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OPTICALLY ACTIVE TRIORGANOSILYL ESTERS OF PHOSPHORUS

SYNTHESIS AND STRUCTURE

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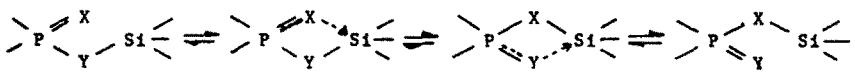
Abstract - *We report the synthesis of the first optically active silyl esters of phosphorus having two centres of chirality : one on silicon and the other on phosphorus. Compounds are obtained of general formula : t-BuPhP(X)YSiaNpPhMe X,Y=O,O(1); S, O(2); Se, O(3); S, S(4); doublet, O(5) including 1 and 3 with optical activity located on Si, 2 and 5 with the activity on Si or P and on both these centres, 4 only racemic. Absolute configurations are determined.* ^{31}P *and* ^{29}Si *NMR spectra of these models and their trimethylsilyl analogues are reported. The triorganosilyl group is always preferentially bound to phosphorus through oxygen atom. Surprisingly, diastereotopic NMR chemical shifts exclude the fast 1,3 migration in esters 1 and 4.* ^{29}Si *NMR spectra correspond to a tetracoordinate silicon atom.*

Introduction

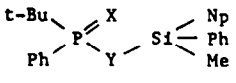
There has recently been increasing interest in silyl esters of phosphorus as intermediates in synthesis of diverse phosphorus compounds, including those important in bioorganic chemistry. These esters are often used in synthesis of various acids and polyacids of phosphorus[1-8], phosphorus anhydrides[9], important intermediates containing phosphorus and sulfur[10,11] and carbon functional compounds of phosphorus[12,13].

Their potential reactivity at both silicon and phosphorus render these esters very convenient models for mechanistic studies. New theory of the stereochemistry of substitution at silicon has recently been developed[14] and there are many observations permitting to suppose that this theory could be extended to phosphorus[15 16].

Since these esters are ambident electrophiles, the question arises which is the reactive centre for substrates and nucleophiles of diverse structure. The nature of these esters constitutes another problem as they may appear in various isomeric forms. The knowledge of their geometry could give a better insight into their reactivity. Intramolecular migration of triorganosilyl group between nucleophilic centres is commonly encountered in organosilicon chemistry[17-19] and pentacoordinate silicon species with intramolecular nucleophilic coordination are also well documented[20-24], thus these esters are expected to show following equilibria :

(1) 

The present paper describes the synthesis of optically active triorganosilyl esters of phosphorus acids with two chiral centres, one on silicon and the other on phosphorus, having general intended formula :



	1	2	3	4	5
X :	O	S	Se	S	-
Y :	O	O	O	S	O

Np = α-Naphtyl

The optically active esters were created as a result of stereospecific reactions using optically active silicon and/or phosphorus reactants. The absolute configurations were obtained by chemical correlation method. NMR spectroscopy was used as the tool for elucidation of structure and behaviour of these esters.

We hope that studies of these models shed some light on the possible isomerization presented in scheme (1). In addition they could give some information about the role of pentacoordination of silicon in the electrophilic reactivity of silyl esters of phosphorus at silicon and phosphorus centers. To our knowledge there has not been so far any report concerning optically active esters of phosphorus having chiral silicon in the ester group. On the other hand successful attempts of synthesis of the silyl esters with optical activity on chiral phosphorus are not numerous[25-27].

1 - Synthesis of optically active silyl esters of phosphorus with optical activity originating from chiral silicon atom

There are many known reactions leading to the silyl esters of phosphorus (see for ex. [4,28,29]), however, no synthesis of these esters with chiral silicon atom has so far been reported. The synthesis of an optically active species of this type may be a problem since a considerable mobility of the silyl group in these esters and their particularly high reactivity towards nucleophiles may lead to racemization during the synthetic procedure.

Three general routes to optically active silyl esters of phosphorus have been developed in this study : 1) The reaction of optically active triorganosilanolates with chloroanhydrides of P(III) acids followed by the addition of oxygen, sulfur or selenium ; 2) Reactions of optically active triorganohalogenosilanes with phosphorus salts[28] or esters ; 3) Dehydrocondensation of optically active triorganosilyl hydride with acids of phosphorus.

The reaction of naphtylphenylmethylsilanolate with chloroanhydrides of phosphorus acids

This method permits to convert the silanolate to esters of various acids of phosphorus without cleavage of any bond to silicon atom. However, the silyl ester formed is very sensitive to silanolate or another nucleophile present in the system.

1) $R_2PCl + NpPhMeSiOK \longrightarrow R_2POSiNpPhMe + KCl$

2) $R_2POSiNpPhMe + NpPhMeSiOK \longrightarrow R_2POK + NpPhMeSiOSiNpPhMe$

3) $R_2POK + R_2PCl \longrightarrow R_2P\text{-}P(O)R_2 + KCl$

4) $R_2POSi\equiv + R_2PCl \longrightarrow R_2P\text{-}P(O)R_2 + \equiv SiCl$

A process similar to (1)-(3) also makes difficult the synthesis of P(IV) esters from the silanolate and chloroanhydrides of P(IV) acids. We have found that in the case R=OEt only 13 % of the silyl ester was formed when stoichiometric amounts of the substrates were used.

