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A Novel Synthesis of α,β-Unsaturated Phosphonates

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ABSTRACT

A stereoselective synthesis of α,β-unsaturated phosphonates based on the reaction of S-(β-oxoalkyl)-dithiophosphates and Se-(β-oxoalkyl)selenophosphates with sodium dialkyl phosphites is described.

INTRODUCTION

We recently reported a new strategy for the conversion of aldehydes and ketones into olefins and functionalized olefins [1]. The reaction sequence illustrating this strategy is shown in Scheme 1. The starting aldehydes and ketones are routinely converted into silyl enol ethers [2], which are subjected to thiophosphorylation to give the corresponding phosphates **3** [3]. The addition of a selected nucleophile to **3** results in the formation of the oxyanion **4**, which rearranges by the phosphoryl group migration, affording thiolate **5**. Cyclization of **5** provides episulfide **6**, which is finally transformed into the corresponding olefin **7**.

This paper describes further extention of our approach, which, by utilizing sodium dialkyl phosphites as the nucleophile, gives access to α,β-unsaturated phosphonates **7**. The phosphonates **7** have proved to be particularly valuable precursors in the synthesis of various organophosphorus and organic compounds [4]. Although a number of methods for introducing α,β-unsaturation into a carbon chain connected with a phosphoryl group are available, the majority of them afford exclusively the phosphonates **7** of E configuration [5]. The method we present here is highly stereoselective and provides preferentially the (Z)-phosphonates **7**.

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RESULTS AND DISCUSSION

The reaction of S-(β-oxoalkyl) *O,O*-dialkyl dithiophosphates **3** with sodium dialkyl phosphites proceeds smoothly in benzene solution at ambient temperature giving episulfides **6** in excellent yield (90–95% according to ^{31}P NMR data). Under treatment with triethyl phosphite or triphenylphosphine, the crude **6** is easily converted into the corresponding α,β-unsaturated phosphonates **7** (Scheme 2).

In light of the known analogy between thio- and selenophosphates, we have anticipated that similar reaction sequences could be performed with Se-(β-oxoalkyl) *O,O*-dialkyl selenophosphates **11** as the key intermediates. Indeed, the addition of sodium dialkyl phosphites to **11** leads to episelenides **12** which spontaneously and almost quantitatively decompose into the corresponding phosphonates **7** (Scheme 3). The synthesis of **11**, which is a new class of compounds, was performed by selenophosphorylation of silyl enol ethers **2** with the phosphonium salt **10**. All attempts to use oxophosphoraneselenyl chloride $(RO)_2P(O)SeCl$ for the preparation of **11** failed due to the low stability of the chloride even at −40°C.

The transformations shown in Schemes 2 and 3 can also be accomplished as a one-pot reaction.

The representative examples of the olefination are summarized in Table 1. Several points of in-

