Synthesis and Cyclization of Diethylphosphono-Substituted α-Allenic Alcohols to 4-(Diethylphosphono)-2,5-dihydrofurans

Valery K. Brel

Institute of Physiologically Active Compounds of Russian Academy of Science, Chernogolovka, Moscow region, 142432, Russia
Fax +7(95)9132113; E-mail: brel@ipac.ac.ru

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Abstract: Various types of diethylphosphono-substituted α-allenic alcohols have been readily prepared. Treatment of these compounds with a catalytic amount of silver nitrate under a nitrogen atmosphere provided the corresponding 4-(diethylphosphono)-2,5-dihydrofurans.

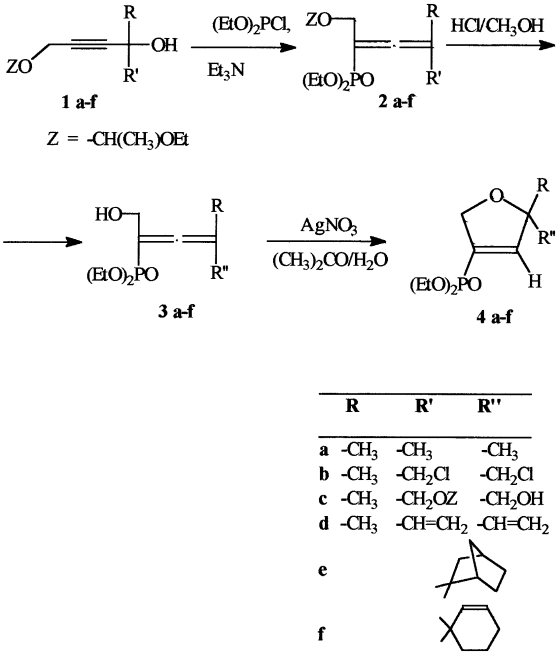
Key words: cyclization, furans, phosphaallenes, phosphorus heterocycles

Allenes have been widely used as building blocks in organic chemistry for construction of five and six-membered carbocyclic and heterocyclic ring systems.[1,2] An impressive number of heterocyclic systems has been prepared from allenic starting materials or via allenes as unstable intermediates.[3–6] Several examples of cyclization of allenic alcohols to derivatives 2,5-dihydrofurans have been described.[7–10]

Application of this approach to phosphorus-containing allenes had opened the way to 4-(diethylphosphono)-2,5-dihydrofurans. In order to investigate the scope and limitations of the new approach and synthetic strategies for synthesis of phosphorus-containing heterocyclic compounds,[1c,11,12] we have synthesized and studied interaction of several γ,γ-disubstituted allenylphosphonic acid derivatives having different substituents on the allenic system with silver nitrate. In this paper we would like to report our findings on the intramolecular cyclization of diethylphosphono-substituted α-allenic alcohols. Our aim was to synthesize 2,2-dialkyl-4-(diethylphosphono)-2,5-dihydrofurans **4a–f**, new phosphonic heterocycles.

The 4-(diethylphosphono)-2,5-dihydrofurans **4a–f** were synthesized by a simple and efficient three-step procedure: synthesis of the alkynols **1a–f**; synthesis of the phosphorylated allenes **2a–f**; and cyclization of α-allenic alcohols **3a–f** (Scheme).

The acetylenic alcohols **1a–f** were prepared in 60–70% yield by a standard procedure starting from propargyl alcohol.[11] Phosphorylated allenes **3a–f** were prepared directly from alcohols **1a–f** in 60–80% yields by Horner–Mark [2,3]-sigmatropic rearrangement of the unstable phosphites generated in situ by reaction with diethyl chlorophosphite in the presence of triethylamine in diethyl ether at –40 °C and then kept at 20 °C. Compounds **2a–f** were stable enough to be handled at ambient temperature. The hydroxyl group was deprotected by stirring the methanol solution of the reaction mixture in the presence of HCl, at room temperature. Analytically pure phosphorylated allenes **3a–f** were isolated as colorless or pale yellow oils by column chromatography on silica gel.



