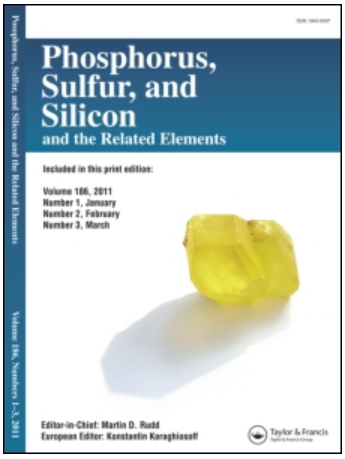

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SYNTHESIS OF POLYOLS BEARING PHOSPHONATE GROUPS. PART II: EPOXIDES USED AS STARTING MATERIALS

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SYNTHESIS OF POLYOLS BEARING PHOSPHONATE GROUPS. PART II: EPOXIDES USED AS STARTING MATERIALS

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Three epoxyphosphonates were prepared. These compounds have the following general formula: $CH_2(O)C(R)$-Z-$PO(OCH_2CH_3)_2$with (II): R=H, Z=CH_2; (V): R=H, Z=$CH_2O(CH_2)_3S(CH_2)_3$; (VI): R= CH_3. (II) is obtained by epoxidation of diethyl allylphosphonate by hydrogen peroxide in the presence of benzonitrile with a yield superior to 60%. (V) is obtained by photoaddition of $HS(CH_2)_3PO(OCH_2CH_3)_2$ to allyl glycidyl ether $CH_2(O)CH$ CH_2-O- $CH_2CH=CH_2$ with a high yield. (VI) is obtained by addition of diethyl hydrogenophosphonate $HPO(OCH_2CH_3)_2$ to 1-chloropropan-2-one $CH_3C(O)$ CH_2Cl with a yield of 80%.

These epoxides then lead to polyols bearing a phosphonate group by ring opening with diethanolamine $(HOCH_2CH_2)_2NH$: $(HOCH_2CH_2)_2NCH_2C(OH)(R)$-Z-$PO(OCH_2CH_3)_2$ with (VII): R=H, Z=CH_2; (VIII): R=H, Z=$CH_2O(CH_2)_3S(CH_2)_3$; (IX): R= CH_3.

This reaction appears to be an easy method without any need for solvent or catalyst, and could be of industrial interest.

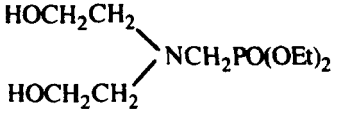
Keywords: Epoxides; diethanolamine; polyols; phosphonates; amino - methylphosphonic acids

INTRODUCTION

The huge expansion of polymer use in most industrial areas (building, packaging, transport, energy...) has raised the problem of flame retardancy.

* Correspondence Author.

Concerning polyurethanes, many studies have been made to improve their flame retardancy. Inorganic compounds ($Al(OH)_3$, $Mg(OH)_2$, H_3BO_3[1]) have been tested and also non functional additives containing halogen or phosphorus ($CH_3PO(OCH_3)_2$: DMMP[2], tri (2-chloroisopropyl) phosphate: TCPP[3]) have been introduced in great quantities in formulations. In each case, problems of migration in the structure and decrease of the mechanical properties have been observed. This has been avoided by the incorporation of halogen atoms on the main polymer chain by the synthesis of very efficient halogen containing polyols (Ixol B 251 (SOLVAY)[4]). But because of the possibility of toxic and corrosive emissions of hydrogen halides, this kind of product is not an environmently acceptable solution. As described in[5], we have chosen phosphorus compounds in order to reduce the flammability of polyurethanes. But polyols bearing a phosphonate group are preferred to phosphates or phosphites giving a sensitivity to hydrolysis because of the presence of the (P-O)-C bond. Moreover, the presence of both phosphorus and nitrogen atoms is very interesting because of their synergy in flame retardancy phenomena[6]. Such phosphonates, FYROL 6 for example:



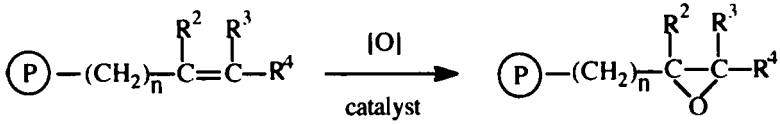
are already used in polyurethane industry[7]. According to Sturtz's works[8], diols obtained with a longer spacer between the phosphorus and the nitrogen than in the FYROL 6 improve the flame retardancy properties. In this paper, we describe the synthesis of epoxides bearing a phosphonate group leading to triols bearing a phosphonate group with different spacer between P and N by opening with diethanolamine.

RESULTS AND DISCUSSION

A) Synthesis of epoxides bearing a phosphonate group

We give below a summary of the principal methods of phosphonate epoxide synthesis used today.

