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Studies on the Free Radical Carbon-Carbon Bond Formation in the Reaction of α-Phosphoryl Sulfides and Selenides with Alkenes [1]†.

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Abstract: α-Mono- and α, α-disubstituted α-phosphoryl radicals **9** were generated from the easy accessible α-phosphoryl sulfides **4**, **5** and α-phosphoryl selenides **11**, **12** and reacted with the electron rich alkenes **6** under the reductive (n-Bu_3SnH/AIBN) conditions to give the functionalized phosphonates **7** in 32÷68% yield. Two fragmentation processes of the phosphonate α-alkoxy alkyl radicals are also described.
Key words: α-phosphoryl sulfides, α-phosphoryl selenides, intermolecular radical reaction, radical fragmentation, phosphonates, tri-n-butyltin hydride, α,α'-azaisobutyronitrile

INTRODUCTION

Phosphonates are one of the most important classes of organophosphorus compounds that play a peculiar role in organic synthesis, medicine, agriculture and technology[2,3]. The following phosphonates are good examples to illustrate this thesis: Fosfomycin (antibacterial activity), Foscarnet sodium (antiviral activity), Clodronic acid (calcium regulator) and its analog Pamidronic acid (inhibitor of tumor induced hypercalcemia, radioactive imaging agent as technetium complex), Glyphosate (herbicide), Trichlorfon (insecticide, anthelmintic activity), Glyphosine (chemical ripener), cyclohexyloammonium salt of (±) 1,1-difluoro-3,4-dihydroxybutyl phosphonate (a substrate for NADH linked glycerol-3-phosphate dehydrogenase)[4]. More recently nucleobases modified phosphonates like (phosphonomethoxyethoxy)adenine (PMEA, a promising anti-HIV agent) or 3' and 5'-C-phosphonate analogues of nucleotides and sugars may be added to this list[5]. Although several methods for the synthesis of phosphonates have so far been elaborated, the application of the radical based approach, which is an established method for the inter- and intramolecular C-C bond formation, has not been recognized sufficiently. A limited number of papers related to this problem, describing addition of the radical type species to vinylphosphonates[6-8] or alkenes[8,9], utilized substrates for special purposes (for instance α,α-difluoro-compounds or the AZT analogues). Therefore, such approaches did not bear features of generality. Moreover, in some cases the products obtained were not isolated and identified[10,11]. Recently, we have reported a direct synthesis of α-phosphoryl radicals from α-halophosphonates using the classical n-Bu_3SnH/AIBN system for their generation[12]. These studies are currently continued because we plan to utilize these radicals for the construction of the early stage molecules in total synthesis of natural

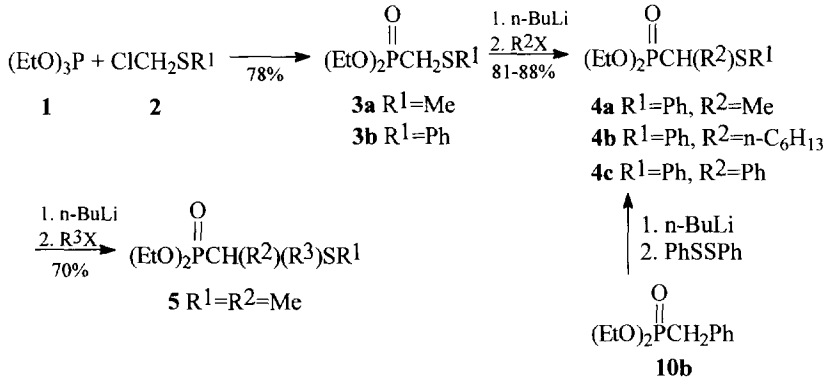
† Dedicated to Professor Richard Neidlein on the occasion of his 65th birthday.

products[13]. For this purpose we have elaborated a new synthesis of phosphonates harnessing the free radical reaction of the phosphorus containing C-centered radicals derived from α-phosphoryl sulfides and α-phosphoryl selenides with alkenes. The particular aim of our investigations was optimization of the reaction and a further recognition of its scope and limitation especially in regard to the structure of substrates, new initiators and reducing agents.

RESULTS AND DISCUSSION

Radical Reaction of α-Phosphoryl Sulfides with Alkenes.

α-Phosphoryl sulfides are excellent precursors of radicals **9** for their easy accessibility and possibility of functionalization in the α-phosphonate position. Thus, unsubstituted α-phosphoryl sulfides **3a** and **3b** were obtained in the Arbuzov reaction of the corresponding α-chlorosulfides **2** with triethylphosphite **1**[14]. The mono- and disubstituted α-phosphoryl sulfides **4** and **5** were synthesized either by alkylation of the corresponding α-litho-derivatives **3-Li** and **4-Li** or in the case of **4c** by sulfenylation of diethyl α-lithiobenzylphosphonate **10b-Li** with diphenyl disulfide[15] (Scheme 1).



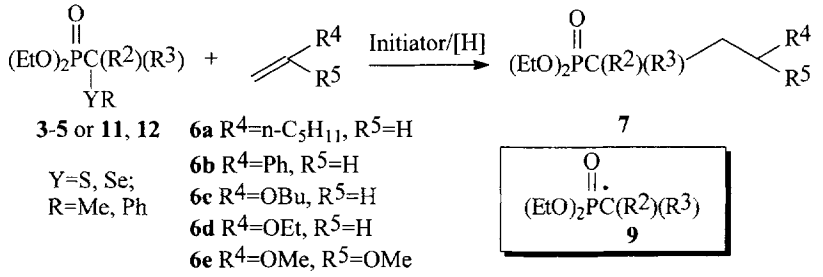
Scheme 1.

Considering the electrophilic (or less nucleophilic than methyl radical) character of the α-phosphorylalkyl radicals **9** and the reactivity requirements for radical reactions[16] (electrophilic radical + electron rich alkene), n-butoxyethene **6c** was chosen as a radical acceptor for comparison of the reactivity of the variously α-substituted radicals **9**. The latter generated under the reductive (Bu_3SnH/AIBN) free radical conditions from α-phosphoryl sulfides **3-5** are involved in the reaction depicted in Scheme 2. This process is synthetically useful when a propagation step, which affords the adduct radicals $(EtO_2)P(O)C(R^2)(R^3)CH_2\dot{C}(R^4)(R^5)$-**8** and subsequently the final reaction products **7**, effectively competes with the undesired reduction of the radical substrates **9** leading to the reduced phosphonates $(EtO_2)P(O)CH(R^2)(R^3)$-**10**.

TABLE 1: Optimization of stoichiometry for the reaction of **7a, 7c, 7i** with **6c**.

