according to optical purity of starting silanolate.

Hydrolysis

To 0.14g of 3, $[\alpha]^{25}_D$-18.5° (e.e 56%), in 2 ml of benzene, 0.1g (5.5 mmol) H_2O was added in 0.5 ml dioxane. The reaction was checked by ^{31}P NMR. After it was complete, the solvents were removed in vacuo, and the products were dissolved in CCl_4. Optical rotation of NpPhMeSiOH (GC) was $[\alpha]^{25}_D$=0

Alcoholysis

To 0.14g of 3, $[\alpha]^{25}_D$ -18.5°, in 2 ml of benzene, 0.1 ml MeOH in 0.5 ml of benzene was added. After the reaction was complete (^{31}P NMR) the optical rotation of NpPhMeSiOMe was $[\alpha]^{25}_D$ 2.7° (e.e. corrected 27%).

A second experiment performed with (+)3 $[\alpha]_D$ + 17.8° (e.e 54%) gives the alkoxysilane $[\alpha]_D$ -2.1° (e.e. corrected 22.5%).

Reaction with n-BuLi

To 0.0925g of 3, $[\alpha]^{25}_D$+ 17.8°, in 2 ml of benzene, 0.3 ml of 20% of nBuLi-hexane was added.

After usual work-up, NMR spectrum was registered and optical rotation measured. (1 ml Et_2O), $[\alpha]^{25}_D$ + 1.3°.e.e. corrected 74.5% (+)NpPhMeSiBu was identified by GC; standard was prepared by an independent route.
In another experiment (-) 3 ($[\alpha]_D$ -19°) was mixed with a small excess of nBuLi in hexane, as before. After work-up, the organosilane was optically active $[\alpha]_D$ -2.02° (e.e. 63%).
Reaction with Grignard reagent
0.14g (0,3 mmol) of 3 in 2 ml of benzene, $[\alpha]^{25}_D$ +17.8°, was added to 1 ml solution of EtMgBr in Et_2O. After the reaction was complete (shown by ^{31}P NMR), the excess of EtMgBr was decomposed ; NpPhMeSiEt was extracted with Et_2O, dried with $MgSO_4$. Measured optical activity of NpPhMeSiEt was $[\alpha]^{25}_D$=- 1.8° (e.e. corrected 54%).

Reactions of α-naphthylphenylmethylsilyl t-butylphenylselenophosphate (4).
Obtained[1] by addition of selenium to 1, $[\alpha]_D$ max -19°. Enantiomeric excess calculated like above.
Reductions with $LiAlH_4$.
0.204g (0.4 mmol) of 4 in 2 ml of benzene, $[\alpha]^{25}_D$ -11°, was carefully added to 0.05g $LiAlH_4$ in 2 ml of Et_2O. After the reaction was complete (^{31}P NMR), excess of $LiAlH_4$ was decomposed, NpPhMeSiH was extracted with Et_2O, dried and concentrated.
Optical rotation of NpPhMeSiH was $[\alpha]^{25}_D$=+15.4°, (e.e. corrected 78%).
Methanolysis
To 0.204g (0.4 mmol) of 4 in 2 ml of benzene, $[\alpha]^{25}_D$=-8.1°, 0.1 ml of MeOH in 0.5 ml benzene was added. After the reaction was complete (^{31}P NMR) optical rotation of NpPhMeSiOMe was $[\alpha]^{25}_D$=+3.1°, (e.e. corrected 43%).

Reactions with optically active NpPhMeSiOK

Diphenylchlorophosphine : to a solution of 0.495g (1.6 mmol) of (+) NpPhMeSiOK, ($[\alpha]_D$ +35°) in 2 ml of dioxane was introduced 0.38g (1.7 mmol) of Ph_2PCl. The immediately formed precipitate of KCl was filtered off. The main phosphorus product was $Ph_2P(O)PPh_2$. [$\delta^{31}P$ ppm(37.6, 28.5 and -20.6, - 29.8), J_{P-P} = 220Hz]. Disiloxane was identified by comparison with an authentic sample, $[\alpha]_D$ - 2.16°.
$(EtO)_2P(O)Cl$
To a solution of 0.3g (1.75 mmol) of $(EtO)_2P(O)Cl$ in 2 ml of freshly distilled THF, was added 0.488g (1.6 mmol) of (+) αNpPhMeSiOK, $[\alpha]_D$ + 61°, in 4 ml of xylene. After completion of the reaction, the composition of the P products was the following :
$(EtO)_2P(O)P(O)(OEt)_2$ (75%), $(EtO)_2P(O)OSiMePhNp$ (13%), $(EtO)_2P(O)Cl$ (12%).
The optical activity of NpPhMeSiOSiMePhNp was measured only after 30 mn, to avoid contamination with residual $(EtO)_2P(O)O$-SiMePhNp. The silylphosphate is fully epimerized in less than 15 mn. $[\alpha]_D$ of the siloxane - 3.6°.
The same reaction run at -50°C gave a similar result.

Preparation of diphenylphosphinic and diphenylthiophosphinic acids
Diphenylphosphinic acid was prepared by oxidative hydrolysis of Ph_2PCl with H_2O_2 Diphenylthiophosphinic acid was prepared in two stages : $Ph_2P(S)Cl$ was obtained by addition[17] of sulfur to Ph_2PCl, followed by hydrolysis with NaOH water solution[18]. Both acids were purified by crystallisation from toluene.
Trimethylsilyl diphenylphosphinate was obtained by the reaction[1] of diphenylphosphinic acid with Me_3SiCl in the presence of Et_3N in methylene chloride. After filtering off $Et_3N.HCl$ and evaporation of the solvent, the product was crystallized from benzene. Yield : 75%. Spectral data : ^{31}P 20.7 ppm, ^1H 0.3 ppm (s, $Si(CH_3)_3$), 7.3-8.0 ppm (m, PPh_2).
Triphenylsilyldiphenylphosphinate was obtained by exchange of silyl groups[7] between $Ph_2P(O)OSiMe_3$ and Ph_3SiCl. After evaporating the solvent, the crude product was dissolved in hot benzene, precipitated by addition of n-hexane. Yield 85%, spectral data ^{31}P : 21.2 ppm, ^1H : 7.3-8.0 ppm (m, Ph).
Triphenylsilyldiphenylthiophosphinate was obtained from thiophosphinic acid, Ph_3SiCl and Et_3N. The crude product was crystallized from toluene. Yield 76%, spectral data : ^{31}P 70.9 ppm, ^1H : 7.3-8.0 ppm (m, Ph).

Reaction of triphenyl diphenylphosphinate and thiophosphinate with nucleophiles : general procedure.
All reactions were directly performed in 10 mm NMR tubes using the proper solvents reported in table 1, and were followed by ^{31}P NMR spectroscopy. Phosphorus containing products were identified by their chemical shifts. As an example, a solution of 0.25g (0.52 mmol) of silyl ester in 1ml of CH_2Cl_2 was introduced in the NMR tube and an equimolar amount of nucleophile was added. The tube was tightly closed and warmed for 2 hrs at 40°C. After this time the spectrum

was taken. The sample was then stored for 24 hrs at room temperature and the NMR measurement repeated.

ACKNOWLEDGMENTS

The authors express their appreciation to the CNRS for financial aid and to the donors of the Polish Academy of Sciences for support of this research under grant CPBP 01.13. We also thank Pr. J. MICHALSKI and Pr. R. CORRIU for their kind interest and encouragement. Helpfull comments from C. YOUNG on the english version of the manuscript were appreciated.

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