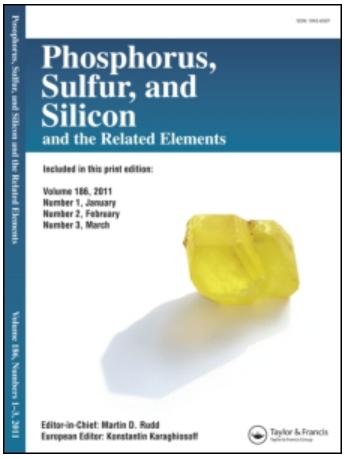

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Andrzej Łopusiński[a]
[a] Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lódź, Poland

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TRANSFORMATION OF ORGANOPHOSPHORUS S-TRIFLUOROMETHYLTHIOATES RR'P(O)SCF$_3$ INTO FLUORIDATES RR'P(O)F. STEREOCHEMICAL ASPECTS OF THIOCARBONYL FLUORIDE EXTRUSION

ANDRZEJ ŁOPUSIŃSKI

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland

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The stereochemical course of the thermal or by nucleophiles catalyzed extrusion reaction of thiocarbonyl fluoride from two diastereoisomeric (**6**) and optically active (**10**) organophosphorus S-trifluoromethylthioates has been investigated. To explain the observed retention of configuration at phosphorus in fluoridates **7** formed in the thermal reactions, a four center transition state for such reactions has been proposed. The lack of the stereoselectivity in the catalyzed reactions of **6**, and the observed racemization of the final product **11** are briefly discussed.

Key words: O,O-dialkyl-S-trifluoromethyl phosphorothioate, *cis*- and *trans*-2-S-trifluoromethyl-2-oxo-4-methyl-1,2,2-dioxaphosphorinans, *cis*- and *trans*-2-fluoro-2-oxo-4-methyl-1,3,2-dioxaphosphorinans optically active t-butyl(phenyl)-S-trifluoromethyl phosphinothioate, dialkylphosphorofluoridate.

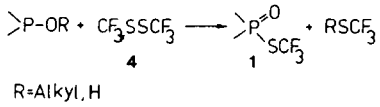
In our previous papers[1–3] we described the synthesis of organophosphorus esters **1** containing the trifluorothiomethyl group RR'P(O)SCF$_3$. They were obtained in the reaction of various tricoordinated phosphorus compounds with bis-(trifluoromethane)disulfide $(CF_3S)_2$ **4**. We have found, that the esters **1**, undergo a

$$\underset{\mathbf{1}}{RR'P(O)SCF_3} \xrightarrow[0\text{-}20^\circ C]{\text{Nucleophile}} \underset{\mathbf{2}}{RR'P(O)F} + \underset{\mathbf{3}}{SCF_2} \qquad (1)$$

decomposition[2] which is catalyzed by nucleophilic reagents.[3] This extrusion reaction of thiocarbonyl fluoride **3** from **1** serves as a convenient method for the synthesis of the structurally diversified organophosphorus fluoridates. The present paper describes our study on the stereochemistry of this reaction.

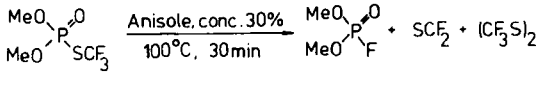
RESULTS AND DISCUSSION

The first step in our investigations was to test the stability of the esters **1** (R = R' = alkoxy) prepared from tricoordinated phosphorus compounds and the disulfide **4** (Equation 2). Esters **1** obtained according to the method described in Equation (2), are thermally relatively stable. This stability can be explained by the absence of the nucleophilic catalysts in the reaction medium. The second

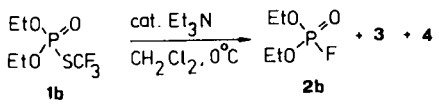


(2)

product of the reaction (Equation 2) is highly volatile and readily removable from the reaction solution. However, when the esters **1** are warmed to 100°C in aprotic solvent, a slow extrusion of thiocarbonyl fluoride **3** takes place and the formation of the corresponding fluoridates **2** is observed. This can be exemplified by the transformation of O,O-dimethyl S-trifluoromethyl phosphorothioate **1a** into O,O-dimethylphosphorofluoridate **2a** in anisole solution at 100°C. After 30 minutes, **2a** is formed with ca. 10% yield. The reaction is completed in two hours. The formation of thiocarbonyl fluoride **3** as a second major reaction product and some amounts (15%) of trifluoromethyl disulfide **4** as well as the traces of the unidentified fluorine compounds were detected by ^{19}F NMR spectroscopy. Similar behavior of some trihalogenomethylthiophosphorochloridates was observed by Haas and Winkler.[4] In contrast, the decomposition of S-trifluoromethyl organophosphorothioates **1** by extrusion of the thiocarbonyl fluoride in the presence of a catalytic amount of nucleophile such as trialkylamine, proceeds violently already at 0°C as it is shown in Equation (4).



