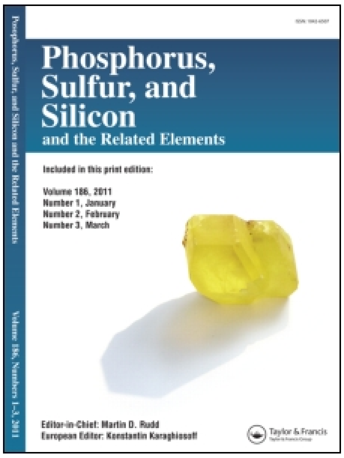

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SYNTHESIS OF DIOLS BEARING PHOSPHONATE GROUPS PART III. THIOLS USED AS STARTING MATERIALS

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SYNTHESIS OF DIOLS BEARING PHOSPHONATE GROUPS PART III. THIOLS USED AS STARTING MATERIALS

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This article describes the synthesis of diols bearing a phosphonated group. The method used is the monoaddition of a thiol on unsaturated compounds. Two ways are possible depending on the species bearing either the phosphonated group or the diol function. First we added a thiol bearing a diol function onto dialkylallylphosphonates. Then a thiol bearing phosphonated groups was added onto an allylic diol. On the other hand we compared radical and UV additions. We also compared the reactivity of similar phosphonated compounds (dimethyl and diethyl phosphonates). All the reactions gave very good yields and the different products have been analyzed by NMR studies. Finally, we succeeded in the synthesis of the corresponding phosphonic diacids by the bromosilane method.

Keywords: Diols; phosphonates; radical; thiols; UV

Diols are generally well-known as precursors of polyesters and polyurethanes. In order to modulate the properties of these polymers, one possibility of the ways is to modify the initial diol structure. That is the main reason we have synthesized new diols bearing a phosphonate group.

We previously have described such polyols using epoxides as starting material.[1] So the epoxy compounds bearing a phosphonated group lead to polyols by ring opening with diethanolamine. We also have prepared a phosphonated hydroxy telechelic polybutadiene (PBHT)[2] by grafting the thiol HS-$(CH_2)_3$-$PO(OC_2H_5)_2$[3] on PBHT. The method led to new

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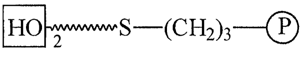
macromolecular polyols containing 3% to 5% weight of phosphorus. A similar study had been published with another thiol $HS\text{-}(CH_2)_2\text{-}PO(OC_2H_5)_2$.[4] We also must mention the family of Fyrol compounds well-known as flame retardants: For example, $(HO{-}CH_2CH_2)_2N{-}CH_2{-}PO(OC_2H_5)_2$ (Fyrol 6) often had been used as diol in polyurethanes synthesis.[5,6] Phosphorus can improve either the adhesiveness or the flame retardancy compared to usual commercial products.

As the mercaptans are well-known as good transfer agents,[7] we intended to prepare new phosphonated diols by addition of alkylmercaptans onto allylphosphonates with the general structures:



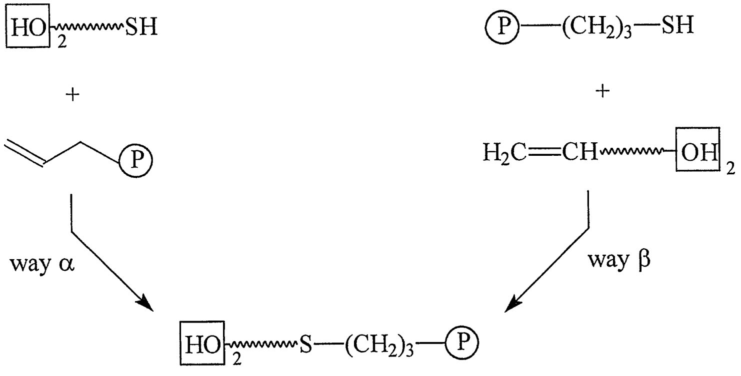
$\boxed{HO}_2$ represents two hydroxyl groups

P represents a phosphonic group such as $P(O)(OR)_2$

$R = CH_3, C_2H_5$

We obtain the structure of thioethers including a phosphonic group and two hydroxyl groups.