5) $R_2P(O)Cl + NpPhMeSiOK \longrightarrow R_2P(O)OSiNpPhMe + KCl$

6) $R_2P(O)OSiNpPhMe + NpPhMeSiOK \longrightarrow R_2P(O)OK + NpPhMeSiOSiNpPhMe$

7) $R_2P(O)OK + R_2P(O)Cl \longrightarrow R_2P(O)OP(O)R_2 + KCl$

The key problem in the synthesis of the silyl esters by this method was, therefore , the choice of the proper phosphorus reagent which enter into the reaction with potassium naphtylphenylmethylsilanolate faster than the silyl ester which appears as the product of this reaction. Tertiary butylphenylchlorophosphine was found to meet this requirement. Its reaction with NpPhMeSiOK leads to high yield of the ester 5 and no diphosphine oxide is observed. The formation of 5 may be easily followed by ^{31}P NMR.

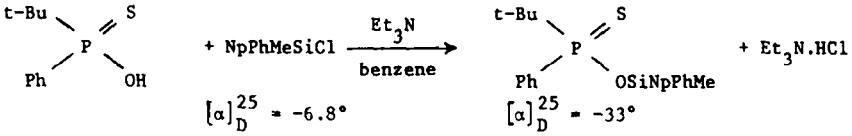
Since the ester is highly sensitive to hydrolysis and oxidation and also shows some tendency for loosing its optical activity when kept in the system, it was used without isolation for further syntheses. The ester reacts readily with oxygen, sulfur and selenium, thus it can be easily transformed to corresponding optically active silyl esters of P(IV) acids (see the experimental section) :

8) $NpPhMeSiOK + ClPtBuPh \xrightarrow[-KCl]{} NpPhMeSiOPtBuPh \xrightarrow{X} NpPhMeSiOP(X)tBuPh \quad X = O, S, Se$

Reactions of naphtylphenylmethylhalogenosilane with phosphorus acid salts and esters

These reactions have some potential in synthesis of optically active silyl esters with asymmetric silicon.

For example, the reaction of t-butylphenylthiophosphinic acid with naphtylphenylmethylchlorosilane in the presence of triethylamine proceeds smoothly at ambient temperature and with a high stereospecificity according to the scheme :



The reaction with oxyphosphoryl analogue leads to racemic ester.

The analogous silylation of tert-butylphenylphosphinous acid goes fast in methylene chloride and, when performed at low temperature,it gives the silyl ester 5 :

10) $t\text{-}BuPhP(O)H + NpPhMeSiCl \xrightarrow[CH_2Cl_2]{Et_3N} t\text{-}BuPhPOSiMePhNp + Et_3N.HCl$

$[\alpha]_D^{25} = -6.4°$ $\qquad$ $[\alpha]_D^{25} = -2.7°$

On the other hand, the thiophosphinous and dithiophosphinic acids are not reacting with the chlorosilane in the presence of amine or using ammonium salt of these acids . In contrast, the silylation may be performed using the corresponding bromosilane, but the products are racemic.

11) $t\text{-}BuPhP(S)S^- \overset{+}{N}H_3C_6H_{11} + NpPhMeSiBr \xrightarrow{CH_2Cl_2} t\text{-}BuPhP(S)SSiNpPhMe + C_6H_{11}NH_2.HBr$

12) $t\text{-}BuPhP(S)H + NpPhMeSiBr \xrightarrow{Et_3N} t\text{-}BuPhSSiNpPhMe + Et_3N.HBr$

The reaction with P(IV) acid proceeds fast giving almost 100 % yield of the silyl ester (^{31}P NMR). However, low optical stability of the bromosilane or the ester renders the reaction not applicable to synthesis of optically active product.

The reaction of naphtylphenylmethylhalogenosilanes with the stannyl ester[4] corresponding to 1 proceeds stereoselectively, according to the scheme :

13) $t\text{-}BuPhP(O)OSnMe_3 + NpPhMeSiCl \xrightarrow[CCl_4]{} t\text{-}BuPhP(O)OSiNpPhMe + Me_3SnCl$

$[\alpha]_D^{25} = -6.8°$ $\qquad$ $[\alpha]_D^{25} = +9°$

However, the reaction is very chimeric. Stoichiometry seems to be important. In particular, all experiments in which ^{31}P NMR spectra of products showed traces of the stannyl ester gave racemic products. The excess of the silyl chloride should be also avoided.

Dehydrocondensation of naphtylphenylmethylsilane with acids of phosphorus

A serious limitation of the synthesis of optically active silyl esters of phosphorus is connected to the presence of nucleophiles in these reaction systems. Therefore we were looking for an other synthetic approach which would permit us to perform the synthesis in the absence of nucleophilic species responsible for racemization during the synthetic operation and for the low optical stability of these esters. The condensation reaction between triorganosilyl hydrides and acids of phosphorus in the presence of transition metal catalysts seemed to give this possibility.

14) t-BuPhP(S)OH + NpPhMeSiH $\xrightarrow{Pd/C}$ t-BuPhP(S)OSiNpPhMe

$[\alpha]_D^{25} = +34°$ $[\alpha]_D^{25} = -40°$

The above reaction with Pd catalyst requires heating for rather long time, but it gives a high yield of the product, with also a better optical stability than that obtained on other routes.

The reaction, applicable to the oxygen analogue of the acid, proceeds too slowly to be suitable for the synthesis of the optically active P=O ester, whose optical stability is very poor. In addition, it is very difficult to remove water from the acid which under the reaction conditions readily converts the hydrosilane to optically active silanol. The reaction does not seem to proceed with dithioacids, nor it is applicable to P(III) acids. Also, it is worth to note that the rate of the reaction depends to a considerable extent on the way of the preparation of palladium catalyst.

The dehydrocondensation of the P=O acid with the hydrosilane was performed using rhodium Wilkinson catalyst. However, it proceeded slowly and we were not successful in synthesis of the optically active product.