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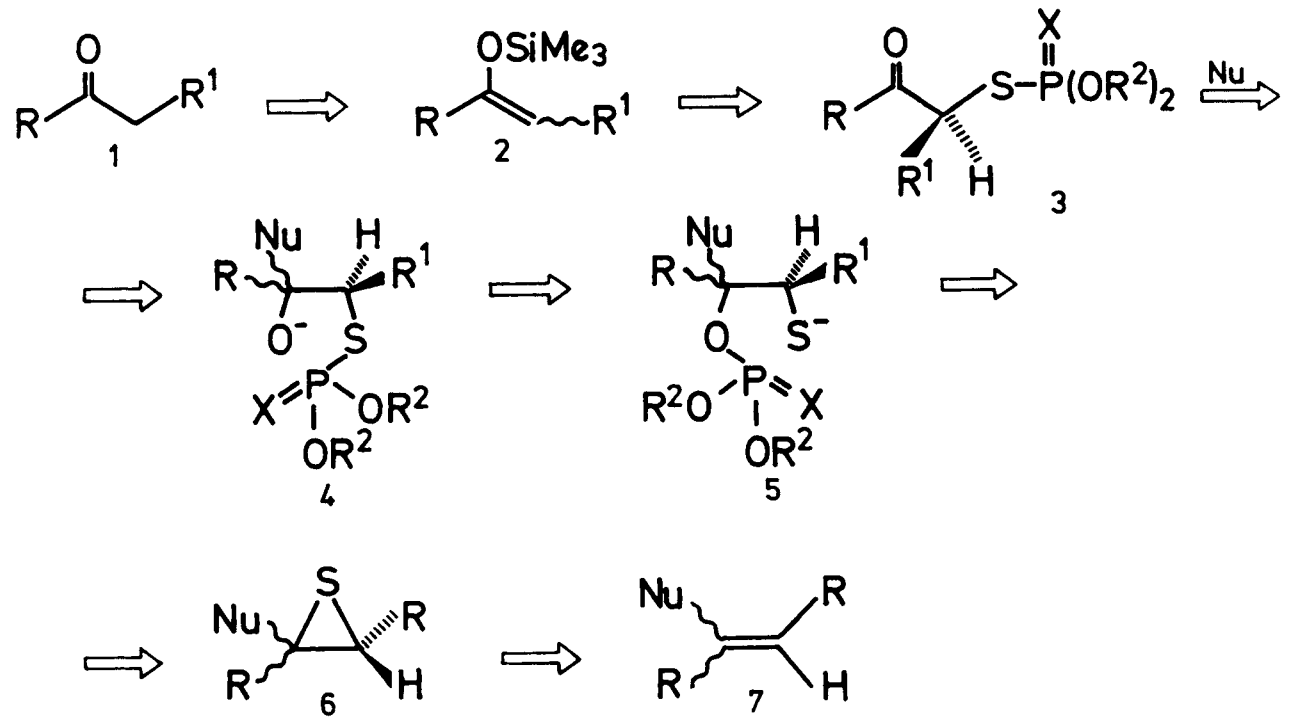
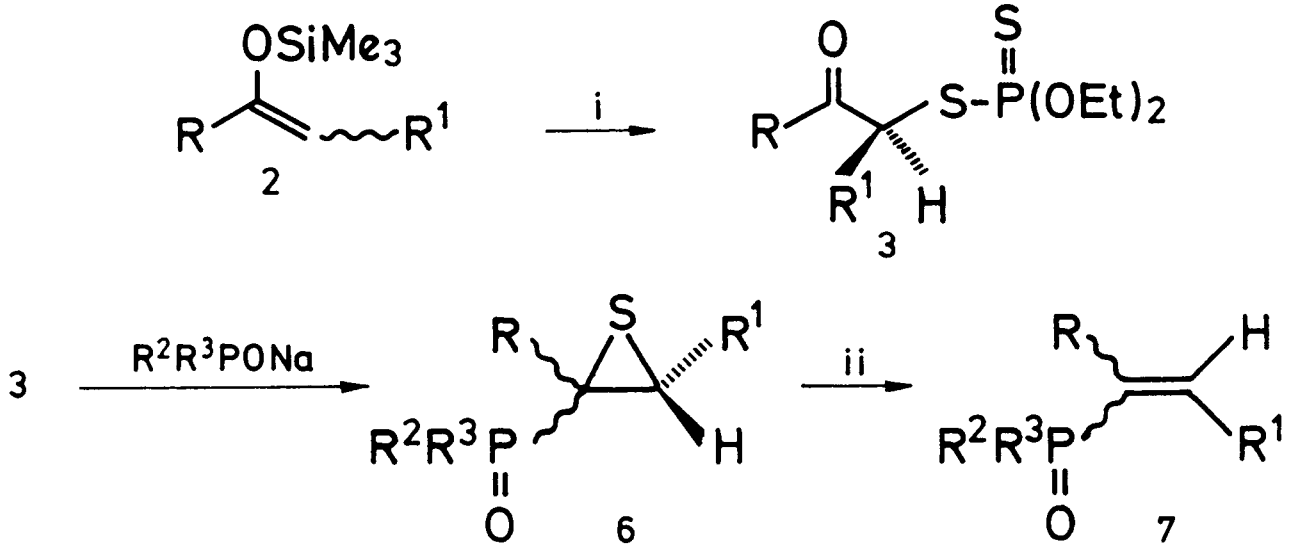


