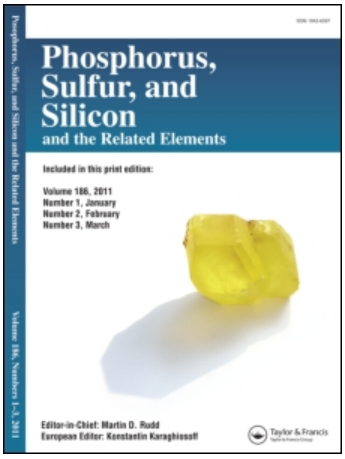

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Enchev, D. D. and Kirilov, M.(1998) 'NEW APPROACH TO 1-SUBSTITUTED-l,2-ALKADIENEPHOSPHONATES I', Phosphorus, Sulfur, and Silicon and the Related Elements, 141: 1, 1 — 8
To link to this Article: DOI: 10.1080/10426509808033716
URL: http://dx.doi.org/10.1080/10426509808033716

Phosphorus, Sulfur and Silicon, 1998, Vol. 141, pp. 1-8
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NEW APPROACH TO 1-SUBSTITUTED-1,2–ALKADIENEPHOSPHONATES I

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(Received 18 February, 1998)

The possibility of the substitution of the H atom at C1-position of the phosphorylated allenes with different kind of electrophiles have been discussed and evidence for the mechanism of the heterocyclization of allenephosphonates by the reaction with electrophilic reagents have been supplied. The new approach for synthesis of 1-substituted-1,2-alkadienephosphonates via acetylene-allene rearrangement of acetylenecarboxylic acid have been discussed

Keywords: Allenephosphonates; electrophilic reagents; heterocyclization; acetylenecarboxylic acid

INTRODUCTION

The C=C and C-H bond lengths in the allene chromophore exhibit only slight deviation from those for ethene. For example, in allene the C=C and C-H bond lengths are 1.309 and 1.061 A[1] compared to 1.337 and 1.086A in ethene[2]. All other data such as absorbtion maximums, PES ionization potentials and calculated HOMO and LUMO energies[3–8] indicate that the two orthogonal π-systems of an allene are virtually identical with the π-system of simple alkenes.

The introduction of different substituents onto allene chromophore results not only in a change in the energy of the π-system to which the substituent was attached but also affects the energy of the other π-system[9].

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In general, the introduction of an alkyl group raises the energy of both π-systems. The influence of an heterofunctional group depend on its electronic properties. The electron-donating groups raise the energy of $\pi_{1,2}$ and lower energy of $\pi_{1,2}$* -, $\pi_{2,3}$- and $\pi_{2,3}^{*}$ -MO's.

The electron withdrawing groups lower the energies of all the π-type MO's. These change in orbital energies are responsible for chemoselectivity and reactivity of substituted allenes.

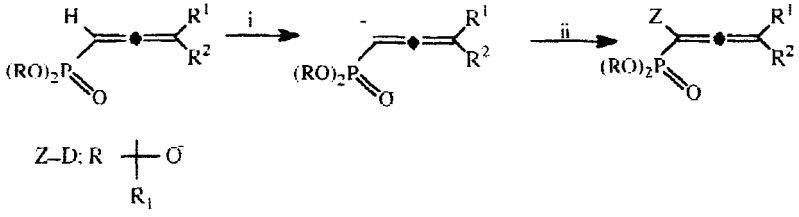
The electrophilc addition of a raagent ENu to allenic derivatives can occur as it does for simple alkenes stereospecifically (suprafacial or antarafacial)[10] and regioselectively with Markovnikov or anti-Markovnikov orientation.

The phosphorylated allenes, which are easily prepared via acetylene-allene rearrangement of acetylene phosphites[11] contain a system of double bonds which provide unusual character of their interactions with numerous electrophiles and nucleophiles.

Numerous inverstigations show, that allenephosphonates have to be taken in consideration as a source for synthesis of many interesting compounds, whose preparation are restricted, to some extent, by using other approaches.[12–15]

On the other hand the discovered oxaphospholic cyclization of the allenephosphonates in the reaction with electrophilic reagents, give the possibility for obtaining of number of cyclic compounds, in many cases with very interesting properties[16,17].