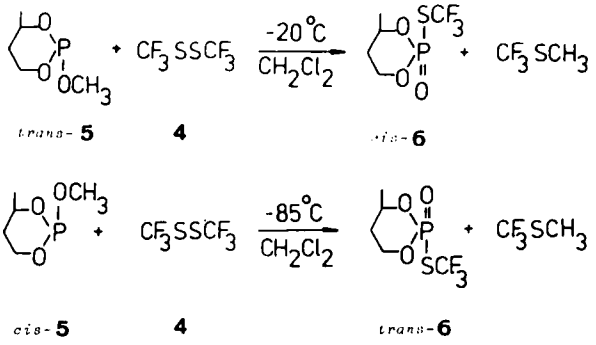
(3)



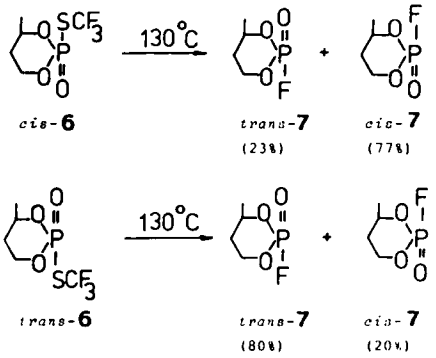
(4)

The diastereoisomeric *cis*- and *trans*-2-S-trifluoromethyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinames **6** obtained by the disulfide method,[2] were used as models for stereochemical studies of thiocarbonyl fluoride extrusion. Stability of the *cis*- and *trans*-**6** is high and they do not decompose up to 115°C and can be readily distilled under reduced pressure. However, when the pure sample of **6** is heated without solvent at 130°C the corresponding *cis*- and *trans*-2-fluoro-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes **7** are formed.

Thus, the reaction of *cis*-**6** gave 77% of fluoridate *cis*-**7** accompanied by 23% of *trans*-**7**. Under the same conditions *trans*-**6** gave *trans*-**7** (80%) and *cis*-**7** (20%) In both cases, the formation of 2–3% of disulfide **4** as well as the oligomeric thiocarbonyl fluoride **3** and unidentified fluorine compounds were observed. The distribution of products **7** shown on the Scheme 2 was registered after 55 min of the reaction time using ^{31}P and ^{19}F NMR spectroscopy. The stereochemical assignments concerning the products *cis*- and *trans*-**7** was based on the spectral analysis in accordance with the literature data.[5] After this time only 30% conversion of *trans*-**6** and 45% of the *cis*-**6** was observed. Prolonging the reaction time to 6 hr, affords the mixture of products **7** containing thermodynamically more stable[5] *trans*-**7** as the major product.