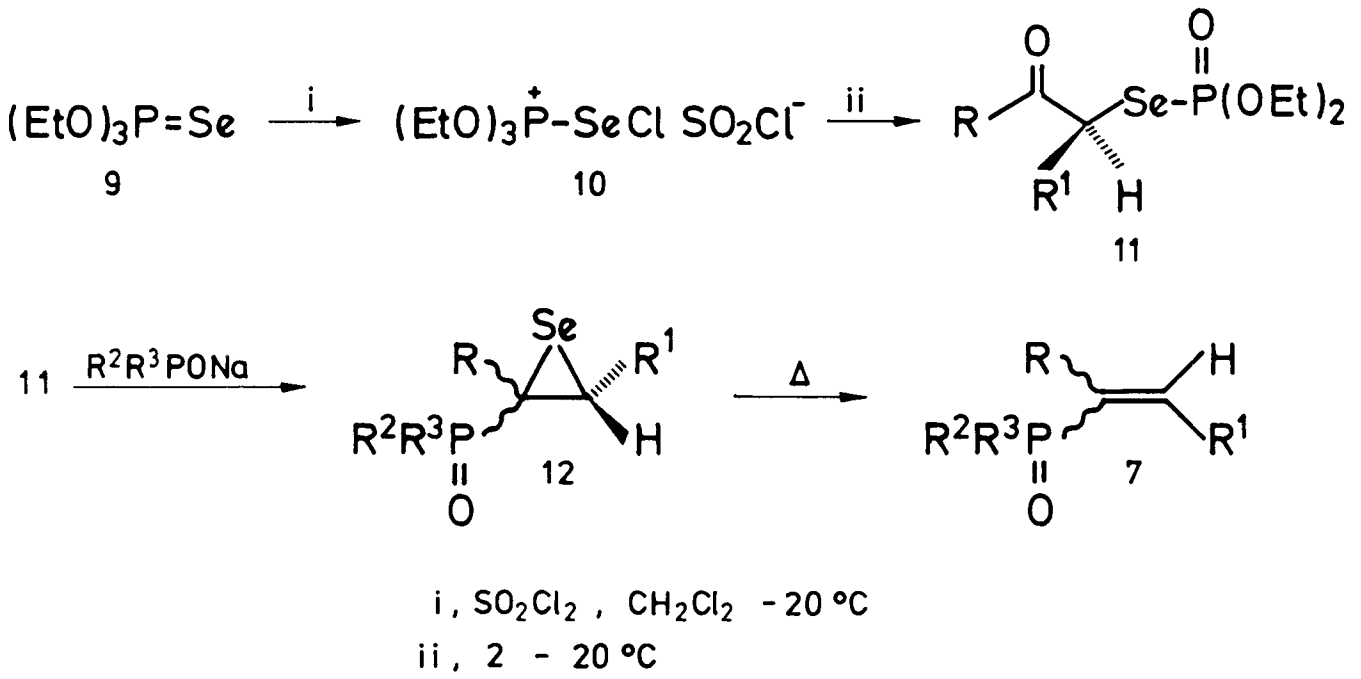
SCHEME 1



i, $(EtO)_2P(S)SBr$ 8, -78 °C, 2h

ii, $(EtO)_3P$ or Ph_3P

SCHEME 2



SCHEME 3

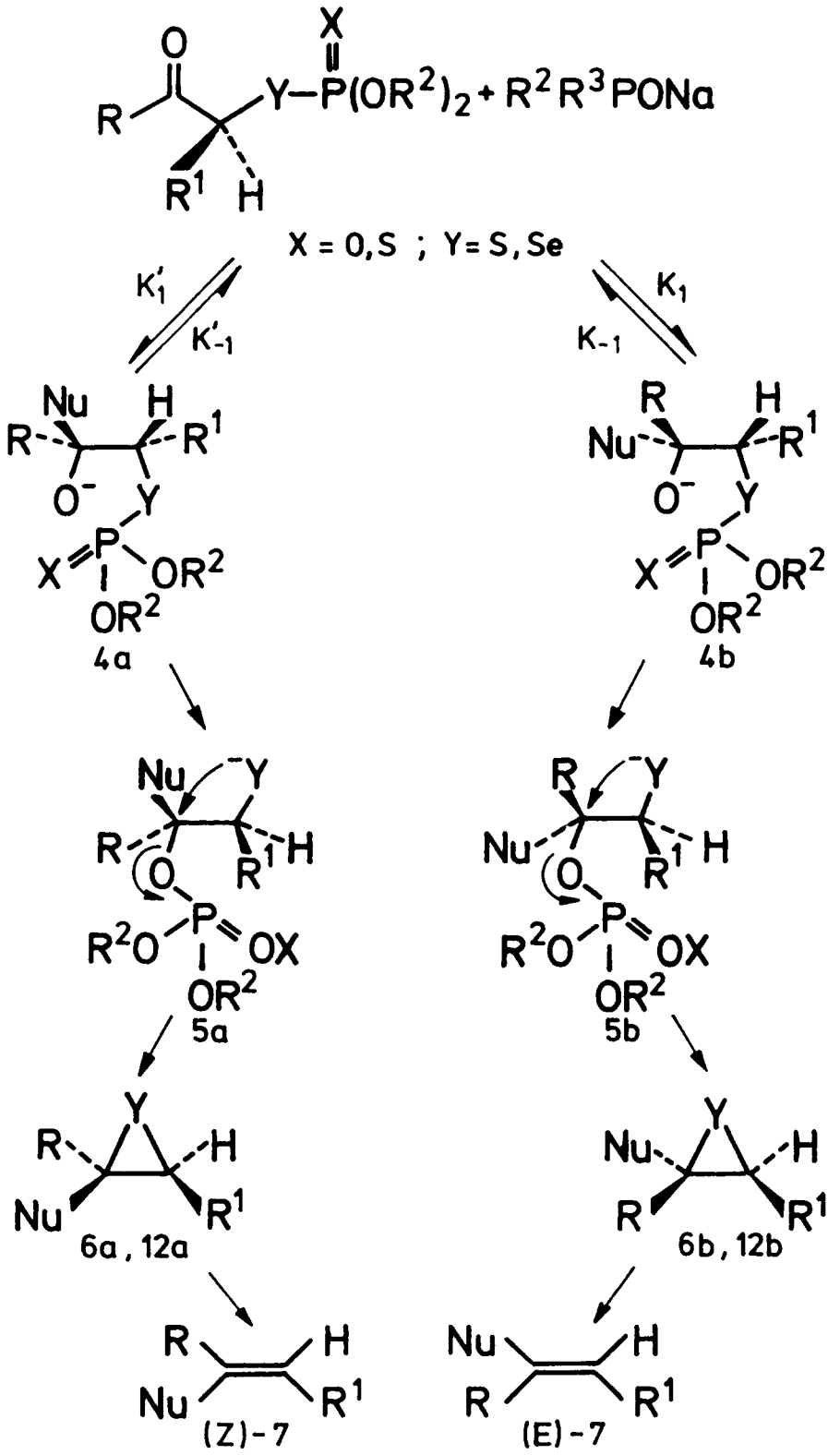
terest should be noted from the presented data: i) when R ≠ H, the olefination occurs with high stereoselectivity producing predominantly, or even exclusively, α,β-unsaturated (Z)-phosphonates **7** (entries 8–12); ii) the highest stereoselectivity is achieved when **11** is used as starting material (entries 8, 9); iii) in contrast to different reported methods, the general efficiency of the olefination does not depend on steric factors (entry 11).