	R	R'	R''
a	-CH$_3$	-CH$_3$	-CH$_3$
b	-CH$_3$	-CH$_2$Cl	-CH$_2$Cl
c	-CH$_3$	-CH$_2$OZ	-CH$_2$OH
d	-CH$_3$	-CH=CH$_2$	-CH=CH$_2$
e			
f			

Scheme

Treatment of the γ,γ-disubstituted phosphorylated allenic alkohols **3a–f** with a catalytic amount of silver nitrate in water/acetone led to complete cyclization, affording the 2,5-dihydrofurans **4a–f** within 0.5 h at 50–52 °C. Reactions were monitored by TLC on SiO_2; detection was made using a $KMnO_4$ basic solution and ^1H NMR spectral data. All of the 4-(diethylphosphono)-2,5-dihydrofurans were isolated as stable colorless oils by column chromatography on silica gel.

Compounds **3a–f** and **4a–f** were identified by IR, ^1H, ^{13}C, ^{31}P and MS spectral data. For example, IR spectra of all compounds **3a–f** contained absorption bands of the phosphoryl group at 1249–1259 cm^{-1}, the allenic system double bonds at 1948–1960 cm^{-1} and hydroxy group 3610–3593 cm^{-1}. The ^1H NMR spectrum of the phosphorylated allenes **3a–f** contained signals of the protons for ethoxy groups and for groups connected to the allenic system. The chemical shift of phosphorus for **3a–f**, δ_P = 16–18.1 ppm was characteristic for derivatives of phosphory-

lated allenes.[7,11,12c] The extremely low-field position of the allenic central carbon atom resonance (near 200 ppm relative to tetramethylsilane) allows the immediate identification of the allenic moiety by ^{13}C NMR spectroscopy.[13] The chemical shift of signals of the allenic central carbon atom for phosphorylated allenes **3a–f** is δ = 204–207 ppm.

The mass spectra of the phosphorylated allenic alcohols **3a–f** contained signal of molecular ion M^+ (intensity about 10%).

The structure of **4a–f** was clearly assigned by NMR spectral data. NMR spectra of **4a–f** were in good agreement with NMR spectral data for phenyl[2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl]iodonium salts.[1c] For instance, the ^1H NMR spectrum of the 4-(diethylphosphono)-2-methyl-2-vinyl-2,5-dihydrofuran (**4d**) contained a set of resonances characteristic of the CH_3, $CH{=}CH_2$, $(RO)_2P(O)C{=}CH$ and $(RO)_2P(O)CCH_2O$ groups. The chemical shift of phosphorus, δ_p = 12.10–13.12 ppm, is characteristic for compounds with a 4-coordinate phosphorus atom linked with an sp^2-hybridized carbon atom.

In summary, we have described an easy and convenient synthesis of the 2,2-dialkyl-4-(diethylphosphono)-2,5-dihydrofurans **4a–f.** Compounds **4a–f** and allenes **3a–f** have been highlighted as interesting building blocks which, hopefully, can be used in the synthesis of molecules of biological and pharmaceutical interest. Future studies on this potentially important synthetic methodology are currently in progress. Applications of phosphorylated allenes to the synthesis of interesting phosphonic heterocycles will be reported in due course.

NMR spectra were recorded on a Bruker CXP-200 spectrometer at 200 MHz (^1H NMR), 81.01 MHz (^{31}P NMR) and 50.3 MHz (^{13}C NMR). Chemical shifts for ^1H NMR and ^{13}C NMR are reported in ppm relative to TMS as internal standard. ^{31}P downfield shifts (δ) are expressed with a positive sign, relative to external 85% H_3PO_4 in H_2O. LRMS were measured on a Finnigan INCOS-50 system (ionization voltage 70 eV). Significant fragments are reported as follows: *m/z* [intensity relative to base (100)]. Infrared spectra were recorded on a Bruker IFS-113 spectrometer. Samples were typically prepared as films or in CCl_4 solution. Band frequencies (ν) are reported in (cm^{-1}).