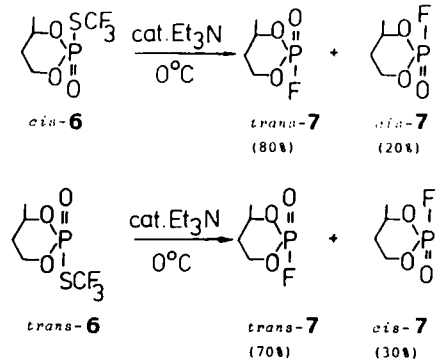


SCHEME 1

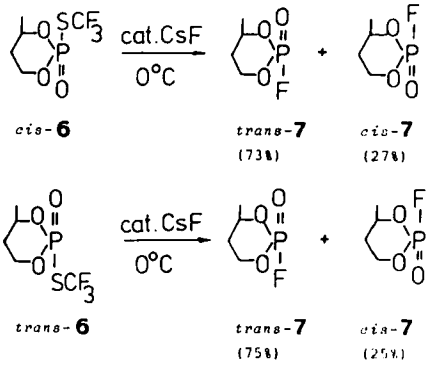


SCHEME 2

In spite of the fact that the stereoselectivity of the thermal reactions involving *cis*- and *trans*-**6** is not high, we can conclude that it takes place with retention of configuration at the phosphorus atom. The same diastereoisomeric compounds **6** were used to follow the stereochemistry of the extrusion reaction of thiocarbonyl fluoride catalyzed by triethylamine and cesium fluoride. The exothermic reaction occurs after the addition of the catalytic amount of triethylamine to the dichloromethane solution of *cis*-**6** at 0°C. The ^{31}P NMR spectra of the reaction mixture recorded immediately after the addition show, that the signal of *cis*-**6**, δ 5.1 disappeared and two doublets characteristic for *cis*-**7** and *trans*-**7** at δ −15.22, δ −15.28, respectively, appeared in 2:8 ratio (Scheme 3).



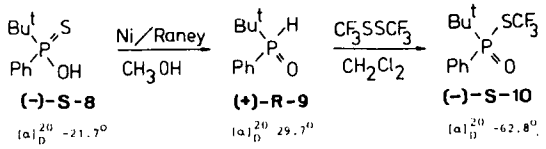
SCHEME 3



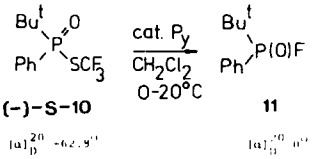
SCHEME 4

The ^{19}F NMR showed also the presence of disulfide **4**, fluoride **3**, and several unidentified fluorine-containing compounds. Under the same conditions, starting from *trans*-**6**, δ ^{31}P 3.3, a mixture of *trans*-**7** and *cis*-**7** in the 7:3 ratio was formed. Similar product distribution, was observed in the reaction catalyzed by cesium fluoride, as shown in Scheme 4.

The stereochemistry of the thiocarbonly fluoride extrusion was also investigated with t-butyl(phenyl)-S-trifluoromethyl phosphinothioate **10** used as the optically active model. For the synthesis of **10** the literature procedure,[3] involving reaction of t-butylphenylphosphine oxide **9**[6] with disulfide **4** was adopted. It is most likely that the retention of configuration at phosphorus results in the **9**→**10** transformation (Equation 5).[7,8] The ester **10** is a stable compound and was isolated from the reaction mixture by distillation without decomposition. Unfortunately, the optically active t-butylphenyl S-trifluoromethyl phosphinothioate **10** does not undergo extrusion of SCF_2 up to 125°C without solvent. The formation of minute amount of the t-butylphenylphosphinofluoridate **11** was observed only after raising the temperature to 145°C. However, these conditions were considered too drastic for the stereochemical studies. In the presence of catalytic amount of pyridine the optically active **10** undergoes the SCF_2 extrusion at room temperature. The obtained t-butyl(phenyl)phosphinofluoridate **11** was found to be racemic.



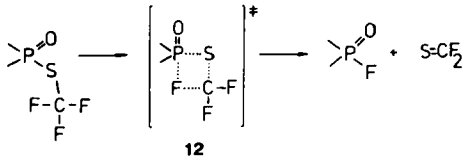
(5)



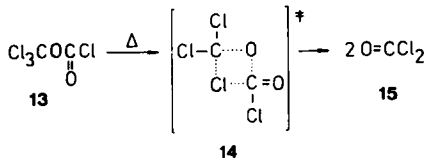
(6)

The overall transformations depicted in Equations (1), (3), (4) and (6) and Schemes 2, 3 and 4 can be formally viewed, as the nucleophilic substitution of the

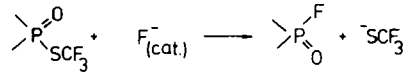
SCF_3 group at the phosphorus atom by the fluoride anion. The trifluoromethyl group, with the electronegativity of 2.7 which is comparable with the electronegativity of halogens, displays halogen-like behavior [9–12] and is a good leaving group when bonded to the electrophilic center.[2,3,10,11] Taking this into account, the internal delivery of F^- nucleophile involving a four-center transition state structure **12** can be postulated for the uncatalyzed transformation of **6** into **7**. Such a process would involve retention of configuration at phosphorus which was indeed observed. The thermal extrusion of carbonyl chloride **15** from trichloromethyl chloroformate **13**, was explained by the analogous mechanism.[13]



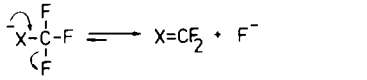
12 (7)



13 **14** **15** (8)



