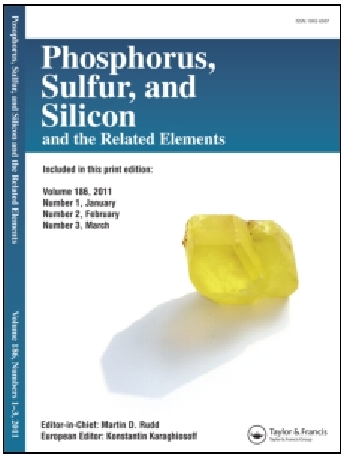

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Christo M. Angelov[a]; Dobromir D. Enchev[a]
[a] Department of Chemistry, Higher Pedagogical Institute, Shoumen, Bulgaria

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HETEROCYCLIC PHOSPHONIUM SALTS BY REACTION OF DIMETHYL(1,2-ALKADIENYL)-PHOSPHINE OXIDES WITH ELECTROPHILIC REAGENTS

CHRISTO M. ANGELOV and DOBROMIR D. ENCHEV
Department of Chemistry, Higher Pedagogical Institute, 9700, Shoumen, Bulgaria.

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Salts of 2,5-dihydro-1,2-oxaphosphole have been prepared by reaction of dimethyl(1,2-alkadienyl)phosphine oxides with halogens, sulfenyl and selenenyl chlorides. The essential influence of tertiary carbenium ions for realization of oxaphospholic cyclization of phosphorylated allenes has been established.

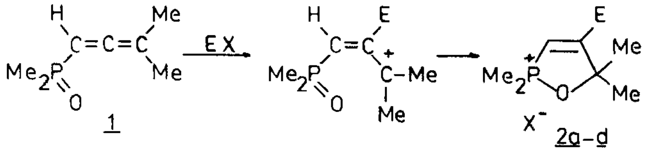
INTRODUCTION

In the past 10 years the heterocyclization of phosphorylated allenes by reaction with electrophilic reagents is studied mainly at 1,2-alkadienylphosphonic dialkyl esters and dichlorides.[1]

The detailed investigation of this reaction shows that in many cases together with oxaphospholes, 1,2- and 2,3-adducts are obtained as well.[2–4] In the literature there is scant information on the chemical behaviour of tertiary allene phosphine oxides when treated with electrophiles.[5,6] In the present paper we describe the results from interacting of dimethyl(3-methyl-1,2-butadienyl)phosphine oxide with halogens, sulfenyl and selenyl chlorides and of dimethyl(1,2-hexadienyl)-phosphine oxide with chlorine.

RESULTS AND DISCUSSION

Bromine and iodine as well as methylsulfenyl and methylselenenyl chloride with phosphine oxide **1** give cyclic phosphonium salts in good yields:



EX = Br_2, I_2, RSCl, RSeCl.

SCHEME 1

The salts **2a–d** are air-stable powders which are soluble in water and insoluble in nonpolar solvents. Upon heating the compounds **2a–d** decompose. The ^{31}P chemical shift is typical that of phosphonium salts (Table I). The formation of

^1H, ^{31}P NMR and IR spectral data of 2,5-dihydro-1,2-oxaphosphonium salts **2a–d**

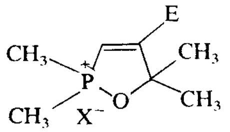


TABLE I

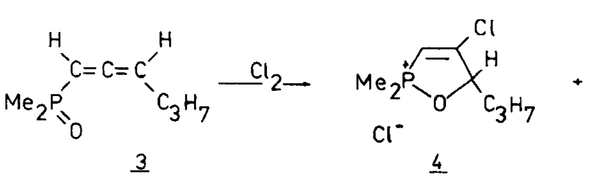
No	E	X	Chemical shift, ^{31}P	H	Me_2P	Me_2C	Coupling constant, J Hz H—P	Me—P	IR spectra, cm^{-1} C=C	P—O—C
2a	Br	Br	107.1	6.35d	1.86s	1.34s	33.6	15.6	1550	950
b	I	I	107.1	6.48d	1.92s	1.38s	32.4	15.4	1545	990
c	MeS	Cl	—	6.50d	2.44s	1.60s	31.2	15.6	1520	980
d	MeSe	Cl	—	6.22d	2.42s	1.72s	36.0	15.8	1575	990