Column chromatography on silica gel was performed with Fluka Silica gel 60 (0.035–0.070 mm) Preparative TLC was performed on Fluka Silica gel/TLC-cards (20 × 20 × 0.2 cm). All reagents were of commercial quality or were purified before use. Organic solvents were purified and dried by standard procedures. The details of the preparation of **1** have been described in the earlier articles.[11] Propargyl alcohol was protected by reaction with ethyl vinyl ether to afford the ether in nearly quantitative yield by standard procedures.[14]

Phosphorylated Allenes 3a–f

2-(Diethylphosphono)-4-methylpenta-2,3-dien-1-ol (3a); Typical Procedure

To a solution of EtMgBr (2.66 g, 0.02 mol) in anhyd Et_2O (50 mL) was added dropwise over 30 min at –5 °C, *O*-protected propargyl alcohol (2.56 g, 0.02 mol). The mixture was then stirred at r.t. for 1 h and at 34 °C for 2 h. After the evolution of ethane ceased, the mixture was cooled in an ice bath, then acetone (1.22 g, 0.021 mol) in Et_2O (5 mL) was added dropwise over 15 min. The mixture was then stirred and heated to reflux for additional 1h. The mixture was cooled and sat. aq NH_4Cl was added carefully to dissolve the solid components. The two layers were separated and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic fractions were dried (K_2CO_3) and solvent was evaporated in vacuo. The crude acetylene **1a** (2.53 g, 0.013 mol) was dissolved in Et_2O (50 mL) under N_2, Et_3N (1.52 g, 0.015 mol) was added and the mixture was cooled to –50 °C. The solution of diethyl chlorophosphite (2.03 g, 0.013 mol) in Et_2O (10 mL) was added dropwise over 20 min. The mixture was then stirred at –50 °C over 1h and at r.t. for 5 h. The solid was removed by filtration and the solvent was evaporated in vacuo. The crude phosphorylated allene **2a** (2.39 g, 0.0078 mol) was dissolved in CH_3OH (20 mL) and 35% of HCl (1–2 drops) was added. The solution was stirred at r.t. over 30 min, and the solvent was evaporated in vacuo. The crude product was chromatographed on a silica gel column with Et_2O/acetone (1:1) as eluent to give **3a** (1.83 g, 60%).

^1H NMR ($CDCl_3$): δ = 1.34 (6H, dt, *J* = 0.6, 7.0 Hz, $2CH_3$), 1.8 (6H, d, *J* = 7.6 Hz, $2CH_3$), 3.8 (1H, br s, OH), 4.10 (4H, dq, *J* = 7.0, 6.8 Hz, $2CH_2OP$), 4.24 (2H, d, *J* = 14.0 Hz, CH_2OH).

^{13}C NMR[$CD_3C(O)CD_3$]: δ = 16.57 (d, J_{c-p} = 6.4 Hz), 19.61 (d, J_{c-p} = 7.2 Hz), 60.63 (d, J_{c-p} = 12.0 Hz), 62.62 (d, J_{c-p} = 6.4 Hz), 94.16 (d, J_{c-p} = 184.7 Hz), 99.07 (d, J_{c-p} = 15.26 Hz), 207.08 (d, J_{c-p} = 4.8 Hz).

^{31}P NMR ($CDCl_3$): δ = 18.50.

IR (film): ν = 1254 (P=O), 1950 (C=C=C), 3621 (OH).

MS: *m/z* (%) = 234(M^+,10), 204(81), 169(25), 148(100), 133(12), 123(48), 99(35), 81(73), 65(48).

Calcd for $C_{10}H_{19}PO_4$: C; 51.28%, H; 8.12%, P; 13.25%. Found: C; 51.33%, H; 8.20%, P; 13.18%.

5-Chloro-2-(diethylphosphono)-4-methylpenta-2,3-dien-1-ol (3b)
yield 67%.

^1H NMR ($CDCl_3$): δ = 1.35 (6H, dt, *J* = 1.0, 7.8 Hz, $2CH_3$), 1.92 (3H, d, *J* = 7.0 Hz, CH_3), 3.3 (1H, br s, OH), 4.11 (6H, m, $2CH_2OP$, CH_2Cl), 4.28 (2H, d, *J* = 13.75 Hz, CH_2OH).

^{13}C NMR[$CD_3C(O)CD_3$]: δ = 15.84 (d, J_{c-p} = 6.4 Hz), 16.57 (d, J_{c-p} = 6.4 Hz), 47.26 (d, J_{c-p} = 6.4Hz), 60.37 (d, J_{c-p} = 11.2 Hz), 63.20 (d, J_{c-p} = 6.5 Hz), 97.36 (d, J_{c-p} = 183.1 Hz), 101.37 (d, J_{c-p} = 14.5 Hz), 206.79 (d, J_{c-p} = 4.8 Hz).