The stereochemical course of the olefination is shown in Scheme 4. It is reasonable to assume that the addition of sodium dialkyl phosphites to thio- **3** or selenophosphates **11**, producing diastereoisomeric anions **4a** and **4b**, occurs reversibly. A number of precedents of similar reactions is known [7]. In such a situation one can conclude that the ratio of the final olefins is at least partially controlled by thermodynamic factors and cannot be predicted on the basis of the asymmetric induction models. It is obvious that the cyclization of the intermediates **5** must take place with inversion of configuration at the carbon adjacent to the phosphate moiety. On the other hand, the transformation of the episulfides **6** and the episelenides **12** into olefins **7** is known to proceed stereospecifically with retention of configuration [8].

TABLE 1

Entry	**3, 11**	**7**	*R*	*R'*	R^2R^3	*Z/E*	*Yield*[a] %
1	**3**	**a**	Me	H	EtO	—	71
2	**3**	**b**	Me	H	*i*-PrO	—	71
3	**3**	**c**	Me	H	*n*-PrO	—	68
4	**3**	**d**	Me	H	*t*-Bu,Ph	—	60
5	**11**	**e**	H	Me	EtO	50/50	63
6	**3**	**f**	H	Me	EtO	65/35	80
7	**3**	**g**	H	*n*-Bu	EtO	42/58	77
8	**3**	**h**	Et	Me	EtO	72/28	83
9	**11**	**i**	Et	Me	EtO	100/0	62
10	**11**	**j**	*n*-Pr	Et	EtO	79/21	58
11	**11**	**k**	*i*-Bu	*i*-Pr	EtO	100/0	85
12	**3**	**l**	Ph	Me	EtO	78/22	75

[a] Yield of pure isolated product based on **3** and **11**.



SCHEME 4

EXPERIMENTAL

All reactions were performed under argon. Nuclear magnetic resonance spectra were recorded on MSL 300 and AC 200 Bruker spectrometers. Chemical shifts are in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in Hertz. Silica gel (70–230 mesh) was used for the chromatographic separations.

Materials

Sodium dialkyl phosphites were freshly prepared prior to use by a standard method [9]. Silyl enol ethers **2** [2] and diethoxythioxaphosphoranesulfenyl bromide **8** [10] were prepared by the known literature procedures. S-(β-oxoalkyl) *O,O*-diethyl dithiophosphates **3** [3] and Se-(β-oxoalkyl) *O,O*-diethyl selenophosphate **11** [6] were obtained according to the Skowrońska et al. procedures.

General Procedure for the Preparation of α,β-Unsaturated Phosphonates **7** *from* **3**

A solution of freshly prepared sodium dialkyl phosphite (0.01 mol) in benzene (50 mL) was added to a stirred solution of an appropriate S-(β-oxoalkyl) *O,O*-diethyl dithiophosphate **3** (0.01 mol) in benzene (20 mL) at ambient temperature. Stirring was continued for an additional 1–24 h. The reaction mixture was washed several times with water and dried over $MgSO_4$. The solvent was evaporated in vacuo to give the crude episulfide **4**. The **4** was then refluxed for 12 h with triethyl phosphite (2 mL). Excess triethyl phosphite and triethylphosphorothionate were removed in vacuo to yield a mixture of α,β-unsaturated (Z)- and (E)-phosphonates **7**. The diastereoisomers were separated by column chromatography (benzene–ethyl acetate from 20:1 to 1:1) to give pure (Z)- and (E)-**7** as the colorless oils.

General Procedure for the Preparation of α,β-Unsaturated Phosphonates **7** *from* **11**

Freshly prepared sodium dialkyl phosphite (0.01 mol) in benzene (40 mL) was added to a solution of an appropriate Se-(β-oxoalkyl) *O,O*-dialkyl selenophosphate **11** (0.01 mol) in benzene (20 mL) at room temperature and the resulting solution was stirred for 1–12 h. The reaction mixture was then washed four times with water and dried ($MgSO_4$), and the solvent was evaporated to give the mixture of isomeric phosphonates **7**. The diastereoisomers were separated as indicated in the previous general procedure to give pure (Z)- and (E)-**7** as the colorless oils.

Yields of analytically pure compounds are listed in Table 1.

