Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 187-191
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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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(Received 26 November, 1997)

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 phosphites[1] contain a system of double bonds which provide 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 preparationsare restricted, to some extend, 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 properties[6–8] from practical point of view.

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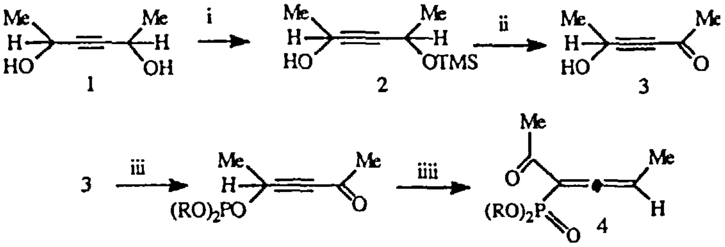
In this paper we report our results on the synthesis of different 1-keto-substituted derivatives using the acetylene-allene rearrangement of α- substituted acetylenic compounds

RESULTS AND DISCUSSION

Continuing our investigations of the chemical behavior of 1-substituted 1,2-alkadienephosphonates we successfully synthezised 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 sylilated hydroxyl group using the Jones reagent [10]and interaction finally with dialkylchlorophosphites (see experimental). The reaction follows the scheme given below:



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

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

EXPERIMENTAL

Analytical methods

^{1}H nmr spectra were determined on a Tesla BS(80MHz) 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

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 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%.

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.

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

No	$R\,R^1$	R^2	*Yield(%)*	*Foond% 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

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

No	$R(R^2)$	R^1	^{31}P	*IR spectra* (cm^{-1})	
				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			

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