2 - Synthesis of naphtylphenylmethylsilyl esters of phosphorus acids with optical activity originating from chiral phosphorus centre

Optically active trimethylsilyl esters of tricoordinate and tetracoordinate chiral phosphorus were previously synthesized [25-27]. The principal method used for this purpose was the silylation of the sodium or ammonium salt of the acid with trimethylchlorosilane. We have also explored this method because it permitted the determination of the absolute configuration of esters at the phosphorus centre. Moreover, since the reaction occurs stereoselectively also at silicon centre, therefore it was used for the synthesis of esters with optical activity coming from both these centres.

15) t-BuPhP(O)H + NpPhMeSiCl $\xrightarrow[CH_2Cl_2]{Et_3N}$ t-BuPhPOSiNpPhMe

$[\alpha]_D^{25} = -11.4°$ $[\alpha]_D^{25} = -17.4°$

The addition of sulfur and the oxygenation of phosphorus moiety permitted to obtain the corresponding optically active esters of tetracoordinate phosphorus.

Separate experiments with the silylation of the optically active t-butylphenylthiophosphinic acid with trimethylchlorosilane in the presence of triethylamine confirmed the optical stability at phosphorus (IV). The consecutive methanolysis performed after keeping the ester for 48 hours permitted to regain the acid of the same configuration, preserving about 70 % of its initial rotation.

16) t-BuPhP(S)OH + Me_3SiCl $\xrightarrow{Et_3N}$ t-BuPhP(S)OSiMe$_3$ $\xrightarrow{MeOH}$ t-BuPhP(S)OH

$[\alpha]_D^{25} = -16.8°$ $[\alpha]_D^{25} = +13.8°$ $[\alpha]_D^{25} = -11.6°$

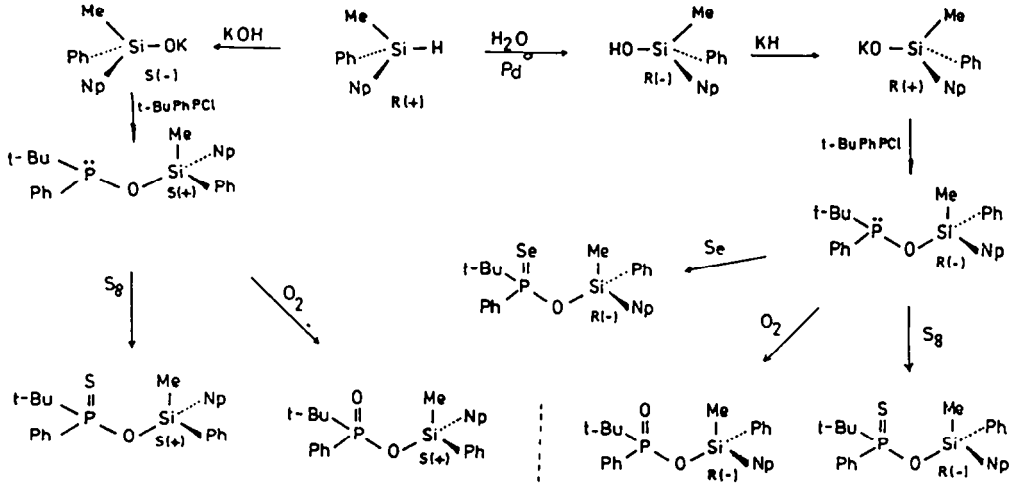
We also used the dehydrocondensation of optically active t-butylphenylthiophosphinic acid with naphtylphenylmethylsilane for producing the ester with the optical activity from chiral phosphorus. The method, which was described in previous section, proved to be particularly suitable to obtain the ester with optical activity shared by both silicon and phosphorus centres.

17) t-BuPhP(S)OH + NpPhMeSiH $\xrightarrow{Pd/C}$ t-BuPhP(S)OSiNpPhMe

$[\alpha]_D^{25} = +24.6°$ $[\alpha]_D^{25} = 31.7°$ $[\alpha]_D^{25} = -47.9°$

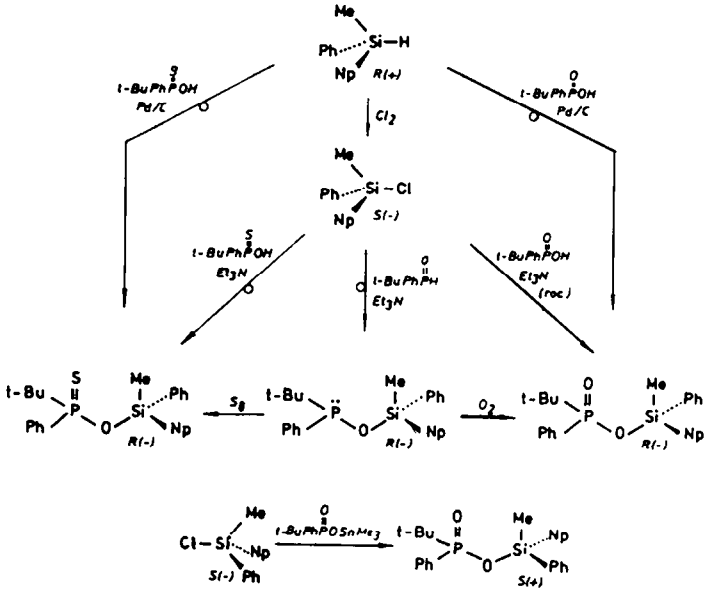
3 - The chemical correlation of the absolute configuration of α-naphtylphenylmethylsilyl esters of phosphorus

The synthesis of silyl esters of phosphorus from optically active potassium naphtylphenylmethylsilanolate of known configuration permitted the determination of their absolute configuration at silicon atom (scheme 18). Both R(+) as well as S(-) enantiomers of the silanolate were used for this purpose. S(-) isomer had been prepared by Sommer's method reacting R(+) NpPhMeSiH with KOH (retention)[30], while R(+) isomer was obtained by hydrolysis of R(+) NpPhMeSiH on palladium[31] (inversion) followed by the reaction of the silanol formed with potassium hydride (retention). The reaction with t-BuPhPCl does not change the configuration at silicon atom nor does it the subsequent step i.e. oxidation, sulphur addition or selenium addition.