SPECTRAL DATA AND NOTES

7a: ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.82 (td, 6H, J_1 = 7, $\Delta\nu$ = 0.5, $C\underline{H}_3CH_2O$); 1.42 (ddd ≈ dt, 3H, J_{PH} = 19, $J_1 \cong J_2$ = 1.5, $CH_3\underline{C}H$=); 3.56 (m, 4H, $OC\underline{H}_2CH_3$); 5.24 (d quin, 1H, J_{PH} = 47, J_2 = 2, =CH trans to P); 5.46 (d sext, 1H, J_{PH} = 22 $J_2 \cong$ 1, =CH cis to P). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 18.87. IR (neat): ν(C=C) 1650 cm^{-1} ν(P=O) 1260. Anal. Calcd. for $C_7H_{15}O_3P$: C, 47.19; H, 8.43; P, 17.40. Found: C, 46.98; H, 8.31; P, 17.12.

7b: ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.02 (dd, 12H, J = 6.5, $\Delta\nu$ = 6.5, $(C\underline{H}_3)_2CHO$); 1.62 (dt ≅ ddd, 3H, J_{PH} = 14, $J_2 \cong J_3$ = 1, $CH_3\underline{C}H$=); 4.36 (d sept, 2H, J_{PH} = 8, J_2 = 6.5, $(CH_3)_2C\underline{H}O$); 5.40 (d quin, 1H, J_{PH} = 48, J_2 = 1.7, =CH trans to P); 5.67 (d sext, 1H, J_{PH} = 22, J_2 = 1.5, =CH cis to P). ^{31}P NMR (C_6H_6, 24.289 MHz): δ 15.94. IR (neat): ν(C=C) 1648 cm^{-1}, ν(P=O) 1260. Anal. Calcd. for $C_9H_{19}O_3P$: C, 52.42; H, 9.29; P, 15.02. Found: C, 52.39; H, 8.97; P, 14.85.

7c: ^1H NMR ($CDCl_3$, 80.018 MHz): δ 0.98 (t, 6H, J = 7, $C\underline{H}_3CH_2CH_2O$); 1.68 (sext, 4H, J = 7, $CH_3C\underline{H}_2CH_2O$); 1.93 (dt, 3H, J_{PH} = 14, J_2 = 1, $CH_3\underline{C}H$=); 3.98 (q, 4H, J = 7, $CH_3CH_2C\underline{H}_2O$); 5.75 (d quin, 1H, J_{PH} = 48, J_2 = 2, =CH trans to P); 5.96 (d sext, 1H, J_{PH} = 21, J_2 = 1, =CH cis to P). ^{31}P (neat, 24.289 MHz): δ 18.86. IR (neat): ν(C=C) 1650 cm^{-1}, ν(P=O) 1260 broad. Anal. Calcd. for $C_9H_{19}O_3P$: C, 52.42; H, 9.29; P, 15.02. Found: C, 51.94; H, 9.03; P, 14.76.

7d: ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.17 (d, 9H, J_{PH} = 14.7, *t*-Bu); 2.02 (dt, 3H, J_1 = 11, J_2 = 1.3, $CH_3\underline{C}H$=); 5.85 (d quin, 1H, J_{PH} = 37.2, J_2 = 1.7, $\underline{H}CH$= trans to P); 5.96 (d quin, 1H, J_{PH} = 17, J_2 = 1.0, $\underline{H}CH$= cis to P); 7.35 – 7.82 (m_c, $5H_{arom}$). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 40.0. IR (neat): ν(C=C) 1645 cm^{-1} (low) ν(P=O) 1270 (low). Anal. Calcd. for $C_{13}H_{19}OP$: C, 70.25; H, 8.62; P, 13.94. Found: C, 69.89; H, 8.25; P, 13.80.

7e-*cis*: ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.35 (td, 6H, J_1 = 7, J_2 = 1, $C\underline{H}_3CH_2O$); 2.08 (ddd, 3H, J = 7, J_2 = 4, J_3 = 1.5, $C\underline{H}_3CH$=); 4.18 (m, 4H, $OC\underline{H}_2CH_3$); 5.62 (ddq, 1H, J_{PH} = 20, J_{cis} = 13, J_3 = 1.5, PCH=); 6.59 (ddq, 1H, J_{PH} = 53, J_{cis} = 13, J_3 = 7, $CH_3C\underline{H}$=). ^{31}P NMR (C_6H_6, 24.289 MHz): δ 16.24. R_F (AcOEt/C_6H_6 1:1): 0.329. IR (neat): ν(C=C) 1655 cm^{-1}, ν(P=O) 1220 broad.

7e-*trans*: ^1H NMR ($CDCl_3$, 300.13 MHz): δ 1.37 (td, 6H, J_1 = 7, J_2 = 1, $C\underline{H}_3CH_2O$); 1.94 (ddd, 3H, J = 6.6, J_2 = 2.2, J_3 = 1.5, $C\underline{H}_3CH$=);

4.23 (m, 4H, $OC\underline{H}_2CH_3$); 5.70 (ddq, 1H, J_{PH} = 21.8, J_{trans} = 17, J_3 = 1.8, PCH=); 6.83 (ddq, 1H, J_{PH} = 21.8, J_{trans} = 17, J_3 = 6.8, $CH_3C\underline{H}$=). ^{31}P NMR (C_6H_6, 24.289 MHz): δ 17.23. R_F (AcOEt/C_6H_6 1:1): 0.192. IR (neat): ν(C=C) 1640 cm^{-1}, ν(P=O) 1245. Anal. Calcd. for $C_7H_{15}O_3P$: C, 47.19; H, 8.49; P, 17.38. Found: C, 47.41; H, 8.62; P, 17.07.

