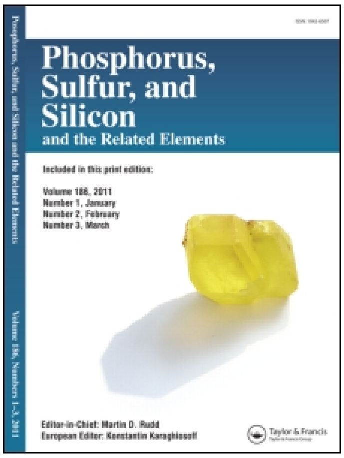

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New Synthetic Approach to 1-Substituted-1,2-alkadiene Phosphonates

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NEW SYNTHETIC APPROACH TO 1-SUBSTITUTED-1,2-ALKADIENE PHOSPHONATES

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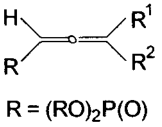
The application of a new synthetic approach to 1-substituted-1,2-alkadiene phosphonates is discussed.

Keywords: 1,2-Alkadiene phosphonates; sylilated acetylenic diols

INTRODUCTION

Over the past several years there has been noticeable interest to the chemistry of phosphorylated 1,2-alkadienic hydrocarbons. They are possible precursors for the synthesis of many valuable industrial compounds whose syntheses are restricted using other synthetic ways.

Many authors[1–8] indicate that the proton at C_1-atom of the 1,2-alkadienephosphonic system can be substituted easily by different electrophilic reagents (Scheme 1):



SCHEME 1

The reaction conditions of the above mentioned reactions included low temperatures (−78°C), inert atmosphere, as well as using of strong bases.

In this article we report our results connected with the creation of a new synthetic way to target compounds, namely 1-substituted-1,2-alkadiene phosphonates.

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RESULTS AND DISCUSSION

The 1-substituted-1,2-alkadiene phosphonates have been prepared via acetylene-allenic rearrangement of acetylenic phosphites. The last are readily available by the reaction of acetylenic diols and dialkylphosphites in nonpolar media.

Due to the symmetrical constitution of the starting acetylenic diols, the first step of the reaction included their interaction with trimethylchlorosilan (TMSCl). Under these conditions the H-atom from the OH-group has been successfully displaced by TMS-group.

The reaction takes place in benzene media, at $0 \div -5^\circ$C and in the presence of pyridine.

After adding of a mixture of the corresponding acetylenic diol and TMSCl the reaction mixture was heated to boiling. The reaction mixture was then left stand to reach room temperature; the precipitate was filtered, the solvent was evaporated, and the residue was distilled.

The IR-spectra of the prepared sylilated acetylenic diols exhibit broad bands in the area of 3340–3370 cm^{-1} characteristic for the stretching vibrations of the associated OH-group, as do the characteristic bands for the C—O bond at 1080 cm^{-1} for the secondary alcohols and at 1150 cm^{-1} for the tertiary alcohols.[9]

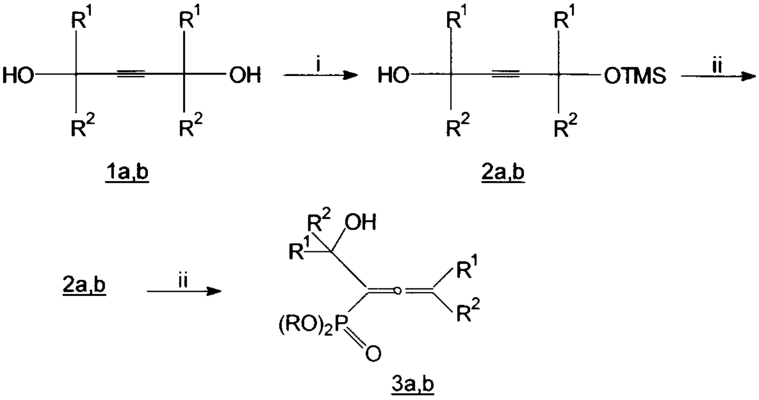
Despite of the different kind of substituents at C-atoms of the triple bond the IR-spectra do not exhibit bands for the stretching vibrations ($\nu_{\text{C}\equiv\text{C}}$) because of their equal induction effect.[9] The appearance of the intensive characteristic bands at 700 cm^{-1}, 845 cm^{-1} ($\nu_{\text{Si–C}}$), 1250 cm^{-1} ($\delta^{\text{s}}_{\text{SiMe}_3}$), and 1100 cm^{-1} ($\nu_{\text{Si–O–C}}$)[10] is evidence for the successful displacement reaction.

The isolated sylilated acetylenic diols smoothly react with dialkylchlorophosphites in the presence of organic base.

The reactions conditions include low temperature ($-8 \div -10^\circ$C) and nonpolar solvent.

To the solution of the corresponding dialkylchlorophosphite, a mixture of the equivalent amounts of pyridine and sylilated alcohol was added drop-wise. The reaction mixture was then left standing for 24 h, and the precipitate was filtered, the solvent evaporated, and the residue distilled. IR spectra of the end products compared to those of the sylilated precursors exhibit:

1. the appearance of a new band at 1945–1950 cm^{-1} for the stretching vibrations of the allenic system;[10]
2. the appearance of new bands at the region 1000–1300 cm^{-1} for:



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

ii = 1. Pyr., 2. $(RO)_2PCl$, ether

	R	R^1	R^2
a	Me	H	Me
b	Et	Me	Me

SCHEME 2

- stretching vibrations of the P=O-group[9]—1230–1240 cm^{-1}
- stretching vibrations of the P—O—C-group[9]—band at 1030–1040 cm^{-1}, which for some of the products appears as doublet—970–980 cm^{-1};

3. retaining of the band for OH-group at 3360–3370 cm^{-1}, as well as the band for C—O-group (for the secondary alcohols, this band was overlapped from the band for the P—O—C-group).
4. disappearance of the bands for —O—$SiMe_3$.

In the ^1H NMR spectra of the end products there were signals for the protons of the alkyl- and alkoxy-groups as well as signals for the OH group.

The spectral investigations and the elemental analysis data show that the suggested mechanism of the discussed reaction is most probable.

According to the described procedure the previously unknown 1-hydroxy-1,2-alkadiene phosphonates were synthesized with good yields via a two-step reaction (Scheme 2).

EXPERIMENTAL

Starting Compounds

TMSCl and acetylenic diols were products of "Fluka," Switzerland. Dialkylchlorophosphites were synthesized from the corresponding alcohols and PCl_3, which were products of the same firm.

Synthesis of Monosylilated Acetylenic Alcohols 2a, b. General Procedure

In the temperature range of 0–5°C, the solution of TMSCl in benzene as a solvent was added for 30 min to a mixture of the corresponding acetylenic diol and pyridine in the same solvent and under continuous mixing. After the addition, the reaction mixture was heated to the boiling of the solvent, then the reaction mixture was left standing to reach room temperature; the precipitate of pyridine hydrochloid was filtered, the solvent evaporated under vacuum, and the residue distilled. Yield: 78–82%, b.p.: **2a**—77–79°C/1 mm Hg; **2b**—78–80°C/1 mm Hg.

Synthesis of Hydroxyalkadiene Phosphonates 3a, b. General Procedure

An equimolar quantity of pyridine was added to a solution of **2a,b** in ether for 15 min, then an equimolar quantity of the corresponding dialkylchlorophosphite was added to the reaction mixture during 1 h. The reaction mixture was left standing for 24 h; the precipitate was filtered, the solvent evaporated under vacuum, and the residue distilled. Yield: 75–80%, b.p.: **3a**—95–97°C/1 mm Hg; **3b**—98–100°C/1 mm Hg.

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