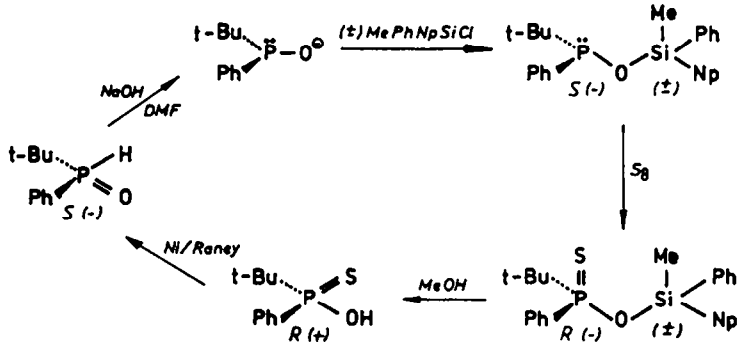
Scheme 18

The knowledge of the absolute configuration of the silyl esters of phosphorus permitted also to establish the stereochemistry of other reactions leading to the formation of these esters (scheme 2). The dehydrocondensation process of the thiophosphinic acid and the hydrosilane proceeds with inversion of the configuration similarly to analogous reactions involving carboxylic acid studied by Sommer et al.[32]. The reaction of naphtylphenylmethylchlorosilane with the ammonium salt of the thioacid takes also place with inversion. In contrast, the reaction of the chlorosilane with the stannyl ester of t-butylphenylphosphinic acid takes place with retention of the configuration at silicon atom (scheme 19).



Scheme 19

The absolute configuration at phosphorus centre was determined exploring the reaction of optically active sodium salt of t-butylphenylphosphinous acid with racemic naphtylphenylmethylchlorosilane according to scheme 20.



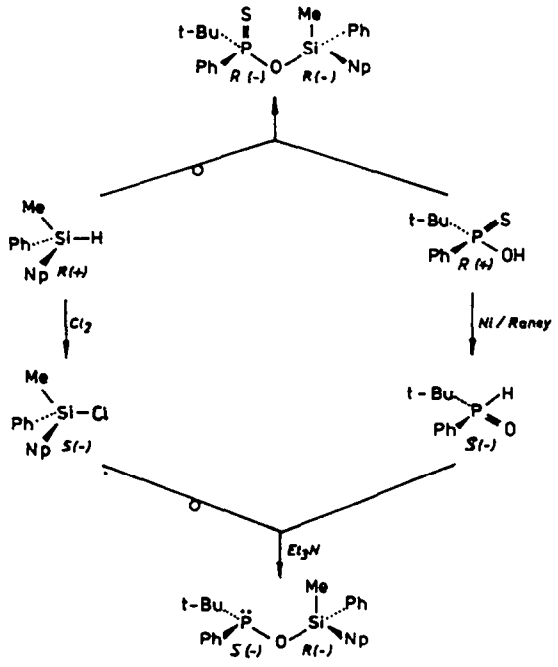
Scheme 20

The optically active phosphinous acid of known configuration, S(-) isomer, was obtained in result of the reduction with Raney nickel of R(+) enantiomer of t-butylphenylthiophosphinic acid (retention) according to the method described in [33]. The formation of the sodium salt and its reaction with the chlorosilane should go with retention at phosphorus atom leading to S enantiomer[25]. Similarly, the addition of sulphur to the phosphorus in the silyl ester of the phosphinous acid was reported to give retention of the configuration[34] leading thus to R isomer. The absolute configuration at phosphorus was confirmed by methanolysis of the thioester. The methanolysis involves the attack at silicon centre and consequently gives the thioacid with retention at phosphorus. Thus all steps in this correlation circle proceed with retention. Indeed, the thioacid was of the same configuration as the starting one.

We have also performed set of correlation experiments of the synthesis of these bichiral esters using both phosphorus as well as silicon reagents optically active (scheme 21). This approach gave us the possibility of the application of ^{31}P and ^{29}Si NMR spectroscopy as a tool for verification of the stereochemistry of theses reactions. Since the fully stereospecific process of two pure enantiomers leads to one enantiomer and one diastereomer only, valuable information about the stereospecificity of the reaction may be deduced from the proportion of signals of diastereomers. It is of value since the optical activity itself is not here the tool precise enough for quantitative determination of the stereoselectivity.

The dehydrocondensation of (+)napthylphenylmethylsilane with (+)t-butylphenylthiophosphonic acid gave the silyl ester showing the ratio of diastereomers 90/10, as judged from the integration of two doublets centre at 2.06 ppm and 1.63 ppm in ^{29}Si NMR spectrum. The main doublet corresponds to the $(-)R_P$ $(-)R_{Si}$ diastereoisomer. Taking into account the optical purity of the substrates the stereospecificity of the reaction was above 90 %.

In a similar way a highly stereoselective course of the reaction of phenyl-t-butylphosphine oxide with naphtylphenylmethylchlorosilane in the presence of triethylamine was confirmed.



Scheme 21

4 - Properties and structure of the naphtylphenylmethylsilyl esters of t-butylphenyl acids of phosphorus

The listing of the many methods we tried in order to obtain optically active compounds are obvious evidences of the high tendency of these esters to loose there optical activity, at least the part connected to chiral silicon. The racemization or the epimerization is presumably induced by contamination with some nucleophilic or electrophilic reagents. Particularly prone to a "spontaneous" racemization is compound 1 having >P(O)O-structure. In fact, for none of the esters 1-5 we have been able to isolate optically pure compounds. The compound 4 >P(S)S- was not eventually obtained as optically active product.