7f-*cis:* ^1H NMR ($CDCl_3$, 300.13 MHz): as **7e**-cis. ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 16.24. IR (neat): ν(C=C) 1650 cm^{-1}, ν(P=O) 1220 broad.

7f-*trans:* ^1H NMR ($CDCl_3$, 300.13 MHz): as **7e**-trans. ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 17.45. IR (neat): ν(C=C) 1640 cm^{-1}, ν(P=O) 1250. Anal. Calcd. for $C_7H_{15}O_3P$: C, 47.19; H, 8.49; P, 17.38. Found: C, 47.39; H, 8.71; P, 17.03.

7g-*cis:* ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.88 (t, 3H, J = 7, $C\underline{H}_3(CH_2)_3CH$=); 1.32 ($m_c$, 6H and 2H, $C\underline{H}_3CH_2O$ and $CH_3C\underline{H}_2(CH_2)_2$); 2.19 (m, 2H, =$CHCH_2C\underline{H}_2CH_2CH_3$); 2.50 (m, 2H, =$CHC\underline{H}_2$—); 4.10 (m, 4H, $OC\underline{H}_2CH_3$); 5.54 (ddt, 1H, J_{PH} = 19.6, J_{cis} = 13, J_3 = 1.5, PCH=); 6.44 (ddt, 1H, J_{PH} = 50.0, J_{cis} = 13, J_3 = 7.9, CH_3—$C\underline{H}$=). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 17.83.

7g-*trans:* ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.88 (t, 3H, J = 7, $C\underline{H}_3(CH_2)_3CH$=); 1.32 ($m_c$, 6H and 2H, $C\underline{H}_3CH_2O$ and $CH_3C\underline{H}_2(CH_2)_2$); 2.20 (m, 2H, =$CHCH_2C\underline{H}_2CH_2CH_3$); 2.50 (m, 2H, =CH—$C\underline{H}_2(CH_2)_2CH_3$); 4.10 (m, 4H, $OC\underline{H}_2CH_3$); 5.61 (ddt, 1H, J_{PH} = 21.5, J_{trans} = 17, J_3 = 1.5, PCH=); 6.75 (ddt, 1H, J_{PH} = 21.5, J_{trans} = 17, J_3 = 6.7, $CH_3C\underline{H}$=). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 19.45. IR (neat): ν(C=C) 1635–1655 cm^{-1}, ν(P=O) 1230 broad. Anal. Calcd. for $C_{10}H_{21}O_3P$: C, 54.45; H, 9.61; P, 14.06. Found: C, 53.98; H, 9.32; P, 14.43.

7h-(*Z*): ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.97 (t, 3H, J = 7.5, $C\underline{H}_3CH_2C$=); 1.22 (t, 6H, J = 7, $OCH_2C\underline{H}_3$); 1.93 (ddt, 3H, J_1 = 7.5, J_{PH} = 3.5, J_3 = 1.5, $C\underline{H}_3CH$=); 2.12 (dq quin, 2H, J_{PH} = 13.5, J_2 = 7.5, J_3 = 1.5, $CH_3C\underline{H}_2C$=); 3.95 (m, 4H, $OC\underline{H}_2CH_3$); 6.16 (dqt, 1H, J_{PH} = 50.7, J_2 = 7.5, J_3 = 1.5, $CH_3C\underline{H}$=). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 20.04.

7h-(*E*): ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.98 (t, 3H, J = 7.5, $C\underline{H}_3CH_2C$=); 1.23 (t, 6H, J = 7, $OCH_2C\underline{H}_3$); 1.93 (ddt, 3H, J_1 = 7.5, J_{PH} = 3.5, J_3 = 1, $CH_3C\underline{H}$=); 2.13 (m, 2H, $CH_3C\underline{H}_2C$); 4.0 (m, 4H, $OC\underline{H}_2CH_3$); 6.62 (dq, 1H, J_{PH} = 23, J_2 = 7, $CH_3C\underline{H}$=). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 20.06. IR (neat): ν(C=C) 1630 cm^{-1}, ν(P=O) 1250. Anal. Calcd. for $C_9H_{19}O_3P$: C, 52.42; H, 9.29; P, 15.02. Found: C, 52.40; H, 9.21; P, 14.94.

7i-(*Z*): ^1H NMR ($CDCl_3$, 300.13 MHz): as **7h**-(Z). ^{13}C NMR ($CDCl_3$, 50.288 MHz, DEPT): δ 14.15 (=$CHC\underline{H}_3$); 14.20 ($C\underline{H}_3CH_2C$=); 16.32 and 16.40 ($OCH_2C\underline{H}_3$); 28.19 (d, J = 12.3, $CH_3C\underline{H}_2C$=); 61.13 (d, J = 5.4, $OC\underline{H}_2CH_3$); 131.49 (d, J = 170, C-4°); 141.33 (d, J = 11.5, =$C\underline{H}CH_3$). ^{31}P NMR ($CDCl_3$, 121.49 MHz): as **7h**-(Z). IR (neat): as **7h**. Anal. Calcd. for $C_9H_{19}O_3P$: C, 52.42; H, 9.29; P, 15.02. Found: C, 52.39; H, 9.02; H, 14.69.

