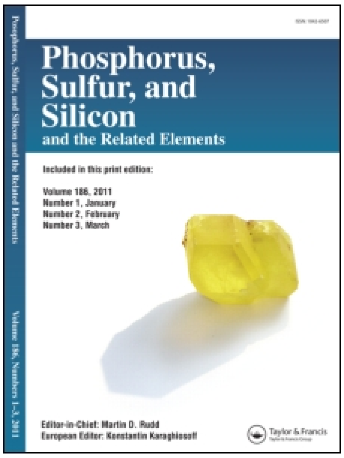


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

HETEROCYCLIZATION OF 1,2,4- AND 1,3,4-ALKATRIENYLPHOSPHONIC DICHLORIDES WITH ELECTROPHILIC REAGENTS

Christo M. Angelov[a]; Dobromir D. Enchev[a]; M. Kirilov[b]
[a] Department of Chemistry, Higher Pedagogical Institute, Shoumen, Bulgaria [b] Department of Organic Chemistry, Faculty of Chemistry, Sofia University, Sofia, Bulgaria

To cite this Article Angelov, Christo M. , Enchev, Dobromir D. and Kirilov, M.(1988) 'HETEROCYCLIZATION OF 1,2,4-AND 1,3,4-ALKATRIENYLPHOSPHONIC DICHLORIDES WITH ELECTROPHILIC REAGENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 35: 1, 35 — 39

To link to this Article: DOI: 10.1080/03086648808079361

URL: http://dx.doi.org/10.1080/03086648808079361

Phosphorus and Sulfur, 1988, Vol. 35, pp. 35–39
Photocopying permitted by license only

HETEROCYCLIZATION OF 1,2,4- AND 1,3,4-ALKATRIENYLPHOSPHONIC DICHLORIDES WITH ELECTROPHILIC REAGENTS

CHRISTO M. ANGELOV,† DOBROMIR D. ENCHEV and M. KIRILOV‡

† Department of Chemistry, Higher Pedagogical Institute, 9700 Shoumen Bulgaria
‡ Department of Organic Chemistry, Faculty of Chemistry, Sofia University, 1000 Sofia, Bulgaria

(Received February 3, 1987; in final form April 2, 1987)

By the reaction of 1,2,4- and 1,3,4-alkatrienylphosphonic dichlorides with sulfuryl, sulfenyl and selenenyl chlorides, the different P-containing heterocyclic compounds have been prepared. The obtained heterocycles contained one or two chorine atoms at phosphorus which have great reactivity and can change with another functional groups.

INTRODUCTION

In the past several years the reaction of 1,2,4- and 1,3,4-alkatrienylphosphonic dialkyl esters, i.e. esters of 3- and 1-vinylsubstituted allenylphosphonic acids, respectively with electrophilic and nucleophilic reagents[1–9] were intensively studied. These compounds are of great interest owing to the presence of both the 1,2- and 1,3-dienic fragment in their triene system of double bonds, as well as, phosphonate group whose influence on the reaction considerably depends on its position in the system. We have recently found[1–4,6–8] that depending on the nature of the reagents the reaction of above phosphonic esters with electrophiles lead to a variety of products—2,5-dihydro-1,2-oxaphosphole 2-oxides, P-containing thiophenes and selenophenes, and adducts.

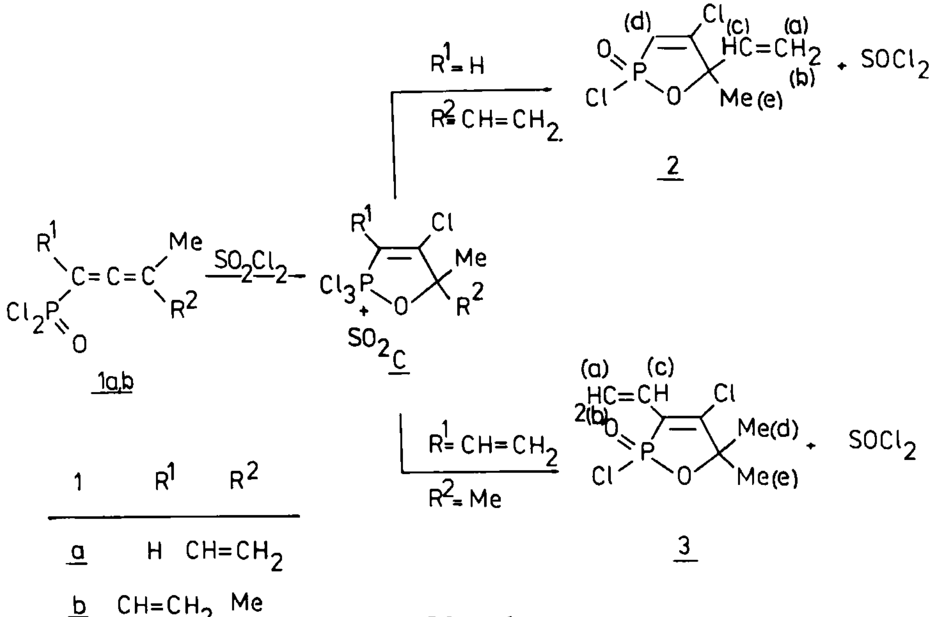
Now we report the results of our further investigations in this field.

