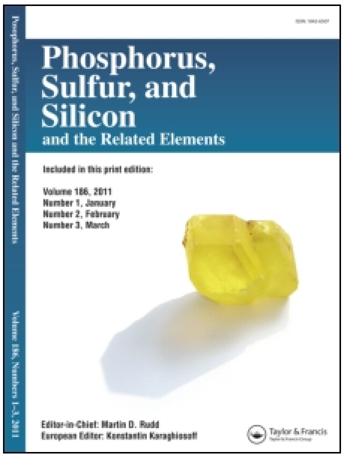


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF 2-(TRIMETHYLSILYL)- AND 2-(DIETHOXYPHOSPHONYL)-1,3-BUTADIENES

Valerij Ch. Christov[a]
[a] Department of Chemistry, University of Shoumen, Shoumen, Bulgaria

To cite this Article Christov, Valerij Ch.(1998) 'SYNTHESIS OF 2-(TRIMETHYLSILYL)- AND 2-(DIETHOXYPHOSPHONYL)-1,3-BUTADIENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 132: 1, 79 — 83

To link to this Article: DOI: 10.1080/10426509808036976

URL: http://dx.doi.org/10.1080/10426509808036976

Phosphorus Sulphur and Silicon, Vol. 132 pp. 79–83
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF 2-(TRIMETHYLSILYL)- AND 2-(DIETHOXYPHOSPHONYL)-1,3-BUTADIENES

VALERIJ CH. CHRISTOV

Department of Chemistry, University of Shoumen, BG-9700 Shoumen, Bulgaria

(Received 16 December 1997)

Synthesis of the 2-(trimethylsilyl)- (**3**) and the 2-(diethoxyphosphonyl)-1,3-butadienes (**4**) by Horner-Emmons and Peterson reactions respectively, of the 1-(trimethylsilyl)-2-propenylphosphonic diethyl ester (**1**) is described.

Keywords: 1-(trimethylsilyl)-2-propenylphosphonate; Horner-Emmons reaction; 2-(trimethylsilyl)-1,3-butadiene; Peterson reaction; 2-(diethoxyphosphoryl)-1,3-butadiene

