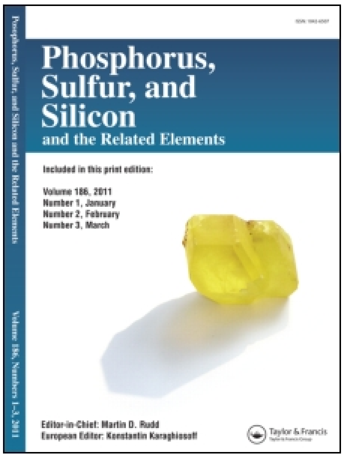

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,2-ALKADIENEPHOSPHONIC AMIDOESTERS AND THEIR OXAPHOSPHOLIC CYCLIZATION IN REACTION WITH ELECTROPHILIC REAGENTS

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To cite this Article Angelov, Christo M. and Enchev, Dobromir D.(1987) '1,2-ALKADIENEPHOSPHONIC AMIDOESTERS AND THEIR OXAPHOSPHOLIC CYCLIZATION IN REACTION WITH ELECTROPHILIC REAGENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 34: 3, 163 — 168

To link to this Article: DOI: 10.1080/03086648708074321

URL: http://dx.doi.org/10.1080/03086648708074321

Phosphorus and Sulfur, 1987, Vol. 34, pp. 163–168
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1,2-ALKADIENEPHOSPHONIC AMIDOESTERS AND THEIR OXAPHOSPHOLIC CYCLIZATION IN REACTION WITH ELECTROPHILIC REAGENTS

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(Received March 31, 1987)

By the reaction of 1,2-alkadienephosphonic dichlorides with dialkylamines and aliphatic alcohols, the 1,2-alkadienephosphonic amidoesters **2a–k** have been prepared. The synthesized 1,2-alkadienephosphonates **2a–k** have been cyclized in reactions with different electrophiles. The obtained 2,5-dihydro-1,2-oxaphosphole derivatives are characterized by spectral data and elemental analyses.

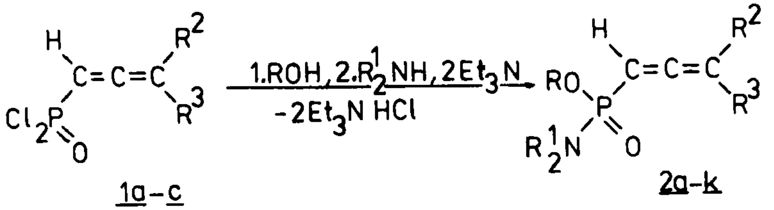
INTRODUCTION

The phosphorylated allenes, which are easily prepared via acetylene-allene rearrangement of acetylene phosphites,[1] contain an interesting system of double bonds (O=P—C=C=C); their unusual chemical behavior in reactions with other reagents soon attracted the attention of organophosphorus chemists. Improved synthetic methods for 1,2-alkadienephosphonic derivatives[2–4] contributed to the discovery of the heterocyclization of these compounds in electrophilic reactions at the beginning of the 1970s.[5]

The oxaphospholic cyclization of allene phosphororganic compounds is studied in the reaction of 1,2-alkadienephosphonic acids, and their diesters and dichlorides. This reaction, however, is not investigated for the amidoesters of substituted allenephosphonic acids, which until our investigations, were not published in the literature. In the present work, using the method described by A. A. Petrov and co-workers[6] for the preparation of 1,2-alkadienephosphonic dichlorides, we successfully obtained a few amidoesters and studied their cyclization in reaction with halogens, sulfenyl-, and selenenylchlorides.

RESULTS AND DISCUSSION

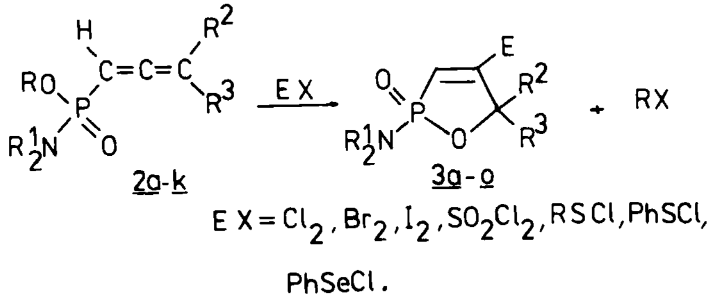
The 1,2-alkadienephosphonic amidoesters are obtained in high yield (72–85%) by substitution of two chlorine atoms in corresponding dichloride with aliphatic alcohol and secondary amine in the presence of triethylamine. The reaction is carried out in ether at −10 to −8°C in one hour:



SCHEME 1

The ^{1}H NMR spectra of the isolated and vacuum distilled allenephosphonates exhibited signals of protons at C-1 and two groups of signals for alkoxy and dialkylamino groups. The chemical shift of ^{31}P corresponds to phosphorylated allenes (16.7 to 18.2 ppm). The data from elemental analysis confirm the structure of the obtained compounds (Table I).

The amidoesters isolated by us in preparative amounts allowed us to study their chemical behavior in the reaction with halogens, sulfenyl-, and selenenyl chlorides. We established that irrespective of the electrophile, 4-substituted-2N,N-dialkylamido-2,5-dihydro-1,2-oxaphosphole 2-oxides are isolated in high yields (72–86%) in all cases.



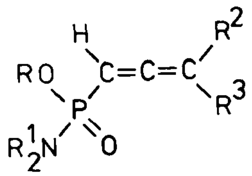
SCHEME 2

Comparison of ^{1}H NMR spectra of starting phosphonates with those of the end products shows that during the reaction, a five-membered heterocyclization of allenephosphonic system of double bonds occurs. Thus, in the spectrum of **2b**, a doublet is observed at 3.87 ppm for the methoxy group and signals at 2.99 ppm and 1.00 ppm for the protons of the diethylamino group. After chlorination of **2a**, the signals for the protons from the methoxy group vanish and at the same time the signals for the protons of the diethylamino group are observed again, which is direct confirmation of the fact that in the second step of the reaction, the heterocyclization proceeds via intramolecular rearrangement of the Arbuzov type. Moreover after cyclization the chemical shift of ^{31}P appears at lower field (27.9 to 32.3 ppm) which correlated with the results obtained earlier.[7–9] The obtained amido derivatives of 2,5-dihydro-1,2-oxaphosphole 2-oxides are colorless crystals with a definite melting point (Tables II and III).

The successful five-membered cyclization of 1,2-alkadienephosphonic amidoesters with electrophilic reagents allowed us to synthesize new amido derivates of 2,5-dihydro-1,2-oxaphosphole.

TABLE I

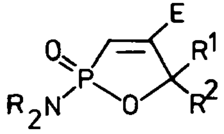
IR spectra, Yields, Physical Constants and Elemental Analysis of 1,2-Alkadienephosphonates **2a–k**



No.	R (R^1)	R^2 (R^3)	IR spectra, cm^{-1} P=O	C=C=C	P—O—R	Yield (%)	b.p. (°C/mm Hg)	n_D^{20}	Found % P (N)	Formula	Calcd. % P (N)
1	2	3	4	5	6	7	8	9	10	11	12
2a	Me (Et)	Me (Me)	1225	1957	900	75	136–8/0.5	1.4250	14.42 (5.93)	$C_{10}H_{20}NO_2P$	14.25 (6.40)
b	Et (Et)	Me (Me)	1230	1959	1004	82	138–40/0.5	1.4740	13.26 (5.89)	$C_{11}H_{22}NO_2P$	13.39 (6.00)
c	Pr^i (ET)	Me (Me)	1230	1960	1000	76	139–41/0.5	1.4950	12.45 (5.70)	$C_{12}H_{24}NO_2P$	12.62 (6.58)
d	Me (Et)	$(CH_2)_5$	1248	1966	1003	80	148–50/0.5	1.4925	11.99 (5.03)	$C_{13}H_{24}NO_2P$	12.03 (5.44)
e	Et (Et)	$(CH_2)_5$	1235	1959	1000	77	149–51/0.5	1.4969	11.28 (5.08)	$C_{14}H_{26}NO_2P$	11.41 (5.10)
2f	Pr^i (Et)	$(CH_2)_5$	1240	1987	1000	85	150–2/0.5	1.4939	10.53 (4.76)	$C_{15}H_{28}NO_2P$	10.85 (4.90)
g	Me (Pr^i)	Me (Me)	1235	1967	1004	82	125–7/0.5	1.4860	12.53 (5.98)	$C_{12}H_{24}NO_2P$	12.62 (6.58)
h	Pr^i (Pr^i)	Me (Me)	1225	1984	1002	79	126–8/0.5	1.4760	11.02 (4.89)	$C_{14}H_{28}NO_2P$	11.33 (5.12)
i	Me (Pr^i)	$(CH_2)_5$	1230	1978	1000	76	129–30/0.5	1.5345	10.62 (4.85)	$C_{15}H_{28}NO_2P$	10.85 (4.90)
k	Pr^i (Pr^i)	$(CH_2)_5$	1225	1980	900	78	135–7/0.5	1.5099	9.63 (4.25)	$C_{17}H_{32}NO_2P$	9.88 (4.46)

