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Chemical modification of 1,4-polydienes by di(alkyl or aryl)phosphates

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Abstract

Synthesis of 1,4-polydienes bearing di(alkyl or aryl)phosphate groups in side position of the polydiene chains was considered by using a chemical modification procedure. The synthesis was carried out according to a two-step process. Firstly, functionalized intermediate polydienes were prepared by partial epoxidation of 1,4-polyisoprene or 1,4-polybutadiene units. Secondly, the introduction of the di(alkyl or aryl)phosphate groups was realized by using the reactivity of the acidic function P–OH of di(alkyl or aryl)phosphate reagents toward oxirane rings.

A preliminary study on model molecules of epoxidized 1,4-polydienes (4,5-epoxy-4-methyloctane for epoxidized 1,4-polyisoprene, 4,5-epoxyoctane for epoxidized 1,4-polybutadiene) allowed the characterization of polymers derived from the various types of polydienes: epoxidized synthetic 1,4-polybutadiene, and epoxidized synthetic 1,4-polyisoprene or epoxidized liquid natural rubber (ELNR), as well as that of the side reactions. In all cases, the oxirane rings are opened and two categories of 1:1 phosphate adducts are obtained: five-membered cycle adducts (2-(alkoxy or aryloxy)-2-oxo-1,3,2-dioxaphospholane structures) and 1:1 β-hydroxyphosphate adducts, in proportions depending on the di(alkyl or aryl)phosphate that is the alkyl (or aryl) group nature (methyl, ethyl, butyl, phenyl), and the model structure. The whole phosphate adduct yields are generally limited to about 80%, due to the side reactions.

The addition of di(alkyl or aryl)phosphates on the epoxidized units of epoxidized liquid 1,4-polydienes proceeds in a way nearly similar to that observed on the model molecules. The partial modification of oxirane rings by the phosphate compounds lets unreacted epoxides so available for a latter reaction, for instance for a crosslinking process.

1. Introduction

Elastomers present a commercial interest because of their own properties (elasticity, electric insulation) required for special applications in various industrial sectors (tyres, adhesives, housing,...). However, they have one considerable drawback: they are combustible. They form during decomposition volatile breakdown products and radicals which combine with the surrounding air to supply the combustion process.

One way to improve the flammability of polymeric materials is chemical modification by using phosphorus-containing reagents or monomers [1]. The advantage of this method is that active species cannot diffuse toward the polymer surface and remain efficient longer [2]. Phosphorus-containing polymers are well know for their flame-retardant properties and they are on the increase over their halogen counterparts because they generally release less toxic and corrosive volatile combustion products [3].

In a previous paper [4], we related the flammability improvement obtained after incorporation of phosphate groups onto polydiene backbone. It was demonstrated that flame resistance of 1,4-polydienes can be improved by grafting low proportions of di(alkyl or aryl)phosphate groups (about 1.1–1.2 wt.% of phosphorus) on the polydiene backbone, especially diphenylphosphate groups.

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The purpose here is to give the results of the syntheses leading to polydienes having phosphate groups in side position of polydiene backbone. For that, the chemical introduction of phosphate groups onto polydienes was envisaged by a two-step process. In the first step, partial epoxidation of 1,4-polyisoprene or 1,4-polybutadiene units produced functionalized intermediate polydiene. The second step of the chemical modification was the introduction of the di(alkyl or aryl)phosphate group using the reactivity of the acidic bond P–OH of di(alkyl or aryl)phosphates toward oxirane rings. A preliminary study on model compounds of 1,4-polydienes was considered in order to allow the characterization of products according to both types of polydienes, epoxidized 1,4-polybutadiene or epoxidized 1,4-polyisoprene (natural or synthetic), and to the nature of the ester substituent of the di(alkyl or aryl)phosphate, as well as the side reactions.

2. Experimental

2.1. Materials

Dichloromethane is dried on calcium sulfate, then filtered and distilled on phosphoric anhydride after 1 h of reflux. Acetone is distilled on calcium sulfate and is stored on molecular sieves 3 Å. Methanol is distilled on calcium sulfate after 2 h of reflux, and then stored on molecular sieves 3 Å. Hexane is distilled and stored on molecular sieves 4 Å.

Dibutylphosphate (DBP) (Acros Organics; purity 97%) is distilled before use. Diethylphosphate (DEP) results from the hydrolysis of diethyl chlorophosphate (Acros Organics; purity 95%). After 1 h of agitation at room temperature in distilled water excess (fast and exothermic reaction), the aqueous phase is extracted by dichloromethane and the organic solution is dried on anhydrous sodium sulfate. After filtration of the solution and evaporation of dichloromethane, DEP is purified by distillation under reduced pressure (yield: 100%; $\mathrm{Eb}_{0.3\,\mathrm{mmHg}} = 36$–37°C). The substitution of chlorine by a hydroxyl group is noticed in ^{1}H-NMR spectroscopy by a displacement of the signals of the methyl and methylene hydrogens toward the high fields (Table 1). In ^{31}P-NMR, the hydrolysis is confirmed by the disappearance of the phosphorus signal of diethyl chlorophosphate at $\delta = 4.77$ ppm and the appearance of a new signal at $\delta = 0.83$ ppm characteristic of DEP.

Diphenylphosphate (DPP) results from the hydrolysis of diphenyl chlorophosphate (Acros Organics; purity 98%) which is carried out according to the procedure described above. Contrary to that of diethyl chlorophosphate, the hydrolysis of diphenyl chlorophosphate is very slow as shown by the kinetic of the reaction at room temperature followed by ^{31}P-NMR by comparing the heights of the peaks respectively characteristic of diphenyl chlorophosphate and DPP (Fig. 1). At room temperature, 5 h of reaction are necessary to obtain the total hydrolysis of diphenyl chlorophosphate. DPP which crystallizes after concentration of the solution, is purified by recrystallization in hexane, then dried under vacuum ($F = 59$°C). It is characterized in ^{31}P-NMR by a signal at $\delta = -9.75$ ppm.

Dimethylphosphate (DMP) was prepared from phosphorus oxychloride (Acros Organics) (Scheme 1).

Two equivalents of methanol are added drop by drop on one equivalent of phosphorus oxychloride at 0°C. The mixture is stirred at 0°C for 1 h. The formed hydrochloric acid is extracted using a dry air flow, then neutralized by a concentrated solution of potassium hydroxide [5] (Fig. 2). The dimethyl chlorophosphate is distilled under reduced pressure ($\mathrm{Eb}_{0.3\,\mathrm{mmHg}} = 29$°C) (yield = 56%). It is hydrolyzed according to the proce-

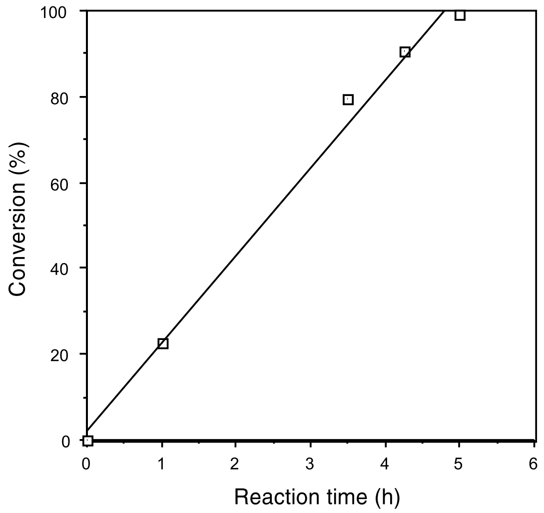
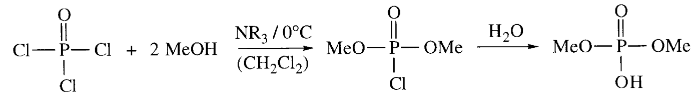


Fig. 1. Hydrolysis kinetic of diphenyl chlorophosphate.

Table 1
^{1}H-NMR characterization of diethyl chlorophosphate and DEP (solvent: $CDCl_3$, internal reference: TMS)

Compound	CH_3	CH_2
$(EtO)_2P(O)Cl$	1.40–1.50 ppm (triplet)	4.20–4.50 ppm (quintuplet)
$(EtO)_2P(O)OH$	1.30–1.35 ppm (triplet)	4.05–4.15 ppm (quintuplet)



$$Cl-P(O)(Cl)-Cl + 2\,MeOH \xrightarrow[(CH_2Cl_2)]{NR_3\,/\,0°C} MeO-P(O)(Cl)-OMe \xrightarrow{H_2O} MeO-P(O)(OH)-OMe$$

Scheme 1.

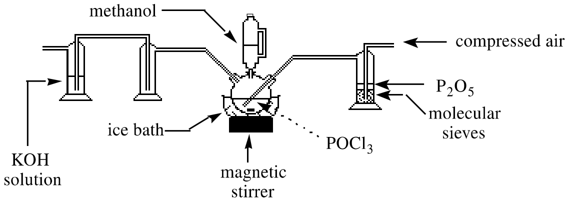


Fig. 2. Synthesis of dimethyl chlorophosphate.