7a	1.5 eq.	3 eq.	5 eq.	10 eq.	**7c**	10 eq.	30 eq.	**7i**	10 eq.	30 eq.
Yield	22	36	51	58	Yield	50	44	Yield	35	27
P/R	0.27	0.63	1.04	3.73	P/R	1.92	1.29	P/R	0.54	0.51

Table 1 shows that 10 equivalents of **6c** per 1 equivalent of the starting phosphonate is the optimum amount from the economical point of view and this amount was used in our further comparative investigations. The increase of the quantity of **6** to 30 eq. caused formation of the side, phosphorus containing products (16-17%). Upon evaluation of the amount of olefin, we synthesized a series of the phosphonates **7** which are collected together with their P/R ratios in Table 2. The synthesis of the phosphonates **7** containing tertiary (**7c-7j**) and quarternary **7k** α-carbon atoms nicely illustrates an advantage of the free radical approach to the synthesis of phosphonates over the commonly used ionic Arbuzov reaction.

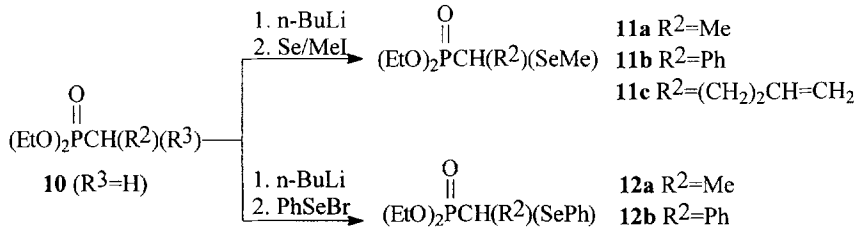


Scheme 2.

It is interesting to note that the α-phenyl substituent limited the reactivity of **9** (R^2=H, R^3=Ph) most probably due to the additional delocalization of the radical onto the aromatic ring. In this case, the chain reaction was not maintained and the reduction product was only isolated. The same reaction course was observed with **3a**. The α-alkyl substitution slightly decreased the yield of the desired products **7c**,**7i** and **7k** in comparison to the yield of the unsubstituted one **7a**. The use of acrylonitrile as the radical acceptor, although stands in contrast to the general selectivity requirements, gave the 19% yield of the product **7b**. The use of n-heptyne-1 brought the recovery of the phosphorus substrate what may suggest a competition between the phosphonyl and stannyl radicals towards this alkyne. The replacement of n-Bu_3SnH by tris(trimethylsilyl)silane brought in the case of **7a** only the 12% yield. The deaerating of the solvent used improved the yield of **7a** by 20% relative to the yield of the reaction carried out in nonaerated solvent under continuous flow of argon.

Radical Reaction of α-Phosphoryl Selenides with Alkenes.

α-Selenenylated phosphonates **11** and **12**, which were further used as the radical precursors for their low energetic C-Se bond, were synthesized from the corresponding α-phosphoryl carbanions either by selenenylation with phenylselenenyl bromide or by addition of elemental selenium followed by methylation with methyl iodide[17] (Scheme 3).



Scheme 3.

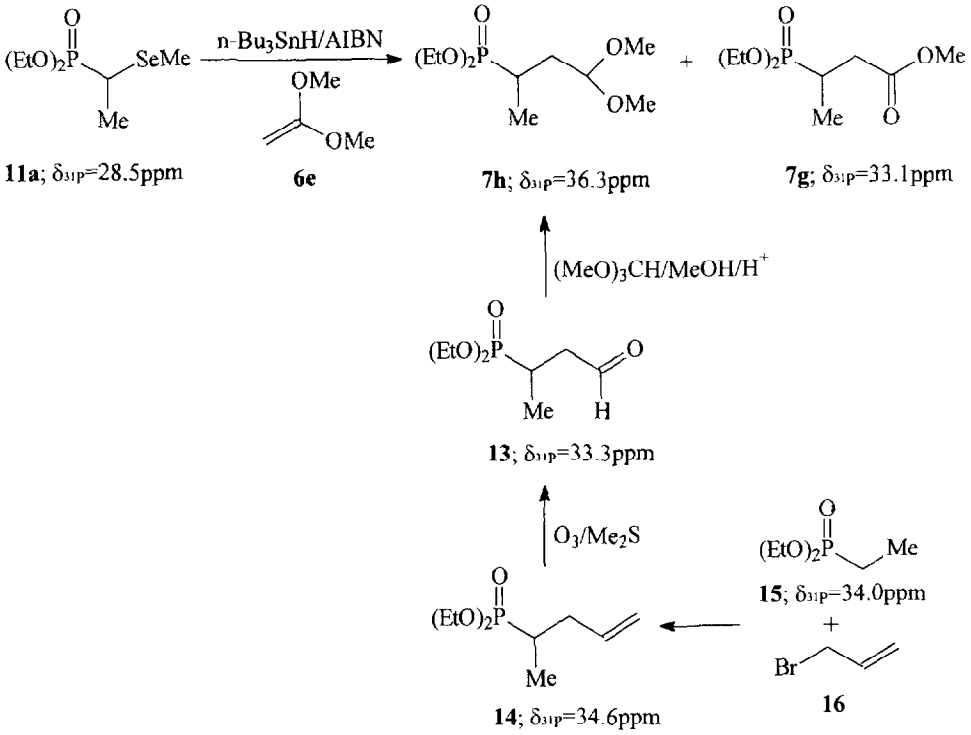
The phosphonates thus obtained were submitted to the radical reaction initiated by AIBN, Et_3B/O_2, and the UV light with various alkenes to give the phosphonates **7** according to the reaction equation depicted earlier in Scheme 2. Most of these radical reactions were carried out using the syringe pump technique in various solvents. The standard procedure with n-Bu_3SnH or Ph_3SnH/AIBN (Procedure **A**) or Et_3B/O_2[18] (Procedure **D**) was performed in toluene. The modification employing n-Bu_3SnCl or Me_3SnBr (from the syringe)/$NaBH_4$ (in the reaction mixture) was carried out in a mixture of solvents: toluene/i-PrOH when the initiator was AIBN (Procedure **B**) and t-BuOH//i-PrOH (or only EtOH) when the reaction was initiated photochemically (Procedure **C**). Other modifications comprised the use of $(Me_3Si)_3SiH$ instead of n-Bu_3SnH or Ph_3SnH and the use of Ph_3SnCl instead of n-Bu_3SnCl or Me_3SnBr. In some photochemical reactions $NaBH_4$ was replaced by $NaBH_3CN$. (see Table 2 and Figure 1)