Two ways of synthesis have been developed leading to the same products family as shown on Scheme 1.



Ⓟ ≡ $P(O)(OR)_2$

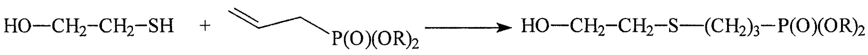
$R = CH_3, C_2H_5$

SCHEME 1 Two diols synthesis routes.

RESULTS AND DISCUSSION

Addition of Thiols onto Dialkyl Allylphosphonates: Method $\underline{\alpha}$

Before adding a diol onto allylphosphonates, we tested the behavior of a monoalcohol, the mercaptoethanol, in order to compare UV and thermal addition. The reaction is:



1a : R = CH_3

1b : R = C_2H_5

This radical reaction already has been described in the literature.[3,4,8] The addition was initiated by AIBN [azobis (isobutyronitrile)] and the authors used diethyl allylphosphonate. In our study, we compared the reactivity of dimethyl and diethyl allylphosphonate. We have carried out the reaction under UV irradiation photoinitiated by benzophenone.

The structure of the monoadduct easily was identified. The results of the thermal addition and the photochemical addition are summed up respectively in Figures 1 and 2. The conversion rates are calculated from the ^{31}P NMR spectra on which we only see two signals corresponding

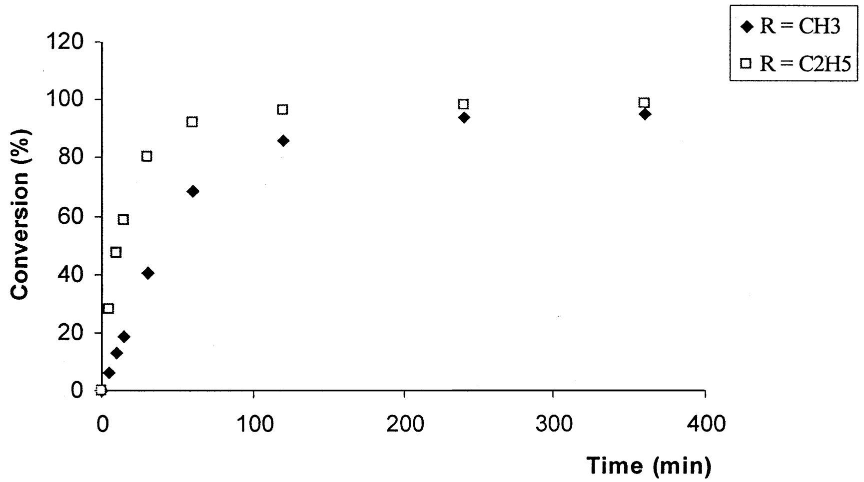


FIGURE 1 Evolution of conversion rate versus time during the radical addition of mercaptoethanol onto dialkylallylphosphonates. a: R = CH_3, b: R = C_2H_5.

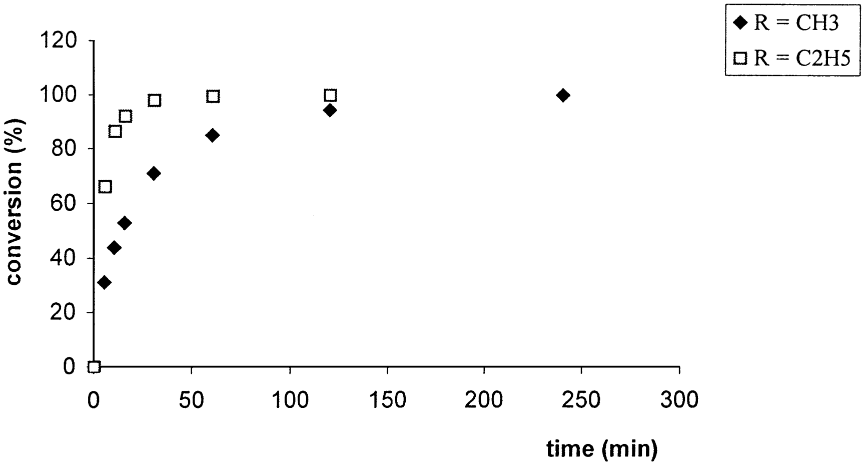
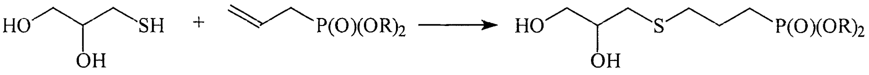