Table 2
^{1}H- and ^{31}P-NMR characterization of dimethyl chlorophosphate and DMP (solvent: $CDCl_3$, internal reference: TMS)

$(MeO)_2P(O)X$	X=Cl	X=OH
^{1}H-NMR: δ (ppm)	3.90 (doublet)	3.75 (doublet)
^{31}P-NMR: δ (ppm)	7.91	2.84

dure described above (yield = 97%). The intermediate and final products were analyzed by ^{1}H-NMR and ^{31}P-NMR (Table 2).

2.2. Synthesis and epoxidation of 1,4-polydiene models

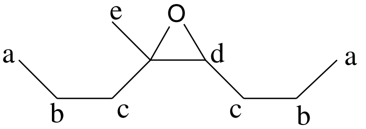
4-Methyloct-4-ene and oct-4-ene were selected like respective models of 1,4-polyisoprene and 1,4-polybutadiene. These molecules (*cis*/*trans* mixtures) were synthesized by Wittig–Schöllkopf reaction, according to the method developed by Reyx [6]. The 100% *trans* oct-4-ene was supplied by Acros Organics. Their epoxidation was carried out by action of metachloroperbenzoic acid in dichloromethane at 0°C. The use of aromatic peracids makes it possible to better control the epoxidation, the soft conditions of action of these reagents thus make it possible to limit the side reactions of ring opening of the oxiranes and the formation of β-hydroxyester or glycol [7]. The metachloroperbenzoic acid solution in dichloromethane is added slowly in the two-phase system: model in dichloromethane and 5% aqueous solution of sodium bicarbonate, cooled to 0°C and stirred magnetically. After addition, agitation is continued for 2 h. The two phases are separated, and the organic phase is washed with a 0.1 M solution of NaOH, then with distilled water. The aqueous phase is extracted by dichloromethane. The two organic phases are joined together, and then dried on anhydrous Na_2SO_4. After filtration of the solution, the dichloromethane is eliminated using a rotary evaporator.

The epoxidized model molecules are purified by distillation under atmospheric pressure (4,5-epoxy-4-methyloctane (**1**) Eb = 164–165°C; 4,5-epoxyoctane (**2**) Eb = 155–156°C). They were characterized by ^{1}H-NMR (Table 3) by the disappearance of the signals between 5.0 and 6.0 ppm (hydrogens on carbon–carbon double bonds) and the appearance of a signal corresponding to hydrogens of the oxirane ring at δ = 2.76 ppm.

2.3. Synthesis and epoxidation of 1,4-polydienes

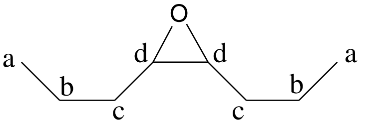
Selected 1,4-polyisoprene is a synthetic product of low molecular weight supplied by the Kuraray Company (LIR-30). It was purified beforehand by dissolution–precipitation using the couple benzene/methanol, then

Table 3
^{1}H-NMR chemical shifts of the various hydrogens present in **1** and **2** prepared according to Wittig–Schöllkopf reaction (solvent: $CDCl_3$, internal reference: TMS)



57% cis

(1)



85% cis

(2)

H_a	H_b, H_c	H_d	H_e	H_a	H_b, H_c	H_d
1.00 ppm	1.50–1.53 ppm	2.76 ppm	1.26, 1.30 ppm	0.98 ppm (t)	1.42–1.57 ppm	2.91 ppm (*cis*) 2.66 ppm (*trans*)
				$^3J_{a,b}$ = 7.18 Hz	$^3J_{c,d}$ = 4.07 Hz (*cis*)	
				$^3J_{b,c}$ = 7.33 Hz	$^3J_{c,d}$ = 4.52 Hz (*trans*)	

dried under vacuum. It comprises 94% of 1,4-polyisoprene units (*cis* 64% and *trans* 36%) and 6% of -3,4.

1,4-polybutadiene was synthesized by anionic polymerization of butadiene in an equipment entirely purged with argon (Fig. 3). The benzene, after 12 h of agitation on $LiAlH_4$, is distilled directly in the three-necked flask used as reactor, then the desired quantity of initiator (*n*-BuLi) is introduced through the rubber stopper using a syringe and the solution thermostated at 40°C. The butadiene is purified right before polymerization by passage through a column filled with molecular sieves 3 Å in order to eliminate any moisture traces, then directly condensed on a cold finger in the three-necked flask. After complete introduction of this one drop by drop into the strongly stirred reactional mixture, polymerization is stopped at the end of the reflux by addition of methanol. Polybutadiene is precipitated in methanol and purified by successive dissolutions and precipitations using the couple benzene/methanol, and finally dried under vacuum until constant weight. It comprises 89.4% of 1,4-polybutadiene units and 10.6% of -1,2. Its number average molecular weight, determined by SEC initially calibrated with *n*-alkane standards, is equal to 1600.

The partial epoxidation of 1,4-polyisoprene and 1,4-polybutadiene was carried out using *meta*-chloroperbenzoic acid, the quantity of introduced peracid depending on the required modification yield. *meta*-Chloroperbenzoic acid in dichloromethane, is added drop by drop to the heterogeneous mixture cooled to 0°C: 1,4-polydiene in solution in dichloromethane and 5% aqueous solution of sodium bicarbonate. The reaction is continued for 3 h. The two phases are separated. The organic phase is washed with a 0.1 M NaOH solution, then with distilled water. The epoxidized polymers are isolated by precipitation in methanol, then purified by successive dissolutions and precipitations using the couple dichloromethane/methanol, and finally dried under vacuum until constant weight. The number average molecular weight $\overline{M}_n$, determined by SEC initially calibrated with polystyrene standards, is equal to 25 600 ($I = 1.3$).

Epoxidized LIR-30 is characterized in ^{1}H-NMR by the presence of signals at 1.25–1.30 and 2.70 ppm which correspond respectively to the hydrogen and the methyl group on the oxirane ring formed from the starting 1,4-polyisoprene units. In ^{13}C-NMR spectroscopy, carbons of the oxirane rings are characterized by peaks at 64.54 ppm for the *cis* form and 63.29 ppm for the *trans* form (carbon bearing hydrogen), and at 60.83 ppm (carbon bearing the methyl group).

Epoxidation yields were determined from ^{1}H-NMR spectra by comparing the respective integrations of the signals of the hydrogens on carbon–carbon double bonds $\text{-3,4C}H_2\text{=C(Me)–}$, and $\text{–1,4-C}H\text{=C(Me)–}$ with that of the hydrogens of the oxirane rings. The epoxidation occurs essentially on the internal carbon–carbon double bonds of the 1,4-polyisoprene units. LIR-30 epoxidation can be also conveniently followed by IR spectroscopy by observation of the reduction in intensity of the band characteristic of the carbon–carbon double bond (*cis* and *trans*) at 839 cm^{-1} and the concomittant increase in intensity of the band at 894 cm^{-1} due to the

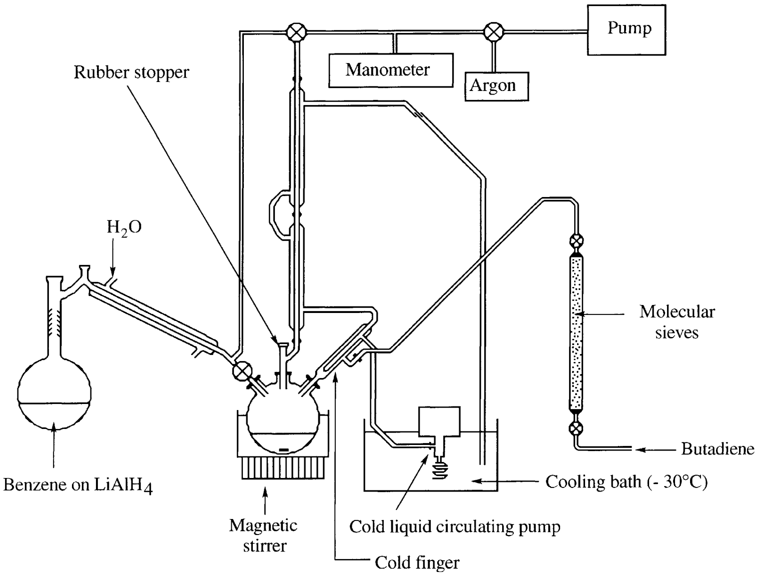


Fig. 3. Apparatus used to synthesize 1,4-polybutadiene.

C–O bonds of the oxirane rings overcapped by the vinyl structures of 3,4-polyisoprene units.

Polybutadiene epoxidation is controlled in ^{1}H-NMR by the intensity reduction in the integrations of the hydrogen signal of the carbon–carbon double bonds between 4.95 and 5.55 ppm, and the appearance and increase of the signal corresponding to the hydrogens on the oxirane rings at 2.65–2.90 ppm. As in the case of the model **2**, the epoxidation allows to distinguish and to quantify the epoxidized *cis* 1,4- (49%) and *trans* 1,4- (51%) polybutadiene units. Epoxidized 1,4-polybutadiene is characterized in ^{13}C-NMR by the chemical shifts of carbons of the oxirane rings at $\delta = 58.12$ (*cis*) and 56.49 ppm (*trans*), and those of the internal carbon–carbon double bonds at $\delta = 129.71$ (*cis*) and 129.14 ppm (*trans*).