* from unsaturated phosphonates:[9–12]

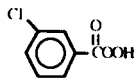


(P) = $PO(OR^1)_2$ R^1 = alkyl R^2, R^3, R^4 = H, alkyl n = 0,1

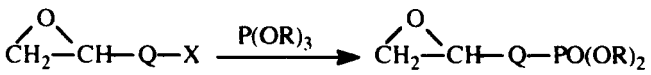
TABLE I gives the main results from diethyl allyl phosphonate:

$$R^1 = C_2H_5, R^2 = R^3 = R^4 = H \text{ and } n = 1.$$

TABLE I Epoxidation of diethyl allylphosphonate: main literature results

Oxidation agent: O	*catalyst*	$\frac{[O]}{[alcene]}$	*Yied (%)*	*References*
H_2O_2	Na_2WO_4	18.6	70	[9]
$tBuO_2H$	$Mo(CO)_6$			
			85	[10,11]
$(CF_3COO)_2$, NaOAc			65	[12]

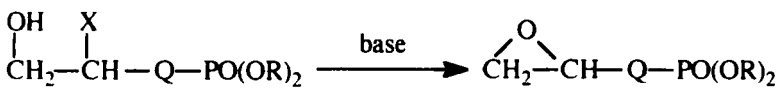
* from halogenated epoxides[13]:



X = Cl, Br.

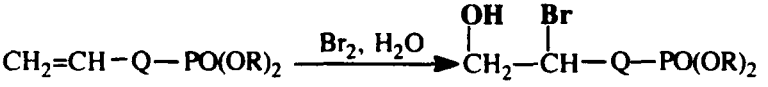
Q is a spacer group , R is alkyl.

* from phosphonates bearing a halohydrin function[14,15]:

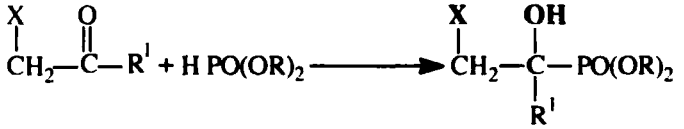


In this case several routes lead to halohydrin phosphonates:

- from unsaturated phosphonates[16,17]

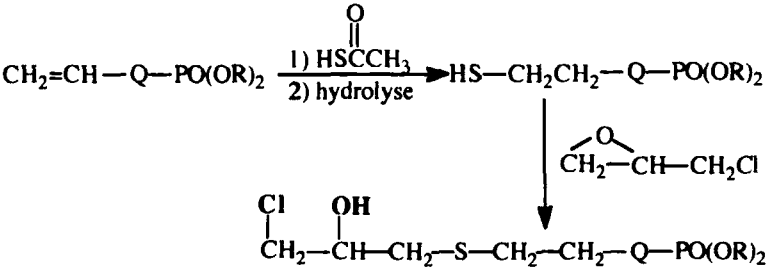


- by addition of dialkyl hydrogenphosphonates to α-haloketones[18]:

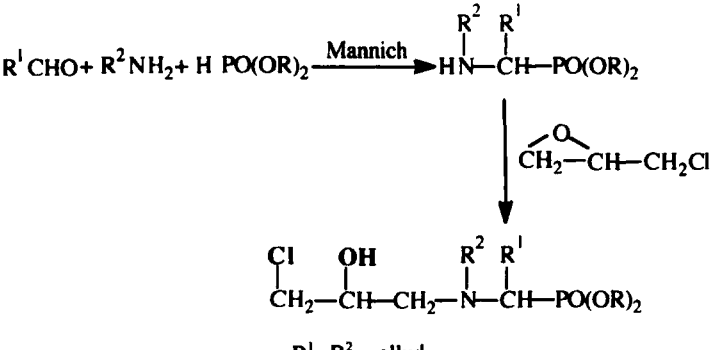


R^1 = alkyl

- by addition of epichlorhydrin[19] to a thiol phosphonate[20,21]:

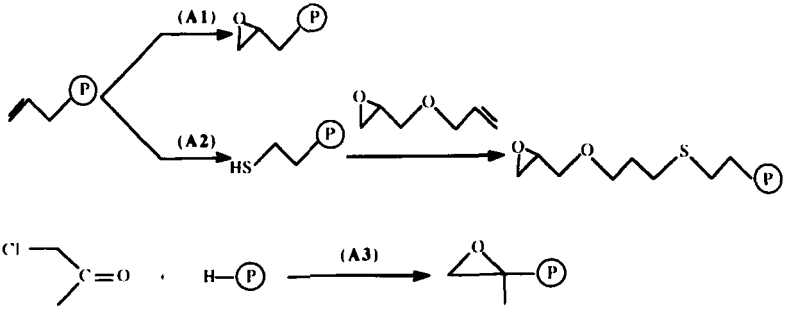


- by addition of epichlorhydrin to amino phosphonate[22,23]:



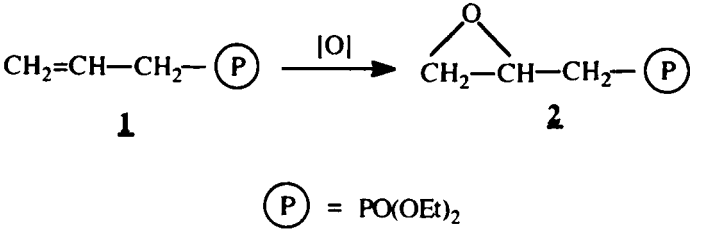
R^1, R^2 = alkyl

We have selected the three following syntheses:

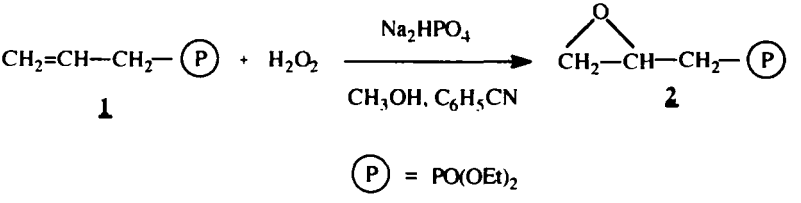


A1) Epoxidation of diethyl allylphosphonate

We have considered the following reaction:



The phosphonate **1** has been widely studied in our laboratory[24–26]. We succeded in the epoxidation reaction, using the results of Payne[27,28] and Hebermeir[29,30]. So our reaction can be summed up as follows:



The mixture is heated for 3 hrs at 55°C and the pH is maintained at 8.8. After distillation we obtained 62 % of pure **2**. The ^{31}P NMR spectra shows

only one peak at 27.6 ppm ($CDCl_3$ as solvent). All the results of ^1H NMR are given in TABLE II. FIGURE 1 represents the expanding part between 1.5 and 2.1 ppm, related to the two methylenic protons at the α position of the phosphonate group. All the values confirm the structure **2**, already described by Phillips[13] but in less detail than we have shown.

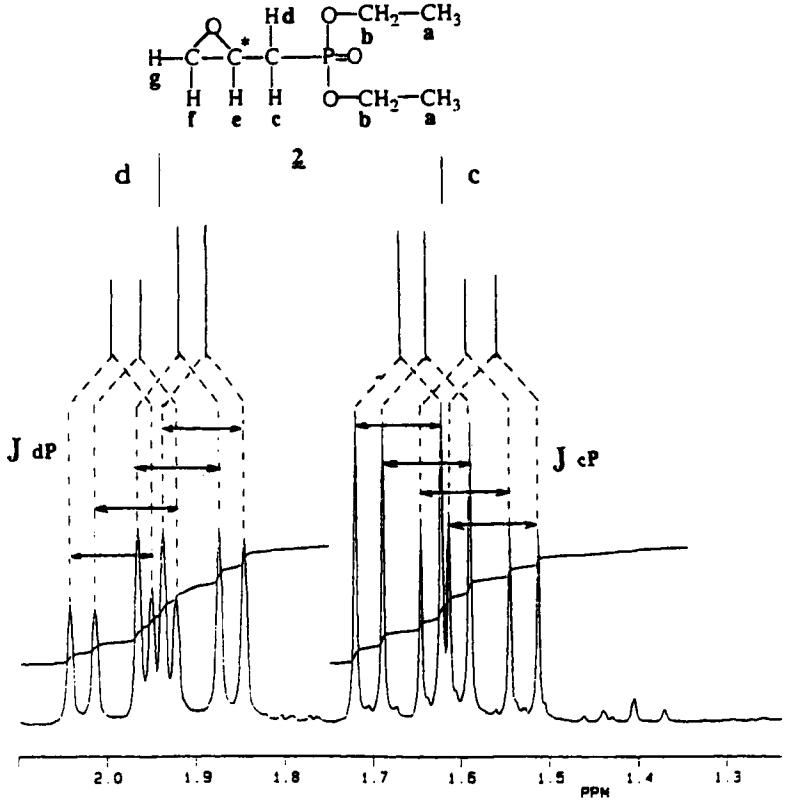


FIGURE 1 ^1H NMR of epoxide **2**: expanding part related to protons **c** et **d**

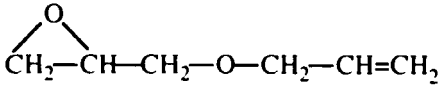
TABLE II ^1H NMR characteristics ($CDCl_3$) of epoxide **2**

Protons	δ *(ppm)*	*Signal appearance*	*Coupling (Hz)*
a	1.09	t	$^3J_{ab} = 7.0$
b	3.88	q, d	$^3J_{ab} = 7.0$ $^3J_{bP} = 8.0$
c	1.62	part AB of ABX	$^2J_{cd} = 15.3$ $^2J_{cP} = 18.2$
		system split	$^3J_{ce} = 5.1$

Protons	δ *(ppm)*	*Signal appearance*	*Coupling (Hz)*
d	1.94	by phosphorus	$^3J_{de} = 5.8$ $^2J_{dP} = 19.8$
e	2.91	m	$^3J_{eP} = 2.6$
f	2.33	m	$^2J_{fg} = 5.0$
g	2.54	m	$^4J_{gP} = 2.6$

A2) The fixation of a phosphonate group onto allyl glycidyl ether

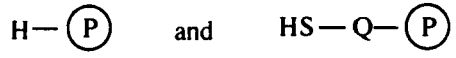
In order to obtain epoxide phosphonates, a second route consists of fixing a phosphonate group onto allyl glycidyl ether **3**:



3

To achieve this, the radical addition of a good phosphonate transfer agent, onto the allylic bond seems to be a convenient solution.