FIGURE 2 Evolution of conversion rate versus time during the UV addition of mercaptoethanol onto dialkylallylphosphonates. a: $R = CH_3$, b: $R = C_2H_5$.

to allylphosphonate (height h_1) and the phosphonated diol (height h_2). The conversion rates are the ratio $h_2/(h_1 + h_2)$.

We noticed that the photochemical addition was more efficient than the thermal addition: The maximum conversion rate is always higher than 95%. On the other hand, diethyl allylphosphonate is more reactive than dimethyl allylphosphonate.

Considering these good results, the addition of thioglycerol on allylphosphonates was performed.



2a : R = CH3

2b : R = C2H5

As we did with mercaptoethanol, we compared the thermal addition initiated by AIBN and the photochemical addition initiated by benzophenone. The results are summed up in the Figures 3 and 4.

The kinetic study leads to the same conclusions: The photochemical method is better than the thermal, and diethyl allylphosphonate is more reactive than dimethyl allylphosphonate. We can notice that the photochemical addition is quantitative with both reactives. Thioglycerol seams to be a better transfer agent than mercaptoethanol.

The ^{1}H NMR (CD_3COCD_3) agrees with the structures of **2a** and **2b**, especially concerning the characteristics of the two CH_2 groups in the

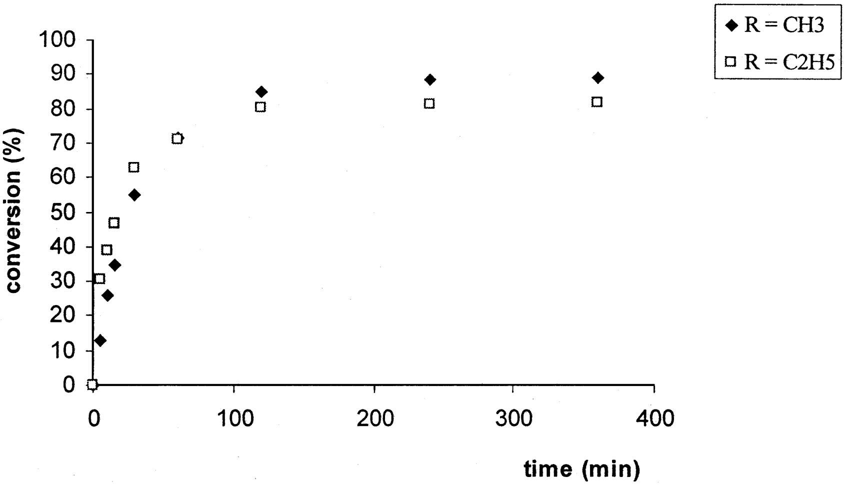


FIGURE 3 Evolution of conversion rate versus time during the radical addition of thioglycerol onto dialkylallylphosphonates. a: R = CH_3, b: R = C_2H_5.

α position of the sulfur atom (2.5–2.6 ppm) and the glycidyl group between 3.5 to 4.2 ppm. The ^{31}P NMR chemical shifts of **2a** and **2b** are respectively at 29.7 ppm and 34.7 ppm in good agreement with the expected value. We give as example the spectrum of **2b** (Figure 5).

The results of the hydroxyl group titrations by phthalylation are in good agreement with the molecular weight of the diol.