ELNR latex: The latex used was provided by the Matériaux department of the Centre de Transfert et de Technologie du Mans. It results from the depolymerization of natural rubber in latex medium by action of phenylhydrazine in oxidative medium (air) leading to low molecular weight 1,4-polyisoprenes (7000–20 000) (LNR). The entirely *cis* 1,4 structure of the initial natural rubber is preserved [8,9]. The epoxidation of LNR is also carried out in latex medium by using performic acid prepared in situ by action of formic acid on hydrogen peroxide.

To determine the structural characteristics of the ELNR contained in the ELNR latex, the latter was precipitated in methanol and then purified by successive dissolutions and precipitations using the couple dichloromethane/methanol, and finally dried under vacuum until constant weight. Its epoxidation rate, determined from its ^{1}H-NMR spectrum by comparison of the integration of oxirane ring hydrogens at 2.70 ppm with that of hydrogens of non-modified carbon–carbon double bonds at 5.10 ppm, is equal to 26%.

2.4. Reaction of di(alkyl or aryl)phosphates with epoxidized 1,4-polydienes and their respective models

2.4.1. Reaction onto epoxidized models

Equimolecular quantities of epoxide and di(alkyl or aryl)phosphate are placed in a Pyrex glass tube equipped with a magnetic stirrer and closed by a screwed stopper with a joint of sealing covered with Teflon. The reaction mixture is heated in an oil bath thermostated at 70°C and magnetically stirred for 3 h.

2.4.2. Reaction onto epoxidized 1,4-polydienes

In solution: the epoxidized polydiene (1 g) and the di(alkyl or aryl)phosphate, in stoichiometric quantity compared to polymer oxirane rings, is dissolved in 10 ml of dichloromethane and the whole is placed in a tube closed by a screwed stopper. After 12 h of magnetic stirring at 30°C, the solution is concentrated by partial elimination of dichloromethane using a rotary evaporator, and then the modified product is isolated by precipitation in methanol (or hexane, when it is partially soluble in methanol), and then dried under vacuum until constant weight. The modified polymers were analyzed by NMR.

Without solvent: the reactions were carried out as in solution, at room temperature for 24 h or at 70°C for 3 h. The crude products were directly analyzed by NMR.

In biphasic system (ELNR latex): 5 ml (1 g) of latex and 3.5 mmol of dialkylphosphate in 5 ml of solvent (dichloromethane or toluene), placed in a Pyrex glass tube closed by a screwed stopper, are magnetically stirred very strongly at room temperature for 24 h. The modified polymer is isolated by precipitation in hexane or methanol, and then dried under vacuum until constant weight.

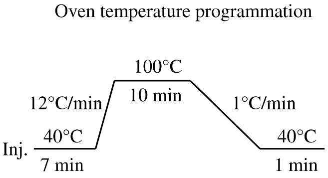
2.5. Measurements

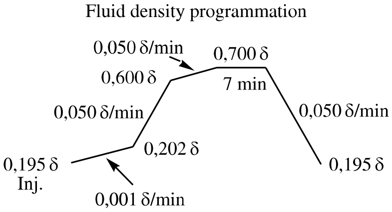
NMR spectra were recorded on a Bruker AC 400 Fourier-transform spectrometer, at 400.13 MHz for ^{1}H, at 161.98 MHz for ^{31}P, and at 100.61 MHz for ^{13}C. Samples were analyzed in solution in deuterated chloroform or methanol. In ^{1}H- and ^{13}C-NMR, the chemical shifts are expressed in ppm in the δ scale, compared to the singlet of tetramethylsilane, as internal standard. In ^{31}P-NMR, the chemical shifts of various phosphorus are expressed in δ scale with reference to the phosphoric acid peak as external standard.

The IR spectra were recorded with a Perkin–Elmer 1750 Fourier-transform spectrometer. Liquid samples were analyzed in the form of films between two NaCl disks. Solid samples were analyzed in KBr pellets.

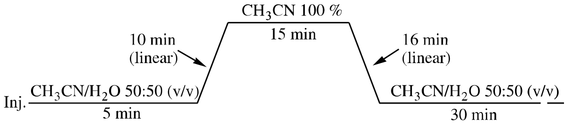
Analyses in supercritical fluid chromatography (SFC) were performed using a Erba Science modular equipment including a SFC 300 tandem pumping installation comprising two electric syringe pumps, a SFC 3000 chromatograph equipped of a thermostated split semi-automatic injection system, of an oven with temperature programmer, of a Durabond® DB5 open tubular capillary column (100 μm ID, and 10 m in length) coated with a 0.4 μm film of diphenyldimethylpolysiloxane, of a 15 cm × 10 μm right fused-silica tube used as restrictor to maintain the pressure inside the column, and of a FID 40 flame ionization detector. The command of the various modules, the acquisition of the data and the data processing were carried out using a IBM PS2-30-286 microcomputer. The fluid vector was carbon dioxide.

The chromatographic analyses were led under the following conditions: detector temperature, 300°C; injection duration: 100 ms; injection temperature, 250°C





Analyses in high performance liquid chromatography (HPLC) were performed on a Waters modular equipment including a Model 510 pump module, a Model U6K injector, a Waters Radial-PAK C18 column (5 mm ID, and 10 cm in length; particle size: 10 μm), and a double detection system (a Model 990 photodiode array spectrophotometer and a Model 410 differential refractometer). The mobile phase flow was adjusted to 1 ml min^{-1} and the analyses were carried out according to the following conditions:



Polyisoprene analyses in steric exclusion chromatography (SEC) were performed in THF using a Waters apparatus with 5 μ-styragel columns (100, 3 × 500, 1000 Å) and a double detection (UV detector and differential refractometer), calibrated with polystyrene standards. That of polybutadiene were performed in THF with a modular equipment including a set of two columns (Polymer Laboratories, PL-gel 100 Å, 60 cm × 7.5 mm), a Gilson pump (Model 302), a Toilets injector (WISP 710), a Toilets UV detector (Model 440) with variable wavelength and a Toilets differential refractometer (Model 410). The calibration was realized with *n*-alkane standards.

3. Results and discussion

3.1. Addition of dibutylphosphate onto 1,4-polydiene models: analysis of the adducts formed and characterization of side products

All the reactions were carried out without solvent at 70°C for 3 h, with stoichiometric molar proportions of epoxide and DBP.

*3.1.1. Reaction onto 4,5-epoxy-4-methyloctane (**1**) (Fig. 4)*

The ^{1}H-NMR analysis of the crude mixture indicates a total transformation of **1** (total disappearance of the signal characteristic of the oxirane ring hydrogens at $\delta = 2.76$ ppm). The signals characteristic of the phosphate groups are localized between 4.00 and 4.40 ppm. The presence of butanol is also noticed (chemical shifts at $\delta = 0.95$, 1.40, 1.60 and 3.65 ppm respectively characteristic of hydrogens of groups $-\mathrm{C}H_3$, Me–$\mathrm{C}H_2$–, –$\mathrm{C}H_2$–$\mathrm{C}H_2$–O and –$\mathrm{C}H_2$O–); also characterized by SFC. It is explained by the formation of 2-butoxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane (**1a**) (result of internal condensation reaction between a butylphosphate function and the tertiary alcohol function of the initial 1:1 adduct formed) which is characterized in ^{31}P-NMR by four peaks between 14 and 18 ppm, zone characteristic of five atom cyclic phosphates (no peak characteristic of the 1:1 β-hydroxyphosphate adduct) [10]. The condensation reaction between two butylphosphate functions have been rejected because in drastic conditions these reactions do not occur (attempts were realized between DBP and tributylphosphate, but also between tributylphosphate and an epoxide).

Each peak characteristic of **1a** observed in ^{31}P-NMR corresponds to a precise isomer form of the molecule which, having three asymmetry centers (two asymmetrical carbons and the phosphorus), exists with eight isomer forms (diastereomers and enantiomers). The presence of four peaks is explained by the fact that the optical isomers are not differentiated in ^{31}P-NMR. The four diastereomers are represented in Scheme 2.

1a is characterized in ^{1}H-NMR (Table 4) by signals at $\delta = 4.15$ and 4.22 ppm (doublet of doublet) corresponding to the hydrogens –CH_2–O–P and –CH–O–P of the respective phosphate groups.

In ^{13}C-NMR, butanol is characterized by chemical shifts at 14.14, 18.85, 34.75 and 62.53 ppm. Those of tertiary and quaternary carbons of the dioxaphospho-

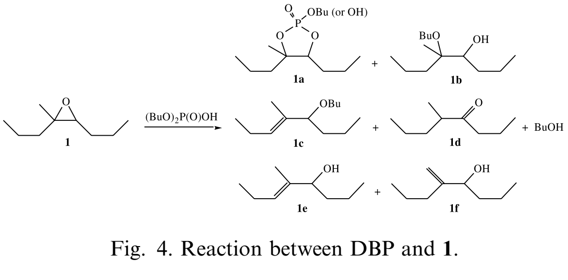
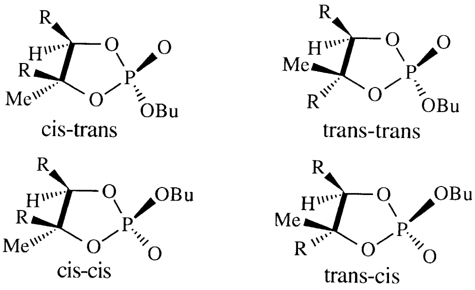


Fig. 4. Reaction between DBP and **1**.