We have studied the interaction of 3-methyl-1,2,4-pentatrienyl-1- and 5-methyl-1,3,4-hexatrienyl-3-phosphonic dichlorides **1a** and **1b** with some electrophilic reagents.

RESULTS AND DISCUSSION

The reaction of the dichlorides **1a** and **1b** with sulfuryl, sulfenyl selenenyl chlorides and with sulfur dioxide were carried out in dry tetrachlormethane at low temperature. The reaction of **1a** and **1b** with SO_2Cl_2 proceeds in analogous manner to that of the corresponding esters,[1,4,7] i.e. with participation of the 1,2-dienic fragment of the trienic system of double bonds and P=O group as an inner nucleophile, affording 3- and 5-vinylsubstituted 2,5-dihydro-1,2-

oxaphosphole 2-oxides **2** and **3**, respectively:

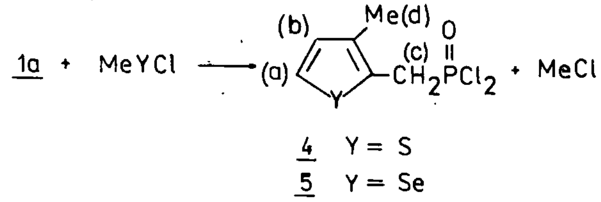


Scheme 1.

The formation of a cyclic intermediate *C* with phosphorane structure could be supposed as in the case of the corresponding esters.[1,4] Such an intermediate was obtained by other authors[10] in the reaction of **1b** with chlorine, which slowly undergoes dehydrochalogenation affording conjugated alkatrienylphosphonate. In our case, however, the generated sulfur dioxide immediately reacts with the trichlorphosphorane group which transferes into chlorphosphoryl group stabilizing in this way the cyclic structure in the end products.

Unlike of the above alkatrienylphosphonic dialkyl esters[11,12] the dichlorides **1a** and **1b** do not react with sulfur dioxide. This is probably due to the lowered reactivity of the 1,3-dienic fragment of **1a** and **1b** caused by the stronger electron-withdrawing effect of $P(O)Cl_2$ in comparison with $P(O)(OR)_2$ group, thus making the reactivity of **1a** and **1b** unsufficient for 1,4-cycloaddition reaction with weak electrophiles as SO_2. Analogous results have been obtained by the reaction of the same reagent with 1,3-alkadienes containing other electron-withdrawing groups.[13-15]

With methylsulfenyl and methylselenenyl chlorides, the trienylphosphonates **1a** and **1b** react in different ways. The dichloride **1a** participates in the reaction with both reagents with its 1,3-dienic part, heterocyclization takes place analogous to the case of the corresponding esters:[2,6]



Scheme 2.

TABLE I

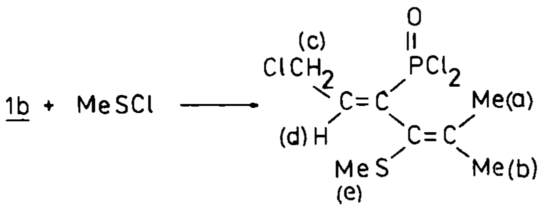
^{1}H NMR and IR spectral data of the compounds **2–7**