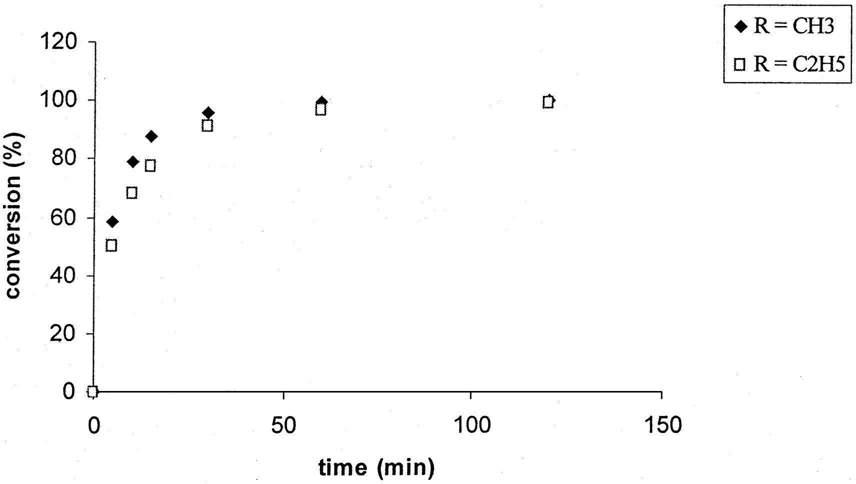


FIGURE 4 Evolution of conversion rate versus time during the UV addition of thioglycerol onto dialkylallylphosphonates. a: R = CH_3, b: R = C_2H_5.

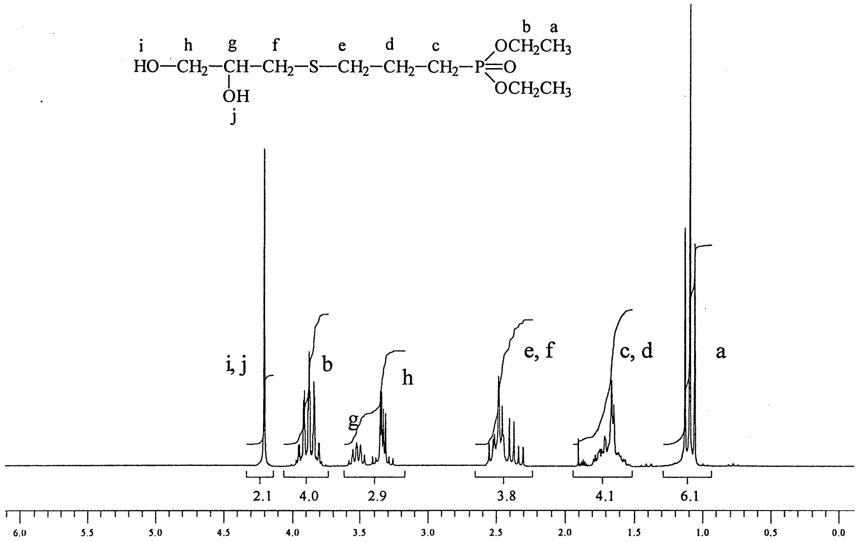
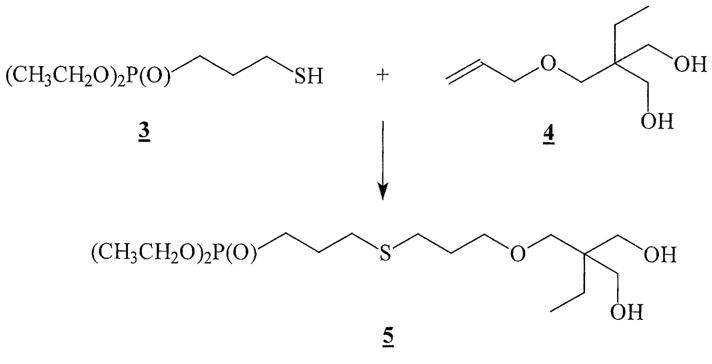


FIGURE 5 ^1H NMR (CD_3COCD_3) of the phosphonated diol **2b**.

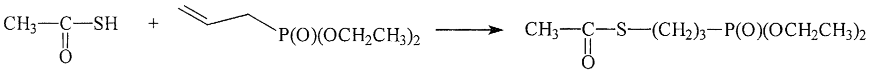
Addition of Thiol onto Unsaturated Diol: Method β

Another strategy consists on adding a phosphonated thiol onto an unsaturated diol. First, we synthesized the diethyl 3-sulfanylpropylphosphonate **3**, and then it was added onto a commercial diol: the trimethylolpropane allylether.