Scheme 2.

lane cycle are localized toward the low fields (from 85.6 to 88.6 ppm).

In IR, the absorption bands characteristic of the formation of **1a** are noticed at 977, 1032 and 1283 cm^{-1} (Table 5).

Table 5
IR absorption bands characteristic of dioxaphospholane formation

Wavelength (cm^{-1})	Group	Literature values [11] (cm^{-1})
1283	$(RO)_3P(O)$	1286–1258
1064	C–O–P	1080–990
1032	$P(O)CH_2R$	1042–987
977	$P(O)CHR_2$	1018–950

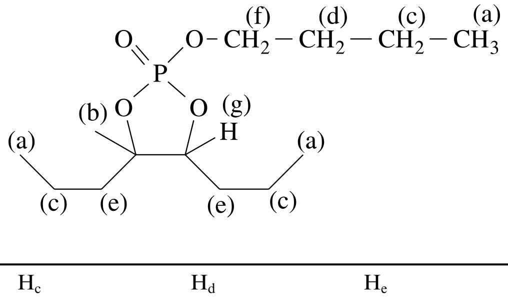
It was also noticed that **1** is not solely transformed into 1:1 phosphorated adducts. Several other non-phosphorated side derivatives were identified by comparing their spectroscopic characteristics with those of derivatives issued from **1**, beforehand synthesized according to a reactional process able to occur during the studied reaction, such as for example, the addition of the butanol formed on the oxirane rings [12], the reactions of rearrangement of oxirane rings or the alcoholysis of the phosphate bonds. While thus operating, the presence of allyl alcohols (**1e** and **1f**), allyl ether (**1c**), β-hydroxyether (**1b**) and ketone (**1d**) derivatives could be confirmed (Fig. 4). The two allyl alcohols are characterized in ^{1}H-NMR (Table 6) by the hydrogens of the carbon–carbon unsaturations: triplet at 5.40 ppm (internal carbon–carbon double bonds) for **1e** and two singlets at 4.80 and 5.00 ppm (external carbon–carbon double bonds) for **1f**. The β-hydroxyether **1b** is characterized by the singlet of the methyl group in α of the hydroxyl at $\delta = 1.05$ ppm. The ketone **1d** (5-methyloctan-4-one) is characterized in IR (absorption band at 1708 cm^{-1}) and ^{1}H-NMR (triplet at $\delta = 2.4$ ppm characteristic of hydrogens of the methylene in α position of ketone function, and sextuplet at $\delta = 2.52$ ppm for the hydrogen –C*H*(CH$_3$)–). On the other hand, it was not possible to verify if the α,β-diol **1g** is formed during the reaction. The analysis by SFC was considered to confirm the presence of the side products supposed to be formed according to the ^{1}H-NMR analysis of the mixture obtained after reaction between DBP and **1**. For that, the chromatograms obtained after fractionation of the crude mixtures resulting from the respective reactions **1**/butanol/ceric ammonium nitrate (CAN) and **1**/DBP were compared, which allows to note in the both cases the presence of products at $t_R = 4.42$, 8.62, 8.74, 9.37 and 10.27 min, respectively characteristic of the presence of butanol, **1d**, **1e** and **1f**, **1c** and **1b** respectively (Table 7).

The respective proportions of **1b**, **1c**, **1d**, **1e** and **1f** were determined from the ^{1}H-NMR spectrum of the crude mixture of the reaction between DBP and **1**, and expressed in relation with the quantity of initial epoxide **1** (Fig. 4). The total yield in side products (15%) corresponds approximately to the ratio of residual DBP (17%) measured on the ^{31}P-NMR spectrum.

3.1.2. Reaction onto 4,5-epoxyoctane (2) (Fig. 5)

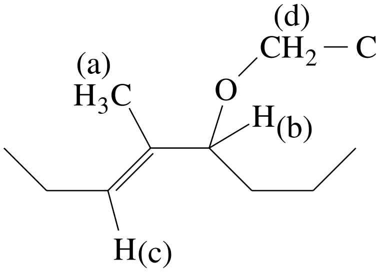
On contrary to the study realized with **1**, the addition of DBP upon **2** occurs with formation of a mixture of two types of phosphorated adducts, accompanied by a

Table 4
^{1}H-NMR characterization of **1a** (solvent: CDCl$_3$, reference: TMS)



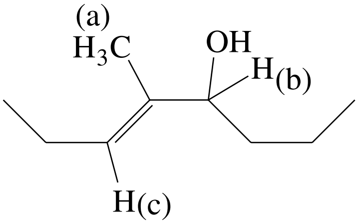
H_a	H_b	H_c	H_d	H_e	H_f	H_g
0.95 ppm (two triplets)	1.30 ppm (s) 1.35 ppm (s)	1.40 ppm	1.55 ppm	1.65 ppm	4.15 ppm (triplet)	4.22 ppm (d d)

Table 6
^{1}H-NMR and IR characterization of side products formed during DBP addition on **1**



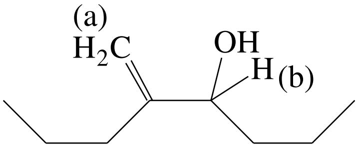
(1c)

^{1}H-NMR (ppm)	IR (cm^{-1})
H_a 1.60 (singlet)	C=C 1670
H_b 4.00	C–O–C 1123
H_c 5.40 (triplet)	
H_d 3.30 (triplet)	



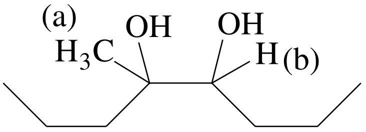
(1e)

^{1}H-NMR (ppm)	IR (cm^{-1})
H_a 1.60 (singlet)	C=C 1667
H_b 3.95	–OH 3350
H_c 5.35 (triplet)	



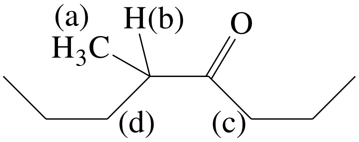
(1f)

H_a 4.80, 5.00 (two singlets)	CH_2=C 1640
H_b 4.05	–OH 3350



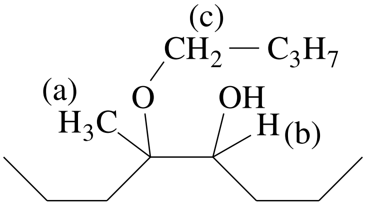
(1g)

H_a 1.10, 1.20 (two singlets)	–OH 3350
H_b 3.40 (triplet)	



(1d)

H_a 1.05 (doublet)	C=O 1708
H_b 2.52 (sextet)	
H_c 2.40 (triplet)	



(1b)

H_a 0.98, 1.05 (two singlets)	–OH 3413, 1380
H_b, H_c 3.25–3.30	C–O–C 1123

small quantity of 4,5-dihydroxyoctane as side product, characterized in ^{1}H-NMR by a signal at $\delta = 3.40$ ppm corresponding to the –C*H*OH– hydrogens (Fig. 5). Moreover, the addition of the formed butanol on the oxirane rings does not occur.

The composition depends on the isomerism (*cis* or *trans*) of **2** (Table 8). The addition of DBP upon 85% *cis* 4,5-epoxyoctane (meso (R,S)) (the 15% remainder being the form *trans* (racemic $(R,R)+(S,S)$)) occurs with principal formation of 2-butoxy-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane (**2b**). On the other hand, the same addition realized upon 100% *trans* 4,5-epoxyoctane (racemic $(R,R)+(S,S)$) occurs with formation of the 1:1 β-hydroxyphosphate adduct **2a** as main product (57%).

The formation of only one isomer characterized in ^{31}P-NMR at $\delta = 15.56$ ppm for the dioxaphospholane resulting from the 85% *cis* epoxide (Table 8) can be explained by the mechanism proposed in Fig. 6. Initially,

Table 7
SFC characterization of products commonly present in the two mixtures resulting from the respective reactions: **1**/butanol/CAN and **1**/DBP

Product identified	t_R (min)	Proportions	
		1/BuOH/CAN	**1**/DBP
Butanol	4.42	Low	Very high
1d	8.62	Medium	Low
1e, **1f**	8.74	High	Low
1c	9.37	Low	Low
1b	10.27	Very high	Medium

there would be a nucleophilic opening of the *cis* oxirane ring by the DBP anion (SN2 substitution) with inversion of configuration of the carbon bearing the phosphate group. The *n*-propyl groups being in *syn* position, an unstable configuration, would be repositioned then in the more stable *trans* configuration, by rotation around C–C bond (C(*R*), C(*R*)). This rotation would have then for consequence to bring closer the hydroxyl group with the phosphorated center, making easier the formation of dioxaphospholane by cyclization with elimination of alcohol. The dioxaphospholane molecule would be thus entirely *trans*, which is in agreement with the presence of only one peak on the ^{31}P-NMR spectrum.

The less significant proportions of dioxaphospholane compared to the 1:1 β-hydroxyphosphate adduct observed with the *trans* epoxide can be explained by the fact that the *n*-propyl substituents adopt in this case, immediately after the addition of the dialkylphosphate anion, an antiposition, i.e. a stable configuration, and the rotation around C–C bond (C(*R*), C(*S*)) would not occur (Fig. 7).

