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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; Jones reagent; allenephosphonates

INTRODUCTION

The phosphorylated allenes, which are easily prepared via acetylen-allene rearrangement of acetylene phosphites¹ contain a system of double bonds which provide unusual character of their interactions with numerous electrophiles and nucleophiles¹.

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.^{2-5,9}

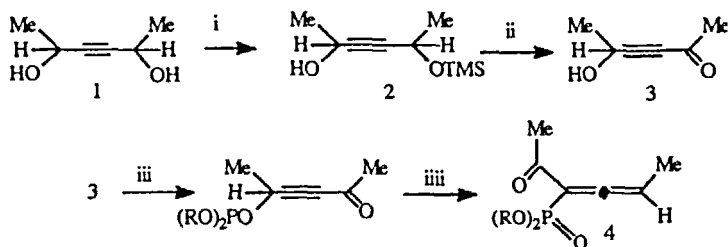
On the other hand the discovered oxaphospholic cyclization of the allenephosphonates in the reaction with electrophilic reagents, give cyclic compounds, in many cases with very interesting properties⁶⁻⁸ from practical point of view.

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In this paper 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 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 silylated hydroxyl group using the Jones reagent¹⁰ and interaction finally with dialkylchlorophosphites (see experimental). The reaction follows the scheme given below:



i= TMSCl, Pyr., ether

ii= Johns reagent

iii= $(RO)_2PCl$, Pyr. ether

iii= isomerization

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

EXPERIMENTAL

Analytical methods

¹H nmr spectra were determined on a Tesla BS(80MHz) at normal temperature as CDCl₃ 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

1. Synthesis of silylated acetylenic diols

General procedure

To a solution of the acetylenic diol and triethylamine in dry benzene an equimolar amount of TMSCl in the same 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 $\text{CrO}_3 \cdot \text{H}_2\text{O}$ and H_2SO_4 was added. After appropriate work-up (see references) the crude ketone was distilled.

Yield 78–80%.

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 evaporated and the residue was distilled.

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

TABLE I Constants and elemental analysis data for compounds 2a-d

<i>No</i>	<i>R R^I</i>	<i>R²</i>	<i>Yield(%)</i>	<i>Foond% P</i>	<i>Formula</i>	<i>Calcd.% P</i>
2a	Me H	Me	85	15.12	C ₈ H ₁₃ O ₄ P	15.17
b	Et H	Me	87	13.25	C ₁₀ H ₁₇ O ₄ P	13.34
c	n-Pr H	Me	92	11.87	C ₁₂ H ₂₁ O ₄ P	11.9
d	i-Pr H	Me	95	11.88	C ₁₂ H ₂₁ O ₄ P	11.9

TABLE II ¹H-, ³¹P and IR spectral data for compounds 2a-d

<i>No</i>	<i>R(R²)</i>	<i>R^I</i>	<i>³¹P</i>	<i>IR spectra (cm⁻¹)</i>	
				<i>C=O</i>	<i>P-O</i>
2a	Me	0.67	16.8	1670	1235
	(Me)	1.34			
	H	5.02			
b	Et	CH ₃ -0.98	17.4	1660	1230
		CH ₂ -3.78			
	(Me)	1.34			
	H	5.02			
c	n-Pr	CH ₃ -0.89	17.8	1665	1234
		CH ₂ -3.77			
	(Me)	1.34			
	H	5.02			
d	i-Pr	CH ₃ -0.90	18.4	1660	1225
		CH-0.65			
	(Me)	1.34			
	H	5.02			

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