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A GENERAL PROCEDURE LEADING TO PHOSPHOLANES AND PHOSPHORINANES : POLYMERIZATION AND CHARACTERIZATION

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Résumé : Dans la littérature de nombreuses façons de procéder à la synthèse de phospholanes et de phosphorinanes ont été décrites . Un résumé et un schéma global pouvant conduire à ces synthèses de phospholanes et de phosphorinanes sont ici proposés.Sur cette base, de nouveaux monomères ont été synthétisés il s'agit du 2-p-nitrophenoxy-2-oxo-1,3,2-dioxaphospholane et du 2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane. La polymerisation par ouverture de cycle des phospholanes et des phosphorinanes est également discutée et décrite selon les méthodes contenues dans la littérature. Sur cette base, la polymérisation des nouveaux monomères a été éalement réalisée.

Mot-clés : monomère, polymérisation, catalysateur, spectre organophosphate, proton, phosphorinane, dioxaphospholane.

INTRODUCTION

The ordinary demand of a severe environmental control of human activities in industrialized countries may find more localized and specific orientations in some third world regions devoted to agricultural production of only one harvest extended in time and space. Here, once ascertained the possibility of climate and/or biological decay of a specific pesticide, the insecticidal action should be oriented to the extension better than to the intensity of activity.

This valuable property of agricultural drugs spurred some research groups to study the anchorage of a pesticide function to the polymeric support by chemical bonds [1] which allow drug release upon prolonged

exposure to environment chemicals such as H_2O or oxygen. Besides the economical cost of these supported drugs,the anchorage or fixation appears restricted to some peculiar cases and it cannot encompass the variety of classes of pesticides used in modern agriculture. However, in the case of organophosphates, it is possible to produce self polymerization of monomeric species with appropriate structural functions [2][3] : these polymers can be hydrolysed affording in the time the monomer whith insecticidal action. It is noteworthy that the insecticidal activity of organophosphates is related to the fixation of organophosphorus moiety to the alcoholic group of serine [4][5][6] : these features are promoted by the presence of p-Nitrophenyl group in the phosphoric esters like parathion and paraoxon although short-lived. The polymeric organization of such units should improve their time of living particularly in subtropical regions of Africa subjected to sudden change of rainfall in correspondence to the need of definite insecticidal activity.

These facts spurred us to investigate the possibility to prepare polymers structurally analogous to paraoxon. The first part of the work here presented is devoted to the synthesis of new monomers suitable for polymerization, the preparation of polyorganophosphates, their characterization and the determination of physical properties. Owing to the limited attention paid to these polymers in the past, some systems already described in the literature have been prepared again for comparison with new products here obtained.

EXPERIMENTAL

All chemicals were handled under dry nitrogen. Solvents were dried and purified by standards methods [7] and were degassed before each reaction. ^1H NMR spectra were recorded on a Varian, operating at 90 MHz using TMS as internal standard. IR spectra were recorded using KBr pellets or NaCl windows. Spectrum calibration was made with a polyethylene film. Chemicals were used without further purification.

PREPARATION OF MONOMERS

The monomers $\overline{O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}PO(R)}$, (X=Cl, OCH_3, OC_2H_5, p-$NO_2C_6H_4$-O)

$\overline{O\text{-}(CH_2)n\text{-}O\text{-}PO(R)}$, (R=Cl, OCH_3, OC_2H_5) were prepared by the literature procedures [8][9], according to methods A or B

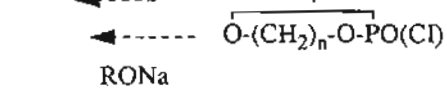
$POCl3 + ROH \dashrightarrow ROPOCl2 + HCl$

A :

$ROPOCl_2 + HO\text{-}(CH_2)n\text{-}OH \dashrightarrow \overline{O\text{-}(CH_2)_n\text{-}O\text{-}PO(OR)} + 2HCl$

$PCl_3 + HO\text{-}(CH_2)n\text{-}OH \dashrightarrow \overline{O\text{-}(CH_2)n\text{-}O\text{-}P\text{-}Cl} + 2\ HCl$

B :



$\overline{O\text{-}(CH_2)_n\text{-}O\text{-}P(OR)}$ $\overline{O\text{-}(CH_2)_n\text{-}O\text{-}PO(Cl)}$

(n = 2,3)

In particular, route B has been applied for the synthesis of 2-Methoxy-2-oxo-1,3,2-dioxaphospholane which cannot be got according to process A.