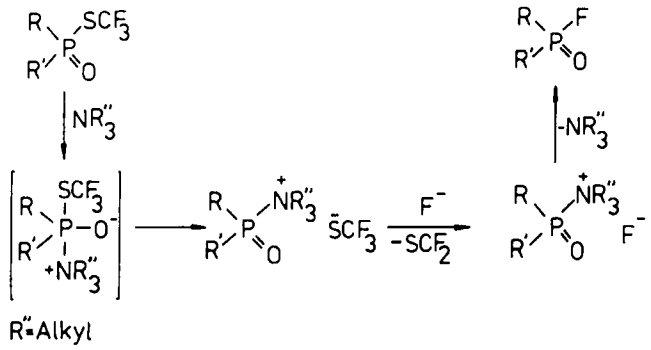
(9)



(10)

On the other hand, for the catalyzed reaction, it is possible that the first step involves the nucleophilic substitution of the SCF_3 group by the "externally" introduced nucleophile (Equation 9). It is most likely that fluoride ion is liberated during decomposition of the leaving group F_3CS^-. It is known that the CF_3S^- anions as well as its oxygen analog exists in solution in equilibrium with the $X = CF_2$ molecule ($X = S$ and $X = O$ respectively) and fluoride anion.[14,15] The fluoride anion, generated in such a process, reacts with the ester $\rangle P(O)SCF_3$, to give the corresponding phosphorofluoridate and this cycle can then be repeated. The catalytic activity of tertiary amine and other nucleophiles in this process can be explained using the same rationale (Scheme 5).[16]

Thus, it can be concluded that the studied reactions catalyzed by nucleophiles constitute rather complex chemical processes. The observed formation of fully racemized fluoridate **11** during the reaction of optically active **9** may likely result from the multiple substitution process involving F^- anion exchange, or other processes of similar nature proceeding through structures with five- and six-coordinated phosphorus atom.[17–23] The observed ratios of the epimeric *cis-trans* fluoridates **7** formed in the reactions described in Schemes 3 and 4 reflect probably the differences in their thermodynamic stability.[5,18] In summary, despite



SCHEME 5

the fact that the retention of configuration during thermal (non-catalyzed) formation of *cis*- and *trans*-**7** from *cis*- and *trans*-**6** respectively, was detected, it is known that, many organophosphorus fluoridates RR'P(O)F are characterised by low optical stability.[24] Therefore the conclusions drawn from studies on catalyzed extrusion of thiocarbonyl fluoride from optically active **10** have to be regarded as tentative.

EXPERIMENTAL

The solvents and reagents were purified by standard methods before use. The boiling points are uncorrected. ^{31}P NMR spectra were recorded on a Jeol-JNM-FX60FT and Bruker MSL-300 spectrometers using 85% H_3PO_4 as internal standard. ^{19}F NMR spectra were recorded on a Bruker MSL-300 spectrometer with $CFCl_3$ as internal standard. The esters **1a**, **1b**, *cis*- and *trans*-**6** were synthesized from the corresponding phosphites and disulfide **4** as described previously.[1,2]
Warning: Because of the high toxicity of organophosphorus fluoridates their preparation and handling must be carried out with precautions.

The conversion of the esters **1a** *and* **1b** *into fluoridates* **2a** *and* **2b**. (a) *Thermal reaction of* **1a** *in anisole* The sample of 1.6 g (0.0076 Mole) of freshly distilled O,O-dimethyl-S-trifluoromethyl phosphorthioate **1a** was heated with stirring in 5 ml of dry anisole on the oil bath at 100°C in a dry inert atmosphere. The ^{31}P NMR spectra of the solution recorded after total 30 min of the reaction time show the presence of two organophosphorus compounds: the substrate **1a** δ 16.2 and O,O-dimethylphosphorofluoridate **2a** δ −9.6 in 9:1 ratio. Stirring was continued under these conditions for the next 90 min. After this time the reaction was completed and the presence of the fluoridate **2a**, thiocarbonyl fluoride **3** δ ^{19}F −40.4 (lit.[25] δ −40.5) and probably their oligomers δ ^{19}F −40.8 and δ ^{19}F −41.3 as well as ca. 15% of bis-(trifluoromethane)disulfide δ ^{19}F −46.78 (lit.[26] δ ^{19}F −46.88) and traces of other unidentified fluorocompounds δ ^{19}F −43.9 to δ ^{19}F −44.8 were observed in the reaction mixture by means of ^{19}F NMR. From the resulting mixture the fluoridate **2a** was separated by distillation: colorless liquid b.p. 20–23°C/4 mmHg; δ ^{31}P −9.7 (neat), J_{P-F} 981 Hz.