TABLE II

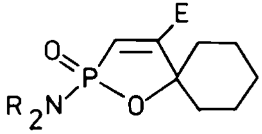
IR spectra, Yields, m.p., and Elemental Analysis data of 2,5-Dihydro-1,2-oxaphospholes **3a–g** (R^1 = Me)



No.	E (R^2)	Ir spectra, cm^{-1} P═O	C═C	P—O—C	Yield (%)	m.p. (°C)	Found, % P (N)	Halogen (S)	Formula	Calculated, % P (N)	Halogen (S)
1	2	3	4	5	6	7	8	9	10	11	12
3a	Cl (Et)	1225	1589	1003	85	85–88	13.02 (5.54)	14.67 (—)	$C_9H_{17}ClNo_2P$	13.31 (5.88)	14.91 (—)
b	Br (Et)	1230	1590	1000	77	74–75	10.94 (4.81)	27.99 (—)	$C_6H_{17}BrNO_2P$	11.05 (4.99)	28.52 (—)
c	SMe (Et)	1234	1587	1002	87	87–89	12.10 (5.23)	— (13.45)	$C_{10}H_{20}NO_2PS$	12.43 (5.61)	— (13.66)
d	Cl (Pr^i)	1225	1586	1004	72	93–95	11.24 (5.10)	12.98 (—)	$C_{11}H_{21}ClNO_2P$	11.65 (5.26)	13.34 (—)
e	Br (Pr^i)	1230	1580	1000	79	98–100	9.79 (4.25)	26.59 (—)	$C_{11}H_{21}BrNO_2P$	9.98 (4.51)	27.76 (—)
f	I (Pr^i)	1225	1578	1004	81	100–103	8.33 (3.55)	— (—)	$C_{11}H_{21}INO_2P$	8.67 (3.91)	— (—)
3	SPh (Pr^i)	1230	1590	1000	84	105–107	9.31 (4.05)	— (9.87)	$C_{17}H_{26}NO_2PS$	9.45 (4.27)	9.81 (9.81)

TABLE III

IR spectra, Yields, m.p. and Elemental Analysis of Spirocompounds **4a–g**



No.	E R	IR-spectra, cm^{-1} P=O	C=C	P—O—C	Yield, (%)	m.p. (°C)	Found, % P (N)	Halogen (S)	Formula	Calculated, % P (N)	Halogen (S)
1	2	3	4	5	6	7	8	9	10	11	12
4a	Cl (Et)	1236	1590	1000	76	88–90	11.00 (4.98)	12.45 (—)	$C_{12}H_{21}ClNO_2P$	11.15 (5.04)	12.76 (—)
b	Br (Et)	1225	1589	1004	86	99–100	9.52 (4.28)	24.66 (—)	$C_{12}H_{21}BrNO_2P$	9.61 (4.34)	24.80 (—)
c	SPh (Et)	1225	1588	1000	85	89–90	8.79 (3.56)	— (9.05)	$C_{18}H_{26}NO_2PS$	8.81 (3.98)	— (9.12)
d	I (Et)	1230	1598	990	79	104–106	6.69 (3.10)	— (—)	$C_{12}H_{21}INO_2P$	6.94 (3.13)	— (—)
e	Cl (Pr^i)	1235	1580	1000	80	99–100	9.87 (4.33)	11.28 (—)	$C_{14}H_{25}ClNO_2P$	10.12 (4.57)	11.59 (—)
f	Br (Pr^i)	1225	1578	1002	81	100–102	8.69 (3.53)	22.69 (—)	$C_{14}H_{25}BrNO_2P$	8.84 (3.99)	22.82 (—)
4g	SePh (Et)	1235	1589	990	85	98–100	9.93 (4.35)	— (—)	$C_{18}H_{26}NO_2PS$	10.40 (4.76)	— (—)