In the same way, the monomers

$\overline{O\text{-}C_2H_4\text{-}O\text{-}P(O)R}$ (R=OCH_3, P-NO_2-C_6H_4-O)

were prepared by route B whereas method A was used for the synthesis of ethyl analogue.

In table I are reported the preparation procedures used for the monomers here studied, and some physical properties of prepared compounds. The preparation procedure is described in details in case of the new compounds.

2-p-Nitrophenoxy-2-oxo-1,3,2-dioxaphospholane and 2-Ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane, the synthesis of other monomers being already described in literature (see table I).

PREPARATION OF p-Nitrophenoxy-2-oxo-1,3,2-dioxa-phospholane.

Method A : 12 g (0.5 mol) of p-NO_2-$C6H_4$-O-P(O)Cl_2,obtained according to the literature[10], dissolved in 600 mL of CH_2Cl_2 where placed into a 4-necked flask equipped with a mechanical stirrer, a dropping funnel, a condenser and a thermometer. To this solution kept at 0°C on a ice bath, a solution of ethylene glycol (25 mL, 0,5 mol) in pyridine (160 mL, 1 mol) is added dropwise, the temperature being kept below 10°C, during 90 minutes. The mixture is left aside for additional 90 minutes under stirring, then extracted in a separating funnel four times with 500 mL of H_2O. The CH_2Cl_2 solution is dried over $CaCl_2$ and concentrated under reduced pressure. The solid residue is crystallized from CCl_4 (yield 37%, melting point 40°C).

Method B : 161 g (1 mol) of sodium paranitrophenoxide, prepared by neutralization of paranitrophenol with NaOH, dissolved in 600 mL of CH_2Cl_2, is reacted in a 4-necked flask equipped as above, at 0°C, with 142 g (1 mol) of 2-chloro-2-oxo-1,3,2-dioxaphospholane, (see table I) added dropwise under stirring, keeping the solution below 10°C, then the solution is maintained under stirring for additional 60 minutes and left at room temperature over night till separation of NaCl has occurred. The solid residue obtained from the filtered solution after evaporation of the solvent is crystallized from CCl_4 (yield 88% ,melting point 40°C).

TABLE I : Preparation of monomers

PREPARATION OF 2-Ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane

This product is prepared according to method A above described. Starting from $Cl_2P(O)OC_2H_5$, got according to reference [11] and trans-2-hydroxymethyl-1-cyclohexanol, obtained with the procedure reported in reference [12]. The product is obtained with a 48% yield as viscous oil (boiling point at 0.003 torr 115-120°C)

PREPARATION OF THE POLYMERS

The polymerization of monomers reported in table I was carried out in the presence of cationic and anionic catalysts. Some physical properties of polymers and the experimental conditions of their preparation are reported in table II for the products already reported in the literature and in table III and IV for the polymerization of 2-Ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane and 2-p-Nitrophenoxy-2-oxo-1,3,2-dioxaphospholane respectively. The polymerization of these latters will be described in details.

POLYMERIZATION OF p-Nitrophenoxy-2-oxo-1,3,2-dioxaphospholane

Here is reported the polymerization in $CHCl_3$, (other solvents, see table III, afford the same products).

20 g of the solid monomer are dissolved in 250 mL of chloroform under reflux with stirring in a three-necked flask. The catalyst (see table IV) is added in molar ratio ranging from 1 to 9% and precipitation of a solid product is observed as the polymerization reaction proceeds. At selected time intervals, the polymer is filtered off, washed with $CHCl_3$ and dried under reduced pressure.

POLYMERIZATION OF 2-Ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane

5 g of monomer are introduced into a polymerization tube with the catalyst (see table IV) in a molar ratio from 0.03 to 10% The tube is heated up to 80-140 °C. After the selected time, the reaction mixture is dis-

solved in ethanol or methanol and the polymer is recovered by dilution with ether. The solid is filtered and dried under vaccuum.

