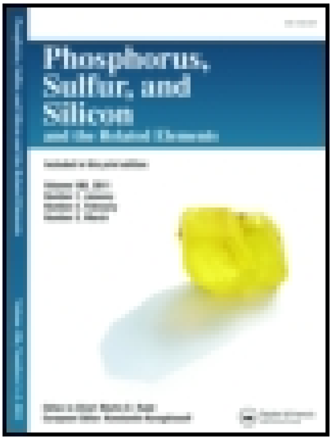

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ARYLOXY DERIVATIVES OF 3-METHYL-1,2-BUTADIENEPHOSPHONIC ACID AND THEIR OXAPHOSPHOLIC CYCLIZATION IN THE REACTIONS WITH ELECTROPHILIC REAGENTS

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ARYLOXY DERIVATIVES OF 3-METHYL-1,2-BUTADIENEPHOSPHONIC ACID AND THEIR OXAPHOSPHOLIC CYCLIZATION IN THE REACTIONS WITH ELECTROPHILIC REAGENTS

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The preparation of aryloxy derivatives of 3-methyl-1,2-butadienephosphonic acid and their reactions with electrophilic reagents are investigated.

Keywords: 3-methyl-1;2-butadienephosphonates; electrophilic reagents

INTRODUCTION

In the past several years the oxaphospholic cyclization of the allenephosphonates, which are easily prepared by the acetylene-allene rearrangement of acetylene phosphites[1], have been investigated[2–5]. The results of this investigations show that oxaphospholic derivatives were detected as major product and/or as one of the products of the reaction of the allenephosphonates with electrophilic reagents. The amount of the obtained cyclic products depends on the possibilities of the electrophile to supply electrons for formation of an "onium" intermediate in this reaction. The stability of this "onium" intermediate depends on tree main factors:

1. The kind of electrophile—its electronegativity, electron affinity, ionization potential and covalent radius;
2. The kind of the solvent.

3. The kind of substituents in the electrophile[alkyl(aryl)sulfenyl- and selenylhalogenides] and the value of substitution at the allene system.

In this paper we describe our results of the synthesis of some new derivatives of 3-methyl-1,2-butadienephosphonic acid and their interaction with electrophilic reagents.

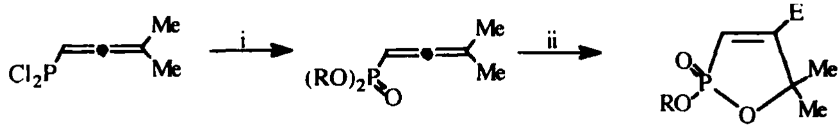
RESULTS AND DISCUSSION

The aryloxy derivatives of the 3-methyl-1,2-butadienephosphonic acid were prepared from the corresponding dichloride of the same acid and aromatic alcohols in presence of organic base by an earlier described procedure, improved by us.[6–8]

The products of the reaction were washed with hexane/benzene and purified by column chromatography(see experimental).

The isolated and purified compounds were investigated in the reactions with electrophilic reagents. Our results show that irrespectively from the nature of the electrophile 4-substituted-2-aryloxy-2-oxo-2,5-dihydro-1,2-oxaphosphole 2-oxides were formed in good yields:

- 2 -



1 2a,b 3a-d 4a-d

i - ROH,Pyr, -5- 0°C, ether
ii - E, -10°C - room tempr., dichlorethane
E= Cl_2, Br_2, I_2, MeSCl, PhSCl

Comparison of the ^{1}H-nmr spectra of the starting aryloxy derivatives of the 3-methyl-1,2-butadienephophonic acid with the spectra of the end products shows that during the reaction a five-membered cyclization of the allenephosphonate system of double bonds takes place. The ^{1}H nmr spectra of the end products exhibit signals at 5.65 to 6.62 ppm for the proton, connected with the C4 atom from the oxaphosphole ring as well as signals for the other groups of protons. Moreover the chemical shift for ^{31}P of the end products (27.9 to 32.3) correlated to our previous results and confirmed that the oxaphospholic cyclization of the allene-phosphonate systems of double bonds take place. The successful isolation of the cyclic oxaphosphole derivatives in this reaction shows that the kind of the ester group at phosphorus does not have an influence on the direction of the reaction.

EXPERIMENTAL

Analytical Methods

^1H nmr spectra were determined on a Tesla BS(80MHz) at normal temperature as $CDCl_3$ solution with TMS as an internal standart.

The IR spectra were recorded on an IR-72-spectrophotometer (Carl Zeiss Jena)

Starting Materials

The 1,2-butadienphosphonic dichloride was prepared by the procedure described earlier. The methyl- and phenylsulfenyl chlorides were prepared from corresponding disulfides and chlorine in CCl_4.