^{31}P NMR ($CDCl_3$): δ = 16.07.

IR (film): ν = 1250 (P=O), 1955 (C=C=C), 3611 (OH).

MS: *m/z* (%) = 233(78), 203(100), 175(60), 159(28), 147(70), 127(53), 81(60), 65(30).

Calcd for $C_{10}H_{18}ClPO_4$: C; 44.69%, H; 6.70%, Cl; 13.22%, P; 11.55%. Found: C; 44.76%, H; 7.30%, Cl; 13.01%, P; 11.41%.

2-(Diethylphosphono)-4-methylpenta-2,3-diene-1,5-diol (3c)
yield 62%.

^1H NMR ($CDCl_3$): δ = 1.34 (6H, dt, *J* = 1.0, 8.0 Hz, $2CH_3$), 1.78 (3H, d, *J* = 7.6 Hz, CH_3), 4.04 (2H, d, *J* = 12.0 Hz, CH_2OH), 4.10 (4H, m, $2CH_2OP$), 4.14 (2H, d, *J* = 12.8 Hz, CH_2OH), 4.34 (2H, br s, 2OH).

^{13}C NMR ($CD_3C(O)CD_3$): δ = 14.88 (d, J_{c-p} = 6.8 Hz), 16.50 (d, J_{c-p} = 6.8 Hz), 60.45 (d, J_{c-p} = 12.2 4Hz), 63.18 (d, J_{c-p} = 6.5 Hz), 63.41 (d, J_{c-p} = 6.5 Hz), 96.39 (d, J_{c-p} = 184.5 Hz), 105.05 (d, J_{c-p} = 15.0 Hz), 205.00 (d, J_{c-p} = 5.4 Hz).

^{31}P NMR ($CDCl_3$) δ = 17.8.

IR (film): ν = 1259 (P=O), 1942 (C=C=C), 3655 (OH).

MS: m/z (%) 250(M^+,12), 220(100), 203(45), 191(10), 175(30), 146(83), 129(23), 109(28), 92(40), 81(48), 65(40).

Calcd for $C_{10}H_{19}PO_5$: C; 48.00%, H; 7.60%, P; 12.40%. Found: C; 48.27%, H; 7.54%, P; 12.13%.

2-(Diethylphosphono)-4-methylhexa-2,3,5-trien-1-ol (3d)
yield 71%.

^{1}H NMR ($CDCl_3$): δ = 1.37 (6H, dt, J = 1.3, 7.6 Hz, $2CH_3$), 1.93 (3H, d, J = 7.5 Hz, CH_3), 3.4 (1H, br s, OH), 4.14 (4H, m, $2CH_2OP$), 4.31 (2H, d, J = 14.0 Hz, CH_2OH) 5.19 (2H, m, $=CH_2$), 6.35 (1H, m, =CH).

^{13}C NMR[$CD_3C(O)CD_3$]: δ = 14.07 (d, J_{c-p} = 6.4 Hz), 16.36 (d, J_{c-p} = 6.4 Hz), 61.44 (d, J_{c-p} = 12.0 Hz), 62.88 (d, J_{c-p} = 6.5 Hz), 93.77 (d, J_{c-p} = 183.8 Hz), 103.65 (d, J_{c-p} = 16.0 Hz), 115.40 (d, J_{c-p} = 4.0 Hz), 132.71 (d, J_{c-p} = 9.0 Hz), 204.85 (d, J_{c-p} = 5.1 Hz).

^{31}P NMR ($CDCl_3$): δ = 16.48.

IR (film): ν = 1249 (P=O), 1948 (C=C=C), 3620 (OH).

MS: m/z (%) = 246(M^+,10), 216(100), 204(23), 188(40), 160(90), 148(22), 120(10), 78(30), 65(20).

Calcd for $C_{11}H_{19}PO_4$: C; 53.66%, H; 7.72%, P; 12.60%. Found: C; 53.96%, H; 7.91%, P; 12.34%.