TABLE II : POLYMERIZATION OF VARIOUS MONOMERS REPORTED IN THE LITERARURE

A : Polymerization of 2-Ethoxy-2-oxo-1,3,2-dioxaphospholane

Catalyst	%mass	Heat of the reac-tion, °C	Time hours	Yield %	Aspect of the product
BF_3OEt_2	0.42	110	30	*	black gum
$SnCl_4$	2.05	110	240	*	black glue
$SnCl_4$	7.3	120	3.0	*	white solid
Na	3.2	110	18	*	solid yellow
nBuLi	1.6	110	96	*	yellow gum
nBuLi	3.2	120	1.0	85	solid yellow
$AlEt_3$	1.2	110	63	12	white solid
$AlEt_3$	1.6	110	63	18	white solid
$AlEt_3$	2.1	110	63	13	solid orange
$AlEt_3$	17.2	110	63	32	white solid
$AlEt_3$	23	110	0.45	28	solid yellow
$AliBu_3$	0.31	120	30	35	white solid
$AliBu_3$	9.1	25	5	29	white solid

B : Polymerization of 2-Ethoxy-2-oxo-1,3,2-dioxaphosphorinane

Catalyst	%mass	Heat of the reaction, °C	Time hours	Yield %	Aspect of the product
BF_3OEt_2	0.38	110	25	*	brown gum
$SnCl_4$	7.64	120	54	*	white solid
NaOH	2.1	110	240	*	yellow gum
nBuLi	3.5	120	48	11	yellow gum
nBuLi	5.3	120	60	15.4	yellow solid
nBuLi	7.9	120	26	9.5	yellow solid
$AlEt_3$	1.3	110	0.45	18.5	white solid
$AlEt_3$	1.4	110	1.0	17.4	white solid
$AlEt_3$	1.6	110	72	16.6	white solid
$ALiBu_3$	2.5	120	60	33	yellow solid

* no yield was measured.

C : Polymerization of 2-Methoxy-2-oxo-1,3,2-dioxaphospholane

Catalyst	%mass	Heat of the reac-tion, °C	Time hours	Yield %	Aspect of the product
NaOH	2.4	110	136	6	yellow solid
nBuLi	2.2	110	144	*	yellow solid
tBuOk	4.0	110	118	*	white glue
$AlEt_3$	1.7	110	1.5	8	white solid
$AlEt_3$	1.9	110	5.5	23	white solid
$AlEt_3$	2.5	110	60	17	white solid

D : Polymerization of 2-Methoxy-2-oxo-1,3,2-dioxaphosphorinane

Catalyst	%mass	Heat of the reac-tion, °C	Time hours	Yield %	Aspect of the product
$AlEt_3$	1.3	110	2	5	white powder
$AlEt_3$	1.1	110	3	8	white powder
$AlEt_3$	1.3	110	5	13	white powder

TABLE III : Polymerization of 2-p-Nitrophenoxy-2-oxo-1,3,2-dioxaphospholane

Solvent	%mass	Heat of the reac-tion, °C	Time hours	Yield %	Aspect of the product
CH_2Cl_2	3.23	-30	16	10	yellow powder
CH_2Cl_2	3.25	-30	20	13	" " "
Dioxan	4.30	-30	19	8	" " "
Dioxan	2.45	+20	24	11	red powder
$CHCl_3$	2.35	-78	48	0.0	----------
$CHCl_3$	2.37	0.0	36	16	green powder
CH_2Cl_2	10.0	+40	5.0	28	elastic gum
CH_2Cl_2	12.0	+40	8.0	41	elastic gum

TABLE IV : Polymerization of 2-Ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane

Catalyst	%mass	Heat of the reac-tion, °C	Time hours	Yield %	Aspect of the pro-duct
nBuLi	9.0	90	1.0	13	brown solid
nBuLi	0.93	110	240	*	----------
CF_3OSO_3H	1.19	110	240	*	----------
tBuOK	2.5	110	240	*	----------
$(Ph)_3C^+$, $SbCl^-_6$	1.78	110	240	*	----------
Na	2.25	120	240	21	brown solid
Na	2.44	110	240	22	" " "
NaOH	2.88	110	60	23	" " "
NaOH	2.32	110	240	19	" " "
$SnCl_4$	0.78	120	120	*	----------
$SnCl_4$	2.5	120	118	*	----------
$SnCl_4$	6.0	120	60	*	----------

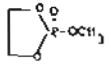
* no yield was measured.

