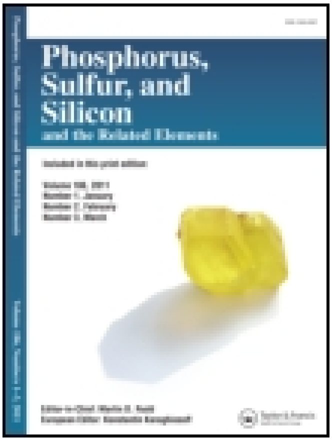

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A New Approach to 1-Substituted-1,2-Alkadiene-Phosphonates III: Synthesis of 2-Keto-5-Methyl-3,4 Hexadienyl-3-Phosphonate Dimethyl Esters

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A New Approach to 1-Substituted-1,2-Alkadiene-Phosphonates III: Synthesis of 2-Keto-5-Methyl-3,4-Hexadienyl-3-Phosphonate Dimethyl Esters

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The synthesis of the titled compounds have been discussed.

Keywords Acetylenic diols; allenephosphonates; Jones reagent

INTRODUCTION

The phosphorylated allenes, which are easily prepared via acetylen-allene rearrangement of acetylene phosphites,[1] contain a system of double bonds which provide an unusual character of their interactions with numerous electrophiles and nucleophiles.[1]

Numerous investigations show that allenephosphonates have to be taken in consideration as precursors for the synthesis of many interesting compounds, which preparations are restricted, to some extent, by using other approaches.[2–5]

On the other hand, the discovered oxaphospholic cyclization of the allenephosphonates in the reaction with electrophilic reagents gives cyclic compounds, in many cases with very interesting properties[6–8] from a practical point of view.

In this article, we report our results on the synthesis of different 1-keto-substituted derivatives using the acetylene-allene rearrangement of α-substituted acetylenic compounds.

RESULTS AND DISCUSSION

Continuing our investigations of the chemical behavior of 1-substituted 1,2-alkadienephosphonates, we successfully synthesized at C1

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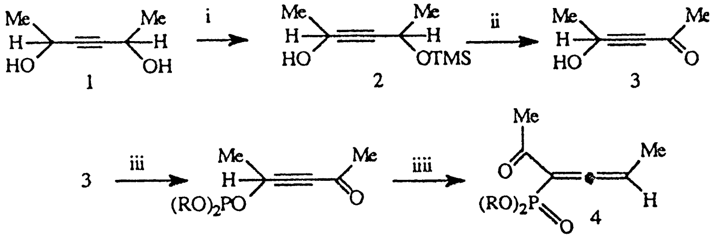
keto-substituted allenephosphonate derivatives. Using the procedure described earlier for the oxidation of the secondary silylated alcohols, we obtained α-keto acetylenic alcohols, which smoothly react with chlorophosphites to 1-keto-substituted-1,2-alkadienephosphonates. The reaction was carried out following the procedures described, involving in the first step a silylation of the secondary acetylenic diol, oxidation of the sylilated hydroxyl group using the Jones reagent[10] and interaction finally with dialkylchlorophosphites (see Experimental section). The reaction follows Scheme 1:



i = TMSCl, Pyr.,ether
ii = Johns reag.
iii = $(RO)_2PCl$, Pyr. ether
iiii = isomerization

SCHEME 1

Thus, new precursors for the synthesis of kumulatriene derivatives by the Wittig-Horner-Emmons reaction have been synthesized.

EXPERIMENTAL

Analytical Methods

^1H nmr spectra were determined on a Tesla BS(80 MHz) at normal temperature as $CDCl_3$ solution with TMS as an internal standard.

The IR spectra were recorded on an IR-72-spectrophotometer (Carl Zeiss Jena).

Starting Materials

The acetylenic diols are commercially available from Fluka, Switzerland.

1. Synthesis of Sylilated Acetylenic Diols

General Procedure. To a solution of the acetylenic diol and triethylamine in dry benzene an equimolar amount of TMSCI in the same

TABLE I Constants and Elemental Analysis Data for Compounds 2a–d

No.	R R^1	R^2	Yield (%)	Fond % P	Formula	Calcd. % P
2a	Me H	Me	85	15.12	$C_8H_{13}O_4P$	15.17
b	Et H	Me	87	13.25	$C_{10}H_{17}O_4P$	13.34
c	n-Pr H	Me	92	11.87	$C_{12}H_{21}O_4P$	11.9
d	i-Pr H	Me	95	11.88	$C_{12}H_{21}O_4P$	11.9

solvent was added dropwise. The resulting mixture was heated to 50°C and then allowed to reach room temperature. After filtration of the triethylaminehydrochloride and evaporation of the solvent, the residue was distilled. Yield 85–90%.

2. Oxidation of the Silylated Diols

General Procedure. To a solution of the silylated diol in acetone at 0°C a solution prepared from CrO_3H_20 and H_2SO_4 was added. After appropriate work-up (see references) the crude ketone was distilled. Yield 78–80%.

TABLE II ^{1}H-, ^{31}P and IR Spectral Data for Compounds 2a–d

				IR spectra (cm^{-1})	
No.	R(R^2)	R^1	^{31}p	C=O	P—O
2a	Me	0.67	16.8	1670	1235
	(Me)	1.34			
	H	5.02			
b	Et	CH3-0.98	17.4	1660	1230
		CH2-3.78			
	(Me)	1.34			
	H	5.02			
c	n-Pr	CH3-0.89	17.8	1665	1234
		CH2-3.77			
	(Me)	1.34			
	H	5.02			
d	i-Pr	CH3-0.90	18.4	1660	1225
		CH-0.65			
	(Me)	1.34			
	H	5.02			

3. Synthesis of 1-Ketosubstituted-1,2-alkadienephosphonates

General Procedure. To a solution of the ketone 3 in dry ether a solution of dialkylchlorophosphite and triethylamine was added dropwise at -10°C with stirring. After 24 hours the triethylamine hydrochloride was filtered off, the solvent was evaporaled, and the residue was distilled.

Yield 68–70%. The elemental analysis and spectroscopic date are given in Tables I and II.

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