Yields and analysis data of salts **2a–d**

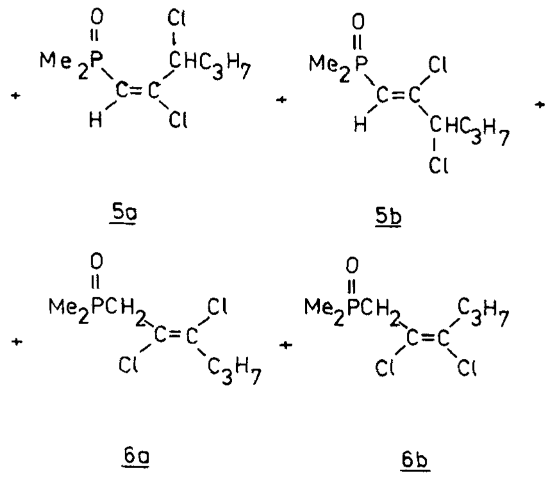
No	Yield (%)	Found, % P	Cl	Br	S	Formula	Calculated, % P	Cl	Br	S
2a	87	9.98	—	52.36	—	$C_7H_{13}Br_2OP$	10.17	—	52.57	—
b	85	7.54	—	—	—	$C_7H_{13}I_2OP$	7.78	—	—	—
c	90	13.12	15.35	—	13.98	$C_8H_{16}ClOPS$	13.66	15.63	—	14.14
d	87	10.99	12.74	—	—	$C_8H_{16}ClOPSe$	11.31	12.95	—	—

cyclic salts only in the cases where MeSCl is used as reagent is a result which differs from that obtained in the reaction of 3,3-disubstituted allenephosphonic dialkyl esters with the same reagent. In the last case, together with cyclic esters, the 1,2- and 2,3-adducts are obtained as well.[2,3]

The high chemo-, regio- and stereoselectivity of the reaction of tertiary allenic phosphine oxide **1** with electrophiles is probably due to the influence of the +I-effect of the methyl groups at the P-atom (increase of the nucleophility of phosphorylic O-atom) and in C-3 of allenic system of double bonds (a formation of stable carbenium ion as intermediate of the reaction). The isolation of cyclic phosphonium salts with excellent yields is an indirect proof for the formation of a tertiary carbenium ion as intermediate in the reaction. A confirmation for this assumption is the fact that chlorination of dimethyl(1,2-hexadienyl)phosphine oxide which proceeds through a secondary carbenium ion leads to the formation of mainly 2,3-adducts and products of their further 1,3-sigmatropic rearrangement. The heterocyclic salt is obtained in only 10% yield:



SCHEME 2



5a 5b 6a 6b

SCHEME 2 (continued)

The formation of the products mentioned in scheme 2 is seen well in the ^{1}H-NMR spectrum of the reaction mixture. The different groups of signals are similar to the signals in spectra of the mixtures obtained in the reaction of 3-monosubstituted allenephosphonic dialkyl esters with electrophilic reagents.[7]

The experimental results obtained in the present work confirm again the essential role of tertiary carbenium ion for the successful passing of the heterocyclization of phosphorylated allenes, which allowed provisions to be made for carrying out a purposeful synthesis for preparation of 2,5-dihydro-1,2-oxaphosphole derivatives.

EXPERIMENTAL

Methods of Analysis. ^{1}H NMR and ^{31}P NMR spectra were determined on Jeol PS 10 and FX-90 Q spectrometers at normal temperature as solution in $CDCl_3$ with TMS as internal standard. The IR spectra were recorded on a spectrophotometer IR-72 (Carl Zeiss Jena, GDR).

Starting Materials. The methylsulfenyl and selenenyl chlorides were prepared from the corresponding disulfide and diselenide and chlorine in CCl_4.

Preparation of dimethyl(1,2-alkadienyl)phosphine oxides. General Procedure.[8] To a solution of 0.1 mole 1,2-alkadienylphosphonic dichloride in 100 ml dry ether was added dropwise a Grignard reagent of 0.2 mole Mg and 0.2 mole CH_3I under cooling ($-30 \div -20$°C). The complex with saturated solution of NH_4Cl at $-20 \sim -18$°C was dissociated and the ether solution was separated. The residue was extracted with $CHCl_3$ and both solutions were united and dried over $MgSO_4$ for 24 h. After removing the solvents the residue was distilled under vacuum. Yield 30%.

Synthesis of heterocyclic phosphonium salts. General Procedure. To 0.02 mole dimethyl(1,2-alkadienyl)phosphine oxide dissolved in 50 ml CCl_4 at $-5 \sim 0$°C were added dropwise with stirring 0.02 mole electrophilic reagent (Br_2, I_2, MeSCl and MeSeCl) dissolved in the same solvent. The obtained precipitate within an hour was filtered and dried in vacuum. Yield 85–90%.

In the case of dimethyl(1,2-hexadienyl)phosphine oxide used as starting material and the reaction with chlorine a complex reaction mixture was obtained containing about 10% cyclic product, as well as 2,3-adducts and further 1,3-sigmatropic rearranged products. ^{1}H NMR spectra: **4** 7.26 d (1H, $^2J_{HP}$ 29.0 Hz); **5a** 5.93 dd (1H, $^2J_{HP}$ 13.2 Hz), 4.46 m (1H); **5b** 6.38 d (1H, $^2J_{HP}$ 11.2 Hz), 5.28 m (1H); **6a** 3.34 d (2H, $^2J_{HP}$ 16.0 Hz); **6b** 2.32 d (2H, $^2J_{HP}$ 14.4 Hz).

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