RESULTS AND DISCUSSION

The preparation of monomers reported in table I involves careful control of moisture absence, particularly for processes occuring with evolution of HCl. The presence of H_2O affords oligomeric by-products lowering the reaction yield. Moreover, the distillation of 2-chloro-1,3,2-dioxaphospholane may lead to explosion by the end of the process [13]. Bad yields are obtained by route B since it requires more passages through intermediate products [14]. Moreover, the occurence of good yield is determined by the ring size, in fact 5-membered rings can polymerize more easily than 6-membered rings [15][16][17][18][19]. The characterization of monomers was made by 1H NMR and IR spectroscopy. In figure 1 is reported a typical NMR spectrum, concerning the 2-Methoxy-2-oxo-1,3,2-dioxaphospholane : the doublet centered at 3.78 ppm is attributed to the methyl group, in agreement with the literature report [20]. The multiplets in the range 4.4-3.8 ppm being associated to the CH_2 protons. Another significant example is concerning the six-membered ring in the 2-Methoxy-2-oxo-1,3,2-dioxaphospholane compound (figure 2). The proton assigments are relevant to the inset numerotation. The attribution is made on the basis of literature reports [21] so that multiplet at 1.71 and 1.96 ppm

refer to protons 5a and 5e coupled with axial and equatorial protons on neibouring carbons,other methylenic protons fall in the range 4.4-4.0 ppm.

Figure 1. 1H NMR spectrum of 2-methoxy-2-oxo-1,3,2-dioxaphospholane at 90 MHz (in COCl3 with TMS as reference).



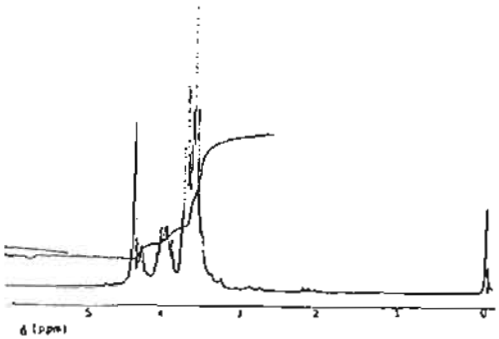
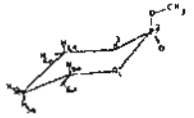
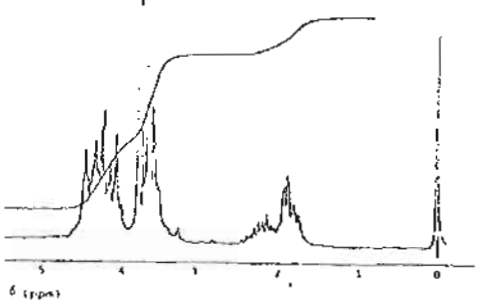


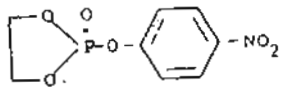
Figure 2. 1H NMR spectrum of 2-methoxy-2-oxo-1,3,2-dioxaphosphorinane at 90 MHz (in $CDCl_3$ with TMS as reference)

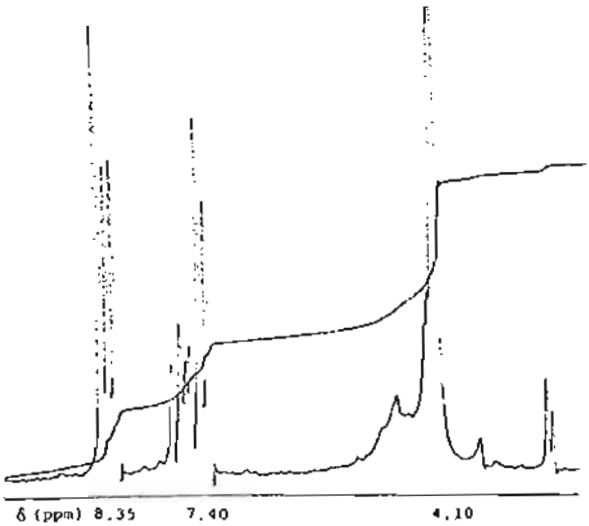




The ^1H NMR spectra of the 2-P-nitrophenoxy-2-oxo-1,3,2-dioxaphospholane (figure 3) has been solved as follow.