The optimization of the amount of alkene was carried out to minimize the formation of phosphorus containing, side products. At the ratio **6/11,12** equalled 10/1, their quantity amounted to only 1-5% with exception of the styrene **6b** for which it increased to 50% (mostly polymeric substance) independently on the method used. In accord with the selectivity requirements[16] for the alkenes **6** containing β-alkoxy groups, the P/R ratio was bigger than unit for all procedures, while for the electron poor alkenes like acrylonitrile and methyl acrylate, the P/R and the reaction yield were very low (0.28-0.33 and 5÷19%, respectivly). The reaction of **11a** with ethyl ethynyl ether representing electron rich alkynes failed. The same bias prefering the electron rich alkenes is observed when one compares the reactivity of the same radical precursor, for instance **11a,** in Procedure **A2** with different olefins **6**. Both P/R and the reaction yield increase simultaneously. The poor result of the reaction of **11a** with cyclopentene shows that the effective radical coupling requires terminally unsubstituted alkenes. For the further optimization of the P/R ratio and the reaction yield, various modifications of the title reaction were examined. Generally, the results with AIBN and the UV light were better in the case of the use of the n-$Bu_3SnCl/NaBH_4$ system than of n-Bu_3SnH itself. Replacement of $NaBH_4$ for $NaBH_3CN$ produced worse results, for instance 68% of **7c** in Procedure **C1** and 13% in Procedure **C3** with P/R=0.14. The same effect brought a replacement of n-Bu_3SnH for Ph_3SnH or $Ph_3SnCl/NaBH_4$. Also, the use of other reducing agents did not improve the yield: Me_3SnBr - **7c** (yield 30%, P/R=0.51); $(Me_3Si)_3SiH$ - the substrate **11a** was recovered. Although the use of Et_3B/O_2 method (Procedure **D**) gave lower yields of the products **7**, than the use of the n-$Bu_3SnCl/NaBH_4$/UV, it complements this and other methods in regard with a possibility of the use of low boiling alkenes and performing reactions at broad range of temperature.

A very important role in the radical reaction plays the addition time of the n-Bu_3SnH (or n-Bu_3SnCl) to the reaction mixture. Usually, a toluene solution of the reagent was added through a syringe pump within 3÷4 hrs and thus guaranteed its low concentration. Shorter reaction times gave worse results (unreacted substrates). Similarly, a simultaneous addition of **11a**, n-Bu_3SnCl, $NaBH_4$, AIBN, and n-butoxyethene **6c** gave only 13% of **7c**. Changes of the quantities of AIBN in the range 5-30% did not affect the yield of the reaction; usually 20% of this initiator was used. For UV light, the reaction results were dependent on the amount of the radicals formed and connected with the reaction time (3 hrs was optimum). For short reaction times (<1h), α-phosporyl selenides were not entirely consumed; for longer ones (>4h) a lot of phosphorus side product were formed. During the optimization investigations, the most interesting results were obtained for the reaction of **11a** and **12a** with n-butoxyethene **6c** carried out without AIBN. In both cases, the 15% (P/R=0.26 and 0.35 respectively) yield of **7c** (Procedure **A2**) was obtained (26 and 20% of **11a** and **12a** left, respectively). Moreover, the same reactions performed without the presence of an olefin gave in both cases

the 31% yield of the reduced, starting phosphonates in the refluxing toluene solution. Without reflux no reaction occurred. Although the effectiveness of the reactions performed without the presence of AIBN cannot compete with that of the reactions initiated chemically or photochemically, they witness the thermal homolysis of the C-Se bond at ~110°C.

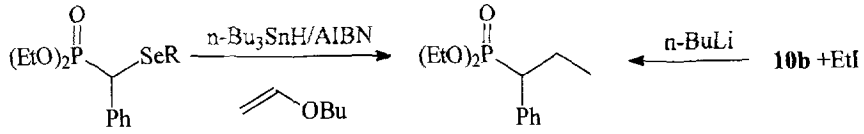
An influence of the concentration of the α-phosphoryl radical precursor on the reaction yield was also investigated. The results of the reaction of α-phosphoryl selenide **11a** with n-butoxyethene **6c** in toluene (Procedure **A**), which are summarized in the Table 3, show the optimum concentration of the radical precursor (c.a. 15ml/1mmol).



11a; δ_{31P}=28.5ppm **6e** **7h**; δ_{31P}=36.3ppm **7g**; δ_{31P}=33.1ppm

13; δ_{31P}=33.3ppm

14; δ_{31P}=34.6ppm **15**; δ_{31P}=34.0ppm **16**

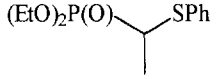
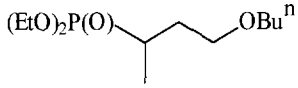
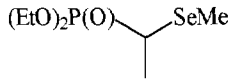
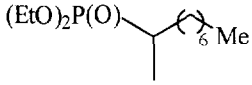
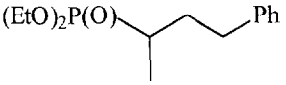
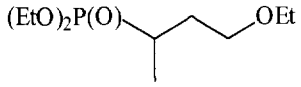
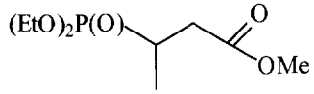
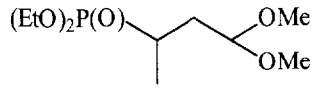
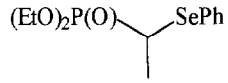
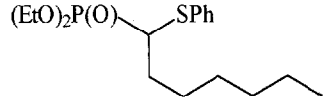
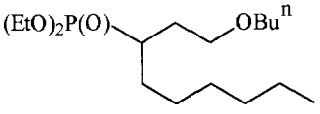


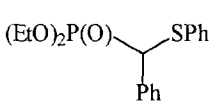
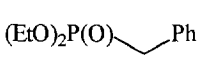
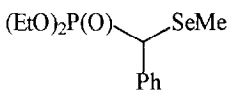
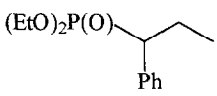
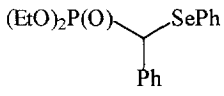
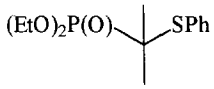
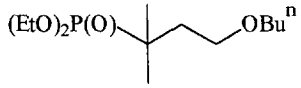
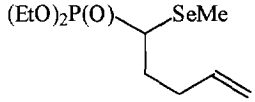
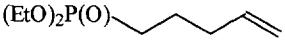
11b; δ_{31P}=23.9ppm **6c** **7j**; δ_{31P}=29.7ppm
12b; δ_{31P}=23.2ppm

R=Me, Ph

Scheme 4.

TABLE 2. Free radical reaction of α-phosphoryl sulfides and selenides with alkenes.

Substrate		Product		Procedure	P/R	Yield [%]
	3a		**10a**	**A1**	-	78
	3b		**7a**	**A1**	3.73	58
			7b	**A1**		19
	**4a**		**7c**	**A1** **A3**	1.92 1.29	50 44
	**11a**	**7c**		**C1**	4.0	68[a]
			**7d**	**A2** **B1**	0.56 1.15	36 51
			**7e**	**A2** **B1**	0.8 3.80	36 42
			**7f**	**C1**	1.30	52
			**7g**	**A2** **B1**	0.93 0.21	41 18
			**7h**	**A2** -		5 98[b]
	**12a**	**7c**		**A2** **B1**	2.34 0.66	44 33
	**4b**		**7i**	**A1** **A3**	0.54 0.51	35 27

	**4c**		**10b**	**A1**	-	78
	**11b**		**7j**	**A2** **B1**	1.12 0.97	48 45
	**12b**	**7j**		**A2**	0.70	32
	**5**		**7k**	**A1**	0.76	32
	**11c**		**10c**	**A4** **D3**	- -	92 96

a - for a reviev of all experimental procedures for synthesis of **7c** see Fig.1 *b* - yield for the acetalization of **13**

Fig.1. A review of experimental procedures for the free radical synthesis of **7c**.

