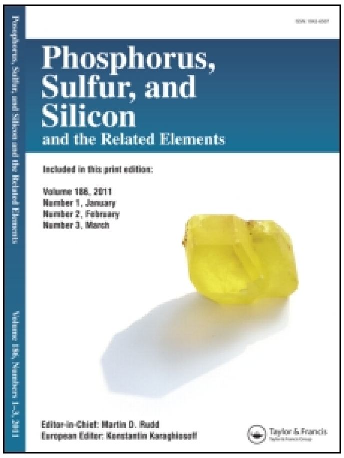

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A New Approach to 1-Substituted-1,2Alkadienephosphonates I

D. D. Enchev[a]; M. Kirilov[b]
[a] Department of Organic Chemistry, K. Preslavski University, Shoumen, Bulgaria [b] Department of Organic Chemistry, Kl. Ohridski University, Sofia, Bulgaria

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A New Approach to 1-Substituted-1,2-Alkadienephosphonates I

D. D. Enchev
Department of Organic Chemistry, K. Preslavski University,
Shoumen, Bulgaria

M. Kirilov
Department of Organic Chemistry, Kl. Ohridski University,
Sofia, Bulgaria

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

Keywords Allenephosphonates; acetylenecarboxylic acid; electrophilic reagents; heterocyclization

INTRODUCTION

The C=C and C—H bond lengths in the allene chromophore exibit only slight deviation from those for ethane. For example, in the 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 absorption maximums, photoelectron spectroscopy (PES) ionization potentials, and calculated higher occupied molecule orbitals (HOMO) and lower unoccupied molecule orbitals (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 the allene chromophore results not only in change in the energy of the π-system to

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Address correspondence to D. D. Enchev, K. Preslavski University, Department of Organic Chemistry, Faculty of Chemistry, 9700 Shoumen, Bulgaria. E-mail: rector@shu-bg.net

which the substituent was attached but also affects the energy of the other π-system.[9]

In general, the introduction of an alkyl group raises the energy of both π-systems. The influence of a heterofunctional group depends 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 $\pi_{2,3}{}^*$-molecule orbitals (MO's).

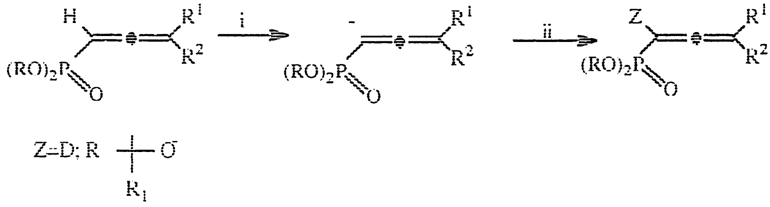
The electron-withdrawing groups lower the energies of all the p-type MO's. These changes in orbital energies are responsible for chemoselectivity and reactivity of the substituted allenes.

The electrophilic addition of a reagent 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 phosphates,[11] contain a system of double bonds which provide an unusual character of their interactions with numerous electrophiles and nucleophiles.

Numerous investigations show that allenephosphonates have to be taken in consideration as a source for the 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 et al.,[18] show the olefinic proton (Scheme 1) at the C1 atom from the allenephosphonate system, easily is displaced in deuterium-exchange reactions and can be used in a Horner-Emmons approach for the generation of an active phosphonate carbanion:

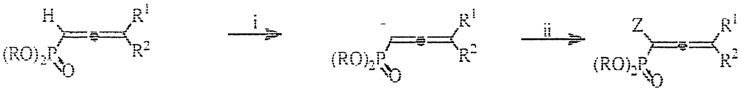


SCHEME 1

In this article, we report our results on the substitution reaction of the olephinic proton at the 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-alkadienephosphonic esters, prepared by the procedure described earlier with LDA and subsequent reactions with sulphenyl-, sulfinyl-, and sulfonylchloride derivatives. The reaction is carried out in ether at −78°C for 1 h under argon atmosphere (Scheme 2):



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

SCHEME 2

In the ^{1}H-nmr spectra of the chromatographic-purified compounds **2a–c** (see Experimental Section) the very characteristic signal for the olephinic proton at the C1-atom of the allenic system, which is in accordance with the data of Macomber et al.[18]