Preparation of the Phosphonated Thiol 3

Various synthetic routes have been described in the literature. Farrington[9] described the addition of triethyl phosphite on acetylsulfanylbromomethane followed by the hydrolysis of thioester by sodium ethanoate. Putvinsky[10] and Randall[11] performed the direct addition of thioacetic acid on diethyl alkenylphosphonates, followed by an hydrolysis by hydrochloric acid. According to our experience of transfer reactions, we have chosen the latter and the addition of thioacetic acid onto diethyl allylphosphonate. The reaction was performed under UV irradiation and photoinitiated by benzophenone. The monoadduct was easily identified and characterized as already described.[3]



3'

The hydrolysis of thioester **3′** was performed by an ethanolic solution of potassium cyanide as previously described,[3] leading to thiol **3**.

Synthesis of the Phosphonated Diol **5**

As we did with thioglycerol and dialkyl allylphosphonates **1a**, **1b**, we added the phosphonated thiol **3b** onto trimethylolpropane allylether. The reaction was performed under UV irradiation and photoinitiated by benzophenone. After purification by distillation, we isolated the compound **5**.

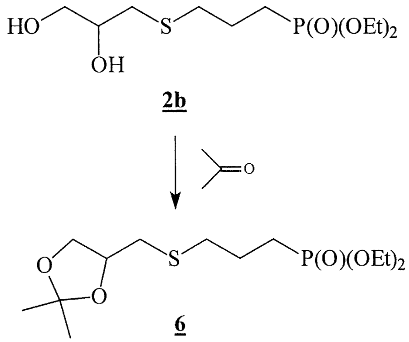
^{1}H NMR confirms the synthesis of phosphonated diols. Actually the protons of the ethoxy group resonate at 1.25 ppm (triplet, J = 7.5 Hz) and 4 ppm (quadruplet). The triplet at 2.5 ppm (characteristic of thioether)confirms the addition of the thiol onto the allyl group.

^{31}P NMR shows a singlet at 32.4 ppm (31.6 ppm for the corresponding thiol).

Hydrolysis of the Phosphonated Diol **2b**

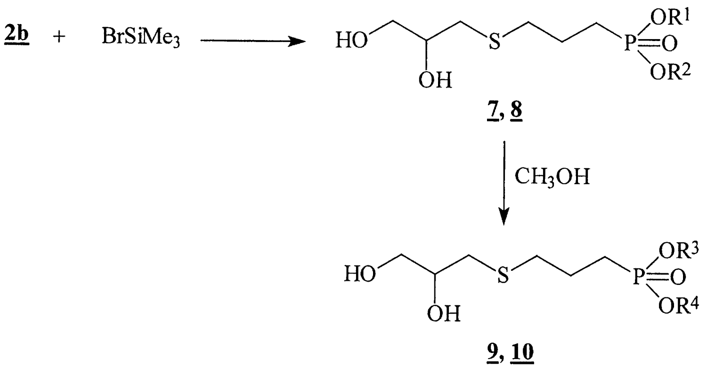
According to the adhesive application of this kind of products it may be interesting to have the mono or diacid form of the phosphonic group.

We have already described monodealkylation of dialkylphosphonates using sodium iodide.[12] But the reaction does not occur with the diol **2b**, neither with the corresponding protected compound **6**. This result is due to the fact that we have diethylphosphonates and not dimethylphosphonates.



The phosphonate **6** results from the acetalizing of **5** with either para-toluene sulfonic acid (PTSA) of BF_3, Et_2O. Rates are respectively 72% and 92%.

We obtained good results with silylated hydrolysis. Depending on the amount of bromotrimethylsilane (the reagent) the reaction led to the phosphonic (mono or di) acids after methanolysis of the corresponding silylated compounds.