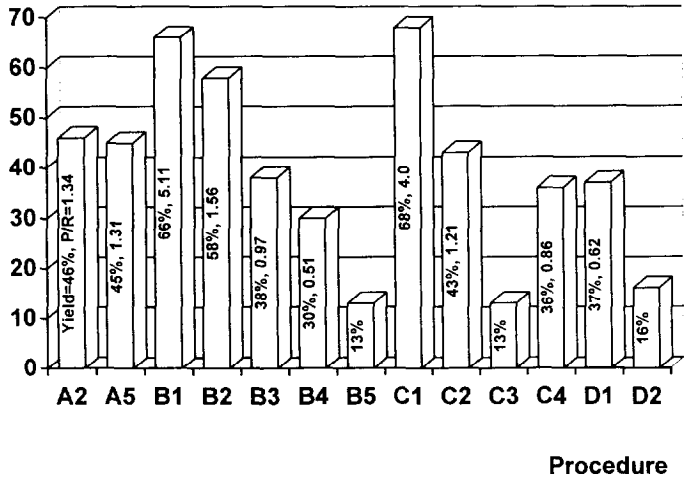
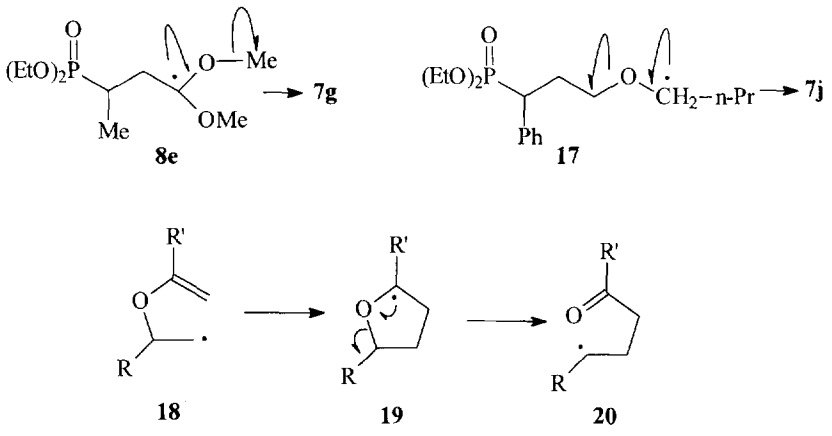


TABLE 3: Optimization of concentration in the reaction of **11a** with **6c** (Procedure **A2**)

Concentration	120ml/1mmol	30ml/1mmol	15ml/1mmol (*)	7.5ml/1mmol	3.25ml/1mmol
Yield	33%	43%	46%	46%	42%
P/R	0.97	1.22	1.34	1.40	1.41

Of special interest is the isolation of two unexpected products **7g** and **7j**, characteristic feature of which is the conversion of the dimethyl acetal function into the methyl ester in the former and the formal reduction of the alkoxy group in the latter one (Scheme 4). In the first case, the main product **7g** is accompanied by a small amount (5%) of the expected product **7h** resulting from a simple addition of **11a** to **6e**. However, when the reaction was stopped after the 50% consumption of the starting phosphonate **11a**, the product **7h** dominated in the reaction mixture and a ratio **7g**/**7h** equalled 5/13. In order to demonstrate that the conversion of **7h** to **7g** involves only radical species and does not occur with neutral molecule, we carried out the reaction between **7h** and stoichiometric amount of n-Bu_3SnH/ AIBN(cat.). However, no reaction occurred and the starting material was recovered. The acetal **7h** necessary for this reaction was synthesized by condensation of diethyl α-lithoethylphosphonate **15-Li** with allyl bromide **16** followed by ozonolysis of the resulting homoallyl phosphonate **14** and final acetalization of the aldehyde **13** formed with trimethyl orthoformate. In our opinion, the formation of the carbonyl compound **7g** can be formally derived from the corresponding strongly nucleophilic adduct radical **8e** (R^2=H, R^3=Me) which may loose **7g** and the methyl radical (Scheme 5).



Scheme 5.

In the second case, the formation of the product **7j** from the reaction of **11b** or **12b** with **6e** is undoubtedly connected with the presence of the α-phenyl substituent because the reactions of the α-alkyl substituted radical precursors **11a**, **12a** gave the "normal products" **7c** and **7f**. This suggests, in turn, the formation of the radical **17** which undergoes fragmentation to give n-butanal and nucleophilic γ-phosphonyl radical derived from **7j**. The latter can be reduced directly by n-Bu_3SnH to give **7j** or further stabilized by the 1,3 α-phosphonate hydrogen shift followed by the reduction with n-Bu_3SnH.

The two fragmentations described above occur thanks to different nucleophilicities and possibilities of stabilization of the involved radicals. Due to these differences, the carbonyl moiety is preserved in the phosphonate residue in the first case **7g** while in the second one (**7j**) is out of it. These two processes involve

acyclic α-alkoxyalkyl radicals **8e** and **17**. It is interesting to mention here two very recent reports on fragmentation of cyclic oxygen stabilized radicals affording the coresponding carbonyl compounds[19,20]. For instance, in the former paper[19] it was proved that rearrangement of 2-(vinyloxy)alkyl radical **18**, proceeds via cyclic α-tetrahydrfuranyl radical **19** which opens to give 4-ketobutyl radical **20**.

In conclusion, we described in this paper a new radical type approach to α, α,α and γ-functionalized phosphonates based on α-phosphoryl sulfides and selenides as the radical precursors. Generally, α-unsubstituted and α,α-alkyl substituted precursors reacted well with the electron rich alkenes in the reactions initiated by AIBN and UV light. In case of α-phenyl substituted α-phosphoryl sulfides (both MeS and PhS substituted), the reduction products of substrates were formed in good yields. High yield of the reduction product was also obtained upon attempted intramolecular cyclisation of **11c**. For α-methyl and α-phenylseleno substituted precursors one did not observe a big difference in reactivity, however, slightly better yields of the products were obtained in case of the MeSe precursors. Although due to the general selectivity requirements, the synthetic value of the radical approach described above is limited to a variety of α-phosphoryl sulfides/ selenides and electron rich alkenes, the yield of the products after optimization of the reaction conditions are sometimes almost twice higher than that in the analogous carboanionic approaches (for instance: **10a-Li** + **6c**→**7a** in the 33% yield, the radical approach - 68% yield). Moreover, the carboanionic C_α -C_β- phosphonate coupling is very difficult in case of the non activated alkenes (**7d**, 51% yield for the radical approach). On the other hand, in the described method, the synthesis of α-mono and α,α-disubstituted phosphonates can be also accomplished what is usually difficult in the Arbuzov C_α-P phosphonate coupling.

EXPERIMENTAL SECTION.