All these compounds are sensitive to hydrolysis, through compounds 2 and 3 are more stable towards traces of water than compounds 1,4,5. The ester of tricoordinate phosphorus 5 is in addition very sensitive to oxygen.

The diastereomeric ratios were determined from the optical rotation of the system, combined with ^{31}P and ^{29}Si NMR measurements in the case of compounds having optical activity both on silicon and phosphorus (Table 1).

Table 1. ^{31}P and ^{29}Si NMR spectroscopic data of triorganosilyl ester of phosphorus acids in CH_2Cl_2.

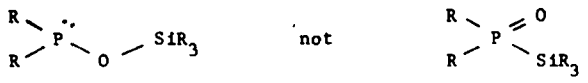
Structure of phosphorus moiety	Structure of silyl group	^{31}P NMR chem. shift(ppm)	^{29}Si NMR chem. shift(ppm)	Coupling constant ^{31}P - ^{29}Si [Hz] (from ^{29}Si NMR)[c]
t-BuPhPO-	$SiMe_3$	113.4	19.35[a]	10.37[a]
	SiMePhNp 5	119.17;118.0[b] 119.47;118.4[b]	1.02;0.46[a] 1.29;0.73[a]	13.92;14.9[a] 13.65;13.97[a]
t-BuPhP(O)O-	$SiMe_3$	43.1	21.77[a]	9.37[a]
	SiMePhNp 1	43.9; 42.1[b] 44.1; 42.6[b]	1.48 2.13	10.39 10.37
t-BuPhP(S)O-	$SiMe_3$	94.6	23.59[a]	10.25[a]
	SiMePhNp 2	97.15 97.6	1.69 2.05	11.15 11.65
t-BuPhP(S)S-	$SiMe_3$	83.33	22.64[a]	4.98[a]
	SiMePhNp 4	84.24 84.64	4.96[a] 6.36[a]	4.96[a] 4.94[a]
t-BuPhP(Se)O-	SiMePhNp 3	98.4[b] 99.2[b]		$J^{31}P-^{77}Se$=800 Hz

a - in C_6D_6

b - in xylene/THF

c - recorded on Bruker WP 200 SY at 39.763 MHz, with internal reference tetramethylsilane.

The ester of phosphinous acid shows ^{31}P NMR chemical shift characteristic for esters of tricoordinate phosphorus and phosphorus-silicon coupling constant value characteristic for P-O-Si structure. Thus the structure of the ester is :



what is in contradiction to what could be expected on the basis of some earlier reports[35, 36] however it confirms the results obtained earlier in one of our laboratories[27].

The spectral data confirm also that thermodynamically stable forms of esters of thiophosphinic and selenophosphinic are those having the silyl group bound to oxygen atom[6].

Particularly important evidence concerning the structure of the selenium derivative is a high value of P-Se coupling constant (J^{P-Se} = 800 Hz). The value characteristic for alternative selenolo structure with selenium in bridging position lies mostly within the range 400-500 Hz[37]. Also values of P-Si coupling constants for these esters (2, 3) are the same as the value for compound 1 giving an additional support for their POSi structure. The dithio derivatives show the coupling constant value much lower i.e. about 5 Hz. It is worth to note that there is some contradiction in the literature concerning the structure of the selenium esters since both isomers having selenolo[36] and selenono[6, 37] structure were postulated to be more stable.

Although dynamic isomerization involving 1, 2 or 1, 3 intramolecular migration of triorganosilyl group between nucleophilic centres is a common feature in organosilicon chemistry[17, 19] and could be expected to occur in silyl esters of phosphorus (scheme 22a, b), present results give no evidence for this migration. In the case of possible erythro-threo isomers the diastereotopic shift is always observed. ^{29}Si NMR spectrum gives two distinguishable doublets with different coupling constants and ^{31}P NMR spectrum shows two signals lying close to each other of intensity ratio close to 50/50. This observation for dithiophosphinic esters as well as for its oxo-phosphoryl analogue excluded the fast, on NMR time scale, migration of the silyl group between two sulfur or two oxygen atoms, since it had to lead to one averaged ^{31}P NMR signal. Certainly, the diastereotopic shift observed for esters 2, 3 and 5 does not eliminate this possibility.

(22)

(a) (b)

Our data permit also to eliminate the possibility of the structures 23a,b with the silyl group bridging two oxygen or two sulfur atoms, since ^{29}Si NMR chemical shift for both these compounds lies in the range typical for tetracoordinate silicon atom.

(23)

(a) (b)

EXPERIMENTAL

All experiments were carried out under inert atmosphere of argon or nitrogen prepurified by passing through a column filled with P_2O_5 and a column filled with copper at 550°.

All solvents and reactants were purified and dried according to[38].

^{31}P NMR spectra were recorded on a Jeol JNM FX-60 Fourier transform spectrometer using sample tubes of 10 mm outside diameter. Chemical shifts are reported relative to external 85 % H_3PO_4.

^{1}H NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer using sample tubes of 5 mm OD. Chemical shifts are reported relative to internal Me_4Si.

Optical rotations were measured at λ = 589 nm with Perkin-Elmer 291MC polarimeter.

Preparation of substrates

(+)α-NpPhMeSiH was prepared by method described in[39], $[\alpha]_D$ = + 32.2° (CCl_4)

(-)Methylphenyl(α-naphtyl)silanol prepared by modified method described in[40], $[\alpha]_D$ = - 19° (dioxane), optical purity 95 %, yield : 98 % (GLC).

