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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

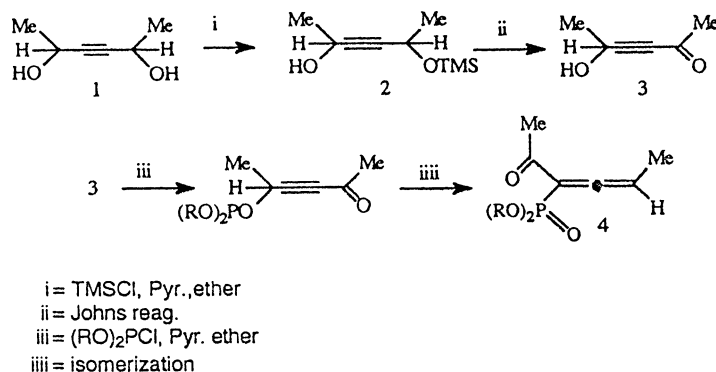
Continuing our investigations of the chemical behavior of 1-substituted 1,2-alkadienephosphonates, we successfully synthesized at C1

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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 silylated hydroxyl group using the Jones reagent¹⁰ and interaction finally with dialkylchlorophosphites (see Experimental section). The reaction follows Scheme 1:



SCHEME 1

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(80 MHz) 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, Switzerland.

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

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 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

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 CrO₃H₂O and H₂SO₄ was added. After appropriate work-up (see references) the crude ketone was distilled. Yield 78–80%.

TABLE II ¹H-, ³¹P 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 CH2-3.78	17.4	1660	1230
	(Me)	1.34			
	H	5.02			
c	n-Pr	CH3-0.89 CH2-3.77	17.8	1665	1234
	(Me)	1.34			
	H	5.02			
d	i-Pr	CH3-0.90 CH-0.65	18.4	1660	1225
	(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 evaporated, and the residue was distilled.

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

REFERENCES

- [1] V. Mark, In *Selective Organic Transformations*, B. S. Thyagarayan, Ed., New York: Wiley (1970), p. 319.
- [2] Ch. M. Angelov, *Phosphorus and Sulfur*, **15**, 177 (1983); CA: **99**, 53800m (1983).
- [3] Ch. M. Angelov and D. D. Enchev, *Phosphorus, Sulfur, and Silicon, and the Related Elements*, **37**, 125 (1988).
- [4] Ch. M. Angelov, and D. D. Enchev, *Phosphorus, Sulfur, and Silicon, and the Related Elements*, **34**, 163 (1988).
- [5] D. D. Enchev, Ch. M. Angelov, et al., *Phosphorus, Sulfur, and Silicon, and the Related Elements*, **57**, 249 (1991).
- [6] R. S. Macomber and G. A. Krudy, *J. Org. Chem.*, **48**, 1420 (1983).
- [7] L. Homer and V. Binder, *Phosphorus*, **1**, 17 (1971).
- [8] P. Cadot, W. Chodgfkiewicz, B. Borecka, C. Charier, and M.-P. Simmonian, *Chem. Abstr.*, **67**, 116923r (1967).
- [9] R. S. Macomber and T. C. Hemling, *Israel J. of Chemistry*, **26**, 136 (1985).
- [10] R. Baker, V. Bhaskar Rao, P. D. Ravenscroft, and C. J. Swain, *Synthesis*, 572 (1983).