The dioxaphospholane **2b** obtained starting from the 100% *trans* epoxide has an isomerism *cis*/*trans* if one considers the position of the butoxy group compared to the two *n*-propyl groups of the dioxaphospholane cycle (Scheme 3). In ^{31}P-NMR, the chemical shifts of the two isomers are observed at 14.82 and 16.11 ppm, values different from that noticed for the dioxaphospholane **2b** formed from the *cis* epoxide.

In the case of the addition of DBP on the 85% *cis* epoxide, the dioxaphospholane **2b** where the two *n*-propyl groups are in *cis* position (obtained starting from *trans* epoxide) was obtained only in the form of traces. This result demonstrates that the dioxaphospholane obtained was practically entirely issued from the starting *cis* epoxide form.

In ^{1}H-NMR (Table 9), **2b** is characterized by a doublet of doublet at 4.16 ppm corresponding to the hydrogen –C*H*–O–P of the dioxaphospholane cycle, as well as a signal at 4.13 ppm characteristic of –CH_2–O–P of the *n*-butyl group. **2a** is characterized by the signals of –C*H*– hydrogens groups at 3.70 and 4.45 ppm corresponding respectively to the hydrogen on the carbon in α position of the hydroxyl group and that on the carbon in α position of the phosphate group, as well as the signal of hydrogens –CH_2–O–P of *n*-butyl group at 4.15 ppm.

In ^{13}C–NMR, the doublets at $\delta = 83.28$ and 83.34 ppm (carbons –*C*H–O–P; $J_{PC} = 6$ Hz) and $\delta = 68.52$ and 68.58 ppm (carbons –*C*H$_2$–O–P; $J_{PC} = 6$ Hz) confirm the formation of the dioxaphospholane **2b**.

3.1.3. Water influence

The dioxaphospholane adducts formed during the addition of DBP onto internal epoxides are easily hydrolyzed. Under the action of water, a selective cleavage of the exocyclic BuO–P bond is noticed (Scheme 4).

This selectivity of the hydrolysis differs from that observed with the non-substituted or monosubstituted dioxaphospholanes, which can as well occur on the

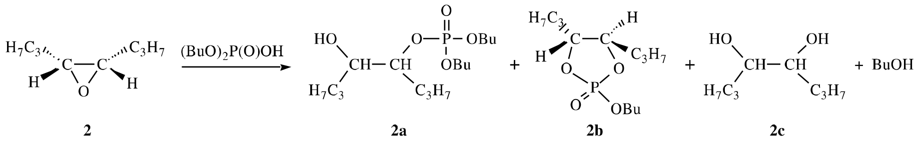


Fig. 5. Reaction between DBP and **2**.

Table 8
Influence of the isomerism of the epoxide on the addition: comparison of the compositions in phosphorated compounds contained in the mixtures obtained versus the initial form (*cis* or *trans*) of **2** (determination made from the ^{31}P-NMR spectra) and ^{31}P-NMR chemical shifts of the various products

4,5-Epoxyoctane (**2**)	Dioxaphospholane adduct **2b**		β-Hydroxyphosphate adduct **2a**		Residual DBP
	Chemical shifts (ppm)	Proportion (%)	Chemical shifts (ppm)	Proportion (%)	
85% *cis*	15.56	69	0.15	21	10
100% *trans*	16.11, 14.82	22	0.20	57	21

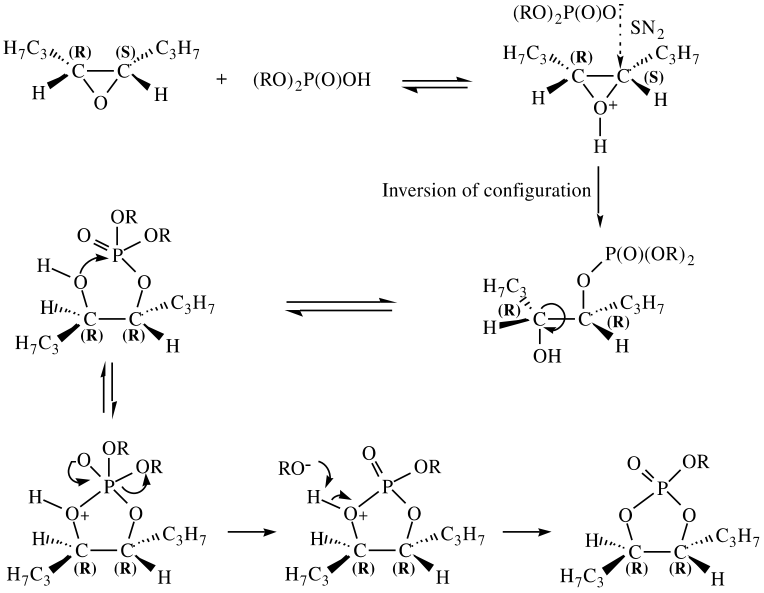


Fig. 6. Mechanism of dioxaphospholane formation (*trans* isomer) from *cis* epoxide **2**.

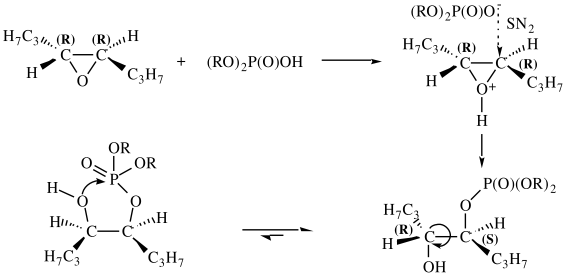
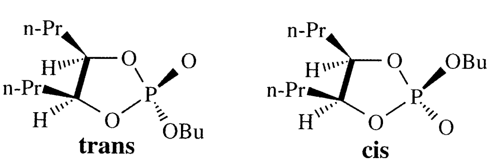


Fig. 7. Mechanism of dioxaphospholane formation (*cis* isomer) from *trans* epoxide **2**.



Scheme 3.

exocyclic phosphate functions as on phosphate bonds of the dioxaphospholane cycle [13,14].

In Fig. 8 are represented ^{31}P-NMR spectra of the mixture issued from the DBP/**1** reaction carried out without solvent, before and after reaction with water. It appears that the 2-hydroxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane formed after reaction with water, is characterized in ^{31}P-NMR by two peaks against four for the initial homologous derivative. This result can be explained by the formation of a hydrogen bond between P=O and P–OH functions, which would suppress thus the chirality of the phosphorus atom (Scheme 5).

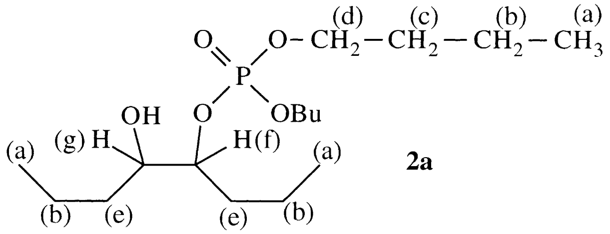
The presence of traces of 2-hydroxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane characterized on the ^{31}P-NMR spectrum of the crude reactional mixture can be explained by action of the water or butanol which are respectively released during formation of the side products (allyl ethers) and the formation of dioxaphospholane structure.

The selective hydrolysis is also characterized on the ^{1}H-NMR spectra by the disappearance of the signals corresponding to the methylene in α position of the oxygen of R–CH_2–O–P butyl group at $\delta = 4.15$ ppm and the transformation of the signal at $\delta = 4.22$ ppm (–C*H*–O–P group; doublet of doublet) into a doublet at $\delta = 4.25$ ppm.

IR also allows to follow this modification by the disappearance of the absorption band at 1032 cm^{-1} (–P(O)OCH$_2$R group) and the appearance of various absorption bands at 1019 and 1712 cm^{-1} corresponding to a –P(O)OH group.

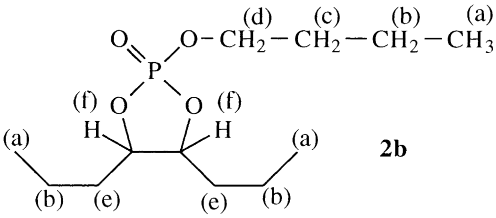
The dioxaphospholane **2b**, obtained after reaction of DBP upon **2** is also hydrolyzed in the presence of water to form only 2-hydroxy-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane, but its hydrolysis is much slower than in the case of **1a** because only 50% of **2b** is transformed after 10 h of stirring at room temperature. The ^{31}P-NMR spectrum presents, in addition to the peak at $\delta = 15.56$ ppm, another peak corresponding to the 2-hydroxy-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane at $\delta = 16.90$ ppm. On ^{1}H-NMR spectra, a decrease of

Table 9
^{1}H-NMR characterization of **2a** and **2b** (solvent: $CDCl_3$, reference: TMS)



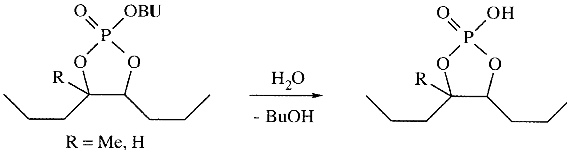
2a

H_a	H_b	H_c	H_d	H_e	H_f	H_g
0.95 ppm	1.45 ppm	1.55 ppm	4.15 ppm	1.65 ppm	4.45 ppm	3.70 ppm

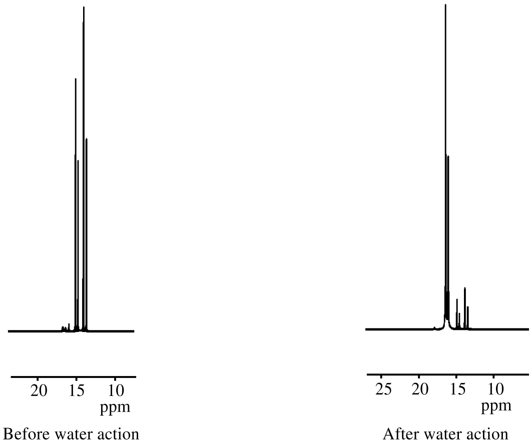


2b

H_a	H_b	H_c	H_d	H_e	H_f
0.95 ppm	1.45 ppm	1.57 ppm	4.13 ppm	1.67 ppm	4.16 ppm



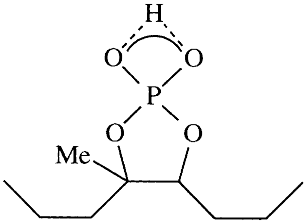
Scheme 4.