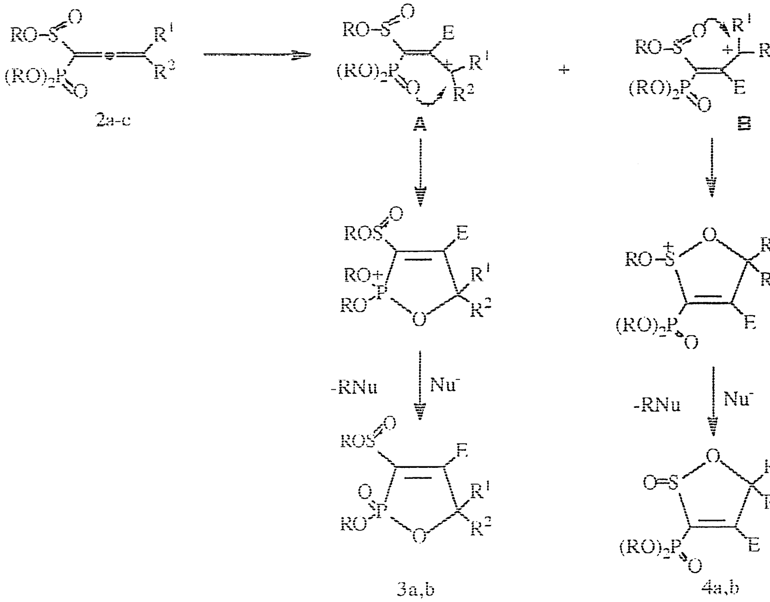
However, the signals for all the other groups of protons are presented, especially the chemical shift for ^{31}P, which is being in accordance with those for phosphorylated allenes (see Table I). The comparison of the ^{1}H nmr spectra of the starting allenephosphonate with those of the end products 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.

TABLE I ^{1}H-, ^{31}P-NMR and IR Spectral Data for Compounds 2a,b, 3a,b, and 4a,b

Chemical shift ppm		IR cm^{-1}				
N	R(R1)	^{31}P	P=O	C=C=C	S=O	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

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

We have studied the isolated compounds in the reactions with chlorine at the conditions we usually used for the preparation of oxaphosphole derivatives in our previous investigations. The results confirmed our suggestions that, in this case, the reactions follow two different pathways, which give two different products (Scheme 3):



SCHEME 3

The spectral characteristics of the chromatographically purified products are given in Table II. The ^{31}P NMR data are especially useful to recognize the two different products of cyclization. Thus, in a one-step reaction, we obtained two different products of cyclization, which, according to us, is 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** directly confirmed the mechanism of the electrophilic addition to allenephosphonate derivatives because the formation of these two products is due to the formation two stereoisomeric ions, **A** and **B**, by the attack of the electrophile on the C2- C3-double bond from its two sides.

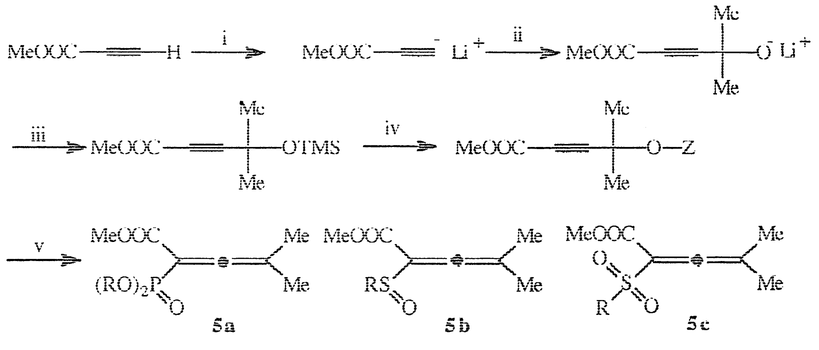
As we continue our investigation of the acetylene-allene rearrangement of α-substituted acetylene compounds as suitable precursors for

TABLE II Constants and Elemental Analysis Data for Compounds 2a,b, 3a,b, and 4a,b

			Calod. (%)				Found (%)		
N	R	Yield (%)	P	S	Cl	Formula	P	S	Cl
2a	Mo	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	81	11.27	11.67	12.91	$C_7H_{12}O_5CIPS$	11.19	11.58	12.89
b	Me	86	10.65	11.03	12.19	$C_7H_{12}O_6CIPS$	10.58	10.98	12.12
4a	Me	78	11.27	11.67	12.91	$C_7H_{12}O_5CIPS$	11.2	11.59	12.58
b	Me	76	10.65	11.03	12.19	$C_7H_{12}O_6CIPS$	10.57	10.97	12.09

the synthesis of different kinds of phosphororganic compounds, we have successfully synthesized phosphorylated allenes, substituted at the 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 the subsequent treatment with dialkylchlorophosphites in THF at −78°C and in an inert atmosphere. The S-containing substituents also can be introduced at the C1 position using in the discussed reaction of other chloro-containing reagents such as sulphenyl- and sulfonylchlorides. The reaction follow Scheme 4:



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

SCHEME 4

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

In the IR spectra of the end products, the band of the allenic bonds is observed instead of the band for the acetylenic bond of the starting compounds. In the same way, the sulfinate and sulfonate derivatives are synthesized, using at the second step of the reaction of sulphenyl- and sulfonylchlorides as regents (see Experimental section).

EXPERIMENTAL

Analytical Methods

^{1}H NMR spectra were determined on a Tesla BS(80 MHz) at normal temperature as a $CDCl_3$ solution with trimethylislane (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 appropriate dialkyl ester of 3-methyl-1,2-butadienephosphonic acid in THF at −78°C and inert atmosphere an equimolar solution of lithium diisopropylamine (LDA) in the same solvent was added. After 15 min of stirring, a solution of equimolar amount of methylsulphenyl-, methylsulphinyl-, and methylsulphonylchloride was added at the same conditions. The reaction mixture was allowed to warm up to room temperature. After standard work-up, the crude products were purified by column chromatography (50 g silicagel benzene/heptane). Yield 65–70%.

2. Interaction of 1-Substituted-1,2-alkadienephosphonates with Chlorine

General Procedure

To a solution of the compounds **2a–c** in methylenechloride at −8 to −5°C an equimolar solution of chlorine in the same solvent was added dropwise for 1 h. The reaction mixture was stirring for 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 2a

General Procedure

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

5a, Yield 78%, Found % P 13.18, $C_9H_{15}O_5P$, Calcd. % P 13.22; ^{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 2b and 1-carboxymethyl-3-methyl-1,2-butadienesulfonates 2c

General Procedure

The procedure was identical as described above except the second step in which 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.

REFERENCES

[1] J. Overend and B. Crawford, Jr., *J. Chem. Phys.*, **29,** 1002 (1958).
[2] H. C. Allen and E. K. Plyer, *J. Am. Chem. Soc.*, **80,** 2673 (1958).
[3] L. H. Suitcliffe and A. D. Walsh, *J. Chem. Soc.*, 849 (1952).
[4] P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23,** 1895 (1955).
[5] F. Brogli, J. K. Crandall, E. Heilbronner, E. Kloster-Jensen, and S. A. Sojka, *J. Electron. Spectroscop. Relat. Phenom.*, **2,** 455 (1973).
[6] C. C. Baker and D. W. Turner, *J. Chem. Soc. D*, 480 (1969).
[7] D. J. Pasto, *J. Am. Chem. Soc.*, **101,** 37 (1979).
[8] D. J. Pasto, *Tetrahedron*, **40,** 2805 (1984).

[9] V. Smadija, *Chem. Rev.*, **83,** 263 (1983).
[10] V. Mark, In *Selective Organic Transformations*, B. S. Thyagarayan, Ed., pp. 319. New York: Willey, 1970.
[11] Ch. M. Angelov, *Phosphorus and Sulfur*, **15,** 177 (1983); CA, **99,** 53800 m (1983).
[12] Ch. M. Angelov and D. D. Enchev, *Phosphorus and Sulfur*, **37,** 125 (1988).
[13] Ch. M. Angelov and D. D. Enchev, *Phosphorus and Sulfur*, **34,** 163 (1988).
[14] D. D. Enchev, Ch. M. Angelov, E. Krawchik, A. Skowronska, and J. Michalski, *Phosphorus, Sulfur and Silicon*, **57,** 249 (1991).
[15] Ch. M. Angelov, M. Kirilov, and B. I. Ionin, *Zh. Obshch. Khim.*, **49,** 1960 (1979).
[16] Ch. M. Angelov, T. S. Mikhailova, V. M. Ignatiev, A. V. Dogadina, and B. I. Ionin, *Compt. Rend. Bulg. Acad. Sci.*, **32,** 619 (1979).
[17] Ch. M. Angelov and Ch. Zh. Christov, *Compt. Rend. Bulg. Acad. Sci.*, **36,** 1559 (1983).
[18] R. S. Macomber and T. C. Hemling, *Israel J. of Chem.*, **26,** 136 (1985).