Among the different possibilities of transfer agents, with phosphorus compounds we noted two main types:



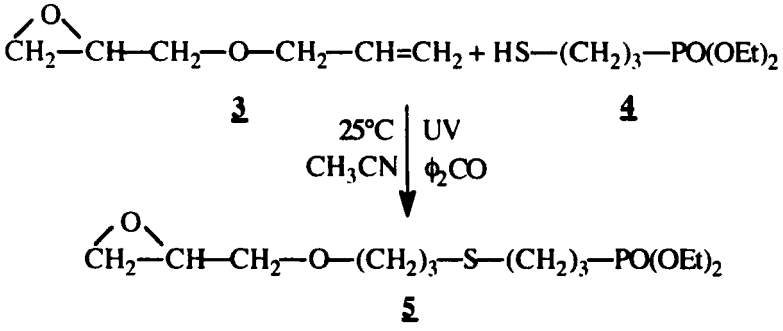
Ⓟ is a phosphonate group, Q is a spacer.

- with the hydrogenophosphonates, the radical conditions are too strong to get a single product and to avoid the decomposition of the epoxide.
- on the other hand with a thiol phosphonate, we expect better results.

So we used the thiol **4** previously described[31]:

4

We achieved the following reaction by a photochemical route:

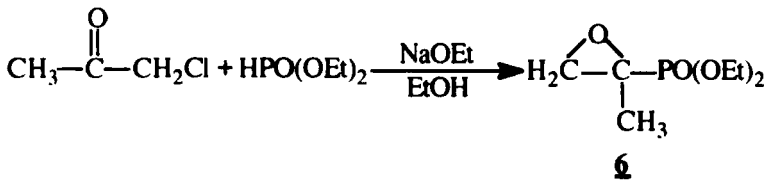


Where the reaction parameters used are $R_o = \frac{[\text{thiol}]}{[\text{monomer}]} = 0.81$ and $c_o = \frac{[\text{initiator}]}{[\text{monomer}]} = 0.04$ the conversion rate is 92% after 40 hrs of reaction. In the ^{31}P NMR spectrum, for the compound **5**, only one peak is observed at 31.9 ppm close to the one observed for **4** (31.6).

The structure of **5** has been confirmed by ^{1}H NMR results (TABLE III and FIGURE 2).

A3) The addition of diethyl hydrogenophosphonate to α-chloroacetone

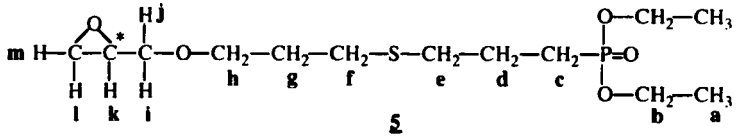
The third epoxyphosphonate has been synthesized by a one step reaction from the diethyl hydrogenophosphonate and the α-chloroacetone according to Spring's works[18]:



After distillation the yield is about 81%.

The ^{31}P NMR spectrum shows a single peak at 21.4 ppm and ^{1}H NMR results (TABLE IV and FIGURE 3) confirm the structure **6** in good agreement with Spring.

TABLE III ^{1}H NMR characteristics ($CDCl_3$) of epoxide **5**



5

Protons	δ *(ppm)*	*Signal appearance*	*Coupling (Hz)*
a	1.17	t	$^3J_{ab} = 7.0$
b	3.93	q, d	$^3J_{ab} = 7.0$ $^3J_{bP} = 8.0$
c	1.72	m	
d	1.72	m	
e	2.44	t	$^3J_{ed} = 7.1$
f	2.44	t	$^3J_{fg} = 7.1$
g	1.72	m	
h	3.42	m	
i	3.58	part AB of	$^2J_{ij} = 11.5$
j	3.20	ABX system	$^3J_{ik} = 2.8$ $^3J_{jk} = 5.9$
k	2.98	m	
l	2.44	part AB of	
m	2.63	ABX system	

TABLE IV ^{1}H NMR characteristics ($CDCl_3$) of epoxide **6**

Protons	δ *(ppm)*	*Signal appearance*	*Coupling (Hz)*
a	1.17	t	$^3J_{ab} = 7.1$
b	3.99	qd	$^3J_{ab} = 7.1$ $^3J_{bp} = 7.2$
c	1.33	d	$^3J_{cP} = 11.2$
d	2.55	t (dd)	$^2J_{ed} = 5.1$ $^3J_{dP} = 5.1$
e	2.93	t (dd)	$^2J_{ed} = 5.1$ $^3J_{eP} = 5.2$