7j-(*Z*): ^1H NMR ($CDCl_3$/TMS, 300.13 MHz): δ 0.91 (t, 3H, J = 7.5, $C\underline{H}_3CH_2CH_2$); 1.02 (t, 3H, J = 7.5, $C\underline{H}_3CH_2CH$=); 1.32 (t, 6H, J = 7.5, $OCH_2C\underline{H}_3$); 1.50 (sext, 2H, J = 7.5, $CH_3C\underline{H}_2CH_2$); 2.17 (dtd, 2H, J_{PH} = 15, J_2 = 7.5, J_3 = 1, $CH_3CH_2C\underline{H}_2$); 2.46 (quin dt, 2H, J_1 = 7.5, J_{PH} = 3.5, $J_3 \cong$ 0.5, =$CHC\underline{H}_2CH_3$); 4.05 (m, 4H, $OC\underline{H}_2CH_3$); 6.13 (dtt, 1H, J_{PH} = 50.8, J_2 = 7.5, $J_3 \cong$ 1, =$C\underline{H}CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 50.288 MHz): δ 13.87 ($\underline{C}H_3CH_2CH_2$); 14.16 ($\underline{C}H_3CH_2CH$=); 16.68 and 16.78 ($OCH_2\underline{C}H_3$); 23.18 ($CH_3\underline{C}H_2CH_2$); 24.00 (d, J = 6.7, =$CH\underline{C}H_2CH_3$); 37.82 (d, J = 12.0, $CH_3CH_2\underline{C}H_2$); 61.45 and 61.55 ($O\underline{C}H_2CH_3$); 129.02 (d, J = 171.4, P$\underline{C}$=CH); 149.76 (d, J = 12.1, PC=$\underline{C}$H). ^{31}P NMR ($CDCl_3$, 80.961 MHz): δ 20.33. R_F (AcOEt/C_6H_6 1:1) = 0.438.

7j-(*E*): ^1H NMR ($CDCl_3$/TMS, 300.13 MHz): δ 0.92 (t, 3H, J = 7, $C\underline{H}_3CH_2CH_2$); 1.04 (t, 3H, J = 7, $C\underline{H}_3CH_2CH$=); 1.32 (t, 6H, J = 7, $OCH_2C\underline{H}_3$); 1.49 (sext, 2H, J = 7, $CH_3C\underline{H}_2CH_2$); 2.20 (m_c, 4H, $CH_3CH_2C\underline{H}_2C$= and =CH—$C\underline{H}_2CH_3$); 4.05 (m, 4H, $OC\underline{H}_2CH_3$); 6.55 (dt, 1H, J_{PH} = 23.9, J_2 = 7, =$C\underline{H}CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 50.288 MHz): δ 13.56 ($\underline{C}H_3CH_2CH_2$); 14.42 ($\underline{C}H_3CH_2CH$=); 16.61 and 16.74 ($\underline{C}H_3CH_2O$); 22.36 (d, J = 20.2, =$CH\underline{C}H_2CH_3$); 22.89 ($CH_3\underline{C}H_2CH_2$); 29.89 (d, J = 11.0, $CH_3CH_2\underline{C}H_2$); 62.08 and 62.19 ($O\underline{C}H_2CH_3$); 129.20 (d, J = 179.1, P$\underline{C}$=CH); 149.18 (d, J = 9.7, PC=$\underline{C}$H). ^{31}P NMR ($CDCl_3$, 80.961 MHz): δ 22.56. R_F (AcOEt/C_6H_6 1:1): 0.263. IR (neat): ν(C=C) 1665 cm^{-1} (major) 1655 (minor), ν(P=O) 1160–1200. Anal. Calcd. for $C_{11}H_{23}O_3P$: C, 56.39; H, 9.90; P, 13.22. Found: C, 56.30; H, 9.94; P, 12.91.

7k-(*Z*): ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.87 and 0.99 (d, 6H, J = 7, $(C\underline{H}_3)_2CHO$); 1.32 (t, 6H, J = 7, $OCH_2C\underline{H}_3$); 1.84 (sept, 1H, J = 7, $(CH_3)_2C\underline{H}CH_2$); 2.03 and 2.08 (d, 1H, CH_2C=); 3.25 (d quin, 1H, J_1 = 11, J_2 = 7, J_3 = 1, =$CHC\underline{H}(CH_3)_2$); 5.86 (dd, 1H, J_{PH} = 50.9, J_2 = 11, =$C\underline{H}CH(CH_3)_2$). ^{31}P NMR ($CDCl_3$, 24.289 MHz): δ 18.76. IR (neat): ν(C=C) 1630 cm^{-1}, ν(P=O) 1250. Anal. Calcd. for $C_{13}H_{27}O_3P$: C,

59.52; H, 10.38; P, 11.81. Found: C, 59.53; H, 10.34; P, 11.50.