7 : $R^1 = Et$; $R^2 = SiMe_3$

8 : $R^1 = R^2 = SiMe3$

9 : $R^3 = Et$; $R^4 = H$

10 : $R^3 = R^4 = H$

When the stoichiometry **2b**/$BrSiMe_3$ is 1/1 we obtain a mixture **2b**/**9** in proportion 50/50. If the stoichiometry is 1/2 the result is a mixture **2b**/**9**/**10** in proportion 1/2/97.

So the silylation is a good method to synthesize the phosphonic acids from the corresponding alkyldiethylphosphonates such as **2b**.

The structures of **7**, **8**, **9**, and **10** have been confirmed by ^{1}H and ^{31}P NMR analysis.

CONCLUSION

Two synthetic ways, depending on the position of the diol and of the phosphonate, lead to diols bearing phosphonate groups. The use of thiols added onto unsaturated compounds, gave very good results. We confirmed that mercaptoethanol and thioglycerol are good transfer agents.

Different kinetics studies show the greater yields obtained with diethyl alkylphosphonates compared to the dimethyl homologues.

In similar conditions we note that the UV additions gave the best results and thioglycerol is a little more reactive than mercaptoethanol.

We also succeeded in the transformation of a dialkyl phosphonate bearing a diol function into the corresponding phosphonic acid compound using the bromosilane method.

EXPERIMENTAL

IR spectra were recorded on a NICOLET 510P FTIR spectrometer. NMR spectra were recorded on BRUKER AC200 or AC250 spectrometers with TMS as reference for ^{1}H NMR and phosphonic acid as reference for ^{31}P NMR. Chemical shifts are reported in ppm: s = singlet, d = doublet, t = triplet, q = quadruplet, and m = multiplet. Addition under UV beams were performed with a Philips HPK 125 W 4A lamp (λ = 360 nm).

Dimethyl 6,7-Dihydroxy-4-thiaheptylphosphonate 2a

^{1}H NMR (CD_3COCD_3): 1.78–2.04 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2P$); 2.52–2.73 (m, 4H, $C\mathbf{H}_2SC\mathbf{H}_2$); 3.49–6.53 (m, 2H, $C\mathbf{H}_2OH$); 3.70 (sd, 6H, $OC\mathbf{H}_3$, $^3J_{PH}$ = 15Hz, $^3J_{HH}$ = 7Hz); 4.27 (s, 2H, O**H**). ^{31}P NMR CD_3COCD_3: 34.7 (s, 1P).

IR (KBr): main bands at 3200 (υ_{O-H}), 2954 (υ_{C-H}), 1448 (δ_{P-C}), 1239 ($\upsilon_{P=O}$), 1189 (δ_{P-O-C}), 1030 ($\upsilon_{(P)-O-C}$), 817 (υ_{P-O-C}) cm^{-1}.

Elementary analysis: $C_8H_{19}O_5PS$ (M = 258); Calc.%: C 37.2, H 7.4, O 31.0, P 12.0, S 12.4; Found%: C 37.63, H 7.88, O 32.03, P-, 11.66.

Diethyl 6,7-Dihydroxy-4-thiaheptylphosphonate 2b

^{1}H NMR (CD_3COCD_3): 1.27 (t, 6H, $OCH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7Hz); 1.82–1.88 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2P$); 2.56–2.70 (m, 4H, $C\mathbf{H}_2SC\mathbf{H}_2$); 3.49–3.51 (m, 2H, $C\mathbf{H}_2OH$); 3.98–4.10 (m, 4H, $OC\mathbf{H}_2CH_3$); 4.20 (s, 2H, $O\mathbf{H}$).

^{31}P NMR (CD_3COCD_3): 29.7 (s, 1P).

IR (KBr): main bands at 3200 (υ_{O-H}), 2956 (υ_{C-H}), 1446 (δ_{P-C}), 1239 ($\upsilon_{P=O}$), 1190 (δ_{P-O-C}), 1030 ($\upsilon_{(P)-O-C}$), 820 ($\upsilon_{P-O-(C)}$) cm^{-1}.

Elementary analysis: $C_{10}H_{23}O_5PS$ (M = 286); Calc.%: C 41.9, H 8.0, O 28.0, P 10.8, S 11.2; Found%: C 42.22, 8.84, O 28.18, P -, S 9.68.