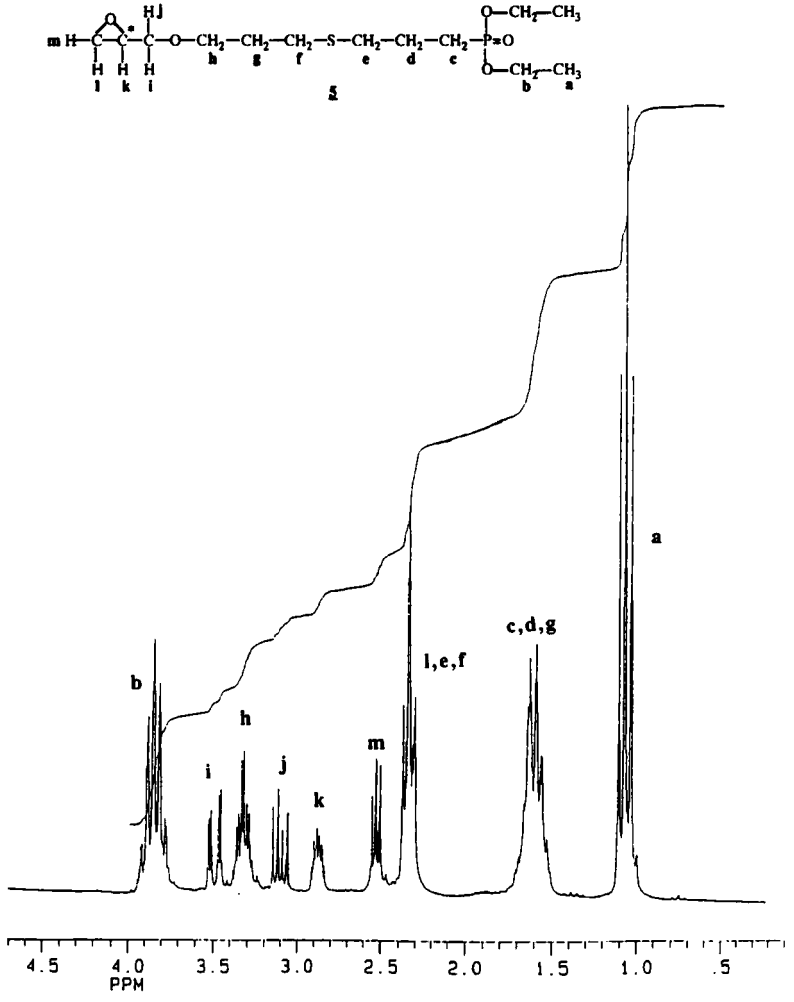
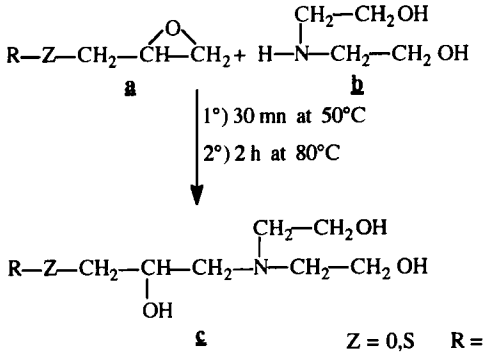
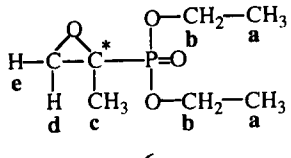


FIGURE 2 ^{1}H NMR spectrum of epoxide **5**

B) Synthesis of polyols bearing a phosphonate group from epoxides

The epoxide ring opening by diethanolamine is largely described in the literature and for example we can quote Chlebicki's works[19,32]. They achieved the following reaction:





6

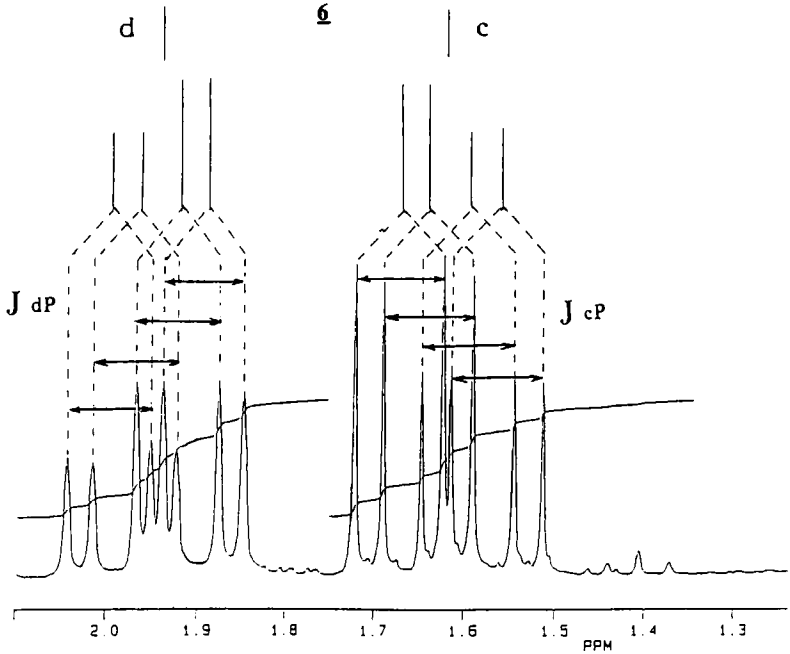
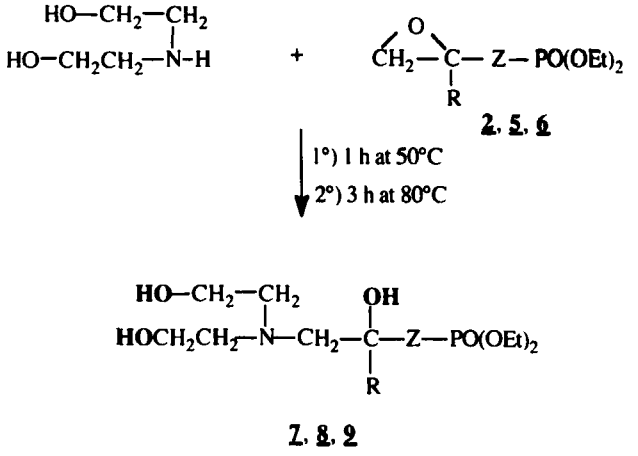


FIGURE 3 ^{1}H NMR spectrum of epoxide 6

We can note in these works an interesting originality: this reaction takes place without any catalyst or solvent. As a matter of fact, this reaction is autocatalysed by the hydroxyl group of the amine and by the formed tertiary amine **c**. The authors describe an induction period of 30 minutes then an accelerated exothermic reaction.

