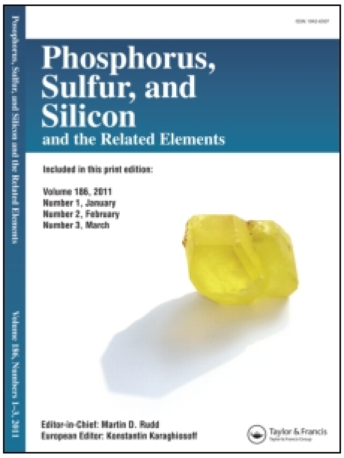

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Enchev, D. D. and Kirilov, M.(1998) 'New Approach to 1-Substituted-1,2-Alkadienephosphonates Ii. Synthesis of 2-Hydroxy-3,4-Alkadiene-3-Phosphonate Dimethyl Esters', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 193 — 197

To link to this Article: DOI: 10.1080/10426509808545463

URL: http://dx.doi.org/10.1080/10426509808545463

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 193-197
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NEW APPROACH TO 1-SUBSTITUTED-1,2-ALKADIENEPHOSPHONATES II. SYNTHESIS OF 2-HYDROXY-3,4-ALKADIENE-3-PHOSPHONATE DIMETHYL ESTERS[1]

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(Received 26 November, 1997)

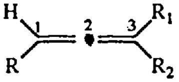
The preparation of unknown 1-substituted-1,2-alkadienephosphonates, possible precursors in the Wittig-Horner-Emmons reaction have been discussed

Keywords: 1-substituted-1,2-alkadienephosphonates; Wittig-Horner-Emmons reaction

INTRODUCTION

In the past several years there is considerable interest to the chemistry of the phosphorylated 1,2-alkadienes. They are possible precursors of many compounds which synthesis are restricted to some extend using other synthetic ways[2–6].

The literature data[7–10] show that the proton at the C1 atom of the allenic system (see scheme 1) is easily displaceable with different kinds of electrophilic reagents: R = $(RO)_2P(O)$



SCHEME 1

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* Corresponding Author.

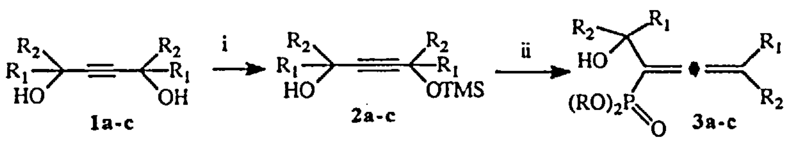
The conditions for such a displacement include however low temperatures(-78°C), inert atmosphere, and the use of strong bases such as buthyllithium, LDA etc.

In this paper we wish to present our results of the new approach to 1-substituted-1,2-alkadienephosphonates.

RESULTS AND DISCUSSION

The new 1-substituted-1,2 -alkadienephosphonates were prepared via an acetylene – allene rearrangement of acetylene phosphites obtained in the reaction of acetylenic diols and dialkylphosphites in nonpolar media. Due to the symmetry of the starting diols in the first step of the reaction, TMSCI has been used to preserve one of the hydroxyl- groups. The reaction is carried out in benzene at 0 to 5°C in the presence of pyridine(see experimental). After adding to the mixture of the appropriate diol and pyridine TMSCI, the reaction mixture was heated to the boiling point of the solvent. After cooling to room temperature the precipitate was filtered off, the solvent was evaporized and the residue was distilled. The IR spectra of the obtained silyated acetylenic diol shows a very characteristic band at 3370–3390cm^{-1} for the -OH group, bands at 1045 –1030cm^{-1} for the TMS-group as well as bands for other characteristic groups.

The isolated compounds smoothly react with dialkylchlorophosphites in nonpolar media(see scheme 2).