2-(Diethylphosphono)-4-(2-norbornylidene)buta-2,3-dien-1-ol (3e)
yield 72%.

^{1}H NMR ($CDCl_3$): δ = 1.78 – 2,12 (10H, m, CH_2, CH), 1.36 (6H, dt, J = 1.6, 8.0 Hz), 3.7 (1H, br s, OH), 4.10 (4H, dq, J = 7.8, 8.0 Hz, CH_2OP), 4.32 (2H, d, J = 12.4 Hz, CH_2OH).

^{13}C NMR[$CD_3C(O)CD_3$]: δ = 16.08 (d, J_{c-p} = 6.1 Hz), 23.18 s, 28.09 s, 35.67 s, 37.42 s, 45.56 s, 46.59 s, 61.53 (d, J_{c-p} = 12.2 Hz), 61.8 (d, J_{c-p} = 5.5 Hz), (d, J_{c-p} = 185.2 Hz), 99.4 (d, J_{c-p} = 6.5 Hz), 210.3 (d, J_{c-p} = 210,3 Hz).

^{31}P NMR ($CDCl_3$): δ = 18.81.

IR (film): ν = 1251 (P=O), 1945 (C=C=C), 3610 (OH).

MS: m/z (%) = 286(M^+,10), 256(100), 228(28), 200(40), 81(75), 65(50).

Calcd for $C_{14}H_{23}PO_4$: C; 58.74%, H; 8.04%, P; 10.84%. Found: C; 58.98%, H; 8.30%, P; 10.52%.

2-(Diethylphosphono)-4-(2-cyclohexenylidene)buta-2,3-dien-1-ol (3f)
yield 63%.

^{1}H NMR ($CDCl_3$): δ = 1.35 (6H, dt, J = 1.6, 8.0 Hz, $2CH_3$), 1.78 (2H, m, CH_2), 2.15 (2H, m, CH_2), 2.46 (2H m, CH_2), 3.60 (1H, br s, OH), 4.09 (4H, dq, J = 7.6, 8.0 Hz, $2CH_2OP$), 4.26 (2H, d, J = 12.4 Hz, CH_2OH) 5.88 (1H, m, =CH), 6.01 (1H, m, =CH).

^{13}C NMR[$CD_3C(O)CD_3$]: δ = 16.36 (d, J_{c-p} = 6.2 Hz), 21.71 s, 24.79 s, 26.51 (d, J_{c-p} = 6.2 Hz), 61.69 (d, J_{c-p} = 11.9 Hz), 62.92 (d, J_{c-p} = 6.2 Hz), 93.47 (d, J_{c-p} = 184.6 Hz), 103.65 (d, J_{c-p} = 15.1 Hz), (d, J_{c-p} = 9.0 Hz), 131.49 (d, J_{c-p} = 11.2 Hz), 205.08 (d, J_{c-p} = 5.0 Hz).

^{31}P NMR ($CDCl_3$): δ = 17.00.

IR (film): ν = 1249 (P=O), 1960 (C=C=C), 3619 (OH).

MS: m/z (%) 272(M^+,8), 242(100), 214(34), 186(69), 167(10), 149(5), 127(8), 81(12), 65(8).

Calcd for $C_{13}H_{21}PO_4$: C; 57.35%, H; 7.72%, P; 11.40%. Found: C; 57.55%, H; 7.90%, P; 11.14%.

Phosphorylated 2,5-Dihydrofurans 4a–f

4-(Diethylphosphono)-2,2-dimethyl-2,5-dihydrofuran (4a); Typical Procedure
To a 30 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar was added silver nitrate (0.425 g, 0.0025 mol). The flask was flushed with N_2, and an acetone/water (4:1) mixture (8 mL) was introduced. To the mixture was added **3a** (1.17 g, 0.005 mol) and the solution was heated to reflux for 0.5 h. Reactions were monitored by TLC on silica gel; detection was made using a $KMnO_4$ basic solution and ^{1}H NMR spectral data. The methanol was evaporated in vacuo and to the mixture was added benzene (30 mL). The benzene (about 20 mL) was evaporated in vacuo, the solid was removed by filtration. The crude product was chromatographed on a silica gel column with Et_2O/acetone (4:1) as eluent to give **4a** 0.82 g (70% yield).