Before water action

After water action

Fig. 8. ^{31}P-NMR of the products of the reaction of DBP with **1**, before and after water action.



Scheme 5.

the intensity of the signals characteristic of R–CH_2O–P protons is observed.

3.1.4. *Comparative study of the action of various di(alkyl or aryl)phosphates on the models*

The addition of DEP, DMP and DPP on **1** and **2** (mainly *cis*) was considered under the same conditions as previously used with DBP.

*Addition upon **1** (Table 10):* Addition of di(alkyl or aryl)phosphates on **1** produces mainly dioxaphospholane derivatives. On the other hand, the type of dioxaphospholane (2-alkoxy(phenoxy) or 2-hydroxy), as well as the proportions of dioxaphospholane and residual phosphate, vary in relation with the nature of the di(alkyl or aryl)phosphate used (Table 10).

Table 10
Results of the addition of di(alkyl or aryl)phosphates on **1**: ^{31}P NMR characterization and yields calculated in comparison with the initial phosphate reagent

Reagent	Dioxaphospholane adduct formed				Side phosphorated products		Residual di(alkyl or aryl) phosphate (%)
	P(O)OH form		P(O)(OR) form				
	Chemical shifts (ppm)	Yield (%)	Chemical shifts (ppm)	Yield (%)	Chemical shifts (ppm)	Yield (%)	
DBP	16.27–16.62	3	13.62–13.99 14.71–15.03	80			17
DEP	15.87–16.22	1	13.22–13.61 14.27–14.60	87	−12.86 $[(EtO)_2P(O)]_2O$	4	4
DMP	16.32–16.68	49	15.03–15.45	4			47
DPP	16.32–16.66	63	7.43–7.47 7.90–7.95	2			35

Contrary to the addition of DEP and DBP on **1**, that of DMP and DPP leads mainly to the 2-hydroxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane which is characterized in ^{31}P-NMR by two peaks at 16.32 and 16.67 ppm. The analysis of the ^{1}H-NMR spectra of the crude mixtures confirms these results: for example, the crude mixture of the reaction of DMP on **1** shows a notable deficiency of the signal intensity of the hydrogens of the CH_3–O–P groups fixed on the dioxaphospholane cycle compared to what it should be without hydrolysis. It is also advisable to note that the total yields in dioxaphospholane adduct derivatives and those in 2-hydroxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane moves in opposite directions; the rates of addition decrease as follows: DEP > DBP > DPP > DMP, whereas the proportions of 2-hydroxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane follow an opposite evolution.

In the case of the addition of DEP on **1**, the pyrophosphate formation (formed by condensation between two ethyl phosphate bonds with water elimination), characterized in ^{31}P-NMR by a chemical shift at −12.86 ppm and in IR by an absorption band at 912 cm^{-1}, was noted.

The significant proportions of 2-hydroxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane observed in particular with DMP and DPP, suppose the use of a significant quantity of water, i.e. a quantity largely higher than that produced by the side reactions simultaneously to the addition process. This establishment thus supposes the existence of another mechanism able to cause the cleavage of the alkoxy (or aryloxy) bond without water intervention. It concerns probably a reaction of alcoholysis owing to the fact that the formation of the dioxaphospholane structures is accompanied by an alcohol release.

Addition upon 2 (Table 11): The addition of dialkylphosphates on **2** (85% *cis*) occurs with mainly formation of dioxaphospholane derivatives. On the whole, the results join those recorded with **1**: the formed products and yields according to the nature of the dialkylphosphate follow the same evolution. Only the results re-

Table 11
Results of the addition of di(alkyl or aryl)phosphates on **2** (85% cis): ^{31}P NMR characterization and yields calculated in comparison with the initial phosphate reagent

Reagent	Dioxaphospholane adduct formed			β-hydroxy-phosphate adduct formed		Side phosphorated products		Residual di(alkyl or aryl) phosphate (%)
	Form	Chemical shifts (ppm)	Yield (%)	Chemical shifts (ppm)	Yield (%)	Chemical shifts (ppm)	Yield (%)	
DBP	P(O)(OBu)	15.56	69	0.15	21			10
DEP	P(O)(OEt)	15.55	91	−0.15	8	−12.97 $[(EtO)_2P(O)_2]O$	0.5	0
DMP	P(O)OH	16.92	32	0.64	10			58
DPP	P(O)OH	16.60	6	8.53	84	−17.60 $[(PhO)_2P(O)]_2O$	2	6

corded with DPP are different since the formation of 1:1 β-hydroxyphosphate adduct is favored. This last is characterized in ^{1}H-NMR by the signal of the hydrogen on the carbon in α position of the hydroxyl group at $\delta = 3.95$ ppm and that of the hydrogen on the carbon in α position of the $(PhO)_2P(O)O$ group at $\delta = 4.30$ ppm, and in ^{31}P-NMR by a peak at $\delta = 8.53$ ppm.

3.1.5. Kinetic studies

Kinetics studies of the addition of DBP on **1** were carried out at 20°C and were followed by SFC. Dodecane was selected as internal reference in order to follow the disappearance with time of **1** and the progressive formation of butanol (issued from the transformation of the β-hydroxyphosphate adduct into a dioxaphospholane derivative) and that of the β-hydroxyether (Fig. 9). The residual DBP was not quantified because of the bad resolution of the chromatographic peak obtained (DBP was too significantly retained in the column), making impossible the calculation of the concentrations.

Butanol immediately appears at the beginning of the reaction. On the other hand, the β-hydroxyether is visible on the chromatograms only after 15–30 min. After 5 h, the epoxide is completely consumed.

The straight line representing the equation $1/(E) - 1/(E)_0$ versus time, where (E) represents the epoxide concentration at time t and $(E)_0$ the epoxide concentration at initial time (Fig. 10), has a correlation coefficient of 0.998, meaning a global order of 2. Order 2 was determined by measurement of the epoxide consumption versus the time. The proportions of side products formed during the reaction are so weak that it is possible to neglect them for the kinetic calculation.

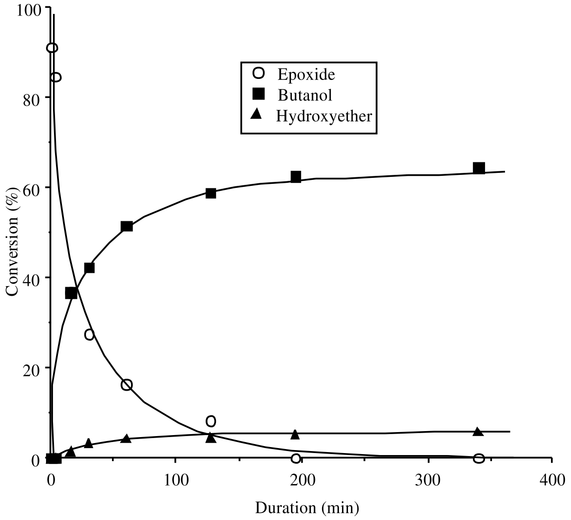


Fig. 9. Kinetic study of the addition of DBP upon **1**.

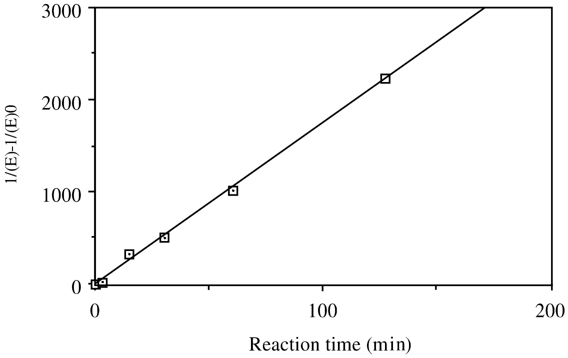


Fig. 10. Representation of the equation in the case of a global order 2 for the equimolecular reaction of DBP on **1**.

At the end of the reaction, the molar quantity of formed butanol represents 64% of the consumed epoxide. This value is lower than that of the dioxaphospholane determined from the ^{31}P-NMR spectrum (80%). The difference between these two values well justifies a partial consumption of butanol by addition on **1** oxirane rings.

3.2. Chemical modification of epoxidized 1,4-polydienes by di(alkyl or aryl)phosphates

3.2.1. Addition of di(alkyl or aryl)phosphates onto epoxidized 1,4-polyisoprene

The study was considered on respectively 18 and/or 39% epoxidized 1,4-polyisoprenes.

