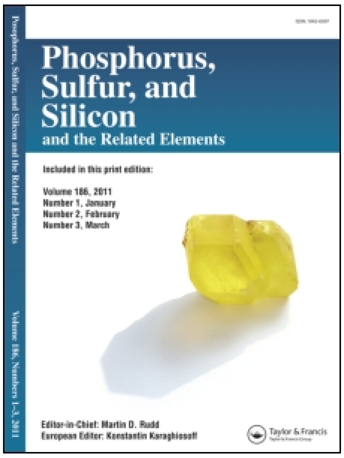

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A New Approach to 1-Substituted-1,2-alkadienephosphonates II: Synthesis of 2-Hydroxy-3,4-alkadiene-3-phosphonate Dimethyl Esters[1]

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The preparation of unknown 1-substituted-1,2-alkadienephosphopnates, 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 has been considerable interest in the chemistry of the phosphorylated 1,2-alkadienes. They are possible precursors of many compounds in which synthesis is restricted to some extent using other synthetic ways.[2–6]

The literature data[7–10] show that the proton at the C1 atom of the allenic system (Scheme 1) is easily displaceable with different kinds of electrophilic reagents.

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

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

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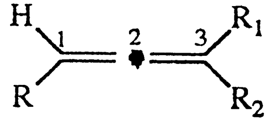
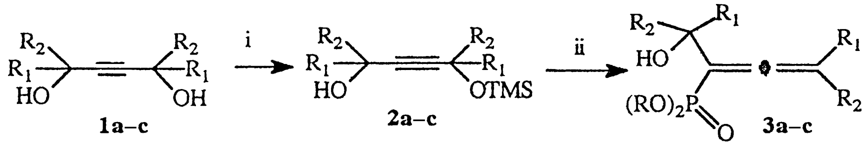


SCHEME 1 R = $(RO)_2P(O)$.

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 0–5°C in the presence of pyridine (see Experimental section). After adding to the mixture of the appropriate diol and pyridine of TMSCI, the reaction mixture was heated up 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 silylated acetylenic diol shows a very characteristic band at 3370–3390 cm^{-1} for the —OH group, bands at 1045–1030 cm^{-1} for the TMS-group, as well as bands for other characteristic groups.

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

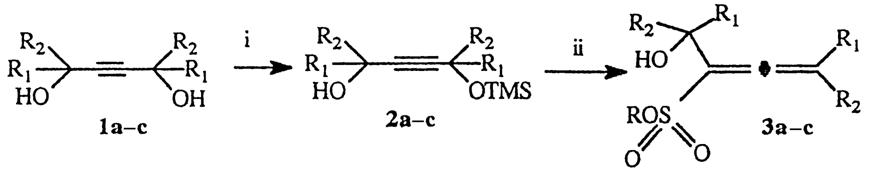


1–3	a	b	c
R_1	Me	Me	H
R_2	Me	H	H

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 the hydroxyl group, phosphoryl group, for ester-groups at phosphorus, for “isopropyl”-linked species at C1 atom, as well as for the allenic system.



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

SCHEME 3

The ^{1}H-NMR spectra of the end products signals for the protons from the alkyl- and alkoxy-groups and no signal for the olefinic proton at C1 atom of the allene system, which is very characteristic for the unsubstituted at C1 position allenephosphonates, has been detected.

The spectral data and elemental analysis confirm that the reaction followed Scheme 2. Thus, the early unknown hydroxyallenphosphonates were prepared in good yield in a two-step reaction. We also were successful in preparing these compounds without using a preliminary protection of a hydroxy-group with TMSCI. 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] (Scheme 3).

Furthermore, the 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 and phosphorus trichloride which also is commercially available from Fluka.

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

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 0–5°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 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 -10–8°C, an equimolar amount of the appropriate dialkylchlorophosphite was added dropwise for 1 h. The reaction mixture was left overnight, the precipitate was filtered off, the solvent was evaporateds and the residue was distilled. Yield 75–80%. The elemental analysis and spectroscopic data are given in Tables I and II.

TABLE II ^{1}H-, ^{31}P-nmr and IR Spectral Data for Compounds 3a–c

N	R[R^1] (R^2)		31P	P=O	C=C=C	HO–
3a	Me[Me](Me)	CH_3-1.7 CH_3-1.34 CH-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
c	Me[H](H)	CH_3-1.7 H-5.04 H-5.04	17.5	1260	1957	3300

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