Figure 3. ^1H NMR spectrum of 2-p-nitrophenoxy-2-oxo-1,3,2-dioxaphospholane at 90 MHz.(in DMSO with TMS as reference.)





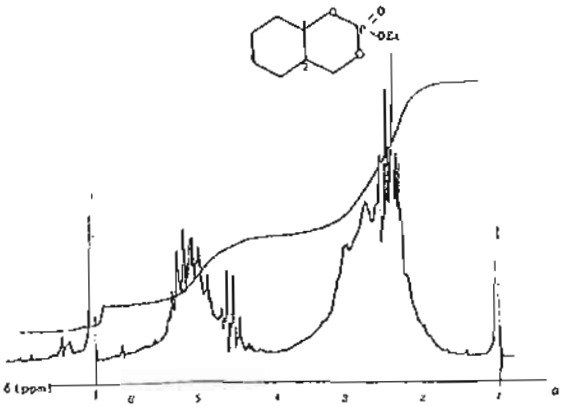
at 4.10 ppm the multiplet of the CH_2 protons of the ring :

at 7.40 ppm, the signal of the protons of phenyl group in ortho position with the P-O bond ;

at 8.35 ppm the signals of the protons of phenyl group on meta position with the P-O bond.

In agreement with the ^1H NMR of the corresponding diol, the spectra of 2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphospholane shows, (figure 4) :

Figure 4. ^1H NMR spectrum of 2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane at 90 MHz. (in $CDCl_3$ with TMS as reference.)



at 2.0 ppm the multiplet of the eight protons of the cycle (except those which are on positions 1 and 2.)

at 5.0 ppm appears the multiplet of CH_2 out of the cyclohexyl ring and those of the proton on C2.

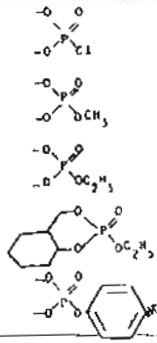
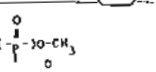
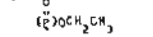
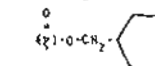
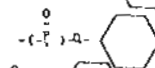
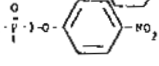
at 1.33 ppm appears the multiplet of the protons of CH_3 group.

at 4.10 ppm we note the signal of the multiplet of protons of CH_2 on the ethyl group.

For a more immediate identification of these products, the IR spectroscopy has been found a very suitable technique. In spite of the few reports on the literature [22][23] we observed that the spectral region 1200-1300 cm^{-1} is diagnostic for P=O bond identification : a strong absorption being observed at 1270 cm^{-1} for 5-membered ring of methyl ester, at 1280 cm^{-1} for the ethyl one and at 1290 cm^{-1} for 6-membered ring species. These data allow a global identification of some compounds with the observation

that C-O band vibration falls at 1190 cm^{-1} for the methyl ester and at 1170 cm^{-1} for the ethyl one. The spectra features and other ones concerning the presence of ordinary absorptions due to substituted phenyl groups are reported in table V. These monomers have been polymerized in the aim to satisfy the overwhelming uncertainty resulting from the literature [24][21a][25][26] where have been reported either occurence of oils with low molecular weight as well of polymers with mass higher than 10. In particular, we focused our attention on the polymerization of new monomers, i.e. 2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane

Table V : Main IR vibrations of monomers and intermediate compounds

Origin of the band	Nature of the radical	Compounds	
		Ring with five atoms	Ring with six atoms
νP-O		1320 cm^{-1} s	1320 cm^{-1} s
		1270 cm^{-1} s	1280 cm^{-1} s
		1280 cm^{-1} s	1290 cm^{-1} s
		"	1290 cm^{-1} s
		1290 cm^{-1} s	"
νP-O-C (νC-O beside ring)		1190 cm^{-1}	1190 cm^{-1}
		1170 cm^{-1}	1170 cm^{-1}
νC-O (inside ring)		—	1150 cm^{-1} 1100 cm^{-1}
		—	1140 cm^{-1}
νP-O		1100-1200 cm^{-1} 1030 cm^{-1}	— 1030 cm^{-1}
νC-C (P-O-C-)		940-950 cm^{-1}	940-980 cm^{-1}

and 2-p-nitrophenoxy-2-oxo-1,3,2-dioxaphospholane.