Total modification: The addition of DBP on the oxirane rings of epoxidized 1,4-polyisoprenes was carried out without solvent and in dichloromethane, for 12 h by using stoichiometric quantities of DBP and epoxidized 1,4-polyisoprene units. The ^{1}H-NMR analysis of polymers obtained in the absence of solvent, as in solution, shows the total disappearance of the signals characteristic of the hydrogens of oxirane rings ($\delta = 2.70$ ppm). The addition of DBP on the oxirane rings is confirmed in ^{31}P-NMR by the presence of four peaks at 13.49, 13.87, 14.64 and 14.87 ppm which correspond to the four isomers of the 2-butoxy-2-oxo-1,3,2-dioxaphospholane structures (*cis–cis*, *cis–trans*, *trans–cis*, *trans–trans*) previously identified during the study carried out with **1**, and in ^{1}H-NMR by the chemical shifts at 4.05 and 4.15 ppm respectively characteristic of hydrogens C_3H_7–CH_2–O–P and –CH–O–P. β-hydroxyphosphate structures are also characterized by ^{31}P-NMR ($\delta = 1.20$ ppm) but in low proportions compared to that of the dioxaphospholane structures (Table 12). The presence of residual DBP (~13%) is always noted on the ^{31}P-NMR spectrum of the crude product obtained after reaction in the absence of solvent. It is the same concerning the modified products obtained in solution,

Table 12
Proportions (determined from ^{31}P-NMR and ^{1}H-NMR spectra) of the various phosphorated polymer units (reaction without solvent or in solution) of the polymer obtained after chemical modification of 39% epoxidized 1,4-polysioprene by DBP

Reaction conditions	Phosphorated polymer units formed (%)		Chemical modification[a] (%)
	Dioxaphospholane	β-Hydroxyphosphate	
Without solvent	97.7	2.3	33.0
In dichloromethane	96.7	3.3	16.5

[a] Yield in phosphorated units compared to the whole of the polymer units.

because of DBP is not completely eliminated after the precipitation in methanol. The best addition yields are observed when the reaction is carried out without solvent.

It was also noticed that 2-butoxy-2-oxo-1,3,2-dioxaphospholane structures are hydrolyzed very easily. The least water trace in the medium is sufficient to cause the P–OBu bond hydrolysis, and to lead to 2-hydroxy-2-oxo-1,3,2-dioxaphospholane structures, characterized in ^{31}P-NMR by a signal at 16.70 ppm.

The general evolution of these reactions is represented on Fig. 11. As previously shown during model molecule study, the presence of residual DBP, inspite of the total opening of the oxirane rings, means that side structures are formed simultaneously to the detriment of addition 1:1. In the case of the addition of DBP on 39% epoxidized 1,4-polyisoprene, two additional signals are noticed at 3.65 ppm (triplet) and 3.40 ppm. Signals of the type of that observed at 3.65 ppm were already announced by some authors in the framework of studies on the epoxidation and crosslinking of epoxidized natural rubber [15,16]. However, interpretations of the authors differ: whereas for Roy et al. this signal characterizes the presence of furan cycles [15], for Roychoudhury it corresponds to the ether or alcohol structures formed after opening of oxirane rings [16]. Perera et al. [17] who studied the action of phosphoric acid on partially epoxidized polydienes noticed also a signal at 3.40 ppm which they attribute either to the formation α,β-diol structures, or to the formation of ether bonds. While referring to the results of the study carried out with **1**, it appears now logical to attribute the signal at 3.40 ppm to hydrogens –C*H*OH– corresponding to α,β-diol structures (4,5-dihydroxy-4-methyloctane, model of the diol microstructure). This attribution is confirmed by the fact that, as in the case of the addition on **1**, the rearrangement reactions of the oxirane rings (formation of allyl alcohol and ketone) do not occur on epoxidized 1,4-polyisoprenes since the signals characteristic of these structures (allyl ethers: $\delta = 3.30$, 4.00, 5.40 ppm and 3.40, 4.05, 4.80 and 5.00 ppm, β-hydroxyether: $\delta = 1.25$, 3.25 and 3.30 ppm, ketone: $\delta = 2.40$ and 2.52 ppm) are not noticed on the ^{1}H-NMR spectrum of the modified polymer. Consequently, the 1:1 addition of DBP on the epoxidized 1,4-polyisoprene units would be disturbed only by reactions leading to the formation of polymer units of type α,β-diols or interchain bonds of type ether.

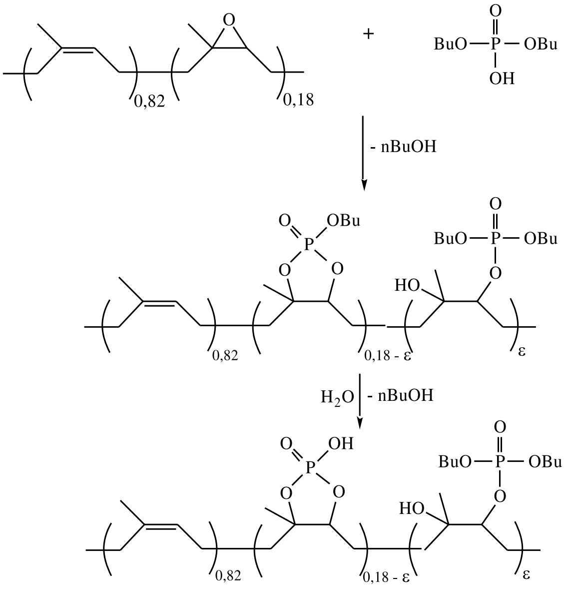


Fig. 11. DBP reaction with epoxidized 1,4-polyisoprene.

Reaction with DEP carried out without solvent and in dichloromethane, under the same conditions that with DBP, leads systematically to the formation of a gel. The elementary analysis of the gel obtained after the reaction led in dichloromethane on a 18% epoxidized 1,4-polyisoprene and washed several times in methanol, indicates a real phosphorus content of 5.8% (theoretical rate calculated for a complete transformation of the oxirane rings in β-hydroxyphosphate structures derived from DEP = 6.2%). This systematic gelation is difficult to explain because the results obtained with model **1** do not make it possible to envisage this phenomenon.

The addition of DPP was only considered without solvent. It causes the total opening of the oxirane rings, with mainly formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane structures (^{31}P-NMR: $\delta = 16.55$ ppm). At the end of the reaction, the quantity of non-transformed DPP represents 28%. Compared to the results recorded with DBP, it appears that the proportion in β-hydroxyphosphate units is more significant (10.5% of the whole of the phosphorated polymer units, whatever the initial content of epoxidized units of the epoxidized 1,4-polyisoprene) and the dioxaphospholane structures are only of type 2-hydroxy-2-oxo-1,3,2-dioxaphospholane (61.4% of the whole of the phosphorated polymer units). Moreover, the side structures are not observed, which supposes a greater selectivity of the reaction with DPP.

Partial modification: The partial modification of epoxidized 1,4-polyisoprene by di(alkyl or aryl)phosphates was carried out in order to check if the epoxide structures present in excess are affected during the reaction. For that, an attempt was carried out without solvent with DBP, by considering a quantity of reagent corresponding to a theoretical modification of 30% of the oxiranes contained in the 39% epoxidized 1,4-polyisoprene. The analysis of the ^{1}H-NMR spectrum of the crude product of the reaction shows that there is addition of DBP onto the oxirane rings (signals at 4.05 and 4.15 corresponding to the hydrogens of butylphosphate groups), but especially that the oxirane rings in excess are not transformed. ^{31}P-NMR analysis also made it possible to note the absence of residual DBP, which shows that under these conditions the addition of the reagent is total. The proportion of the residual oxirane rings is slightly lower than the theoretical value, but this result is logical because of the effect of the side reactions previously described.

3.2.2. Addition of di(alkyl or aryl)phosphates onto epoxidized 1,4-polybutadienes

All the reactions were carried out without solvent on 26 and 46% epoxidized 1,4-polybutadienes.

Total modification: The addition of di(alkyl or aryl)phosphates (stoichiometric quantities compared to the oxirane functions) on epoxidized 1,4-polybutadiene causes the total opening of the oxirane rings (in ^{1}H-NMR, disappearance of the signals characteristic of the oxirane ring hydrogens at 2.70 and 2.90 ppm). Moreover, the ^{1}H-NMR analysis shows that the β-hydroxyphosphate and 2-oxo-1,3,2-dioxaphospholane structures are both present. The β-hydroxyphosphate units are characterized by signals at 3.65 (addition of the dialkylphosphates) or 3.70 ppm (addition of DPP), corresponding respectively to hydrogens –C*H*OH–, and at 4.10 or 4.15 ppm, corresponding to hydrogens –C*H*–O–P. Dioxaphospholane units are characterized by signals at 4.65 (addition of the dialkylphosphates) or 4.45 ppm (addition of DPP) corresponding to hydrogens –C*H*–O–P. In the case of the DPP addition, the chemical shifts of hydrogens –C*H*–O–P are shifted toward low fields because of the diamagnetic aromatic ring current of the phenyl groups. In addition, a signal is always observed at 3.40 ppm whatever the di(alkyl or aryl)phosphate used: its presence is significant of the formation of α,β-diol structures, the only side structure observed.