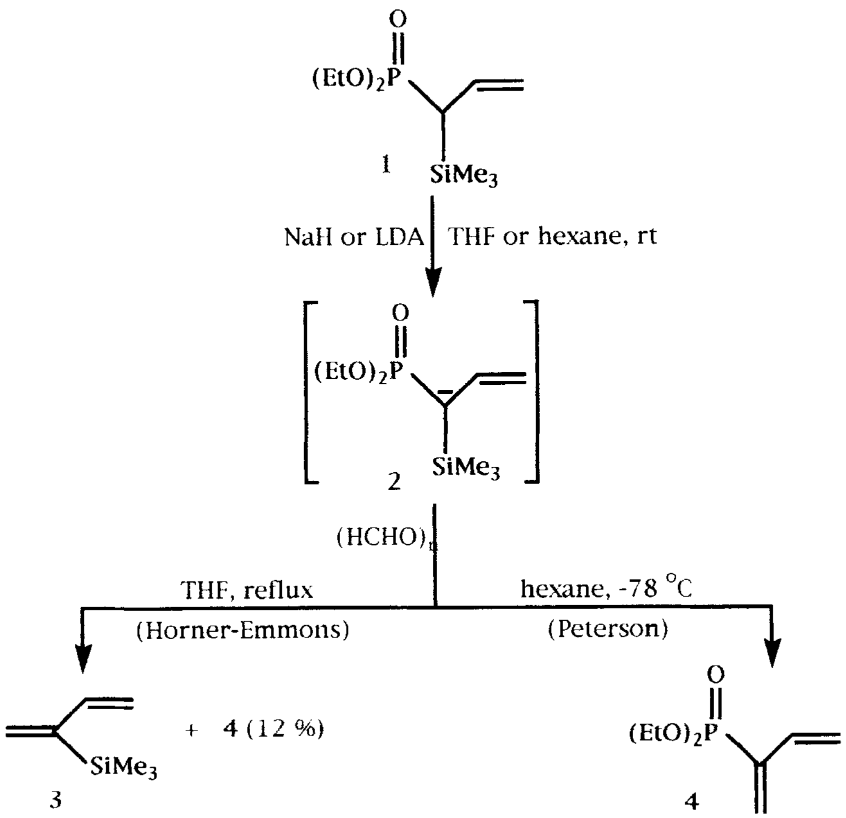
INTRODUCTION

In the past two decades, synthesis and use of vinylphosphonates, containing withdrawing groups at the α- and β-position, have been rapidly expanded in organic synthesis. [1] They are versatile key building blocks for different unsaturated compounds used as monomers as well as for several natural products or related carbocyclic and heterocyclic compounds with good biological activity. We have recently reported the preparation of 1-(trimethylsilyl)-2-propenylphosphonate. [2] On the other hand, the synthesis of dialkyl 1-alkoxy-4-methyl-1,3-pentadiene-2-phosphonate by the Peterson reaction of dialkyl 3-methyl-1-(trimethylsilyl)-2-butenylphosphonate with alkyl formiate has been reported. [3]

In the present paper, we report the successful utilization of the 1-(trimethylsilyl)-2-propenylphosphonate as a versatile reagent for the preparation of highly unsaturated compounds by Horner-Emmons and Peterson reactions. Standard Horner-Emmons [4-7] and Peterson [8-12] olefination of aldehydes and ketones with phosphorylated and silylated carbanions respectively, have found wide application in organic synthesis.

RESULTS AND DISCUSSION

We established that the reaction of phosphoryl- and silyl-stabilized carbanion **2** of the diethyl 1-(trimethylsilyl)-2-propenylphosphonate **1**, generated *in situ* by treatment with sodium hydride (NaH) in tetrahydrofurane at room temperature, with paraformaldehyde and heating at reflux for 5 h gave a mixture of the 2-(trimethylsilyl)-1,3-butadiene (**3**) with 36% yield as a Horner-Emmons product and the 2-(diethoxyphosphonyl)-1,3-butadiene (**4**) with 12% yield as a Peterson product, according to the Scheme. The TLC investigation of the residue showed three chromatographical spots—the one with R_f 0.23 for the silylated 1,3-butadiene **3**, the second with R_f 0.37 for the phosphorylated 1,3-butadiene **4** and the third with R_f 0.51 for the starting material **1**. The products **3** and **4** were



Scheme

separated by preparative TLC on Silica gel using system chloroform:ethylacetate:ether (2:1:1) as an eluent and identified by ^1H, ^{31}P NMP, IR and mass spectra as well as by elemental analysis (see **Experimental**).

In contrast, the similar treatment of the same carbanion **2** of the 1-(trimethylsilyl)-1-(diethoxyphosphoryl)-2-propene **1**, but generated *in situ* by treatment of **1** with lithium diisopropylamide (LDA), generated *in situ* from diisopropylamine (DIA) and n-butyl lithium (n-BuLi), in hexane at room temperature, with paraformaldehyde but at −78°C for 3 h, proceeded regiospecifically with formation of the Peterson product only—2-(dietoxyphosphoryl)-1,3-butadiene (**4**) with 32% yield (the rest is the starting compound **1**) (see the Scheme). The absence of the Horner-Emmons product **3** in the reaction mixture was confirmed by TLC and NMR investigations.

In summary, we have found that the diethyl 1-(trimethylsilyl)-2-propenylphosphonate is a versatile synthon for the synthesis of functionalized 1,3-butadienes, which could be used as monomers of incombustible polymers and copolymers. The results of an initial investigation of the polymerical and copolymerical activity of prepared compounds **3** and **4** were encouraging. This activity is now under extensive investigation.

EXPERIMENTAL

Method of analysis

^1H NMR spectra were obtained on a JEOL JNM-FX-60 spectrometer for solutions in $CDCl_3$ operating at 60 MHz. ^{31}P NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions in $CDCl_3$ operating at 161.9 MHz. Chemical shifts are in parts per million downfield from internal TMS (^1H) and external 85% H_3PO_4 (^{31}P). IR spectra were recorded with an IR-72 spectrophotometer. Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

All reactions were carried out under an argon atmosphere and exclusion of moisture. The solvents were purified by standard methods. All compounds were checked for their purify on TLC plates.