^{1}H NMR ($CDCl_3$): δ = 1.34 (6H, dt, J = 1.0, 7.2 Hz, $2CH_3$), 1.38 (6H, s, $2CH_3$), 4.14 (4H, dq, J = 8.0, 7.2 Hz, $2CH_2OP$), 4.76 (2H, dd, J = 3.0, 2.0 Hz, OCH_2), 6.60 (1H, dt, J = 12.2, 2.0 Hz, HC=).

^{13}C NMR($CDCl_3$): δ = 16.00 (d, J_{c-p} = 6.14 Hz), 26.37 s, 61.85 (d, J_{c-p} = 5.59 Hz), 73.80(d, J_{c-p} = 20.28 Hz), 88.75 (d, J_{c-p} = 19.27 Hz), 127.58 (d, J_{c-p} = 196.25 Hz), 149.58 (d, J_{c-p} = 9.96 Hz).

^{31}P NMR ($CDCl_3$): δ = 12.93.

IR (film): ν = 1250 (P=O), 1609 (C=C).

MS: m/z (%) = 233(M^+–1,80), 219(38), 204(26), 191(22), 177(50), 163(43), 109(90), 81(100), 65(60).

Calcd for $C_{10}H_{19}PO_4$: C; 51.28%, H; 8.12%, P; 13.25%. Found: C; 51.54%, H; 8.43%, P; 13.07%.

2-Chloromethyl-4-(diethylphosphono)-2-methyl-2,5-dihydrofuran (4b)
yield 75%.

^{1}H NMR ($CDCl_3$): δ = 1.32 (6H, dt, J = 1.0, 7.2 Hz, $2CH_3$), 1.4 (3H, s, CH_3), 3.51 (2H, s, $ClCH_2$), 4.06 (4H, dq, J = 8.0, 7.2 Hz, $2CH_2OP$), 4.69 (2H, dd, J = 2.8, 2.1 Hz, OCH_2), 6.48 (1H, dt, J = 12.0, 2.1 Hz, HC=).

^{13}C NMR($CDCl_3$): δ = 16.28 (d, J_{c-p} = 6.00 Hz), 25.67 s, 51.37 s, 62.01 (d, J_{c-p} = 5.4 Hz), 73.76 (d, J_{c-p} = 20.1 Hz), 89.76 (d, J_{c-p} = 19.5 Hz), 127.03 (d, J_{c-p} = 195.3 Hz), 148.01 (d, J_{c-p} = 10.2 Hz).

^{31}P NMR ($CDCl_3$): δ = 12.1.

IR (film): ν = 1249 (P=O), 1611 (C=C).

MS: *m/z* (%) = 267(M^+–1,10), 219(85), 204(5), 191(21), 163(72), 109(48), 81(100), 65(48).

Calcd for $C_{10}H_{18}ClPO_4$: C; 44.69%, H; 6.70%, Cl; 13.22%, P; 11.55%. Found: C; 44.52%, H; 6.53%, Cl; 13.17%, P; 11.52%.

4-(Diethylphosphono)-2-(hydroxymethyl)-2-methyl-2,5-dihydrofuran (4c)
yield 73%.

^{1}H NMR ($CDCl_3$): δ = 1.36 (3H, s, CH_3), 1.38 (6H, dt, J = 1.0, 7.8 Hz, $2CH_3$), 3.62 (2H, s, CH_2OH), 4.14 (4H, dq, J = 8.0, 7.8 Hz, CH_2OP), 4.3 (1H, br s, OH), 4.8 (2H, dd, J = 2.8, 2.0 Hz, OCH_2), 6.58 (1H, dt, J = 12.0, 2.0 Hz, HC=).

^{13}C NMR($CDCl_3$): δ = 16.28 (d, J_{c-p} = 5.6 Hz), 20.03 s, 62.19 (d, J_{c-p} = 5.4 Hz), 64.01 s, 74.22 (d, J_{c-p} = 20.2 Hz), 89.71 (d, J_{c-p} = 18.0 Hz), 128.07 (d, J_{c-p} = 195.87 Hz), 148.32 (d, J_{c-p} = 10.0 Hz).

^{31}P NMR ($CDCl_3$): δ = 12.65.