The proportions of β-hydroxyphosphate and 2-alkoxy-2-oxo-1,3,2-dioxaphospholane units, determined from ^{31}P-NMR spectra, depend on the di(alkyl or aryl)phosphate (Table 13). The addition of the dialkylphosphates occurs with the predominant formation of β-hydroxyphosphate units (Fig. 12), while that of diphenylphosphate leads to a major formation of dioxaphospholane units, results which are surprisingly contrary to those obtained with the model **2**.

On the other hand, some variations in the proportions of the polymer units formed are noticed in relation with

Table 13
Comparison of the results obtained after modification in the absence of solvent of 26% and 46% epoxidized 1,4-polybutadienes by various di(alkyl or aryl)phosphates (yields in phosphorated units are expressed in comparison with the initial epoxidized units and determined from ^{31}P-NMR spectra)

Epoxidized unit content (%)	Reagent[a]	Phosphorated polymer units formed						Residual reagent (%)
		Dioxaphospholane units		β-Hydroxyphosphate units		Side phosphorated product[b]		
		Chemical shifts (ppm)	Yield (%)	Chemical shifts (ppm)	Yield (%)	Chemical shifts (ppm)	Yield (%)	
26	DBP	15.95	13.5[c]	0.22	54.1			32.4
46	DBP	15.95	9.5[c]	0.22	79.2			11.3
26	DEP	15.50	25.6[c]	0.02	51.3			23.1
46	DEP	15.50	17.0[c]	0.02	57.5			25.3
26	DPP	16.51	44.8[d]	8.22	6.8	−17.72	15.1	18.2
46	DPP	16.51	18.5[d]	8.22	59.3	−17.72	5.5	11.2

[a] Stoichiometric quantities in comparison with oxirane rings.

[b] $[(PhO)_2P(O)]_2O$.

[c] 2-Alkoxy-2-oxo-1,3,2dioxaphospholane structures.

[d] 2-Hydroxy-2-oxo-1,3,2-dioxaphospholane structures.

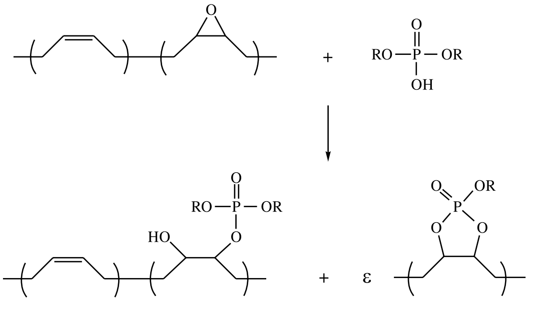


Fig. 12. Reaction of di(alkyl or aryl)phosphates on the oxirane rings of epoxidized 1,4-polybutadiene.

the degree of epoxidation of the 1,4-polybutadiene (Table 13). Globally, when the content in epoxidized units of the epoxidized 1,4-polybutadiene increases, the total yield in phosphorated units increases: the proportions of β-hydroxyphosphate structures increase and, inversely, those of dioxaphospholane structures and residual di(alkyl or aryl)phosphate decrease. This can be explained by the increasing of the polarity of the epoxidized 1,4-polybutadiene when the content of epoxidized units is increased, which would facilitate the approach of the di(alkyl or aryl)phosphate reagent.

Partial modification: To complete the study, a partial modification of the 26% epoxidized 1,4-polybutadiene by DBP (utilization of a DBP quantity corresponding to a theoretical modification of 50% of the oxirane rings) was considered. As in the case of the epoxidized 1,4-polyisoprenes, it is noticed that the excess part of the oxirane rings is not affected at the end of the reaction. Indeed, on the ^{1}H-NMR spectrum of the resulting polymer, the two signals characteristic of the oxirane ring hydrogens (*cis* and *trans*) are noticed at 2.70 and 2.90 ppm.

3.3. Action of dialkylphosphates upon the ELNR latex

The study with the ELNR latex (5 ml of latex contain approximately 1 g of ELNR) was considered only with dialkylphosphates (DBP and DEP), used in stoichiometric quantities compared to the oxirane rings.

Dichloromethane and toluene [18] were chosen as organic solvents with the aim to prepare a reverse emulsion. The latex mixture (pH = 2) and dichloromethane (or toluene) was submitted to the action of some dialkylphosphates during 24 h, at room temperature and under stirring.

With toluene, whatever the dialkylphosphate used, a latex coagulation is always observed during the reaction (the polymer obtained is insoluble in usual solvents).

With dichloromethane, the results depend on the nature of the dialkylphosphate: with DEP, the results join those obtained with toluene (latex coagulation during the reaction), whereas with DBP only a demixing of the reactional medium is noticed when the stirring is stopped, thus allowing the separation of the two liquid phases, and then their separated analysis by NMR. There is transfer of a part of the rubber in the organic phase. The dichloromethane phase, after solvent evaporation, is composed of residual DBP (67%) and ELNR modified by DBP. 32% of the ELNR initial oxiranes are transformed in 2-butoxy-2-oxo-1,3,2-dioxaphospholane units ($\delta = 15.54$ ppm) and 1% in β-hydroxyphosphate units ($\delta = 0.04$ ppm), whereas the ^{1}H-NMR analysis indicates a total transformation of the oxirane rings. Side structures (diol, ethers) are also identified. The modified ELNR recovered in the latex medium shows the same characteristics as that transferred in the dichloromethane phase. Compared to those obtained onto epoxidized LIR (for a reaction carried out without solvent), the yields of the addition of DBP on ELNR obtained in these conditions are much lower.

It was also noticed that, even when there is coagulation of the latex during the reaction, the addition occurs. This was proved by the elementary analysis of the phosphorus contained in the coagulate isolated after action of DEP in dichloromethane. Measurement was realized on the coagulate beforehand washed several times in methanol, and submitted to a final dichloromethane extraction for 8 h by using a soxhlet (in order to eliminate residual DEP). The real phosphorus content amounts to 4% (theoretical content calculated for a complete transformation of the oxirane rings in β-hydroxyphosphate structures derived from DEP = 7.0%).

4. Conclusion

The addition of di(alkyl or aryl)phosphates on oxirane rings is easily realizable without catalyst, under soft conditions. It occurs via P–OH acid bonds, and leads to the formation of the wanted structures. However, there is a competition between the formation of the awaited 1:1 adduct (β-hydroxyphosphate structures) and that of another 1:1 adduct of type 2-(alkoxy or aryloxy)-2-oxo-1,3,2-dioxaphospholane by internal transesterification between one of the *n*-alkyl(or aryl)phosphate bond and the hydroxyl of the same β-hydroxyphosphate, reaction which leads to the release of an alcohol molecule.

The study carried out with the model molecules of the respective 1,4-polydiene chains showed that the addition on internal epoxides always leads to the predominant formation of adducts of type 2-(alkoxy or aryloxy)-2-oxo-1,3,2-dioxaphospholane (their proportions increase with the degree of substitution of the internal epoxide). With **1**, model of the epoxidized 1,4-polyisoprene, the formation of the dioxaphospholane is nearly exclusive, whereas with **2**, model of the epoxidized 1,4-polybutadiene, the result depends on the form of the epoxide (*cis* or *trans*): with *trans* isomer, the formation of β-hydroxyphosphate adducts is favored, result which is explained by problems of steric hindrance, while with the *cis* isomer it is the dioxaphospholane. Moreover, the wanted adducts 1:1 are always accompanied by non-phosphorated side products derived from the initial epoxidized molecule, which explain in part the systematic presence of residual di(alkyl or aryl)phosphate at the end of the reaction (10–20%). Lastly, it must be mentioned that the adducts 2-(alkoxy or aryloxy)-2-oxo-1,3,2-dioxaphospholane are hydrolyzed (or alcoholyzed) rather easily in 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and the importance of this transformation is closely related to the nature of the di(alkyl or aryl)phosphate used: formation favored with DMP and DPP.

The addition of di(alkyl or aryl)phosphates on the epoxidized units of epoxidized liquid 1,4-polydienes proceeds in a way nearly similar to that observed on the model molecules of these various structures, with quasi-single formation of 2-(alkoxy or aryloxy)-2-oxo-1,3,2-dioxaphospholane structures in the case of the epoxidized 1,4-polyisoprene, and obtaining of a mixture of β-hydroxyphosphate and dioxaphospholane structures in the case of epoxidized 1,4-polybutadiene. Globally, the formation of side polymer units is less important than in the case of the addition on model molecules and the side units formed are essentially of type α,β-diol. The best yields of addition (dioxaphospholane or β-hydroxyphosphate structures) are obtained when the reactions are carried out without solvent. The last outstanding point concerns the partial modification of oxirane rings by di(alkyl or aryl)phosphates which can be realized while preserving the excess epoxides. A further study demonstrated the ability to crosslink epoxidized 1,4-polydienes partially modified by di(alkyl or aryl)phosphate by using methylnadic anhydride as crosslinking reagent [4].

The attempts of di(alkyl or aryl)phosphate addition on ELNR latex showed that, in biphasic medium by using for instance dichloromethane or toluene as organic solvent, the formation of dioxaphospholane structures is noticed, but the addition yields are much lower than those obtained with epoxidized 1,4-polyisoprene in the absence of solvent or in organic solvent.

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