(+)Potassium α-naphtylphenylmethylsilanolate

To the suspension of 1.4 g (3.5 mmol) of potassium hydride, washed with pentane, 1.85 g (7.0 mmol) of α-NpPhMeSiOH ($[\alpha]_D$ = -19°) in 5 ml of xylene was added. The evolution of hydrogen was observed. The reaction was exothermic. The product ($[\alpha]_D$ = +63°, 90 %) was optically stable. It had been stored under nitrogen in xylene solution for over two weeks without any lost of the optical activity.

The product obtained by methods of Sommer et al.[30] showed lower optical stability.

(-)α-NpPhMeSiCl and (-)α-NpPhMeSiBr were prepared by Sommer's method[41]. The solution of (-)α-NpPhMeSiBr was used in situ without isolation of the silane. The chemical and optical purities were checked respectively by gas chromatography and polarimetry (CCl_4).

t-BuPhPCl, t-BuPhP(O)H (rac), t-BuPhP(O)OH, t-BuPhP(S)OH (rac), t-BuPhP(S)SH, all were obtained using common procedures[42]. Optically active t-BuPh(O)H and t-BuPhP(S)OH were prepared according to [33-43].

Trimethylstannyl ester of t-butylphenylphosphinic acid was obtained by dehydrocondensation of trimethylstannyl hydride with the phosphinic acid in cyclohexane[44]. After completion of the reaction (checked by ^{31}P NMR) the solvent was evaporated under reduced pressure and the ester was then dissolved in CCl_4 to be used to other reactions.

1 - Preparation of naphtylphenylmethylsilyl t-butylphenyl-phosphinite (5)

a) From potassium naphtylphenylmethylsilanolate and t-butylphenylchlorophosphine (ester with optical activity on silicon).

The solution of 0.090 g (0.3 mmol) of (-)α-NpPhMeSiOK in 5 ml of xylene ($[\alpha]_D$ = -50°, optical purity 71 %) was placed in two necked flask connected to a reservoir of nitrogen and equipped with magnetic stirrer. 0.070 g (0.35 mmol) of t-BuPhPCl in 2 ml of THF (freshly distilled from $LiAlH_4$) was added to the silanolate solution. The reaction was immediate and a colloidal precipitate of KCl appeared. The rotation measured after 10 min. was + 0.335°, $[\alpha]_D$ = +4.8°. $[\alpha]_D$ corrected to the optical purity of silanolate was + 6.8°, ^{31}P NMR showed t-BuPhPOSiMePhNp (70 %), t-BuPhPCl (15 %), t-BuPhP(O)OSiMePhNp and t-BuPhP(O)H (15 %), signals impossible to separate).

The ester 5 obtained from (+)NpPhMeSiOK showed correspondingly the optical rotation of sign (-).

The optical activity of the ester 5 obtained in syntheses repeatedly done was $[\alpha]_D$ = 3° - 14° ; the yield (according to ^{31}P NMR) : 40 - 90 %.

b) From naphtylphenylmethylchlorosilane and t-butylphenylphosphinoxide (ester with optical activity on phosphorus).

A solution of (-)t-butylphenylphosphine oxide (170 mg, 9.4 mmol, $[\alpha]_D$ = -11.4° CH_2Cl_2) in DMF (10 ml) was added gradually to a stirred suspension of sodium hydride (225 mg, 9.4 mmol) in DMF (10 ml), at 0°C. The mixture was left at 50°C for 2 hours, and racemic methylphenylnaphtylchlorosilane in DMF was added dropwise. The solvent was removed in vacuo, and the residual mixture dissolved in 10 ml of C_6H_6. After filtration, the concentrated solution was checked by NMR. We identified (-)t-BuPhPOSiMePhNp $[\alpha]_D$ = -12.7° (C_6H_6).

c) From (-)naphtylphenylmethylchlorosilane and t-butylphenylphosphine oxide (ester with optical activity both on phosphorus and on silicon).

315 mg (1.7 mmol) of (-)t-butylphenylphosphine oxide, $[\alpha]_D$ = -11.4° (CH_2Cl_2) were mixed with 480 mg (1.7 mmol) of the title chlorosilane, $[\alpha]_D$ = -5.7°, and 170 mg (1.7 mmol) triethylamine in 10 ml of dichloromethane, at - 40°C. The solution was filtered off concentrated in vacuo and checked by NMR, $[\alpha]_D$ = -17.4° (CH_2Cl_2).

^{31}P NMR (CH_2Cl_2) : 119.53 ppm (75 %) 119.24 ppm (25 %)

^{29}Si NMR (CH_2Cl_2 + CD_2Cl_2) : 1.29 ppm (13.6 Hz) (80 %) 1.02 ppm (13.9 Hz) (20 %)

d) From (-)naphtylphenylmethylchlorosilane and (±) t-butylphenylphosphine oxide (ester with optical activity on silicon).

In the same conditions as above, 745 mg (4 mmoles) of t-butylphenylphosphine oxide were mixed with 600 µl of triethylamine and 1.15g of the title chlorosilane, ($|\alpha|_D$ - 6,4°), in 10 ml of dichloromethane, at -40°C. After filtration, the product 5 was identified by ^{31}P NMR, $|\alpha|_D$ - 2.7°. The optical activity decreases very quickly.

II - Preparation of naphtylphenylmethylsilyl t-butylphenylphosphinate (1)

a) Dehydrocondensation of t-butylphenylphosphinic acid with (+)naphtylphenylmethylsilane on Pd/C catalyst (racemic ester).