IR (film): ν = 1251 (P=O), 1608 (C=C); 3631 (OH).

MS: *m/z* (%) = 249(M^+–1,25), 235(40), 220(25), 207(10), 81(100), 65(58).

Calcd for $C_{10}H_{19}PO_5$: C; 48.00%, H; 7.60%, P; 12.40%. Found: C; 48.42%, H; 7.92%, P; 12.08.

4-(Diethylphosphono)-2-ethenyl-2-methyl-2,5-dihydrofuran (4d)
yield 74%.

^{1}H NMR ($CDCl_3$): δ = 1.34 (6H, dt, J = 0.8, 7.0 Hz, $2CH_3$), 1.42 (3H, s, CH_3), 4.12 (4H, dq, J = 8.0, 7.0 Hz, $2CH_2OP$), 4.79 (2H, m, OCH_2), 5.82, 5.25 (2H, ddd, J = 11.0, 17.0 Hz, H_2C=), 5.9 (1H, m, *HC*=CH_2), 6.51 (1H, dt, J = 11.6, 2.5 Hz, HC=CP).

^{13}C NMR($CDCl_3$): δ = 16.37 (d, J_{c-p} = 5.4 Hz), 25.02 s, 62.23 (d, J_{c-p} = 5.4 Hz), 74.67 (d, J_{c-p} = 20.9 Hz), 91.06 (d, J_{c-p} = 19.5 Hz), 113.64 s, 128.67 (d, J_{c-p} = 195.4 Hz), 139.92 s, 147.39 (d, J_{c-p} = 10.9 Hz).

^{31}P NMR ($CDCl_3$): δ = 12.48.

IR (film): ν = 1248 (P=O), 1561, 1610 (C=C).

MS: *m*/*z* (%) = 245(M^+–1,21), 231(30), 218(34), 189(33), 175(36), 162(41), 109(80), 81(100), 65(32).

Calcd for $C_{11}H_{19}PO_4$: C; 53.66%, H; 7.72%, P; 12.60%. Found: C; 53.56%, H; 7.68%, P; 12.50%

4-(Diethylphosphono)-2-(2-norbornylidene)-2,5-dihydrofuran (4e)
yield 75%.

^{1}H NMR ($CDCl_3$): δ = 1.18 – 1.8, 2.3 (10H, m, CH_2, CH), 1.34 (6H, dt, J = 0.9, 8.0 Hz, $2CH_3$), 4.16 (4H, dq, J = 8.0, 8.0 Hz, $2CH_2OP$), 6.72 (1H, dt, J = 12.0, 2.25 Hz, HC=CP).

^{13}C NMR($CDCl_3$): δ = 16.08 (d, J_{c-p} = 6.14 Hz), 23.20 s, 28.09 s, 35.69 s, 37.53 s, 45.58 s, 46.69 s, 61.82 (d, J_{c-p} = 5.48 Hz), 73.52 (d, J_{c-p} = 20.08 Hz), 97.73 (d, J_{c-p} = 19.42 Hz), 129.31 (d, J_{c-p} = 196.65 Hz), 147.15 (d, J_{c-p} = 10.77 Hz).

^{31}P NMR ($CDCl_3$): δ = 13.12.

IR (film): ν = 1254 (P=O), 1598 (C=C).

MS: *m*/*z* (%) = 285(M^+–1,100), 257(50), 229(55), 135(40), 107(55), 81(60), 67(40).

Calcd for $C_{14}H_{23}PO_4$: C; 58.74%, H; 8.04%, P; 10.84%. Found: C; 58.71%, H; 8.01%, P; 10.84%.

4-(Diethylphosphono)-2-(2-cyclohexenylidene)-2,5-dihydrofuran (4f)
yield 73%.

^{1}H NMR ($CDCl_3$): δ = 1.32 (2H, m, CH_2), 1.36 (6H, dt, J = 0.9, 8.0 Hz, $2CH_3$), 1.77 (2H, m, CH_2), 2.04 (2H, m, CH_2) 4.11 (4H, dq, J = 8.0, 8.0 Hz, $2CH_2OP$), 4.74 (2H, m, OCH_2), 5.56 (1H, br d, J = 10.0 Hz, *H*C=CH), 5.91 (1H, dt, J = 10.0, 4.0 Hz, HC=C*H*), 6.51 (1H, dt, J = 12.0, 2.0 Hz, HC=CP).