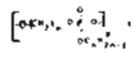
In agreement with previous results, the use of cationic catalyst at high temperature does not give polymers with yield ranging from 65 to 85%. As for anionic catalyst, the most useful seems $Al(Et)_3$ or $Al(Bu)_3$ which lead to white solids in good yield. Unfortunately, the polymerization of the monomers described (2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane and 2-p-nitrophenoxy-2-oxo-1,3,2-dioxaphospholane) required the use of Na or NaOH catalyst affording a white powder whith 20% yield. This polymer is slightly soluble in H_2O and hexafluoroisopropanol.

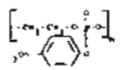
As variant, the AlR_3 catalysts are quite effective for polymerisation of p-nitrophenoxy analogue. In this case, the high viscosity (n=1.99 dl/g) supports that possible cross-linking has occurred.

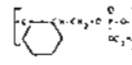
The most important IR spectral features of polymerization products are reported in table VI. It is noteworthy that compounds of general formulation [-O-$(CH_2)_3$-O-PO(OR)-], (R=CH_3, C_2H_5) can be identified by their IR spectrum, whereas spectra of 2-p-nitrophenoxy-2-oxo-1,3,1-dioxaphospholane and 2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphos-

TABLE VI : Main IR vibrations of polymers

bonds	group I	group IIa and IIb
$\nu P=O$	1230 cm^{-1}	II_a : 1265 cm^{-1} II_b : 1270 cm^{-1}
ν-P-O-C-C ν-CO /	1100 - 1200 cm^{-1}	II_a : 1160 cm^{-1} II_b : 1130 cm^{-1}
ν-P-O ν-C-C	1030 cm^{-1} 980 - 990 cm^{-1}	II_a et II_b 1030 cm^{-1} II_a 980 II_b 975 - 1000 cm^{-1}
ν-CH_2 et ν-CH_3 stretching	2850 - 3000 cm^{-1}	2850 - 3000 cm^{-1}
ν-CH_2	1460 - 1470 cm^{-1}	1460 - 1470 cm^{-1}
ν-C-H cycle	-	II_a : 3050 cm^{-1}
ν-NO_2	-	II_a : 1520 - 1350 cm^{-1}
νC-N	-	II_a : 870 cm^{-1}



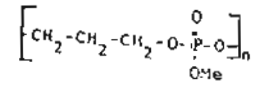


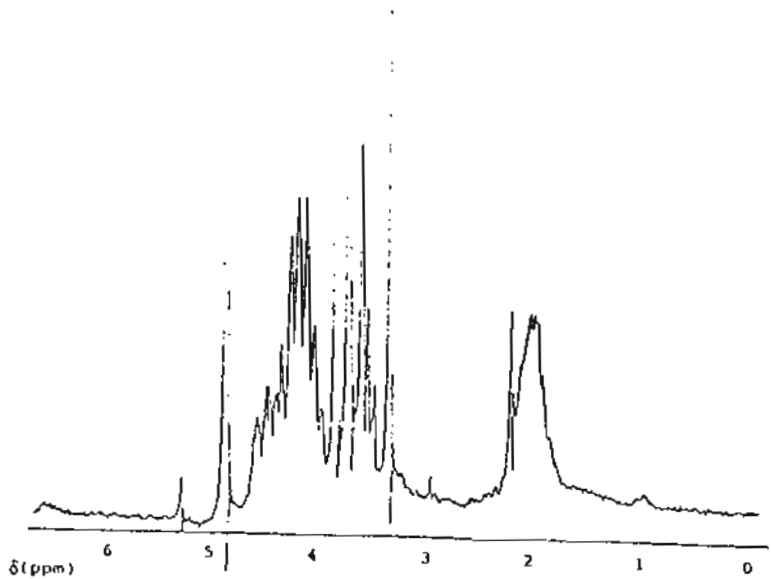


phorinane appear of less immediate identification.