The ^{1}H-NMR (200 MHz) and ^{31}P-NMR (81MHz) spectra were recorded using a Bruker AC 200 spectrometer. The mass spectra were obtained using a Finnigan Mat 95 spectrometr. The models A and A-D of a syringe pump (Razel Scientific Instruments Inc.) were employed for a slow addition of tin reagents. All alkenes **6** with exception of **6e** were commercial reagents (Aldrich Chemical Co). Technically pure styrene (POCh Gliwice) **6b** was low pressure distilled before use. The alkene **6e** was prepared according to the reported procedure[21] and used as a toluene solution.

Preparation of the sulfur containing radical precursors 3, 4, 5.

Phosphonates **3a**, **3b** and **4c** were obtained according to the literature procedure[14,15].

Diethyl 1-Phenylthioethylphosphonate ***4a***

was obtained by alkylation of **3b**-Li (n-BuLi, THF, -78°C, Ar) with methyl iodide (-78°C÷25°C). Yield 81%; n_D^{20}=1.5262; ^{1}H-NMR ($CDCl_3$), δ=1.29 (dt, 6H, $^3J_{H-H}$=7.0Hz, $^4J_{H-P}$=0.3Hz, $POCH_2C\underline{H}_3$); 1.51 (dd, 3H, $^3J_{H-H}$=7.4Hz, $^2J_{H-P}$=16.1Hz, $PCHC\underline{H}_3$); 3.25 (dq, 1H, $^3J_{H-H}$=7.4Hz, $^2J_{H-P}$=16.2Hz, $PC\underline{H}$); 4.13 (m, 4H, $POC\underline{H}_2CH_3$); 7.20÷7.52 (m, 5H, $C_6\underline{H}_5$); ^{31}P-NMR ($CDCl_3$), δ=26.7ppm; Anal. Calcd/Found: C-52.54/52.58; H-6.98/6.94; P-11.29/11.28.

Diethyl 1-Phenylthio-n-heptylphosphonate ***4b***

was obtained by alkylation of **3b**-Li (n-BuLi, THF, -78°C, Ar) with n-hexyl iodide (-78°C÷25°C). Yield 88%; n_D^{20}=1.5102; ^{1}H-NMR ($CDCl_3$), δ=0.85 (t, 3H, $^3J_{H-H}$=6.3Hz, C$\underline{H}_3$); 1.28 (t, 6H, $^3J_{H-H}$=7.0Hz, POCH$_2$C$\underline{H}_3$); 1.18÷2.12 (m, 10H, (C$\underline{H}_2$)$_5$); 3.03,3.12 (2×ddd, 1H, $^3J_{H-H}$=4.0Hz, $^3J_{H-H}$=9.4Hz, $^2J_{H-P}$=16.1Hz, PC$\underline{H}$); 4.13 (m, 4H, POC$\underline{H}_2$CH$_3$); 7.20÷7.54 (m, 5H, C$_6\underline{H}_5$); ^{31}P-NMR ($CDCl_3$), δ=26.4ppm; Anal. Calcd/Found: C-59.28/59.44; H-8.49/8.45; P-8.99/9.03.

Diethyl 1-Methyl-1-phenylthioethylphosphonate ***5***

was obtained by alkylation of **4a**-Li (n-BuLi, THF, -78°C, Ar) with methyl iodide (-78°C÷25°C/2hr; 50° C/20min.). Yield 70%; n_D^{20}=1.5210; ^{1}H-NMR ($CDCl_3$), δ=1.30 (t, 6H, $^3J_{H-H}$=7.1Hz, POCH$_2$C$\underline{H}_3$); 1.39 (d, 6H, $^3J_{H-P}$=15.7Hz, PC(C$\underline{H}_3$)$_2$); 4.18 (dq, 4H, $^3J_{H-H}$=7.1Hz, $^3J_{H-P}$=8.1Hz, POC$\underline{H}_2$CH$_3$); 7.29÷7.70 (m, 5H, C$_6\underline{H}_5$); ^{31}P-NMR ($CDCl_3$), δ=29.3ppm; Anal. Calcd/Found: C-54.15/53.87; H-7.34/7.36; P-10.74/10.61.

Preparation of the selenium containing radical precursors 11, 12.

The precursors **11a** and **11b** were prepared according to the literature procedure[17] with a good agreement of physical and spectroscopic data. The precursor **11c** was obtained according to the same procedure[17] starting from the phosphonate **10c**.

Diethyl n-Pent-4-enylphosphonate ***10c***

To a solution of diethyl methylphosphonate (1.52g,10 mmol) in dry THF (350ml), a solution of n-BuLi in n-hexane (11mmol) was added dropwise at -78°C under argon atmosphere. Then a solution of Br(CH$_2$)$_2$CH=CH$_2$ (1.01ml,10mmol) in THF (10ml) was added and the resulting mixture was stirred for 3hrs., warmed up to room temperature, neutralized with aqueous solution of HCl and evaporated. The crude product was dissolved in $CHCl_3$, washed with water, dried over anhydrous magnesium sulfate, evaporated and distilled using the Kugelrohr apparatus. Yield 74%. ^{1}H-NMR ($CDCl_3$), δ=1.06 (t, 6H, $^3J_{H-H}$=7.1Hz, POCH$_2$C$\underline{H}_3$); 1.35÷1.55 (m, 4H, PCH$_2$C$\underline{H}_2$C$\underline{H}_2$); 1.88 (dt, 2H, $^3J_{H-H}$=6.8Hz, $^2J_{H-P}$=13.5Hz, PC$\underline{H}_2$); 3.75÷3.94 (m, 4H, POC$\underline{H}_2$CH$_3$); 4.72÷4.79 (m, 2H, CH=C$\underline{H}_2$); 5.5 (m, 1H, C$\underline{H}$=CH$_2$); ^{31}P-NMR ($CDCl_3$), δ=32.3ppm; MS-EI (15eV, m/z, %) 207 (45), 206 ($M^{+\cdot}$, 22), 165 (22), 152 (46), 125 (97), 97 (100), 41(67), 29 (41); Anal. Calcd/Found: C-52.43/51.82; H-9.22/9.26.

Diethyl 1-Methylselenenyl-n-pent-4-enyl-phosphonate ***11c***

Yield=94%; ^{1}H-NMR ($CDCl_3$), δ=1.30 (t, 6H, $^3J_{H-H}$=7.1Hz, POCH$_2$C$\underline{H}_3$); 1.58÷2.40 (m, 4H, PCH$_2$C$\underline{H}_2$C$\underline{H}_2$); 2.11 (s, 3H, SeC$\underline{H}_3$); 2.16 (m, 1H, PC$\underline{H}$); 4.0÷4.22 (m, 4H, POC$\underline{H}_2$CH$_3$); 4.95÷5.11 (m, 2H, CH=C$\underline{H}_2$); 5.74 (m, 1H, C$\underline{H}$=CH$_2$); ^{31}P-NMR ($CDCl_3$), δ=27,8ppm; MS-EI (70eV, m/z, %) 300 ($M^{+\cdot}$, 8), 298 ($M^{+\cdot}$, 4.5), 246 (18), 206 (11), 165 (43), 125 (27), 97 (11), 31 (100); Anal. Calcd/Found: C-40.13/39.84; H-7.36/7.37.