7l-(*Z*): ^{1}H NMR ($CDCl_3$ 300.13 MHz): δ 1.30 (t, 6H, J = 7.5, $C\underline{H}_3CH_2O$); 2.31 (dd, 3H, J_1 = 7.5, J_{PH} = 3.8, $C\underline{H}_3CH$=); 4.11 (m, 4H, $CH_3C\underline{H}_2O$); 6.59 (dq, 1H, J_{PH} = 48.6, J_2 = 7.5, $CH_3C\underline{H}$=); 7.30–7.60 (m_c, $5H_{arom}$). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 16.90. IR (neat): ν(C=C) 1615 cm^{-1}, ν(P=O) 1250. R_F (AcOEt/C_6H_6 1:1) = 0.375.

7l-(*E*): ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 1.25 (t, 6H, J = 7.5, $C\underline{H}_3CH_2O$); 1.73 (dd, 3H, J_1 = 7.5, J_{PH} = 3.7, $C\underline{H}_3CH$=); 4.05 (quin d, 4H, J_1 = 7.5, Δν = 2.5, $CH_3C\underline{H}_2O$); 6.97 (dq, 1H, J_{PH} = 23, J_2 = 7.5, $CH_3C\underline{H}$=); 7.18–7.40 (m_c, $5H_{arom}$). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 18.21. IR (neat): ν(C=C) 1635, ν(P=O) 1250. R_F (AcOEt/C_6H_6 1:1): 0.279. Anal. Calcd. for $C_{13}H_{19}O_3P$: C, 61.41; H, 7.53; P, 12.18. Found: C, 61.20; H, 7.31; P, 12.44.

REFERENCES

[1] A. Skowrońska, P. Dybowski, *Phosphorus, Sulfur, Silicon and Relat. Elem., 49/50,* 1990, 275.

[2] P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron, 43,* 1987, 2075.

[3] P. Dybowski, A. Skowrońska, *Synthesis,* 1990, 609.

[4] H. Paulsen, W. Greve, H. Kuhne, *Chem. Ber., 106,* 1973, 2124; H. Paulsen, H. Kuhne, *Chem. Ber., 107,* 1974, 2635; H. Paulsen, H. Kuhne, *Chem. Ber., 108,* 1975, 1239; L. Evelyn, L. O. Hall, L. Lynn, *Carbohydr. Res., 27,* 1973, 21; Y. Kashmann, M. Sprecker, *Tetrahedron, 27,* 1971, 1331; C. Benezra, G. Ourisson, *Bull. Soc. Chim. Fr.,* 1967, 642; C. Benezra, *Tetrahedron Lett.,* 1961, 4471; W. Waszkuć, T. Janecki, R. Bodalski, *Synthesis,* 1984, 1025.

[5] B. Gallenkamp, W. Hoter, B-W. Krüger, F. Maurer, T. Pfister: *Houben-Weyl,* in M. Regitz (ed): *Methoden der Organischenchemie,* Vol. E2, Georg Thieme Verlag, Stuttgart, Germany, pp. 351–386 (1982); N. S. Wadsworth, *Organic Reactions,* Vol. 25, John Wiley, New York, Toronto, Sydney, pp. 98–101, (1977); E. Elia Aboujaoude, S. Lietje, N. Collognon, M. P. Teulade, Ph. Savignac, *Tetrahedron Lett., 26,* 1985, 4435 and references cited therein.

[6] P. Dybowski, A. Skowrońska, unpublished work.

[7] W. S. Abramov, *Dokl. Akad. Nauk SSSR, 73,* 1950, 487; W. S. Abramov, N. S. Nazmutdinova, *Zh. Obshch. Khim., 26,* 1955, 1141; R. C. Miller, J. S. Bradley, L. A. Hamilton, *J. Am. Chem. Soc., 78,* 1956, 5299; R. C. Miller, C. D. Miller, W. Rogers, L. A. Hamilton, *J. Am. Chem. Soc., 79,* 1957, 424; S. A. Buckler, *J. Am. Chem. Soc., 82,* 1960, 4215.

[8] N. P. Neureiter, F. G. Bordwell, *J. Am. Chem. Soc., 81,* 1959, 578; D. B. Denney, M. J. Boskin, *J. Am. Chem. Soc., 82,* 1960, 4736.

[9] K. Sasse: *Houben-Weyl,* in E. Müller (ed): *Methoden der Organischen Chemie.,* Vol. XII/2, Georg Thieme Verlag, Stuttgart, Germany, p. 38 (1964).

[10] J. Michalski, M. Potrzebowski, A. Łopusiński, *Angew. Chem. Int. Ed. Engl., 94,* 1982, 135; A. Łopusiński, M. Potrzebowski, *Phosphorus and Sulfur, 32,* 1987, 5564; A. Łopusiński, L. Łuczak, J. Michalski, *Phosphorus and Sulfur, 40,* 1988, 233.