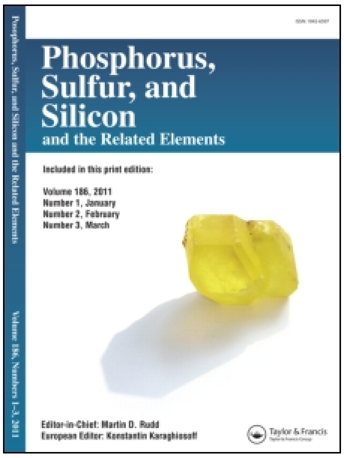

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NMR ^{77}Se, ^{125}Te , ^{31}P AND STRUCTURE OF SELENO- AND TELLURO-PHOSPHORUS COMPOUNDS

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Spectra of a nuclear magnetic resonance of seleno- and telluro-phosphorus compounds on nuclei ^{77}Se, ^{125}Te, ^{31}P are described. The dependences of spectral parameters on a structure of the substitutes at phosphorus atom in these compounds are discussed.

Keyword: nuclei shielding, chemical shift, spin-spin coupling seleno- and tellurophosphorus compounds, enantiomeric purity

INTRODUCTION

NMR spectra of organic compounds widely used for analytical purposes of establishing of the structure of new substances. NMR characteristics of organophosphorus compounds are reviewed in [1,2]. However the information about spectral parameters of seleno- and telluro-phosphorus compounds in is rather poor. In this paper we present results of NMR ^{77}Se, ^{125}Te and ^{31}P study of some seleno-and telluro-phosphorus compounds.

RESULTS AND DISCUSSION

A number of selenophosphorus compounds $R_3P(Se)X_{3-n}$ with R- alkyl, aryl, X- chlorine were investigated with the help of

NMR ^{77}Se and ^{31}P for revealing the dependence of the structural and the spectral parameters. It was established that chemical shifts of ^{77}Se and ^{31}P for these compounds strongly depend on electronegativity of the substitutes near the phosphorus atom[3].

So the increasing of the number of chlorine atoms in molecule of selenophosphorilic compound results 'to displace of ^{77}Se chemical shift to the positive field and to increase the value of $J_{P\text{-}Se}$ (Table1,compounds 1-3,4-6). Similar behaviour of chemical shifts

TABLE 1.

Compounds	δ_{Se}, ppm	$J_{P\text{-}Se}$,Hz	Compounds	δ_{Se}, ppm	$J_{P\text{-}Se}$ Hz
1.$Et_3P(Se)$	-410	686	10.$Et_2P(Se)OPh$	- 268	796
2.$Et_2P(Se)Cl$	- 49	839	11.$Et_2P(Se)SEt$	- 298	761
3.$EtP(Se)Cl_2$	+170	932	12.$ET_2P(Se)NHMe$	- 341	727
4.$Ph_3P(Se)$	-276	756	13.Bu_3PTe	-1098	1718
5.$Ph_2P(Se)Cl$	- 63	854	14.$ET_2P(Te)NMe_2$	-1156	1783
6.$PhP(Se)Cl_2$	+150	935	15.$EtP(Te)(NMe_2)_2$	-1193	1904
7. $EtP(Se)F_2$	+162	1025	16.$EtP(Te)(OBu\text{-}n)_2$	- 696	2142
8. $EtP(Se)Br_2$	+249	857	17.$Et_2P(Te)OPh$	- 840	
9. $Et_2P(Se)OEt$	-307	779	18.$Et_2P(Te)OMent$	- 724	1960

and spin-couplings were revealed for the dihalogeneselenophosphonates (Table1, compounds 7,8). It is obvious that the nucleus ^{31}P in ethyldibromoselenophosphonate is strongly shielded. At the time the value of $J_{P\text{-}Se}$ in ethyldifluorselenophosphonate is about 200 Hz more than in ethyldibromoselenophosphonate. The replacement of one ethyl group of triethylphosphineselenide to the heteroatomic substitutes results in increasing of shielding of ^{77}Se nucleus and in increasing of $J_{P\text{-}Se}$ (Table1,comp.9-12)

NMR ^{77}Se spectrum of dimenthylmethylselenophosphonate, containing chiral centre in the ester fragment consists only two signal due to the spin coupling of ^{77}Se and ^{31}P nuclei.

Double triplets are observed in NMR ^{77}Se spectrum of racemic $CH_3P(Se)[OCH(C_3H_7)CH_3]_2$ Such pattern is caused by the spin-spin interaction of nuclei ^{31}P and ^{77}Se and by the presence of mixture d ,l and meso-isomers in the ratio1:2:1[(δ_{Se} 266,2 ppm, $J_{P\text{-}Se}$ 831Hz (meso 1) , δ_{Se} 272,2 ppm , $J_{P\text{-}Se}$ 841 Hz (meso 2), δ_{Se} 268,9 ppm , $J_{P\text{-}Se}$ 837 Hz (d,l)] . The distinction between nucleus shieldings of meso-1 and meso-2 isomers is 286 Hz, while the distinction between shieldings of meso-1 and d, l and meso-2 and d,l isomers is equal to 130 and 156 Hz accordingly. NMR ^{77}Se spectrum of dibornylmethylselenophosphonate represents two dublets due to the initial alcohole mixture of isoborneol and borneol in the ratio 9:1 with δ_{Se} 285 and 290,2 ppm and $J_{P\text{-}Se}$ 830 and 832 Hz accordingly. The integration of NMR ^{77}Se signal leads to 9:1 ratio also. These results allow to considerate a NMR ^{77}Se spectroscopy as suitable method for determination of enantiomeric purity of optically active alcohols. It is necessary to note that such investigations allow us to determine the spin-spin interaction constants of ^{77}Se and ^{19}F nuclei in difluoroalkylselenophosphonates ($^{2}J_{Se\text{-}F}$). In the same time NMR ^{125}Te spectrum of tellurophosphorus compounds, obtained by addition of elemental tellurium to the derivatives of trivalent phosphorus is considerably complicated by broadened resonance signal which is stimulated likely by the exchange processes in these compounds. In the number of cases it hinders the determination of ^{125}Te chemical shifts.The value of $J_{P\text{-}Te}$ in such cases is more easy to determine from NMR ^{31}P spectrum.

The considered results reveal the peculiarities of NMR ^{77}Se and ^{125}Te spectroscopy with their high sensitivity of magnetic features to the spatial and optically active parameters of the molecules as well as to the near surroundings of heteroatoms.

EXPERIMENTAL

NMR ^{31}P, ^{77}Se and ^{125}Te spectra were recorded on WM-250 CXP-100 and MSL-400 Bruker spectrometers.The substances under investigation were received by known procedures and their structures were confirmed by analytical and spectral methods.

References

[1] J.G.Verkade, J.A.Mosbo, in Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis Organic Compounds and Metal Complexes,edited by J.G.Verkade and L.D.Quin (Verlag Chemie International,New York,1987) , p.453-455.

[2].Cruchfield M.M., Dungan C.H.,Letcher L.H.,Mark V.,J.R.Van Wazer ,Topics in Phosphorous Chemistry, v.5 (John Wiley and Sons, New York, 1967), p.1

[3] I.A.Nuretdinov,E.I.Loginova,E.V.Bayandina,J.obch.chimii (Rus),.48 , 1071(1978)