We have applied these results to the epoxides previously synthetized.

The different reactions can be summed up according to the following scheme:



compounds **2**, **7** : R = H, Z = CH_2,

compounds **5**, **8** : R = H, Z = $CH_2O(CH_2)_3S(CH_2)_3$,

compounds **6**, **9** : R = CH_3.

After elimination of the unreacted compound by distillation under low pressure conditions, the products are obtained with a high purity (95%).

^1H NMR spectrum confirms the structure of the expected products.

The results of the ^{31}P NMR analysis are summed up in TABLE V.

TABLE V Chemical shifts (δ) of the phosphorus atom of epoxides and corresponding triols

epoxide n°	**2**	**5**	**6**
δ (ppm)	26.6	31.9	21.4
triol n°	**7**	**8**	**9**
δ (ppm)	32.2	32.5	27.6

CONCLUSION

A description of three different routes to obtain epoxyphosphonates is given. Firstly, we achieved the epoxidation of diethyl allylphosphonate using hydrogen peroxide in the presence of benzonitrile with a yield superior to 60%. Secondly, we achieved the photoaddition of a phosphonate compound bearing a mercaptan previously described, to the allyl glycidyl ether. The reaction is quantitative but lengthy because the thiol possesses a low reactivity with the presence of a spacer of three carbon atoms between the mercaptan and the phosphonate group. The third epoxyphosphonate was obtained by addition of diethyl hydrogenophosphonate to α-chloroacetone with a yield of 80%.

These epoxides then lead to polyols bearing a phosphonate group by ring opening with diethanolamine. This reaction appears to be an easy method without any need for solvent or catalyst, and could be of industrial interest. These triols bear two primary alcohol functions and one secondary or tertiary alcohol function. Secondary or tertiary alcohol functions are known to be less reactive than primary functions regarding addition to isocyanates. However, the presence of a nitrogen atom can catalyse the reaction between the alcohol and isocyanate. Every alcohol function will then react with the isocyante function and the structure of the obtained polyurethane will be three-dimensional.

EXPERIMENTAL

Solvents and commercially available substrates were provided by Aldrich and Fluka.

Elementary analysis of the products concerning the determination of percentage of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P) and sulfur (S) were carried out by the Central Department of Analysis of CNRS of Vernaison.

NMR spectra were recorded at room temperature on a Brucker AC 250 (or 200) spectrometer for solution in $CDCl_3$, and the chemical shifts values are given relative to $SiMe_4$ (^1H) and phosphoric acid (^{31}P) in ppm and coupling constants are given in Hz.

Vapour phase chromatography (VPC) was carried out by DELSI apparatus with a ionization flame detector, a temperature controller (heating rate 15°C/mn) linked to a Shimadzu C-R6A integrator. The column was of OV1 type (3% silicon grease on chromasorb G) 1 m long and 1/8 inch in diameter.

Reactions under UV radiations were carried out with a Philips HIK 125 W 4A lamp ($\lambda = 360$ nm).

Synthesis of diethyl 2,3-epoxypropylphosphonate 2

Into a three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel and an electrode to control pH, we introduce:

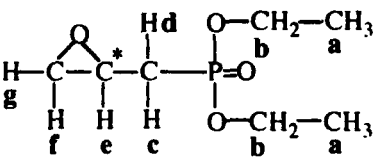
- 20 g of diethyl allylphosphonate (0.112 mole)
- 100 ml of methanol
- 0.73 g of Na_2HPO_4, 12 H_2O($2.2.10^{-3}$ mole)
- 13.04 g of benzonitrile (0.126 mole)
- 7.54 g of hydrogen peroxide (30%)

The mixture is stirred magnetically at 25°C and the pH is maintained at 9.5 by addition of an aqueous solution of NaOH (0.5 N) via the dropping funnel.

After one hour, we introduce 3.58 g of hydrogen peroxide (30%) then 3.44 g one hour later (0.128 mole in total), continously maintaining pH at 9.5.

Then the reaction is continued with stirring at 55°C for 3 hours and pH is maintained at 8.8.

After cooling, we introduce 100 ml of water. The product is extracted by chloroform (3 *45 ml). The organic phase is concentrated to one third by rotary evaporation. Then this phase is cooled by a mixture of water / ice in order to precipitate the benzamide formed. The benzamide is eliminated by filtration and chloroform is evaporated under vacuum. The product **2** is distilled under low pressure and a yield of 62% is obtained.