1-3	a	b	c
R_1	Me	Me	H
R_2	Me	H	H

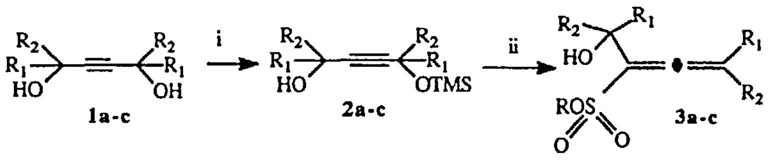
i= 1.Pyr.2.TMSCl,3.benzene
ii= 1.$(RO)_2PCl$, 2.ether

SCHEME 2

The IR spectra of the end products exhibit the characteristic bands for hydroxyl group, phosphoryl group,for ester-groups at phosphorus, for “isopropyl”-linked species at C1 atom as well as for the allenic system.

The ^1H-nmr spectra of the end products show signals for the protons from the alkyl- and alkoxy- groups, as well as the signal for the proton from the hydroxyl group, but no signals for an olephinic proton at C1 atom of the allene system which is very characteristic for the C1 unsubstituted allenephosphonates.

The spectral data and elemental analysis confirm that the reaction followed the scheme shown above. Thus the unknown hydroxyallenphosphonates were prepared in good yield in a two step reaction. We also were successful to prepare this compounds without using a preliminary protection of a hydroxy-group with TMSCl. The direct reaction of the acetylenic diols with dialkylchlorophosphites produced the same hydroxyallenephosphonates in relatively the same yields. This is a direct confirmation of the suggested reaction scheme and gives us reason to assume that the acetylene-allene rearrangement is general for the reactions of α-acetylenic alcohols with chlorophosphites. Moreover, we syntesized a sulfur containing analog of the above mentioned 1-substituted-1,2-allenephosphonates using the same acetylenic diols and sulfonylchlorides via the procedure described by Braverman[11].



1-3	a	b	c
R_1	Me	Me	H
R_2	Me	H	H

i= 1.Pyr.2.TMSCl,3.benzene

ii= 1.ROS(O)Cl, 2.ether

Further work is in progress to investigate the behavior of the obtained compounds in a Wittig-Horner-Emmons reaction.

EXPERIMENTAL

Starting materials

The trimethylchlorsilane and acetylenic diols are commercially available from Fluka.

The dialkylchlorophosphites were prepared from the corresponding alcohols andphosphorus trichloride – also commercially available from Fluka.

Synthesis of monosilylated acetylenic diols 2a-c

General procedure

To a mixture of the appropriate acetylenic diol and a half molar amount of pyridine dissolved in dry benzene at 0 to 5°C and stirring a solution of a half molar amount of trimethylchlorsilane in the same solvent was added dropwise for 30 min. After the addition the reaction mixture was heated up to the boiling point of the solvent for an additional 30 min. Then after cooling to room temperature the precipitate was removed, the solvent was evaporized and the residue was distilled. Yield 78–82%.

Synthesis of hydroxyallenephosphonates 3a-c

General procedure

To a solution of *2a-c* in dry ether at –10 to –8°C an equimolar amount of the appropriate dialkylchlorophosphite was added dropwise for one hour. The reaction mixture was left over night, the precipitate was filtered off, the solvent was evaporated and the residue was distilled. Yield 75–80%.. The elemental analysis and spectroscopic data are griven in tables I and II.

TABLE I Constants and elemental analysis data for compounds 3a-c

N	*$R[R^1](R^2)$*	*Yield(%)*	*Calcd.(%) P*	*Formula*	*Found(%) P*
3a	Me[Me](Me)	87	13.22	$C_{10}H_{19}O_4P$	13.19
b	Me[Me](H)	85	15.09	$C_8H_{14}O_4P$	14.98
c	Me[H](H)	86	17.38	$C_6H_{11}O_4P$	17.22

TABLE II ^1H-,^{31}P-nmr and IR spectral data for compounds 3a-c

N	*$R[R^1]$ (R2)*		*31P*	*P-O*	*C=C=C*	*HO-*
3a	Me[Me](Me)	CH_3-1.7 CH_3-1.34 CH_3-1.42	16.8	1256	1950	3300
b	Me[Me](H)	CH_3-1.7 CH_3-1.32 H-5.02	16.78	1255	1956	3300

N	$R[R^1](R2)$		*31P*	*P-O*	*C=C=C*	*HO-*
c	Me[H](H)	CH_3-1.7 H-5.04 H-5.04	17.5	1260	1957	3300

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