The precursors **12a** and **12b** were prepared according to the following procedure. To a stirred solution of the corresponding phosphonate **10** (10 mmol) in THF (300 ml), n-BuLi was added dropwise within 15 min under argon atmosphere. Then, the solution of PhSeBr [prepared by the bromine addition (129 μl, 5mmol) to the THF (20ml) solution of (PhSe)$_2$ (1.56g, 5.0 mmol), 10min, argon atmosphere] was added dropwise. The resulting mixture was warmed up to room temperature, neutralized with aqueous solution of HCl and evaporated. The crude product was dissolved in $CHCl_3$, washed with water, dried over anhydrous magnesium sulfate, evaporated and distilled through the Kugelrohr apparatus to give: **12a** - 68%; **12b** - 89%.

Diethyl 1-Phenylselenenylethylphosphonate ***12a***

n_D^{20}=1.5523; ^{1}H-NMR ($CDCl_3$), δ=1.31 (t, 6H, $^3J_{H-H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.58 (dd, 3H, $^3J_{H-H}$=7.5Hz, $^3J_{H-P}$=17.5Hz, $PCHC\underline{H}_3$); 3.21 (dq, 1H, $^3J_{H-H}$=7.5Hz, $^2J_{H-P}$=22.0Hz, $PC\underline{H}CH_3$); 4.15 (dq, 4H, $^3J_{H-H}$=7.0Hz, $^3J_{H-P}$=13.2Hz, $POC\underline{H}_2CH_3$); 7.20÷7.35, 7.55÷7.70 (m, 5H,$C_6\underline{H}_5$); ^{31}P-NMR ($CDCl_3$), δ=27.9ppm; Anal. Calcd/Found: C-44.86/45.03; H-5.91/5.92.

Diethyl 1-Phenylselenenylbenzylphosphonate ***12b***

n_D^{20}=1.5742; ^{1}H-NMR ($CDCl_3$), δ=1.11 (t, 3H, $^3J_{H-H}$=7.1Hz, $POCH_2CH_3$); 1.30 (t, 3H, $^3J_{H-H}$=7.1Hz, $POCH_2CH_3$), 3.75÷4.23 (m, 4H, $POCH_2CH_3$); 4.30 (dt, 1H, $^2J_{H-P}$=18.1Hz, $^4J_{H-H}$=2.6Hz, PCHPh); 7.11-7.51 (m, 10H, C_6H_5 and C_6H_5Se); ^{31}P-NMR ($CDCl_3$), δ=23.2ppm; Anal. Calcd/Found: C-53.26/53.33; H-5.48/5.51.

General procedures for synthesis of the phosphonates 7a-7k.

Procedure A1 and A2 : To a stirred solution of the α-phosphoryl sulfides **3**, **4**, **5** or selenides **11**, **12** (1mmol) and the corresponding alkene (10 mmol) in deaerated (water pump/argon) and refluxing toluene (30 ml - procedure **A1**; 15 ml - procedure **A2**), a solution of n-Bu_3SnH (1.4 mmol) and azobisisobutyronitrile (AIBN, 0.2 mmol, 35-40 mg) in toluene (14 ml - procedure **A1**; 7 ml - procedure **A2**) was added through syringe pump within 3 hours under argon atmosphere. After the additional 1h of reflux, the solution was cooled to room temperature and the solvent was evaporated to give the crude product which was purified through a combination of the following methods : 1) distillation using the Kugelrohr apparatus followed by the 8 hr stirring with a saturated solution of potassium fluoride (optionally), 2) flash chromatography over silica gel using a gradient of benzene or toluene/acetone as eluent.

Procedure A3 : As in procedure **A1**. 30 eq. of alkene was used.

Procedure A4 : As in procedure **A2**. For **11c**, reaction time amounted to 14 hr.

Procedure A5 : As in procedure **A2**. n-Bu_3SnH was replaced by Ph_3SnH.

Procedure B1 : To a stirred solution of the α-phosphoryl selenides **11** or **12** (1mmol) and the corresponding alkene (10 mmol) and $NaBH_4$ (75.7mg, 2mmol) in a refluxing mixture of dry toluene and dry ^{i}PrOH (15 ml, 14/1), a solution of n-Bu_3SnCl (0.2 mmol) and AIBN (2 mmol, 35-40 mg) in toluene (7 ml) was added through a syringe pump within 3 hours under argon atmosphere. After the additional 1h of reflux the solution was cooled to room temperature and the solvent was evaporated to give the crude product which was purified as in procedure **A**.

Procedure B2 : As in procedure **B1**. The α-Phosphoryl selenide **11a** was dissolved in a ^{t}BuOH solution.

Procedure B3 : As in procedure **B1**. The α-Phosphoryl selenide **11a** was dissolved in a THF solution.

Procedure B4 : As in procedure **B1**. n-Bu_3SnCl was replaced by Me_3SnBr.

Procedure B5 :As in procedure **B1**. Without a syringe pump. A solution of n-Bu_3SnCl (0.2 mmol) and AIBN (2 mmol, 35-40 mg) in toluene (7 ml) was added for 5min. and the resulting mixture was refluxed for 4 hours.

Procedure C1 : A solution of the α-phosphoryl selenides **11a** or **12a** (1.0 mmol), alkene **6c** or **6d** (10.0 mmol) and $NaBH_4$ (75.7mg, 2mmol) in dry ^{t}BuOH/^{i}PrOH (10ml, 20/1) was irradiated with a low-pressure mercury lamp at room temperature under the argon atmosphere for 3hrs, while the n-Bu_3SnCl (0.2 mmol) solution in dry toluene (2.4 ml) was added.

Procedure C2 : As in procedure **C1**. The α-Phosphoryl selenide **11a** and n-Bu_3SnCl was dissolved in dry EtOH.

Procedure C3 : As in procedure **C1**. $NaBH_3CN$ (2÷4 mmol) was used instead of $NaBH_4$.

Procedure C4 : As in procedure **C1**. n-Bu_3SnCl was replaced by Ph_3SnCl.

Procedure D1 : To a stirred solution of the α-phosphoryl selenides **11a** or **12a** (1mmol) and n-butoxyethene (10 mmol, 1.3ml) in dry toluene (15 ml), a solution of n-Bu_3SnH (1.4 mmol) and Et_3B (1.1 mmol, 1.1 ml, 1M solution in n-heksane) in toluene (7 ml) was added through the A-D model of the syringe pump. Simultaneously dry air (50ml) was injected by a second syringe pump within 3 hours under argon atmosphere at room temperature. The reaction was stirred for additional 30 min and worked up as in procedure **A**.