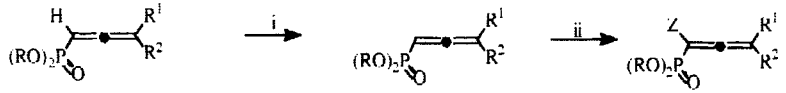
Macomber at al[18], show that the olefinic proton (sheme 1), at C1 atom from the allenephosphonate system is easily displaced in deuterium-exchange reaction and can be used in an Horner-Emmons approach for generation of an active phosphonate carbanion :



In this paper we report our results on the substitution reaction of the olephinic proton at C1-atom with S-containing electrophilic reagents and on the properties of the resulting 1-S-substituted-1, 2-alkadienephosphonates as well as a new approach to the title compounds using the acetylene-allene rearrangement of α-substituted acetylenic compounds.

RESULTS AND DISCUSSION

The 1-substituted-1,2-alkadienephosphonic esters are obtained in good yields by the reaction of 1,2-alkadienephosphonoic esters prepared by the procedure described earlier, with LDA and subsequent reaction with sulfenyl-,sulfinyl- and sulfonylchloride derivatives. The reaction is carried out in ether at −78°C for an hour, under argon atmosphere :



2a-c

i= LDA, -78°C, argon

ii= Z-Cl, -78°C to room temp., argon

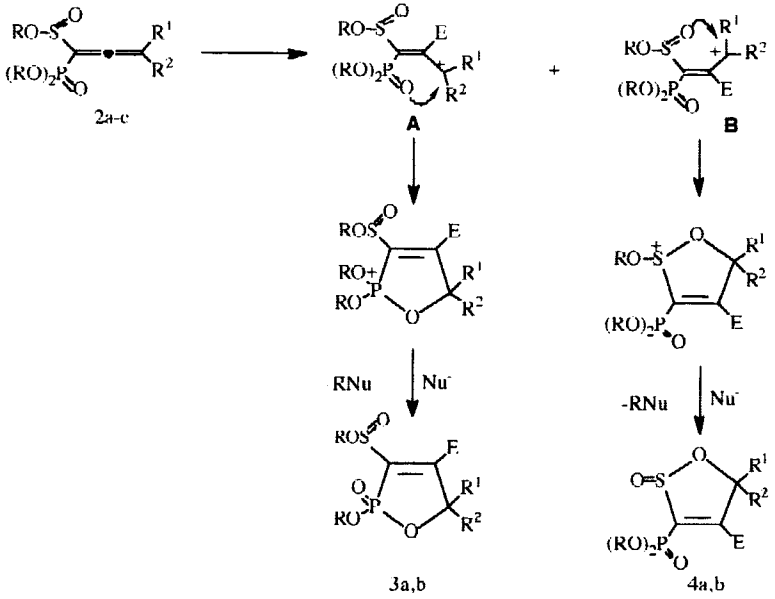
Z-Cl= MeSCl; MeS(O)Cl, MeOS(O)Cl

R=R¹=R²=Me

In the ^{1}H nmr spectra of the chromatografic purified compounds **2a-c** (see experimental is not observed the very characteristic signal for the olephinic proton at C1 -atom of the allenic system, which is in accordance with the data of Macomber *et al* by the deutheroexchange reactions of the same porton[18]. On the other hand the signals for all the other groups of protons are presented, especially the chemical shift for ^{31}P which is being in accordance with those for phosphorylated allenes (see table II). The comparison of the ^{1}H nmr spectra of the starting allenephosphonate with these of the end products confirmed the successful displacement reaction with S-containing electrophiles in this case and indicates the possibility for analogous reactions with the other electrophiles of this kind.

Our investigations give us the synthetic possibilities for preparation of a number of new 1-substituted alkadienephosphonates.