(b) *The triethylamine-catalysed reaction of* **1b**. Into the stirred solution of 2.4 g (0.01 mole) of O,O-diethyl-S-trifluoromethyl phosphorothioate **1b** in 15 ml of dry dichloromethane cooled in an ice bath was added dropwise 0.005 g of dry triethylamine in 1 ml of CH_2Cl_2. The resulting brown colored reaction solution was stirred for the next 10 min at 10°C. The ^{31}P and ^{19}F NMR spectra of a sample showed the mixture of the following reaction products: O,O-diethylphosphorofluoridate **2b**, δ ^{31}P −8.1, δ ^{19}F −79.1; thiocarbonyl fluoride **3**, δ ^{19}F −40.7; bis-(trifluoromethane)disulfide **4**, δ ^{19}F −47.0 as well other unidentified fluorocompounds (resonance lines between δ ^{19}F −40.8 and δ ^{19}F −41.5, and δ ^{19}F −44.0–−44.8). From this mixture the fluoridate **2b** was isolated by the fractional distillation in vacuo: colorless liquid; 1.2 g, 76% yield, b.p. 17–18°C/0.009 mmHg; ^{31}P NMR (neat) −8.0 (d, J_{P-F} 971.1 Hz); ^{19}F NMR (CD_2Cl_2) −79.0 (lit.[27] δ ^{19}F −77.5, J_{P-F} 977 Hz).

The extrusion of **3** *from the cis- and trans-***6**. (a) *Thermal reactions*. The freshly prepared sample of 2.0 g of the *cis*-**6** was placed in a closed NMR tube and was heated without solvent in an oil bath at 130°C for 55 min. After this time, the analysis of the reaction mixture by ^{31}P and ^{19}F NMR revealed

that it contained 65% of the substrate *cis*-**6** δ ^{19}F −34.6 (d, $^3J_{P-F}$ 8.9 Hz); and the products: *cis*-2-fluoro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane **7**, δ ^{19}F 15.22 (J_{P-F} 991.2 Hz), δ ^{19}F −69.24 (lit.[5] δ ^{19}F 17.4, J_{P-F} 1024 Hz; ^{19}F −94.6 using C_6F_6 as standard) and *trans*-**7**, δ ^{31}P 15.28 (d, J_{P-F} 998.5 Hz), δ ^{19}F −85.54 (lit.[5] δ ^{31}P 17.5, J_{P-F} 1030; δ ^{19}F −78.0 using C_6H_6 as standard) in 77:33 ratio. The formation of thiocarbonyl fluoride **3** δ ^{19}F −40.5 and probably its reaction products δ ^{19}F −40.8 to δ −41.4, the disulfide **4** δ ^{19}F −46.8 as well as trace amounts of other fluorocompounds δ ^{19}F −43.5 to δ −45.0 were observed using ^{19}F NMR. The heating of the sample of *cis*-**6** was continued for 5 hr at 130°C to complete the reaction. The formation of *trans*-**7** and *cis*-**7** in the 86:14 ratio was observed from the ^{31}P NMR spectra of the reaction mixture.

Under identical conditions as described above from *trans*-**6** the formation of a mixture of *cis*- and *trans*-**7** in the 1:8 ratio (70%) was observed by means of ^{31}P, ^{19}F NMR after 60 min of the reaction time. The spectral data of *cis*- and *trans*-**7** was in full agreement with the data reported in the literature.[5]

(b) *The triethylamine-catalyzed reaction of* **6**. A sample of freshly prepared *cis*-**6**, 1.18 g (5.0 mmole) in 2 ml dry dichloromethane was placed in the NMR tube. To this solution 1.5 ml of a 0.05 molar solution of triethylamine in CH_2Cl_2 was added at 0°C and the ^{31}P NMR spectrum of the reaction mixture was recorded immediately. The two doublets centered at δ 15.24 (J_{P-F} 990.2 Hz) and δ 15.30 (J_{P-F} 997.3 Hz) in the 20:80 ratio were observed in the spectrum. They are characteristic for the fluoridates *cis*- and *trans*-**7** respectively. After the next 25 min of reaction time at 8–10°C the reaction was completed and the formation of two fluoridates *cis*-**7** δ ^{19}F −69.3 and *trans*-**7** δ ^{19}F −86.3 in ratio 18:82 was confirmed by ^{19}F NMR. The formation of **3**, **4** and trace amount of other fluorocompounds was observed spectroscopically (^{19}F NMR).