	Chemical shift			Coupling const., J Hz			
No.	Ha (Hb)	Hc (Hd)	He	Ha-Hb (Ha-P)	Ha-Hc (Hb-P)	Hb-Hc (Hc-P)	Hc-Hd (Hd-P)
2	5.37d	5.88d	1.70s	—	10.2	17.0	—
	(5.44d)	(6.42d)		(–)	(–)	(–)	(28.2)
3	5.66ddd	6.52ddd	1.67s	—	11.6	17.8	—
	(5.95ddd)	(1.65s)		(2.8)	(1.8)	(28.4)	(–)
4	7.08dd	3.96d	—	5.0	—	—	—
	(6.70dd)	(2.16d)		(0.8)	(1.0)	(15.0)	(–)
5	7.76dd	4.06d	—	5.2	—	—	—
	(6.99dd)	(2.16d)		(0.8)	(1.2)	(16.2)	(–)
6	1.74d	4.00dd	2.06s	—	—	—	7.2
	(2.04d)	(6.91dt)		(5.3)	(7.0)	(2.6)	(25.6)
7	7.60dd	3.92q	—	4.8	—	—	5.8
	(7.27dd)	(1.26d)		(2.8)	(3.8)	(–)	(–)

IR Spectra, cm^{-1}: 1262–1285 (P=O), 1585–1590 (C=C, for **2** and **3**), 1608–1625 (CH=CH$_2$), 1595, 1620 (C=C—C=C, for **6**).

In this way 3-methyl-2-thenylphosphonic and 3-methyl-2-selenophenmethanphosphonic dichlorides **4** and **5** were prepared.

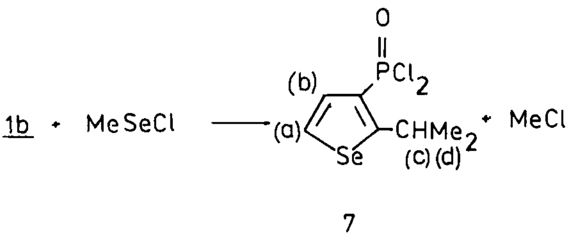
The dichloride **1b** react also with 1,3-dienic part of double bonds but unlike **1a** it gives with methylsulfenyl chloride an 1,4-addition product **6**:



6

Scheme 3.

With methylselenenyl chloride, on the contrary, five-membered heterocyclization takes place yielding 2-isopropyl-3- selenophenphosphonic dichloride **7**:



7

Scheme 4.

The structure of the compounds **2–7** was confirmed by IR- and ^{1}H NMR spectra (see table). The spectral characteristics of **2–7** are analogous to these of the corresponding esters[1–4,6–10] containing alkoxy groups at phosphorus.

EXPERIMENTAL

Analytical Methods. The ^{1}H NMR spectra were measured at the normal probe temperature on Jeol JNM-PS-10 spectrometer at 100 MHz using TMS as internal reference. The IR spectra were run on a IR-72 spectrophotometer (Carl Zeiss Jena GDR).

Starting Materials. The dichlorides **1a** and **1b** were prepared according to the procedure described.[16] Methylsulfenyl and methylselenenyl chlorides prepared from the corresponding disulfide or diselenide and chlorine in tetrachlomethane and used without purification.

1. *2,4-Dichloro-5-methyl-5-ethenyl-2,5-dihydro-1,2-oxaphosphole 2-oxide* **2**. To a solution of 10.4 g (0.05 mole) 3-methyl-1,2,4-pentatrienyl-1-phosphonic dichloride **1a** in 50 ml CCl_4, 6.8 g (0.05 mole) SO_2Cl_2 in 10 ml of the same solvent was added at $-5 \div 0$°C. After 1 h the solvent was distilled off under reduced pressure and the residue distilled in vacuum. Yield 8.5 g (80%). b.p. 95–98°C (0.5 Torr), n_D^{20} 1.5022. $C_6H_7Cl_2O_2P$. Calcd. %: P 14.54, Cl 33.22; Found %: P 14.32, Cl 32.95.

2. *2,4-Dichloro-5,5-dimethyl-3-ethenyl-2,5-dihydro-1,2-oxaphosphole 2-oxide* **3**. Prepared by analogous manner from 10.55 g (0.05 mole) 5-methyl-1,3,4-hexatrienyl-3-phosphonic dichloride **1b** and 6.8 g (0.05 mole) SO_2Cl_2. Yield 9.42 g (83%), b.p. 98–100°C (0.5 Torr), n_D^{20} 1.5139. $C_7H_9Cl_2O_2P$. Calcd. %: P 13.64, Cl 31.23: Found %: P 13.49, Cl 30.99.