2

^{1}H NMR ($CDCl_3$) δ : 1.1 (6H, t, Ha, $^3J_{HaHb}$=7.0); 1.6 (1H, AB of ABX system, Hc, $^2J_{HcHd}$=15.3, $^3J_{HcHe}$=5.1, $^2J_{HcP}$=18.2); 1.9 (1H, AB of ABX system, Hd, $^3J_{HdHe}$=5.8, $^2J_{HdP}$=19.8); 2.3 (1H, m, Hf, $^2J_{HfHg}$=5.0); 2.5 (1H, m, Hg, $^4J_{HgP}$=2.6); 2.9 (1H, m, He, $^3J_{heP}$=2.6); 3.9 (4H, qd, Hb, $^3J_{HaHb}$=7.0, $^3J_{HbP}$=8.0).

^{31}P NMR ($CDCl_3$) δ : 26.6 (1P,s)

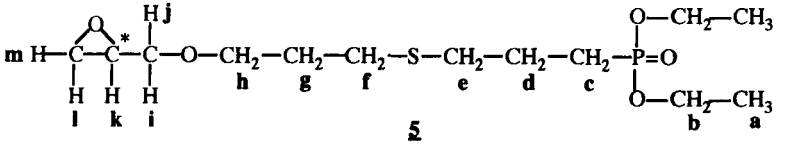
Analysis: $C_7H_{15}O_4P$ (194)	**2**			
% Calc.:	C 43.30	H 7.73	O 32.99	P 15.97
% Found:	42.37	7.69	33.68	15.67

Synthesis of diethyl 10,11-epoxy-8-oxa-4thiaundecylphosphonate 5

In a hermetically closed tube we introduce:

- 3.486 g of diethyl 3-sulfonylpropylphosphonate ($1.642.10^{-2}$ mole)
- 2.307 g of allyl glycidyl ether ($2.021.10^{-2}$ mole)
- 0.131 g of benzophenone ($0.719.10^{-3}$ mole)
- 25 ml of acetonitrile

The mixture is kept under nitrogen for 15 minutes then the tube is closed. The tube is irradiated with a UV-lamp at a distance of 5 cm under rapid stirring for 40 hours. The solvent is evaporated under vacuum and unreacted products are distilled off under low pressure. The product **5** is purified with active carbon in hot acetone followed by a filtration and an evaporation of solvents.



5

^{1}H NMR ($CDCl_3$) δ : 1.2 (6H, t, Ha, $^3J_{HaHb}$=7.0); 1.7 (6H, m, Hc, Hd, Hg); 2.4 (5H, t, He, Hf, Hl $^3J_{HeHd}$=7.1, $^3J_{HfHg}$=7.1); 2,6 (1H, AB of ABX system, Hm); 3.0 (1H, m, Hk); 3.2 (1H, AB of ABX system, Hj, $^3J_{HjHk}$=5.9); 3.4 (2H, m, Hh); 3.6 (1H, AB of ABX system, Hi, $^2J_{HiHj}$=11.5, $^3J_{HiHk}$=2.8); 3.9 (4H, qd, Hb, $^3J_{HaHb}$=7.0, $^3J_{HbP}$=8.0).

^{31}P NMR ($CDCl_3$) δ : 31.9 (1P,s)

Analysis:	$C_{13}H_{27}O_5PS$ (326)	**5**		
% Calc.	C 47.84	H 8.34	O 24.51	S 9.82
% Found	47.52	8.22	24.27	9.67

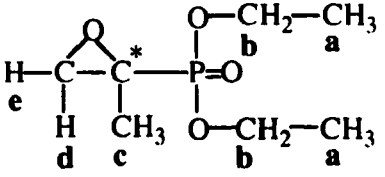
Synthesis of diethyl 1,2-epoxypropyl-2-phosphonate 6

A solution of NaOEt / EtOH is previously prepared by dissolution of 34.06 g of NaOEt (0.5 mole) into 225 ml of ethanol.

Into a three-necked round-bottom flask (1 litre) equipped with a reflux condenser and a dropping funnel we introduce 69.05 g (0.5 mole) of diethyl hydrogenophosphonate, 46.39 g (0.5 mole) of 1-chloropropan-2-one and 100 ml of ethanol.

The solution NaOEt / EtOH is added dropwise for 50 minutes, then stirring is maintained at room temperature for 15 h. The reaction mixture is light yellow at the beginning and changes to an orange colour at the end of the reaction.

The reaction mixture is filtered through cotton and the ethanol is evaporated. Ether is added in order to precipitate NaCl and the mixture is filtered twice through a ground glass filter then the ether is evaporated under vacuum. Product **6** is purifed by distillation under low pressure. VPC purity 97.3%. Yield 81%.



6

^1H NMR ($CDCl_3$) δ: 1.2 (6H, t, Ha, $^3J_{HaHb}$=7.1); 1.3 (3H, d, Hc, $^3J_{HcP}$=11.2); 2.5 (1H, t (dd), Hd, $^2J_{HeHd}$=5.1, $^3J_{HdP}$=5.1); 2.9 (1H, t (dd), He, $^2J_{HeHd}$=5.1, $^3J_{HeP}$=5.2); 4.0 (4H, qd, Hb, $^3J_{HaHb}$=7.1, $^3J_{HbP}$=7.2).