Under identical conditions as was described for *cis*-**6**, *trans*-**6** reacts in the presence of catalytic amounts of triethylamine with formation of a mixture of *cis* and *trans* fluoridate **7** in the 30:70 ratio which was confirmed by the ^{31}P, ^{19}F NMR spectra of the reaction solution.

(c) *The cesium fluoride-catalysed reaction of* **6**. Into the stirred solution of 2.36 g (0.01 mole) of *cis*-**6** in 10 ml of dry dichloromethane a few crystals of finely powdered dry cesium fluoride was added at the temperature of 0°C. The stirring was continued for the next 15 min at 0°C. The cooling bath was removed and the reaction mixture which turned brown was kept standing for the next 30 min at room temperature. The presence of two fluoridates **7** was identified after this time in the solution by means ^{31}P and ^{19}F NMR: *cis*-**7** (yield 27%), δ ^{31}P 15.24 (J_{P-F} 991.3 Hz), δ ^{19}F −70.31 and *trans*-**7**, δ ^{31}P 15.32 (J_{P-F} 998.1 Hz), δ ^{19}F −84.38.

Under the same conditions *trans*-**6** undergoes the extrusion of thiocarbonyl fluoride **3** with the formation of *cis*- and *trans* fluoridates **7** in 25:75 ratio. In both cases, the reactions starting from *cis*- *and trans*-**6**, the formation of **3**, **4** and unidentified fluorine compounds were observed.

*Reaction of (+)-R-***9** *with disulfide* **4**. *(−)-S-t-butyl(phenyl)-S-trifluoromethyl phosphinothioate* **10**. Into the stirred solution of the freshly prepared (+)-R-t-butyl(phenyl)phosphine oxide **9** 5.46 g (0.03 mole), $[\alpha]_D^{20}$ + 29.7° in 15 ml dry CH_2Cl_2, the disulfide **4** 4.1 g (0.04 mole) in 10 ml CH_2Cl_2 was added at temperature of 5–8°C. The stirring was continued for 6 hr at 20°C. The solvent and remaining trifluoromethylmercaptane as well the excess of **4** were removed under reduced pressure (4 mmHg) on the water bath (15°C) to give yellow oily liquid. Distillation gave pure colorless (−)-S-**10** t-butyl(phenyl)-S-trifluoromethyl phosphinothioate yield 7.4 g (88%), b.p. 97–98°C/0.045 mmHg; $[\alpha]_D^{20}$ −62.8° (c = 0.01, CH_2Cl_2); ^{31}P NMR (CH_2Cl_2) δ 66.65 (q $^3J_{P-F}$ 0.75 Hz).

Uncatalyzed extrusion of **3** *from* **10**. The pure sample of (−)-S-**10** 2.8 g(0.01 mole), $[\alpha]_D^{20}$ −62.78° was heated in the closed reaction vessel without solvent at 125°C for the 15 min. The presence of the fluoridate **11** was not observed after this time. Heating was continued at 145°C for the next 15 min. The formation of traces of fluoridate **11**, yield 3–5% was observed by NMR, δ ^{31}P 58.1 (d, J_{P-F} 1046 Hz), δ ^{19}F −69.0 (d).

The pyridine catalyzed reaction of (−1)-*S*-**10**. To the stirred solution of 5.64 g (0.02 mole) of (−)-S1**10**, $[\alpha]_D^{20}$ −62.81° in 15 ml dry CH_2Cl_2 one drop of dry pyridine was added at 0°C. The stirred reaction solution was left at 0°C for the next 15 min and the cooling bath was removed. The solution was stirred for 1 hr at the room temperature and fractionated in vacuo. A colorless oily liquid of fluoridate **11** was obtained: yield 3.5 g (85%); b.p. 60–61°C/0.08 mmHg; $[\alpha]_D^{20}$ 0° (c 0.01, C_6H_6); ^{31}P NMR (CH_2Cl_2) δ 58.1 (d, J_{P-F} 1045 Hz) (lit.[28] δ ^{31}P 58.63, J_{P-F} 1048 Hz).

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