In all cases, the ^1H NMR spectra are very important for identification. Figure 5 constitutes a typical exemple : the doublet at 3.80 ppm remains assigned to methyl group protons as in the spectrum of the parent monomer, whereas signals at 4.22 ppm (multiplet) and at 2.09 ppm are attributed to -O-CH_2 and central -CH_2- protons, respectively.

Figure 5. 1H NMR spectrum of poly (2 methoxy-2-oxo-1,3,2-dioxaphosohorinane) at 90 MHz (in D2O with TMS as reference).





For the poly (2-p-Nitrophenoxy-2-oxo-1,3,2-dioxaphospholane) (figure 6), we can attribute :

at 8.28 ppm the signal of protons of phenyl group ;

at 4.10 ppm those of the CH_2 in the chain.

For the poly (2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane) (figure 7) we can attribute the multiplet at 1.33 ppm to the CH_3 protons. The protons on the carbons C6,C7,C8,C9, are assigned to the multiplet at 1.50 ppm and those on C4 and C5 appear as a multiplet at 2.25 ppm, whereas protons of CH_2 of the ethyl group appear at 4.10 ppm and those on C1 and C2 at 4.20 ppm.

The considerable simplification of this spectrum in comparison with the one of figures 1, 2, 3, 4 indicates the loss of ring organization owing to the occurence of linear -O-$(CH_2)_3$-O-P moiety after polymerization.

FIG.6 ^1H NMR spectrum of the polymer at 90 MHz. (in DMSO with TMS as reference.)

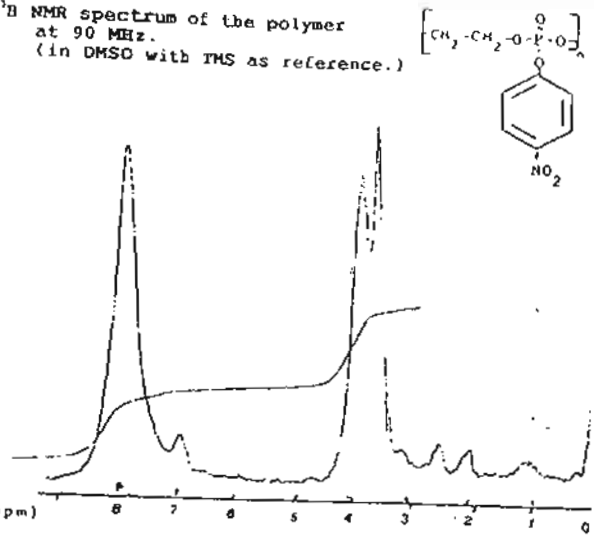
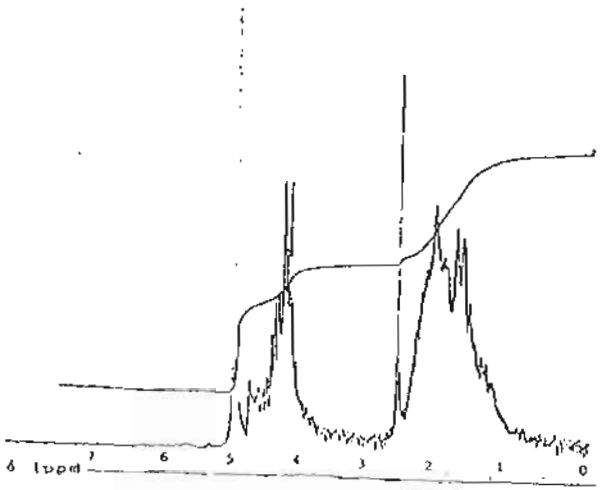


Figure 7. ^1H NMR spectrum of poly.(2-ethoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane) at 90 MHz. (in D_2O with TMS as reference).



CONCLUSION

In this study it is found that an unique and definite synthetic route giving dioxaphospholanes and dioxaphosphorinanes and their polymers was not easy, meanwhile a general method leading to the most of the compounds and their polymerization was realized, completed by ^1H NMR and IR sdudy.

As expected, promissing results, for further technological applications, of insecticidal properties of the intermediates, in controlled systems, may retain great attention.

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