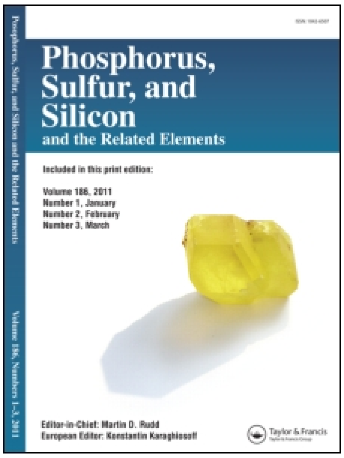

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SYNTHESIS , UV AND CD SPECTROSCOPY OF OPTICALLY ACTIVE SELENOPHOSPHORUS COMPOUNDS

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The synthesis of novel chiral esters of thio- and seleno-phosphorus acids and their UV , CD , and MCD spectra is described.

Keywords : esters of thio- and seleno-phosphorus acids; configuration of chiral alcohols, UV, circular and magnetic circular dichroism

INTRODUCTION

The spectroscopy of circular dichroism is a simple method of the determination of configuration of the chiral center of optically active compounds, especially of bioactive and natural substances. In this paper we are reported on new chromophoric groups for determination of configuration of optically active alcohols.

RESULTS AND DISCUSSION

In our previous papers were shown that in the UV spectra of thio- and seleno-phosphoryl compounds the absorption observed [1].

This absorption is caused by n-π* -transition in P(S) and P(Se) bonds. To a check the possibility of this chromophoric groups can be used for the determination of configuration of chiral alcohols we synthesized the optically active esters of thio- and selenophosphorus acids. These compounds were obtained by addition of elemental sulfur or selenium to tetraethyldiamido-menthyl- or bornyl-phosphites. These amidophosphites were obtained by heating of hexaethyltriamidophosphite with menthol or borneol in toluene (Scheme 1).

$$[(C_2H_5)_2N]_3P + HO\text{-}R \xrightarrow{a,b} [(C_2H_5)_2N]_2P(Se)\text{-}OR$$

ROH - (-)menthol, (+)isoborneol

Scheme 1 Reagents and conditions: a- 1, (-)menthol, toluene,heating at 100 C, 2 h , 2 , Se , heating at 80 C ; b - (+) isoborneol , toluene, heating at 100 C , 2 h, 2, Se, heating at 80 C

The chiral esters of thiophosphorus acids were obtained by addition of elemental sulfur to corresponding diamidophosphites. The structure of optically active esters of thio- and selenophosphorus acids were studied by NMR, IR, UV and circular dichroism (CD) spectroscopy . UV spectra of these compounds shows the absorption maximum in the 200-260 nm cased by n-π* transition in thiophosphorilic and selenophosphorilic groups (TABLE 1).

The investigation of CD spectra of optically esters of seleno- and thio-phosphorus acids shows that sign of Cotton effects depends on the configuration of the chiral center. The sign of Cotton effect for the (-) menthylester of tetraethyl-diamidoselenophosphorus acid was shown to be positive.The negative Cotton effect are observed for esters of selenophosphorus acids obtained from (+) isoborneol (TABLE 1, FIGURE 1).

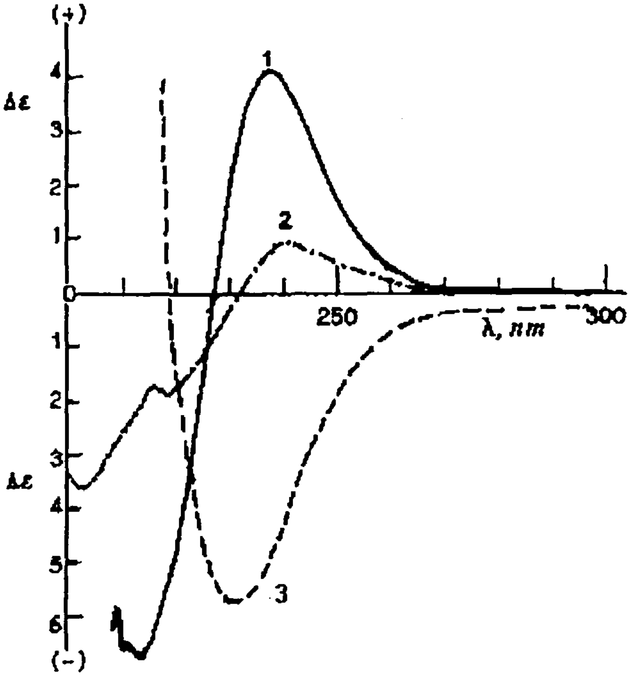

FIGURE 1 1- CD spectra of compound 1 in hexane; 2- MCD spectra of 1; CD spectra of compound 2 in hexane (CD and MCD spectra were recorded on JASCO-500 spectropolarimeter).

For comparison we studied CD spectra of the similar esters of thiophosphorus acids. It is found that selenophosphorus derivatives more convenient for the determination of configuration of chiral centre in optically active alcohols then thiophosphorus derivatives.

We were first to study the magnetic circular dichroism spectra of the optically active selenophosphorus derivatives. It was found that the sign of Cotton effects depended on configuration of chiral fragment of studied molecules (TABLE 1).

TABLE 1.

Compound	UV		CD		MCD	
	λ_{max},nm	lg ε	λ_{max},nm	Δε	λ_{max},nm	Δε
1.$(Et_2N)_2P(Se)$-R	227(sh)	1,94	215	-7	204	-8
			238	+4,1	220	-4
					240	+2
2.$(Et_2N)_2P(Se)$-R'	227(sh)	0,79	-	-		
	243(sh)	0,51	238	-5,8		
3. $Et_2P(Se)$-R	213(sh)	1,68	251	+2	205	- 18
					213	- 16
					251	+0,2
4. $Et_2P(S)$-R	205	4,0	-	-	202	- 30
	287,3	0,056	-	-		
5. $(Et_2N)_2P(S)$-R	205	2,45	-	-	215	-25
	287,4					

(R- (-)-menthol; R' - (+)-isoborneol)

The accumulating information on parameters of MCD spectra of selenophosphorus compounds might provide an answer on nature of electron transition in ground and excited state of these compounds.

The results of this study reveal the possibility of the CD spectroscopy for determination of the configuration of the chiral centre in optically active alcohols by transfer its in the corresponding selenophosphorus derivatives.

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