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1,2-OXAPHOSPHORIN-3-ENE DERIVATIVES IN THE REACTION OF SO_2Cl_2 WITH DICHLORIDES OF 2-CHLORO-3-ALKYL-1,3-ALKADIENEPHOSPHONIC ACIDS

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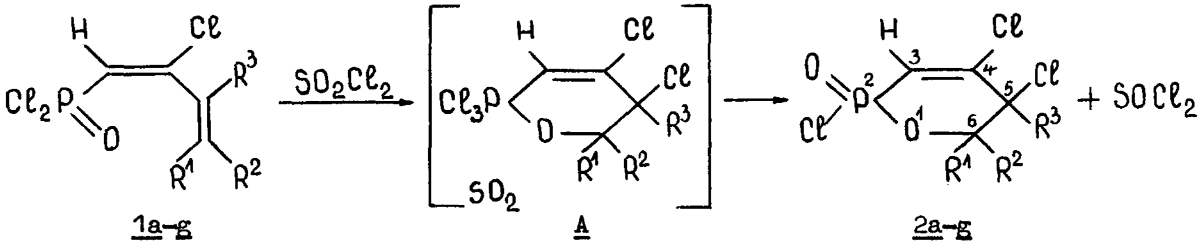
Summary: 2,4,5-Trichloro-2-oxo-1,2-oxaphosphorin-3-enes was sinthesised using the interaction of sulfuryl chloride with dichlorides of 2-chloro-3-alkyl-1,3-alkadienephosphonic acids.

Recently it was reported that during the chlorination of dichloride of 2-chloro-3-methyl-1,3-butadienephosphonic acid, a mixture of addition products is formed[1]. In contrast to this result we found that the reaction of dichlorides of 2-chloro-3-alkyl-1,3-alkadienephosphonic acids 1a-g with sulfuryl chloride leads to the formation of six-membered heterocycles:



R^1, R^2, R^3: see the Table

The reaction takes place in non-polar solvents (CCl_4, $CHCl_3$ etc.) by heating up to 50° or 60°C. The structure of the obtained compounds 2a-g was established by i.r. and n.m.r. spectroscopy (see the Table). Thus, the ^{1}H-n.m.r. spectra of 2a-d and 2g show signals for H^6 (δ 4.50 - 4.99 ppm) with a considerable coupling constant $^3J_{HP}$ (8.6 - 9.2 Hz) characteristic for the CH-O-P group in the six-membered rings[2]. The observation of two doublets for H^3 (δ 6.34 - 6.68 ppm, $^2J_{HP}$ 12.4 - 13.6 Hz) shows that the compounds 2a-g represent mixtures of stereoisomers (chirality at C^5 and P or at C^5, C^6 and P). The chemical shift of ^{31}P of the chloride 2c appears at higher field (δ -13.4 ppm) than in the case of 1,2-oxaphosphol-3-enes[3]. When isolating 2a-g, $SOCl_2$ was also obtained and identified by its physical constants.

The formation of 1,2-oxaphosphorin-3-ene chlorides when SO_2Cl_2 reacts with the compounds 1a-g is probably favoured by the partial dissociation of the reactant to chlorine and sulfur dioxide as well as by the s-cis conformation of 1,3-dienic system in the starting phosphonates 1a-g[4]. Chlorine is presumably attacking the C^3-C^4 double bound, thus forming cyclic chlorides with five-coordinate phosphorus A[5]. These in turn react very fast with sulfur dioxide giving 2a-g.

The reaction described above is a new method for synthesis of 1,2-oxaphosphorin-3-ene derivatives.

^{1}H-n.m.r. and i.r. spectra of 2a-g

№	R^1	R^2 (R^3)	Ch.Shifts δ ppm H	Ch.Shifts δ ppm R^1 (R^2)	J Hz H-P (R^1-P)	i.r. spectra cm^{-1} P=0 (C=C)
2a*	H	H (CH_3)	6.43 6.47	4.76 (4.52)	13.0 (17.0, 19.0)	1305 (1590)
b	H	CH_3 (CH_3)	6.49 6.51	4.90 (1.56)	13.2 (9.0)	1303 (1590)
c	H	CH_3 (C_2H_5)	6.64 6.68	4.99 (1.65)	13.3 (8.6)	1310 (1590)
d	H	C_2H_5 (n-C_3H_7)	6.55 6.60	4.58 (CH_3 1.15, CH_2 2.00)	13.5 (9.2)	1300 (1593)
e	CH_3	CH_3 (CH_3)	6.45 6.48	1.87 (1.89)	12.4 (-)	1298 (1590)
f	CH_3	CH_3 (i-C_3H_7)	6.61 6.64	1.83 (1.85)	13.0 (-)	1301 (1592)
g	H	$-(CH_2)_4-$	6.34 6.36	4.74 (-)	13.6 (9.2)	1310 (1590)

* The substance 2a is obtained together with smoll amounts of 1,2-oxaphosphol-3-ene chloride.

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