Procedure D2 : To a stirred solution of the α-phosphoryl selenide **11a** or **12a** (1mmol), n-butoxyethene (10 mmol, 1.3ml), n-Bu_3SnH (1.4 mmol) and Et_3B (1.1 mmol, 1.1 ml, 1M solution in heksane) in dry toluene (20 ml), dry air (50ml) was injected by a syringe pump within 3 hours under argon atmosphere at room temperature. The reaction was stirred for additional 30 min and worked up as in procedure **A**.

Procedure D3 :As in procedure **D1**. For **11c**, reaction time amounted to 14 hr.

Spectral data of the compounds **7a** and **7b** were identical with those reported by us earlier[12].

Diethyl 1-Methyl-3-n-butoxy-n-propylphosphonate 7c

n_D^{20}=1.4490; ^{1}H-NMR ($CDCl_3$), δ=0.91 (t, 3H, $^3J_{H-H}$=7.0Hz, $(CH_2)_3C\underline{H}_3$); 1.18 (dd, 3H, $^3J_{H-H}$=7.1Hz, $^2J_{H-P}$=19.3Hz, PCHC$\underline{H}_3$); 1.31 (t, 6H, $^3J_{H-H}$=7.0Hz, $POCH_2C\underline{H}_3$); 1.28÷1.66 (m, 6H, $(C\underline{H}_2)_2CH_3$ and PCHC$\underline{H}_2$); 1.95÷2.15 (m, 1H, PC$\underline{H}$); 3.30÷3.53 (m, 4H, $C\underline{H}_2OC\underline{H}_2$); 4.09 (dq, 4H, $^3J_{H-H}$=7.0Hz, $^3J_{H-P}$= 9.2Hz, $POC\underline{H}_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ=35.6ppm; MS-EI (70eV, m/z, %); no $M^{+\cdot}$, 209 (42), 166 (100); MS-HR-CI Found 267.1715, Calcd. for $C_{12}H_{27}O_4P$ 267.1725.

Diethyl 1-Methyl-n-octylphosphonate 7d

^{1}H-NMR ($CDCl_3$), δ=0.87 (t, 3H, $^3J_{H-H}$=6.9Hz, $(CH_2)_6C\underline{H}_3$); 1.15 (dd, 3H, $^3J_{H-H}$=7.1Hz, $^2J_{H-P}$=18.8Hz, PCHC$\underline{H}_3$); 1.25÷1.27 (m,10H, $CH(C\underline{H}_2)_5CH_3$); 1.31 (t, 6H, $^3J_{H-H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.53÷1.92 (m, 3H, PC$\underline{H}$ and PCHC$\underline{H}_2$); 4.09 (2×dq, 4H, $^3J_{H-H}$=7.1Hz, $^3J_{H-P}$= 8.4Hz, $POC\underline{H}_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ =35.2ppm; MS-EI (70eV, m/z, %); 264 ($M^{+\cdot}$, 3), 179 (28), 166 (100), 139 (22), 138 (35), 111 (20); MS-HR-CI Found 264.1840, Calcd. for $C_{13}H_{29}O_3P$ 264.1854

Diethyl 1-Methyl-3-phenyl-n-propylphosphonate 7e

^{1}H-NMR ($CDCl_3$), δ=1.22 (dd, 3H, $^3J_{H-H}$=7.1Hz, $^2J_{H-P}$=18.7Hz, PCHC$\underline{H}_3$); 1.30 (2×t, 6H, $^3J_{H-H}$=7.0Hz, $POCH_2C\underline{H}_3$);1.51÷2.18 (m, 4H, $C\underline{H}_2C\underline{H}_2Ph$); 2.54÷2.89 (m, 1H, PC$\underline{H}$); 3.96÷4.11 (m, 4H, $POC\underline{H}_2CH_3$); 7.13 ÷7.76 (m, 5H, $\underline{Ph}$) ; ^{31}P-NMR ($CDCl_3$), δ=35.2ppm; MS-EI (70eV, m/z, %); 270 ($M^{+\cdot}$, 0.7), 166 (92), 139 (27), 109 (14), 91 (100); Anal. Calcd/Found: C-62.22/61.98; H- 8.52 /8.53

Diethyl 1-Methyl-3-ethoxy-n-propylphosphonate 7f

^{1}H-NMR ($CDCl_3$), δ=1.17 (t, 3H, $^3J_{H-H}$=7.0Hz, $CH_2OCH_2C\underline{H}_3$); 1.17 (dd, 3H, $^3J_{H-H}$=7.1Hz, $^2J_{H-P}$=20.1Hz, PCHC$\underline{H}_3$); 1.30 (t, 6H, $^3J_{H-H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.51÷1.60 (m, 2H, PCHC$\underline{H}_2$); 1.94÷2.17 (m, 1H, PC$\underline{H}$); 3.38÷3.58 (m, 4H, $C\underline{H}_2OC\underline{H}_2$); 4.1 (2×dq, 4H, $^3J_{H-H}$=7.1Hz, $^3J_{H-P}$= 8.2Hz, $POC\underline{H}_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ =35.5ppm; MS-EI (70eV, m/z, %); no $M^{+\cdot}$ 209 (50), 166 (100), 139 (26), 138 (25), 111 (29); Anal. Calcd/Found: C-50.42/50.18; H- 9.66/9.65; P-13.02/13.0

Diethyl 1-Methyl-2-carbomethoxy-ethylphosphonate ***7g***

^{1}H-NMR ($CDCl_3$), δ=1.20 (dd, 3H, $^3J_{H-H}$=7.0Hz, $^2J_{H-P}$=17.9Hz, PCHC$\underline{H}_3$); 1.32 (t, 6H, $^3J_{H-H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.61÷1.82 (m, 2H, PCHC$\underline{H}_2$); 2.22÷2.40 (m, 1H, PC$\underline{H}$); 3.69 (s, 3H, OC$\underline{H}_3$); 4.07 (2×dq, 4H, $^3J_{H-H}$=7.1Hz, $^3J_{H-P}$= 9.5Hz, $POC\underline{H}_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ=33.14ppm; MS-EI (15eV, m/z, %) 238 (9), 223 (3), 207 (17), 179 (96), 165 (28), 151 (28), 138 (100), 111 (33), 69 (21); MS-HR-CI Found 264.1840, Calcd. for $C_{13}H_{29}O_3P$ 264.1854