We have studied the isolated compounds in the reaction with chlorine at the conditions we usually used for the preparation of oxaphosphole derivatives in our previous investigations. The results we have obtained confirmed our suggestions that in this case the reactions follow two different pathways, which give two different products :



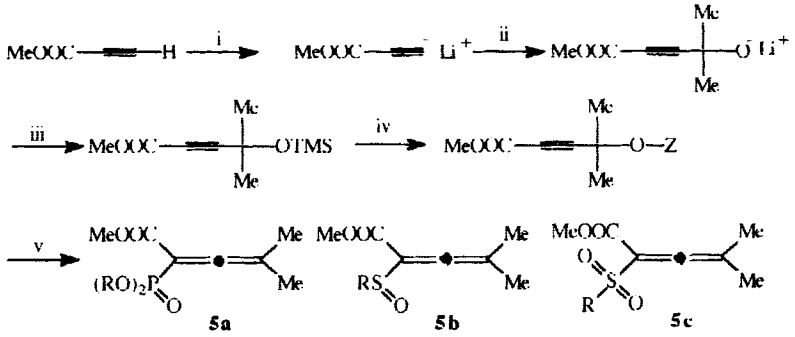
The spectral characteristics of the chromatographically purified products are given in table I. The ^{31}P nmr data are especially useful to recognize the two different products of cyclization. Thus in one step reaction we obtained two different products of cyclization which according to us is a direct evidence for the mechanism and stereochemistry of the reaction of the heterocyclization of the allenephosphonates by the reaction with electrophilic reagents.

The successful isolation of the compounds **3a,b** confirmed directly the mechanism of the electrophilic addition to allenephosphonate derivatives, because the formation of this two products is due to formation of two stereoisomeric ions **A** and **B**, by the attack of the electrophile on the C2-C3-double bond from both sides.

Continuing our investigation of the acetylene-allene rearrangement of α-substituted acetylene compounds as suitable precursors for synthesis of different king of phosphororganic compounds, we have successfully syn-

thesized phophorylated allenes substituted at C1 atom of the allene chromophore.

The 1-substituted-1,2-alkadienephosphonic esters are obtained in good yields by the reaction of acetylenecarboxylic acid methylester with ketones and subsequent treatment with dialkylchlorophosphites in THF at – 78°C and in an inert atmosphere. The S-containing substituents also can be introduced at C1 position using in the discussed reaction other chloro-containing reagents such as sulfenyl and sulfonylchlorides. The reactions follow the scheme :



i= BuLi, THF, -78°C
ii= Me_2C=O, THF, -78°C
iii= TMSCl, THF, -78°C to room temp.
a iv=Z= $(RO)_2PCl$, THF, -8 - -5°C
b iv=Z= RSCl, THF, -8 - -5°C
c iv=Z= RSOCl, THF, -8 - -5°C
v= isomerization

The ^{1}Hnmr spectra of the chromatografically pure compounds **5a-c** (see experimental) do not exhibit the very characteristic signal for the olephinic proton at C1-atom of the unsubstituted allenic system. On the other hand the signals for all the other groups of protons are presented. The chemical shift for ^{31}P being in accordance with those for phosphorylated allenes.

In the IR spectra of the end products the band of the allenic bond is observed instead the band for the acetylenic bond of the starting compounds. In the same way the sulfinate- and sulfonate derivatives are synthezised using (see experimental) at the second step of the reaction sulfenyl- and sulfonylchlorides.

TABLE I Constants and elemental analysis data for compounds **2a,b 3a,b** and **4a,b**

N	R	Yield(%)	Calcd.(%)			Formula	Found(%)		
			P	S	Cl		P	S	Cl
2a	Me	65	12.18	12.61	-	$C_8H_{15}O_5PS$	11.98	12.59	-
b	Me	72	11.46	11.86	-	$C_8H_{15}O_6PS$	11.39	11.78	-
3a	Me	84	11.27	11.67	12.91	$C_7H_{12}O_5ClPS$	11.19	11.58	12.89
b	Me	86	10.65	11.03	12.19	$C_7H_{12}O_6ClPS$	10.58	10.98	12.12
4a	Me	78	11.27	11.67	12.91	$C_7H_{12}O_5ClPS$	11.2	11.59	12.88
b	Me	76	10.65	11.03	12.19	$C_7H_{12}O_6ClPS$	10.57	10.97	12.09

EXPERIMENTAL

Analytical methods

^1H nmrspectra 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.