EXPERIMENTAL

Methods of analysis. ^{1}H NMR and ^{31}P NMR spectra were determined on a Tesla BS 487 B (100 MHz) spectrometer 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, GDR).

Starting materials. The 1,2-alkadienephosphonic dichlorides were prepared by the method described in the literature.[6] The methyl- and phenylsulfenyl chlorides were prepared from the corresponding disulfides and chlorine in CCl_4. The phenylselenenylchloride was prepared in the same way.

Synthesis of N,N-dialkylamido-O-alkyl-3-methyl-1,2-butadienephosphonates and N,N-dialkylamido-O-alkyl-2-(1-cyclohexenyl)ethenephosphonates **2a–k**. *General procedure.* To 0.1 mole 1,2-alkadienephosphonic dichloride dissolved in 300 ml anhydrous ether at −10 to −8°C and continuously stirred were added a mixture of 0.1 mole aliphatic alcohol and 0.1 mole triethylamine dissolved in 50 ml ether and then a mixture of 0.1 mole dialkylamine and 0.1 mole triethylamine in 50 ml of the same solvent while stirring continuously. The reaction mixture was stirred for an hour at the same temperature. Then the precipitate was filtered off, the ether was removed using a water aspirator, and the cresidue was distilled twice in vacuum. Yield 72–85%. ^{1}H NMR spectra: **2a** 5.04 d (1 H, $^2J_{HP}$ 7.5 Hz), 1.68 d (6 H); **2b** 5.04 d (1 H, $^2J_{HP}$ 7.0 Hz), 1.68 d (6 H); **2d** 5.16 d (1 H, $^2J_{HP}$ 6.7 Hz), 1.60 (4 H), 2.60 (6 H); **2e** 5.02 d (1 H, $^2J_{HP}$ 6.8 Hz), 1.55 (4 H), 2.14 (6 H). ^{31}P NMR spectra: **2a** 18.2; **2b** 17.1; **2d** 16.8; **2e** 16.7.

Sythesis of 2-N,N-dialkylamido-2,5-dihydro-1,2-oxaphosphole 2-oxides **3a–o**. *General procedure.* A solution of 0.05 mole of electrophilic reagent (Cl_2, Br_2, I_2, SO_2Cl_2, RSCl, PhSCl, PhSeCl) in anhydrous 1,2-$C_2H_4Cl_2$ or $CHCl_3$ was slowly added, with stirring, at −5 to 0°C, to a solution of 0.05 mole of N,N-dialkylamido-O-alkyl-3-methyl-1,2-butadienephosphonate or N,N-dialkylamido-O-alkyl-2-(1-cyclohexenyl)ethenephosphonate in the same solvent. After stirring the reaction mixture for an hour, the solvent is removed. The residue was recrystallized from heptane. Yield 72–86%. ^{1}H NMR spectra δ: **3a** 5.88 d (1 H, $^2J_{HP}$ 24.2 Hz), 1.40 s (3 H), 1.58 s (3 H); **3f** 5.88 d (1 H, $^2J_{HP}$ 22.4 Hz), 1.70 m (6 H); **3g** 6.08 d (1 H, $^2J_{HP}$ 22.3 Hz), 1.72 m (6 H); **3k** 5.87 d (1 H, $^2J_{HP}$ 23.5 Hz), 1.72 m (6 H). ^{31}P NMR spectra δ: **3a** 28.3, **3f** 27.9, **3g** 28.8, **3k** 32.3.

ACKNOWLEDGEMENT

The authors are indebted to Prof. B. I. Ionin and Dr. A. V. Dogadina (Leningrad Technological Institute, Leningrad, USSR) for ^{1}H and ^{31}P NMR spectra.

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