Thioester 3′

^{1}H NMR ($CDCl_3$): 1.05 (t, 6H, $OCH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7Hz); 1.45–1.69 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2P$); 2.07 (s, 3H, $C\mathbf{H}_3CO$); 2.69 (t, 2H, $C\mathbf{H}_2S$, $^3J_{HH}$ = 7Hz); 3.75–3.90 (m, 4H, OCH_2CH_3).

^{31}P NMR $CDCl_3$): 31.1 (s, 1P).

IR (KBr): main bands at 2953 (υ_{C-H}), 1691 ($\upsilon_{C=O}$), 1448 (δ_{P-C}), 1240 ($\upsilon_{P=O}$), 1190 (δ_{P-O-C}), 1030 ($\upsilon_{(P)-O-C}$), 819 (υ_{P-O-C})) cm^{-1}.

Elementary analysis: $C_9H_{19}O_4PS$ (M = 254); Calc.%: C 42.5, H, 7.5, O 25.2, P 12.2, S 12.6; Found%: C 42.48, H 7.83, O 25.84, P -, S 12.34.

Diethyl 3-Acetylsulfanylpropylphosphonate 3

^{1}H NMR ($CDCl_3$): 1.08 (t, 6H, $OCH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7Hz); 1.53–1.74 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2P$); 2.37 (t, 2H, $C\mathbf{H}_2S$, $^3J_{HH}$ = 7Hz); 3.75–3.93 (m, 4H, $OC\mathbf{H}_2CH_3$).

^{31}P NMR ($CDCl_3$): 31.6 (s, 1P).

IR (KBr): main bands at 2951 (υ_{C-H}), 2527 (υ_{S-H}), 1446 (δ_{P-C}), 1238 ($\upsilon_{P=O}$), 1182 (δ_{P-O-C}), 1030 ($\upsilon_{(P)-O-C}$), 818 (υ_{P-O-C})) cm^{-1}.

Elementary analysis: $C_7H_{17}O_3PS$ (M = 212); Calc.%: C 39.6, H 8.0, O 22.6, P 14.6, S 15.1; Found%: C 39.35, H 8.41, O 23.67, P -, S 14.44.

Compound 5

^{1}H NMR ($CDCl_3$): 0.77 (t, 3H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.5Hz); 1.25 (t, 6H, $OC\mathbf{H}_2CH_3$, $^3J_{HH}$ = 7.5Hz); 1.26 (q, 2H, $C\mathbf{H}_2CH_3$, $^3J_{HH}$ = 7.5Hz); 1.69–1.84 (m, 6H, $C\mathbf{H}_2C\mathbf{H}_2P$, $CH_2C\mathbf{H}_2CH_2$); 2.51 (t, 4H, CH_2SCH_2, $^3J_{HH}$ = 7Hz); 3.33–3.64 (m, 10H, $C\mathbf{H}_2OC\mathbf{H}_2$, $C\mathbf{H}_2O\mathbf{H}$); 3.92–4.11 (m, 4H, $OC\mathbf{H}_2CH_3$).

^{31}P NMR ($CDCl_3$): 32.4 (s, 1P).

Hydrolysis of the Phosphonated Diol 5

A mixture of 10 g (35 mmol) of diol **5a** and 100 mg of BF_3, Et_2O and 100 ml of anhydrous acetone was refluxed during 5 h. Then after drying 10.49 g (32.2 mmol) of liquid **6** were collected.

Protected Diethylthioetherphosphonate 6

^{31}P NMR (CD_3COCD_3): 29.9 (s, 1P).

^{13}C NMR (CD_3COCD_3): 1 quaternary carbon at 109.2.

Phosphonic Acid 9

^{31}P NMR (CD_3OD): 30.7 (s, 1P).

^{1}H NMR (CD_3OD): 6.0 (s, 3H, 2OH alcohol and OH acid).

Phosphonic Acid 10

^{31}P NMR (CD_3OD): 28.5 (s, 1P).

^{1}H NMR (CD_3OD): no signal near 1.3 ppm nor near 4.1 ppm. But singulet at 6.0 ppm (4H, 2 alcohols and 2 acids).

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