Synthesis of 3-Methyl-1,2-butadienephosphonic acid diarylesters 2a,b. General Procedure

To 0.1 mol of 3-methyl-1,2-butadienephosphonic dichloride dissolved in 300ml. of anhydrous diethyl ether at −10 to −8°C and continuously stirred a mixture of 0.2 mol of appropriate aromatic alcohol and 0.2 mol of pyridine at the same solvent were added dropwise in one hour. The reaction mixture was stirred for an additional hour. The precipitate was filtered off, the solvent was evaporated and the residue was purified by chromatography(50g silicagel, benzene/hexane). Yield 87–89%.

Synthesis of 4-Substituted-2-aryloxy-2-oxo-2,5-dihydro-1,2-oxaphosphol 2-oxides 3a–e and 4a–e. General Procedure

A solution of 0.05 mol of the corresponding electrophile (see tables) in anhydrous 1,2-$C_2H_4Cl_2$ was slowly added, with stirring at −5–0°C to a solution of 0.05 mol of the 3-methyl-1,2-butadienephosphonate diaryl esters at the same solvent. After stirring the reaction mixture for one hour, the solvent was re-

TABLE I IR spectra, Yields, Physical Constants and Elemental Analysis for 2,5-dihydro-1,2-oxaphosphole 2-oxides 3a–e and 4a–e

No	*R*	*E*	*IR spectra, cm − 1*			*Yield*	*m.p.(b.p.)*	*Found%(Calcd.%)*			*Formula*
			P=O	*C=C*	*P-O-R*	*(%)*	*°C*	*P*	*Hal*	*S*	
3a	$PhCH_2$	Cl	1235	1589	1004	85	oil	10.96 (11.3)	12.89 (13.00)		$C_{12}H_{14}O_3PCl$
b	$PhCH_2$	Br	1230	1590	1000	87	oil	9.65 (9.76)	25.18 (25.19)		$C_{12}H_{14}O_3PBr$
c	$PhCH_2$	I	1234	1587	1002	86	125–7	8.38 (8.50)	34.78 (34.85)		$C_{12}H_{14}O_3PI$
d	$PhCH_2$	MeS	1225	1586	1004	78	oil	10.76 (10.89)		11.23 (11.27)	$C_{13}H_{17}O_3PS$
e	$PhCH_2$	PhS	1230	1580	1000	76	oil	8.79 (8.94)		9.22 (9.25)	$C_{18}H_{19}O_3PS$
4a	$Ph(CH_2)_2$	Cl	1236	1590	1000	82	oil	10.75 (10.80)	12.33 (12.36)		$C_{13}H_{16}O_3PCl$
b	$Ph(CH_2)_2$	Br	1225	1589	1004	77	oil	9.28 (9.35)	24.10 (24.13)		$C_{13}H_{16}O_3PBr$
c	$Ph(CH_2)_2$	I	1225	1588	1000	78	132–4	8.12m (8.19)	33.52 (33.56)		$C_{13}H_{16}O_3PI$
d	$Ph(CH_2)_2$	MeS	1230	1589	990	87	oil	10.29 (10.38)		10.69 (1074)	$C_{14}H_{19}O_3PS$
e	$Ph(CH_2)_2$	PhS	1235	1580	1000	89	oil	8.50 (8.59)		8.87 (8.59)	$C_{19}H_{21}O_3PS$

TABLE II NMR data for 2,5-dihydro-1,2-oxaphosphole 2-oxides 3a-d and 4a-d

		Chemical shift				*Coupl. const., JHz*
No	*R*	*H*	*R*	*Me*	^{31}P	*H-P*
3a	$PhCH_2$	6.47	7.75		33.09	35.54
			CH_2-4.13	1.68		
b	$PhCH_2$	6.45	7.7		33	22.79
			CH_2-4.12	1.68		
c	$PhCH_2$	6.48	7.8		34.12	27.09
			CH_2-4.15	1.68		
d	$PhCH_2$	6.45	7.7		33.7	24.05
			CH_2-4.11	1.68		
4a	$PhCH_2CH_2$	6.47	7.75		33.09	25.23
			CH_2-4.13	1.68		
			CH_2-4.35			
b	$PhCH_2CH_2$	6.45	7.7	1.68	33.12	22.67
			CH_2-4.12			
			CH_2-4.34			
c	$PhCH_2CH_2$	6.48	7.8		33.23	26.12
			CH_2-4.15	1.68		
			CH_2-4.32			
d	$PhCH_2CH_2$	6.45	7.7		33.67	24.03
			CH_2-4.11	1.68		
			CH_2-4.35			

moved. The residue was purified by chromatography (50 g silicagel, benzene/hexane). In the case of iodine as electrophile the products are crystalline compounds. They are recrystallized from heptane. Yield 72–86%. (Table I).

NMR data **2a** 5.02d(1H, $^2J_{HP}$ 6.7 Hz), 1.68d(6H), 7.70m, 4.13m **2b** 5.05d(1H, $^2J_{HP}$ 7.0Hz), 1.68d(6H), 7.80m, 4.12m, 4.35m; (for **3a–d** and **4a–d** see Table II)

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