1. Synthesis of the 1-substituted-1,2-alkadienephosphonates

General procedure

To a solution of appropriates dialkyl ester of 3-methyl-1,2-butadienephosphonic acid in THF at −78°C and inert atmosphere a equimolar solution of LDA in the same solvent was added. After 15min stirring a solution of equimolar ammount of methylsulphenyl-, methylsuphinyl-, and methylsulphonylchloride was added at the same conditions. The reaction mixture was allowed warm up to room temperature. After standart work-up the crude products are purified by column chromatography (50g silicagel benzene/haptane).

Yield 65–70%.

2. Interaction of 1-substitured-1,2-alkadienephosphonates with chlorine

General procedure

To a solution of the compounds **2a-c** in methylenechloride at -8 to -5°C a equimolar solution of chlorine in the same solvent was added dropwise for an hour. The reaction mixture was stirring an additional hour at the same conditions, the solvent was removed under reduced pressure and the products were purified by HTLC.

Yield 78–80%.

3. Synthesis of 1-carboxymethyl-3-methyl-1,2-butadienephosphonates 5a

General procedure

To a solution of the acetylenecarboxylic acid methyl ester in THF at −78°C and stirring under argon a solution of equimolar ammount of BuLi at the same solution was added. Then an equimolar ammount of dimethylketone in the same solvent at the same conditions was added, followed by treatment of the reaction mixture with TMSCI. The purified 3-silyloxy-3-methyl-1-bityncarboxylic acid methyl ester was treated with an equimolar ammount of corresponding dialkylchlorophosphite in THF and at −8 to −5°C under argon. The crude products are purified by column chromatography.

5a Yield% 78, Found% P13.18 $C_9H_{15}O_5PCacld.\%$ P13.22; ^{1}H-nmr (ppm) 1.34, 1.7 (2Me); ^{31}P 16.8, IRcm^{-1}1235$_{\nu P=O}$, 1956$_{\nu C-C-C}$, 1000$_{\nu P-O-C}$, 1700$_{\nu C-O}$

4. Synthesis of 1-carboxymethyl-3-methyl-1,2-butadienesulfinates 5b and 1-carboxymethyl-3-methyl-1,2-butadienesulfonates 5c

General procedure

The procedure was identical as described above exept the second step in which to the solution of a 3-silyloxy-3-methyl-1-butyncarboxylic acid methyl ester the solutions of the corresponding sulphenyl- and sulphonylchlorides were added.

5b Yield% 76; Found% S 15.89 $C_8H_{12}O_4S$Calcd.% S 15.96; ^{1}H-nmr (ppm)1.72, 1.7(2Me);, IRcm^{-1} $1030_{\nu S=O}$, $1960_{\nu C-C-C}$,$769_{\nu S-O-C}$ $1700_{\nu C=O}$

5c Yield% 74; Found% S 14.52 $C_8H_{12}O_5S$Calcd.% S 14.55; ^{1}H-nmr (ppm) 1.43, 1.7(2Me);, IRcm^{-1}$1420_{\nu SO2}$, $1965_{\nu C-C-C}$, $890_{\nu S-O-C}$$1700_{\nu C=O}$

The physical data are summarized in Tables I and II.

TABLE II ^{1}H-, ^{31}P-nmr and IR spectral data for compounds **2a,b, 3a,b, 4a,b**

	Chemical shift ppm		*IR cm-1*			
N	*R(R1)*	*^{31}P*	*P=O*	*C=C=C*	*S=C*	*C=C*
2a	Me(Me) CH_3-1.34(1.7)	16.8	1235	1950	1120	-
b	Me(Me) CH_3-1.72(1.7)	16.48	1234	1954	1300	-
3a	Me(Me) CH_3-1.86(1.7)	29.8	1235	-	1125	1578
b	Me(Me) CH_3-1.9(1.7)	30.2	1236	-	1300	1586
4a	Me(Me) CH_3-2.44(1.7)	16.34	1235	-	-	1574
b	Me(Me) CH_3-2.34(1.7)	16.95	1235	-	-	1576

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