Diethyl 1-Methyl-3,3-dimethoxy-n-propylphosphonate ***7h***

To a stirred solution of **14** (2.06g, 10mmol) in dry methanol (150ml), a stoichiometric amount of ozone was added at -78°C within 15 min. The resulting mixture was stirred for 1 hour, then warmed up to 0°C. Dimethyl sulfide (1.47ml, 20mmol) was added followed by stirring for 1 hour at room temperature. The solvent was evaporated and the crude product was purified by distillation through the Kugelrohr apparatus followed by flash chromatography over silica gel using a gradient of toluene/acetone as eluent to give 32% yield of aldehyde **13**. ^{1}H-NMR spectrum was identical with that reported in literature[22]. ^{31}P-NMR ($CDCl_3$), δ =33,3ppm (Lit.[22] δ=30.0 ppm). To a stirring solution of **13** (1.04g, 5mmol) in dry methanol (150ml), trimethyl orthoformate (0.6mml, 5.5mmol) and a catalytic amount of p-toluenesulfonic acid were added. The resulting mixture was refluxed for 2 hrs., filtered through a silica gel pad and evaporated to give analytically pure **7h**. Yield 98%. ^{1}H-NMR ($CDCl_3$), δ=1.19 (dd, 3H, $^3J_{H-H}$=7.1Hz, $^2J_{H-P}$=18.6Hz, PCHC$\underline{H}_3$); 1.31 (t, 6H, $^3J_{H-H}$=7.0Hz, $POCH_2C\underline{H}_3$); 1.51÷1.66 (m, 1H, PC$\underline{H}$); 1.90÷2.15 (m, 2H, PCHC$\underline{H}_2$); 3.71 (2×s, 6H, OC$\underline{H}_3$); 4.02 (2×dq, 4H, $^3J_{H-H}$=7.1Hz, $^3J_{H-P}$= 9.0Hz, $POC\underline{H}_2CH_3$) 4.53 (ddd, 1H, $^3J_{H-H}$=7.1Hz, $^4J_{H-P}$= 7.5Hz, $CHOC\underline{H}_3)_2$); ^{31}P-NMR ($CDCl_3$), δ=34.8ppm; MS-EI (15eV, m/z, %) no $M^{+\cdot}$, 239 (12), 233 (50), 194 (12), 152 (18), 138 (18), 85 (22), 75 (100); Anal. Calcd/Found: C-47.24/47.41; H- 9.12/9.12.

Diethyl 1-(n-Butoxyethyl)-n-heksylphosphonate ***7i***

n_D^{20}=1.5215; ^{1}H-NMR ($CDCl_3$), δ=0.87 (t, 3H, $^3J_{H-H}$=7.1Hz, $(CH_2)_5CH_3$); 0.91 (t, 3H, $^3J_{H-H}$=7.0Hz, $O(CH_2)_3CH_3$); 1.31 (t, 6H, $^3J_{H-H}$=7.1Hz, $POCH_2CH_3$); 1.22÷2.32 (m, 17H, $OCH_2(CH_2)_2CH_3$, $(CH_2)_5CH_3$, $PCHCH_2$); 3.39 (t, 2H, $^3J_{H-H}$=6.6Hz, $PCHCH_2CH_2O$); 3.49 (t, 2H, $^3J_{H-H}$=6.5Hz, $OCH_2(CH_2)_2CH_3$); 4.08 (dq, 4H, $^3J_{H-H}$=7.1Hz, $^3J_{H-P}$= 7.7Hz, $POCH_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ=35.3ppm; MS-EI (15eV, m/z, %); 336 ($M^{+\cdot}$, 6); 279 (100), 268 (26), 263 (33), 236 (88), 235 (33), 207 (25), 180 (63), 165 (77), 152 (47), 138 (27), 57 (28); MS-HR-CI Found 337.2510, Calcd. for $C_{17}H_{38}O_4P$ 337.2508.

Diethyl 1-phenyl-n-propylphosphonate ***7j***

^{1}H-NMR ($CDCl_3$), δ=0.79 (dt, 3H, $^3J_{H-H}$=7.1Hz, $^4J_{H-P}$=0.8Hz, $CHCH_2C\underline{H}_3$); 1.03 (t, 3H, $^3J_{H-H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.22 (t, 3H, $^3J_{H-H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.86÷2.13 (m, 2H, PCHC$\underline{H}_2$); 2.99 (ddd, 1H, $^3J_{H-H}$=4.2Hz, $^3J_{H-H}$=11.0Hz, $^2J_{H-P}$=22.3Hz, PC$\underline{H}$); 3.59÷4.62 (m, 4H, $POC\underline{H}_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ =29.7ppm; MS-EI (15eV, m/z, %) 256 ($M^{+\cdot}$, 56), 228 (100), 152 (27), 138 (82), 118 (77), 91 (46); Anal. Calcd/Found: C-60.93/60.88; H- 8.20/8.21; P-12.11/12.09.

This compound **7j** was also obtained by alkylation of **10b**-Li (n-BuLi, THF, -78°C, Ar) with ethyl iodide (-78°C÷25°C) in 85% yield.

Diethyl 1,1-dimethyl-3-n-butoxy-n-propylphosphonate ***7k***

^{1}H-NMR ($CDCl_3$), δ=0.91 (t, 3H, $^3J_{H-H}$=7.1Hz, $(CH_2)_3C\underline{H}_3$); 1.18 (d, 6H, $^3J_{H-P}$=17.0Hz, $PC(C\underline{H}_3)_2$); 1.31 (t, 6H, $^3J_{H-H}$=7.0Hz, $POCH_2C\underline{H}_3$); 1.45÷1.72 (m, 4H, $(C\underline{H}_2)_2CH_3$); 1.74÷1.92 (m, 2H, PCC$\underline{H}_2$); 3.39 (t, 2H, $^3J_{H-H}$=6.5Hz, $OC\underline{H}_2(CH_2)_2CH_3$); 3.55 (t, 2H, $^3J_{H-H}$=7.4Hz, $PCCH_2C\underline{H}_2O$); 4.08 (dq, 4H, $^3J_{H-H}$=$^3J_{H-P}$=7.1Hz,

$POC\underline{H}_2CH_3$); ^{31}P-NMR ($CDCl_3$), δ=36.6ppm; MS-EI (70eV, m/z, %) 280 ($M^{+\cdot}$, 0.4) 223 (11), 180 (100), 138 (46), 111 (17), 69 (17), 57 (23), 29 (20); Anal. Calcd/Found: C-55.69/55.44; H-10.42/10.39%.

Diethyl 1-methyl-n-but-3-enylphosphonate ***14***

was obtained by alkylation of diethyl ethylphosphonate (n-BuLi, THF, -78°C, Ar) with allyl bromide (-78 °C÷25°C) ^{1}H-NMR ($CDCl_3$), δ=1.13 (dd, 3H, $^3J_{H\text{-}H}$=7.1Hz, $^3J_{H\text{-}P}$=15.0Hz, $PCHC\underline{H}_3$);1.31 (t, 6H, $^3J_{H\text{-}H}$=7.1Hz, $POCH_2C\underline{H}_3$); 1.62÷2.16 (m, 2H, $PCHC\underline{H}_2$); 2.46÷2.64 (m, 1H, $PC\underline{H}$); 4.10 (2×dq, 4H, $^3J_{H\text{-}H}$=7.1Hz, $^3J_{H\text{-}P}$= 8.0Hz, $POC\underline{H}_2CH_3$); 5.01÷5.12 (m, 2H, $CH{=}C\underline{H}_2$); 5.65÷5.85 (m, 1H, $C\underline{H}{=}CH_2$); ^{31}P-NMR ($CDCl_3$), δ=32.3ppm; Anal. Calcd/Found: C-52.42/53.12; H-9.29/9.31.

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