To the solution of 0.40 g (2 mmol) of t-BuPhP(O)OH and 0.50 g (2 mmol) of (+)α-NpPhMeSiH in dry dioxane the catalyst (260 mg) 5 % Pd/C (Int. Enzymes Ltd.) was added under nitrogen (commercial catalysts were activated in a stream of hydrogen at 400°C) at room temperature. The mixture was heated up to 80-100°C for some hours while hydrogen was slowly evolved. The reaction progress was monitored by ^{31}P NMR and ^{1}H NMR. After consumption of silane, 80 % of racemic ester was obtained. Some amount of phosphonic acid remained in the system.

b) Dehydrocondensation on Wilkinson catalyst (racemic ester).

Racemic ester was obtained after stirring the benzene solution of 0.40 g (2 mmol) t-BuPhP(O)OH with 0.50 g (2 mmol) of (+)α-NpPhMeSiH ($[\alpha]_D$ = +32°) and 200 mg of Wilkinson catalyst at temperature 50-60° during 4 hours. Yield (^{31}P NMR) of the ester was 50 %. Besides the signals of acid (δ = 49.8 ppm) and ester (δ_1 = 41.86 ppm, δ_2 = 41.16 ppm) the signals δ = 47.6 ppm and δ = 41.86 ppm appeared, which probably corresponded to the complexes of acid and ester with catalyst (the concentration of catalyst was about 0.1 eq/mol).

c) From (-)naphtylphenylmethylchlorosilane and t-butylphenylphosphinic acid (racemic ester).

In 25 ml round flask 1.98 g (10 mmol) of t-BuPhP(O)OH and 1.01 g (10 mmol) of Et_3N was placed in 15 ml of CH_2Cl_2. The solution of 2.83 g (10 mmol) of α-NpPhMeSiCl ($[\alpha]_D$ = -6.8°) in 10 ml of CH_2Cl_2 was quickly added, with vigorous stirring. After several minutes the precipitate was filtered off and the solvent was evaporated under reduced pressure. The ester was an oily sirup which did not crystallize from common solvents.
Yield (^{31}P NMR : 100 % ; $[\alpha]_D$ = 0).

d) From (-)naphtylphenylmethylchlorosilane and trimethylstannylt-butylphenylphosphinate (ester with optical act. on silicon).

To the solution of 0.341 g (0.92 mmol) of t-BuPhP(O)OSnMe$_3$ in 2 ml of dry CCl_4 (^{31}P NMR: 30.87 ppm), 0.260 g (0.92 mmol) of (-)α-NpPhMeSiCl in 1 ml of dry CCl_4 ($[\alpha]_D$ = -6.4°) was added. The reaction progress was monitored by ^{31}P NMR and by polarimetry. Yield of 1 (^{31}P NMR) : 100 % $[\alpha]_D$ = +9°. The optical stability of the product was very poor ; $t_{1/2}$ rac. = 20 min.

e) Oxidation of 5 (Ia) (the product with optical activity on silicon).

2 ml of the solution of 5 (α_D = +3°), obtained by a method Ia, was placed in 10 mm O.D. NMR tube and dried oxygen was passed through within 20 minutes. ^{31}P NMR spectrum indicated 80 % of t-BuPhP(O)OSiMePhNp and 20 % of t-BuPhP(O)OH. Optical rotation was $[\alpha]_D$ = +6.2°. The oxidation of silyl phosphinite was repeated several times giving products of the optical rotations of 3° - 10° (depending on the optical purity of starting phosphinite).

III - Preparation of trimethylsilyl t-butylphenylthiophosphinate (with optical activity on phosphorus)

To the mixture of 1.07 g (5 mmol) of t-butylphenylthiophosphinic acid, $[\alpha]_D$ = -16.8° (MeOH) and 0.505 g (5 mmol) of triethylamine in dichloromethane, at - 10°C, was added quickly, 0.6 g (5.5 mmol) of trimethylchlorosilane. The precipitate was removed and the solution concentrated in vacuo. The product t-BuPhP(S)OSiMe$_3$ was characterized by NMR.
$[\alpha]_D$ = +13.8 ° (C_6D_6, ^{1}H NMR : δ_1 = 0.18 ppm (CH_3)$_3$Si), δ_2 = 1.1 ppm ((CH_3)$_3$C, J_{PCCH} = 18 Hz), (^{31}P and ^{29}Si NMR - see Table 1).

Addition of methanol in excess (5 ml) gave after 48 hours compound identified as (-)t-butylphenylthiophosphinic acid, $[\alpha]_D$ = -11.6° (MeOH).

IV - Preparation of naphtylphenylmethylsilyl t-butylphenylthiophosphinate (2)

a) Dehydrocondensation on Pd/C catalyst (the product with optical activity on silicon).

The solution of 1.07 g (5 mmol) of t-BuPhP(S)OH (mp. 141-142°) and 1.24 g (5 mmol) of (+)α-NpPhMeSiH in 20 ml of dry dioxane with 200 mg of catalyst (5 % Pd/C - Int. Enzymes Ltd.) was heated under reflux for 20 hours. Since the catalyst is partially desactivated during the reaction, new portions of it were occasionally added. The mixture was then centrifugated to remove catalyst and the solvent was evaporated under reduced pressure. The yield (^{31}P NMR) was 85 %. 15 % of unconverted t-BuPhP(S)OH remained. $[\alpha]_D$ = -40° (value corrected to the pure product).

Ester of lower optical activity ($[\alpha]_D$ = -21°) was succesfully crystallized from mixture of pentane and benzene (mp. 100-115°), but that of high optical activity was used in form of the oily sirup. Esters obtained according to this method are optically stable even in solution.

The yield strongly depends on activity of the catalyst. Different catalysts were used giving 10-85 % yields. The racemic ester was prepared in the same route from racemic silane. The crystallization from mixture of benzene and pentane (1:5) gave product mp. : 112-115° (^{31}P an ^{29}Si NMR data - see table 1).

b) Dehydrocondensation (ester with optical activity on phosphorus and silicon).