Preparation of 2-(trimethylsilyl)-1,3-butadiene (3) by the Horner-Emmons reaction

To a suspension of sodium hydride (NaH) (60% dispersion in mineral oil, 0.40 g, 10 mmol) in THF (20 ml) was added a solution of diethyl 1-(trimethylsilyl)-2-propenylphosphonate (**1**) (2.50 g, 10 mmol) in THF (20 ml) at room temperature. The reaction mixture was stirred at this temperature for 1 h. After the addition of a solution of paraformaldehyde (0.29 g, 10 mmol) in THF (10 ml) to the mixture, the reaction mixture was heated at reflux for 5 h. After that the mixture was quenched with 2N HCl, extracted with ethylacetate, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel using chloroform:ethylacetate:ether (2:1:1) as a eluent to give the pure product **3**, which had the following properties:

Yield: 36%; oil; R_f 0.23; $C_7H_{14}Si$, Calcd., %: C 66.58, H 11.18; Found, %: C 66.74, H 11.29. IR (neat), cm^{-1}: 1589, 1631 (C=C-C=C). ^1H NMR δ: 0.24 (s, 9H, 3Me), 5.2-6.4 (m, H_2C=CH and =CH_2, 5H). Mass spectra, m/z: 126 (M^+).

Preparation of 2-(dietoxyphosphonyl)-1,3-butadiene (4) by the Peterson reaction

To a solution of lithium diisopropylamide (LDA), generated *in situ* from diisopropylamine (DIA) (1.11g, 11 mmol) and n-butyl lithium (n-BuLi) (1.6 M in hexane, 6.25 ml, 10 mmol), in hexane (20 ml) was added a solution of the diethyl 1-(trimethylsilyl)-2-propenylphosphonate (**1**) (2.50 g, 10 mmol) in hexane (20 ml) at −78°C. The reaction mixture was stirred at this temperature for 1 h. After the addition of a solution of paraformaldehyde (0.29 g, 10 mmol) in hexane (10 ml) at −78°C to the mixture, the reaction mixture was stirred for 3 h at the same temperature and then at room temperature for 1 h. After that the mixture was quenched with 2N HCl, extracted with dichloromethane, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel using chloroform:ethylacetate:ether (2:1:1) as an eluent to give the pure product **4**, which had the following properties:

Yield: 32%; oil; R_f 0.37; $C_8H_{15}O_3P$, Calcd., %: P 16.29; Found, %: P 16.44. IR (neat) cm^{-1}: 1025 (P-O-C), 1272 (P=O), 1598, 1629 (C=C-C=C). ^1H NMR δ: 1.23 (t, $^3J_{HH}$ 6.2 Hz, 6H, Me), 3.32-3.83 (m, 2H, MeCH_2O), 5.3-6.6 (m, H_2C=CH and =CH_2, 5H). ^{31}P NMR δ,: 18.56. Mass spectra, m/z: 190 (M^+).

References

[1] T. Minami and J. Motoyoshiya, *Synthesis*, 333 (1992).
[2] V. Ch. Christov, *Phosphorus, Sulfur, Silicon*, in press.
[3] H. Al-Badri, E. About-Jandet and N. Collignon, *Tetrahedron Lett.*, **36**, 393 (1995).
[4] L. Horner *et al.*, *Chem. Ber.*, **91**, 61 (1958).
[5] J. Boutagy and R. Thomas, *Chem. Rev.*, **74**, 87 (1974).
[6] A. V. Dombrovskii and V. A. Dombrovskii, *Usp. Khim.*, **35**, 1771 (1966).
[7] B. Deschamps, *et al.*, *Tetrahedron*, **28**, 4209 (1972).
[8] D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).

[9] M. Mikolajczyk and P. Balczewski, *Synthesis*, 101 (1989).
[10] H. Ahlbrecht, W. Farnung and H. Simon, *Chem. Ber.*, **117**, 2622 (1984).
[11] E. E. Aboujaoude, S. Lietje, N. Collignon, M. Teulade and M. P. Savignac, *Synthesis*, 934 (1986).
[12] J. Binder and E. Zbiral, *Tetrahedron Lett.*, **27**, 5829 (1986).