^{31}P NMR ($CDCl_3$) δ : 21.4 (1P,s)

Analysis: $C_7H_{15}O_4P$ (194)		6		
% Calc.	C 43.30	H 7.73	O 32.99	P 15.97
% Found	42.92	7.97	33.22	15.39

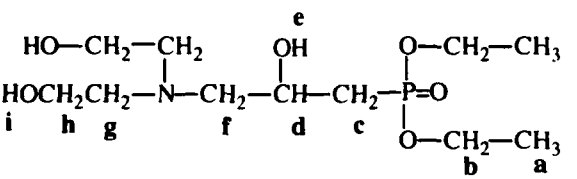
Synthesis of diethyl 4,4-bis(2-hydroxyethyl)-4-aza-2-hydroxybutyl phosphonate 7

Into a round bottom flask equipped with a thermometer, we introduce 3.903 g ($2.01.10^{-2}$ mole) of diethyl epoxy-2,3 propylphosphonate **2** and 2.131 g ($2.03.10^{-2}$ mole) of bis(2-hydroxyethyl) amine.

The mixture is heated to 50°C for 1 hour then to 80°C for 3 hours under magnetic stirring.

A yield superior to 95% is determined by VPC and ^{31}P NMR.

Unreacted products are distilled off under low pressure and product 7 is purified to 98% (^{31}P NMR).



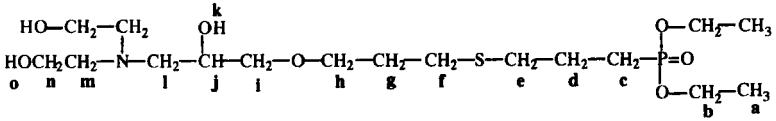
^1H NMR ($CDCl_3$) δ : 1.0–1.2 (6H, t, Ha, $^3J_{HaHb}$=7.0); 1.6–1.8 (2H, m, Hc); 2.2–2.4 (4H, t, Hg); 2.4–2.6 (2H, t, Hf); 3.2–3.6 (4H, m, Hh); 3.7–4.0 (5H, m, Hb, Hd, $^3J_{HaHb}$=7.0, $^3J_{HbP}$=8.0); 4.4–5.0 (3H, broad signal, He, Hi).

^{31}P NMR ($CDCl_3$) δ : 32.2 (1P,s)

Analysis:	$C_{11}H_{26}NO_6P$ (299)	7		
% Calc.	C 44.14	H 8.76	N 4.68	O 32.07
% Found	43.82	9.11	4.75	33.19

Synthesis of diethyl 12,12-bis(2-hydroxyethyl)-12-aza-10-hydroxy-8-oxa-4-thiadodecylphosphonate 8

We introduce 3.268g ($1.00.10^{-2}$ mole) of epoxide **5** and 1.058 g ($1.01.10^{-2}$ mole) of bis(2-hydroxyethyl) amine. The reaction conditions are the same as the ones used for product **7**.



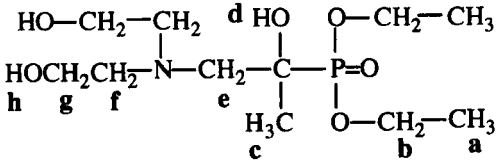
^{1}H NMR ($CDCl_3$) δ : 0.9–1.1 (6H, t, Ha, $^3J_{HaHb}$=7.0); 1.5–1.7 (6H, m, Hc, Hd, Hg); 2.1–2.4 (4H, m, He, Hf); 2.4–2.6 (4H, m, Hm); 3.1–3.2 (2H, d, Hl); 3.2–3.3 (6H, t, Hh, Hn); 3.3–3.5 (2H, d, Hi); 3.5–3.7 (1H, m, Hj); 3.7–3.9 (4H, qd, Hb, $^3J_{HaHb}$=7.0, $^3J_{HbP}$=8.0); 4.3–4.8 (3H, broad signal, Hk, Ho).

^{31}P NMR ($CDCl_3$) δ : 32.5 (1P,s)

Analysis: $C_{17}H_{38}NO_7PS$ (431)	**8**				
% Calc.	C 47.33	H 8.82	N 3.25	O 25.99	S 7.42
% Found	46.74	9.07	3.32	26.25	7.21

Synthesis of diethyl 3,3-bis(2-hydroxyethyl)-3-aza-1-hydroxy-1-methyl-propylphosphonate 9

We introduce 1.946g ($1.00.10^{-2}$ mole) of epoxide **6** and 1.063g ($1.01.10^{-2}$ mole) of bis(2-hydroxyethyl) amine. The reaction conditions are the same as the ones used for product **7**.



^{1}H NMR ($CDCl_3$) δ : 0.9–1.0 (3H, s, Hc); 1.0–1.1 (6H, t, Ha, $^3J_{HaHb}$=7.1); 2.3–2.6 (6H, m, He, Hf); 3.1–3.5 (4H, m, Hg); 3.8–4.0 (4H, qd, Hb, $^3J_{HaHb}$=7.1, $^3J_{HbP}$=8.0); 4.5–5.4 (3H, broad signal, Hd, Hh).

^{31}P NMR ($CDCl_3$) δ : 27.6 (1P,s)

Analysis: $C_{11}H_{26}NO_6P$ (299)	**9**			
% Calc.	C 44.15	H 8.70	N 4.68	O 32.11
% Found	43.91	9.01	4.75	33.82

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