^{13}C NMR($CDCl_3$): δ = 16.33 (d, J_{c-p} = 6.7 Hz), 19.70 s, 24.65 s, 33.72 s, 62.19 (d, J_{c-p} = 5.5 Hz), 74.10 (d, J_{c-p} = 20.8 Hz), 88.53 (d, J_{c-p}=17.8 Hz), 127.81 s, 129.11 (d, J_{c-p} = 194.5 Hz), 131.44 s, 148.00 (d, J_{c-p} = 10.8 Hz).

^{31}P NMR ($CDCl_3$): δ = 13.21.

IR (film): ν = 1251 (P=O), 1540, 1604 (C=C).

MS: *m*/*z* (%) = 271(M^+–1,100), 243(80), 215(95), 133(60), 107(90), 81(70), 65(40).

Calcd for $C_{13}H_{21}PO_4$: C; 57.35%, H; 7.72%, P; 11.40%. Found: C; 57.71%, H; 8.02%, P; 11.00%.

References

(1) (a) Claesson, A.; Olsson, L.-I. In *The Chemistry of Allenes*: Landor, S.R. Ed.; Academic: London, 1982, vol.3, 737.
(b) Fuks, R.; Viehe, H. G. In *The Chemistry of Acetylenes*: Viehe, H.G. Ed.; Marcel Dekker: New York, 1969, 425.
(c) Zefirov, N.S.; Koz'min, A. S.; Kasumov, T. M.; Potekhin, K. A.; Sorokin, V. D.; Brel, V. K.; Abramkin, E. V.; Struchkov, Yu. T.; Zhdankin, V. V.; Stang, P.J. *J. Org. Chem*. **1992**, *57*, 2433.

(2) Claesson, A.; Sahlberg, C.; Luthman, K. *Acta Chem. Scand.* **1979**, *B33*, 309.

(3) Padwa, A.; Meske, M.; Ni, Z. *Tetrahedron* **1995**, *51*, 89.
Luteijn, J.M.; Spronck, H.J.W. *J. Chem. Soc., Perkin ′Trans I.* **1979**, 201.
Mantione, R.; Leroux, Y.; Normant, H. *C. R. Acad. Sci. Ser. C.* **1970**, *270*, 1808.

(4) Gelin, R.; Gelin, S.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1972**, 720.
Toda, F.; Komoda, T.; Akaji, K. *Bull. Chem. Soc. Jpn*. **1968**, *41*, 1493.

(5) Hoff, S.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas.* **1969**, *88*, 84.

(6) Gelin, R.; Albrand, M.; Gelin, S. *C. R. Acad. Sci. Ser. C.* **1969**, *269*, 241.

(7) Claesson, A.; Olsson, L.-I. In *The Chemistry of Allenes*: Landor, S.R. Ed.; Academic: London, 1982, vol.2, 369.

(8) Nikam, S. S.; Chu, K.-H.; Wang, K. K. *J. Org. Chem*. **1986**, *51*, 745.

(9) Carlson, R.M.; Jones, R.W; Hacher, A.S. *Tetrahedron Lett.* **1975**, 1741.

(10) Olsson, L.-I.; Claesson, A. *Synthesis* **1979**, *9*, 743.

(11) Brel, V. K. *Synthesis* **1998**, 710.

(12) (a) Alabugin, I.V.; Brel, V.K. *Usp. Khim.* **1997**, *66,* 225; *Russ. Chem. Rev., Engl. Trans.* **1997**, *66*, 205; *Chem. Abstr*. **1998**, *128*, 114977r.
(b) Brel, V. K.; Abramkin, E. V.; Chekhlov, A. N.; Martynov, I. V. *Dokl. Akad. Nauk SSSR.* **1990**, *312*, 619; *Chem. Abstr.* **1991**, *114*, 122513n.

(13) Wolfgang, R. In *The Chemistry of Allenes*: Landor, S.R. Ed.; Academic: London, **1982**, vol.2, 832–847.

(14) Brandsma, L. *Preparative Acetylenic Chemistry,* Elsevier: Amsterdam, **1988**, 265.