3. *3-Methyl-2-thenylphosphonic dichloride* **4**. To 10.4 g (0.05 mole) 3-methyl-1,2,4-pentatrienyl-1-phosphonic dichloride **1a** in 50 ml CCl_4 a solution of 4.1 g (0.05) mole) methylsulfenyl chloride in 20 ml of the same solvent was added for 1 h at $-12 \div -10$°C. The solvent then was distilled off under reduced pressure and the residue was distilled in vacuum. Yield 6.76 g (53%), b.p. 141–43°C (1.0 Torr), n_D^{20} 1.5365. $C_6H_7Cl_2OPS$. Calcd. %: P 13.52, Cl 30.65, S 14.03; Found %: P 13.33, Cl 30.67, S 13.98.

4. *3-Methyl-2-selenophenemethanphosphonic dichloride* **5**. Analogously to the procedure in (3) from 10.4 g (0.05 mole) of 3-methyl-1,2,4-pentatrienyl-1-phosphonic dichloride **1a** and 6.74 g (0.05 mole) methylselenenyl chloride. Yield 8.94 g (57%), b.p. 145–46°C (1.0 Torr), n_D^{20} 1.5689. $C_6H_7Cl_2OPSe$. Calcd. %: P 11.22, Cl 25.69; Found %: P 10.98, Cl 25.38.

5. *1-Chloro-5-methyl-4-methylthio-2,4-pentadienyl-3-phosphonic dichloride* **6**. By analogous manner as in (3) from 10.55 g (0.05 mole) 5-methyl-1,3,4-hexatrienyl-3-phosphonic dichloride **1b** and 4.1 g (0.05 mole) MeSCl. Yield 7.49 g (51%), b.p. 144–46°C (1.0 Torr), n_D^{20} 1.5403. $C_8H_{12}Cl_2OPS$. Calcd. %: P 10.62, Cl 36.47, S 10.99; Found %: P 10.25, Cl 36.33, S 10.72.

6. *2-Isopropyl-3-selenophenphosphonic dichloride* **7**. Prepared by the procedure described in (3) from 10.55 g (0.05 mole) 5-methyl-1,3,4-hexatrienyl-3-phosphonic dichloride **1b** and 6.74 g (0.05 mole) MeSeCl. Yield 7.12 g (52%), b.p. 145–47°C (1.0 Torr). n_D^{20} 1.5630. $C_7H_9Cl_2OPSe$. Calcd. %: P 10.68, Cl 24.45; Found %: P 10.43, Cl 23.98.

REFERENCES

1. Ch. M. Angelov, M. Kirilov, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **49,** 2225 (1979).
2. Ch. M. Angelov, M. Kirilov, K. V. Vachkov and S. L. Spassov, *Tetrahedron Letters,* **21,** 3507 (1980).
3. Ch. M. Angelov and K. V. Vachkov, *Tetrahedron Letters,* **22,** 2517 (1981).
4. Ch. M. Angelov, N. M. Stojanov and B. I. Ionin, *Zh. Obshch. Khim.*, **52,** 178 (1982).
5. Yu. M. Dangian, G. A. Panosian, M. G. Voskonian and Sh. O. Badanian, *Zh. Obshch. Khim.*, **53,** 61 (1983).
6. Ch. M. Angelov and Ch. Zh. Christov, *Phosphorus and Sulfur,* **15,** 373 (1983).
7. Ch. M. Angelov and Ch. Zh. Christov, *Synthesis,* 664 (1984).
8. Ch. N. Tancheva, Ch. M. Angelov and D. M. Mondeshka, *Heterocycles,* **23,** 843 (1985).
9. Yu. M. Dangian, M. R. Tirakian, G. A. Panosian and Sh. O. Badanian, *Zh. Obshch. Khim.*, **55,** 1631 (1985).
10. V. K. Brel', B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **51,** 2625 (1981).
11. Ch. M. Angelov and D. D. Enchev, *Phosphorus and Sulfur,* **19,** 155 (1984).
12. D. D. Enchev, Ch. M. Angelov and M. Kirilov, in press.

13. S. D. Turk and R. L. Cobb, In: 1,4-Cycloaddition reaction, Ed., J. Hamer, New York, Acad. Press, 1967, pp. 13–45.
14. O. Grummitt and F. J. Christoph, *J. Am. Chem. Soc.*, **73,** 3479 (1951).
15. H. J. Backer, J. Strating and C. N. Kool, *Rec. trav. chim.*, **58,** 778 (1939).
16. Ch. M. Angelov, M. Kirilov and B. I. Ionin, *Zh. Obshch, Khim.*, **49,** 1960 (1979).