In another experiment, 248 mg (1 mmol) of (+)methylphenylnaphtylsilane, $[\alpha]_D$ = +31.7°, was mixed in Et_2O (10 ml) with 214 mg (1 mmol) of (+)t-butylphenylthiophosphinic acid, $[\alpha]_D$ = +24.6° (methanol), and 340 mg Pd/C (10 %). Early after completion of the reaction (checked by thin layer chromatography), the mixture, $[\alpha]_D$ = -47.9° (CH_2Cl_2), was analyzed by ^{29}Si NMR. We obtained two doublets at 2.06 ppm, 1.63 ppm in a 90/10 ratio. The main doublet (downfield) was attribued to the (-)Rp(-)R_{Si} diastereoisomer.

c) From (-)naphtylphenylmethylchlorosilane and t-butylphenylthiophosphinic acid (ester with optical activity on silicon).

To the solution of 0.2 g (0.93 mmol) of t-BuPhP(S)OH and 0.10 g (1 mmol) of Et_3N in 5 ml of benzene placed in 15 ml round-bottom flask, the solution of 0.263 g (0.93 mmol) of (-)α-NpPhMeSiCl ($[\alpha]_D$ = -6.8°) in 5 ml of benzene was quickly added. The precipitate of Et_3N.HCL was filtered off under nitrogen after 3 minutes. The filtrate quickly lost its optical rotation (from α = -1.4° to α = -0.8° in 10 minutes). The attempts of crystallization failed. Yield : 100 % (^{31}P NMR) ; $[\alpha]_D$ = -33°.

d) Addition of sulphur to 5 (Ia) (product with optical activity on silicon)

An excess of powdered sulphur dried on vacuum line was added at room temperature to the solution of (+)t-BuPhPOSiMePhNp (obtained by the method Ia, $[\alpha]_D$ = +4.8°) in xylene/THF. An exothermic effect was observed. After 30 min. the excess of sulphur was filtered off. The optical rotation was $[\alpha]_D$ = +11.2°. Yield (^{31}P NMR) was 80 %. The reaction was repeated several times giving products of the optical rotation of 10°- 17°.

e) Addition of sulphur to 5 (Ic) (product with optical activity on both P and Si)

An excess of sulphur was added at room temperature to the solution of (-)t-BuPhPOSiMePhNp obtained by the method Ic, $[\alpha]_D$ = -17.4°) in CH_2Cl_2. After several minutes the excess of sulphur was filtered off and the ^{31}P NMR spectrum was taken showing two signals 97.6 ppm (70 %) 97.15 ppm (30 %) attributed to the pair of diastereoisomers of silyl ester of thiophosphinic acid, $[\alpha]_D$ = -22.9° (CH_2Cl_2).

f) Addition of sulphur to 5 (Ib) (product with optical activity on phosphorus)

The product 5 (Ib) was added to a suspension of S_8 in C_6H_6, giving after usual work-up (-)t-BuPhP(S)OSiMePhNp, $[\alpha]_D$ = -12.29°, yield (^{31}P NMR) about 100 %.

Finally, subsequent methanolysis in excess methanol afforded (+)t-BuPhP(S)OH, $[\alpha]_D$ = +7.4°, isolated as the ammonium salt.

V - Preparation of naphtylphenylmethylsilyl t-butylphenylselenophosphinate (3) (with optical activity on silicon)

An excess of dried selenium was added to the solution of 5 (obtained according to Ia, $[\alpha]_D$ = -6°, purity estimated from ^{31}P NMR : 80 %) at room temperature. ^{31}P NMR spectrum made after 30 min. showed full conversion of 5 to 3. $[\alpha]_D$ = -8.1° xylene (corrected to optical purity of silanolate : - 11°) (^{31}P NMR data - see table 1).

VI - Preparation of trimethylsilyl t-butylphenyldithiophosphinate

The solution of 3.27 g (0.01 mmol) of t-BuPhP(S)$\overset{+}{S}NH_3C_6H_{11}$ in 20 ml of dry CCl_4 was put into a 3-necked flask equipped with magnetic stirrer, reflux condenser and dropping funnel. The solution of 1.55 g (0.01 mol) of Me_3SiBr in 10 ml dry CCl_4 was added dropwise within 15 minutes. The precipitate of $C_6H_{11}NH_3Br$ was removed by filtration, the solvent was evaporated and the residual sirup was distilled on Glass Tube Oven (Büchi), bp. 141-142°/3.5 x 10^{-2} mm. It slowly crystallized from the sirup (mp. impossible to estimate, as the product is very sensitive to moisture, the range of melting 50° - 90°). Yield (^{31}P NMR) : 100 %, after distillation : 95 %.

VI - Preparation of methylphenyl(α-napthyl)silyl t-butylphenyldithiophosphinate (4) (with optical activity on silicon)

To the solution of 1.59 g (48 mmol) of t-BuPhP(S)$\bar{S}\overset{+}{N}H_3C_6H_{11}$ in the mixture of 4 ml of CH_2Cl_2 and 4 ml Et_2O placed in 15 ml round-bottom flask, the solution of 1.59 g (48 mmol) of (-)α-NpPhMeSiBr ($[\alpha]_D$ = -19°) in 5 ml of Et_2O was added within 2-3 minutes. The tiny precipitate of $C_6H_{11}NH_3Br$ arose immediatly. The mixture was centrifuged and the solvent was evaporated under reduced pressure. Oily sirup was dissolved in CCl_4. Yield : 80 % (^{31}P NMR). 20 % t-BuPhP(S)SH remained in the mixture. Hence the optical activity of the product was very low it was impossible to determine the stereochemistry of the reaction.

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