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DERIVATIVES OF 3-THIENYLPHOSPHONIC ACID AND 1,2-OXAPHOSPHOL-3-ENE

Christo M. Angelov* and Kolio V. Vachkov
Chair of Chemistry, Higher Pedagogical Institute, 9700 Shoumen, Bulgaria

Summary: Alkylsulfenyl chlorides react with 5-methyl-1,3,4-hexatrienyl-3-phosphonic esters giving derivatives of 3-thienylphosphonic acid and 1,2-oxaphosphol-3-ene.

Recently our investigations on 3-methyl-1,2,4-pentatrienylphosphonic esters[1] with chlorine and sulfenylchlorides have shown that the addition of an electrophilic reagent results in an elimination of alkylchloride and the same time a five-membered heterocycles are formed. With chlorine the 1,2-dienic system of π-bonds and the phosphorilic group participate in the reaction, leading to the formation of 1,2- oxaphosphol-3-enes[2], while with sulfenyl chlorid, the 1,3-dienic system and the sulfur atom react, giving thiophenic derivatives[3]. Continuing the studies in this field, we have found that alkylsulfenyl chlorides react with 5-methyl-1,3,4-hexatrienyl-3-phosphonic esters[1] (1a-c) by the 1,2- and 1,3-dienic sections. When the reaction is carried out in chloroform by cooling at -12 ÷ -10°C, a mixture of 3-thienylphosphonic (2a-c) and 1,2-oxaphosphol-3-enyl (3a-e) esters are formed, which could not be separated by vacuum frationation. The esters 2a-c, however, because of their low solubility in CCl_4, are separated as an upper oily layer in this solvent from which the reaction product is obtained as a pure substance after distillation. The esters 3a-e are isolated from the CCl_4 solution, together with very small amounts of 2a-c.

The structure of 2a-c and 3a-e is confirmed by their ^{1}H-, ^{31}P-NMR and IR-spectra. Thus, in the ^{1}H-NMR spectra of 2-isopropyl-3-thienylphosphonic esters 2a-c (Table 1) signals for H^4 and H^5 (δ 7.01 - 7.30) are observed, typical for spin system ABX. In the spectra of 1,2-oxaphosphol-3-enes 3a-e (Table 2) in a

^1H- and ^{31}P-NMR spectra of 2a-c

Table 1

		Chem. shifts, δ			J Hz	
№	R	H^4 (H^5)	H (CH_3)	^{31}P	H^4-P (H^5-P)	H^4-H^5
2a	CH_3	7.14dd (7.30dd)	3.94q (1.32d)	-14.7	4.0 (3.0)	5.0
b	C_2H_5	7.04dd (7.16dd)	3.86q (1.23d)	-11.9	4.0 (3.0)	5.0
c	i-C_3H_7	7.01dd (711dd)	3.92q (1.25d)	-9.7	4.0 (3.0)	5.0

^1H- and ^{31}P-NMR spectra of 3a-e

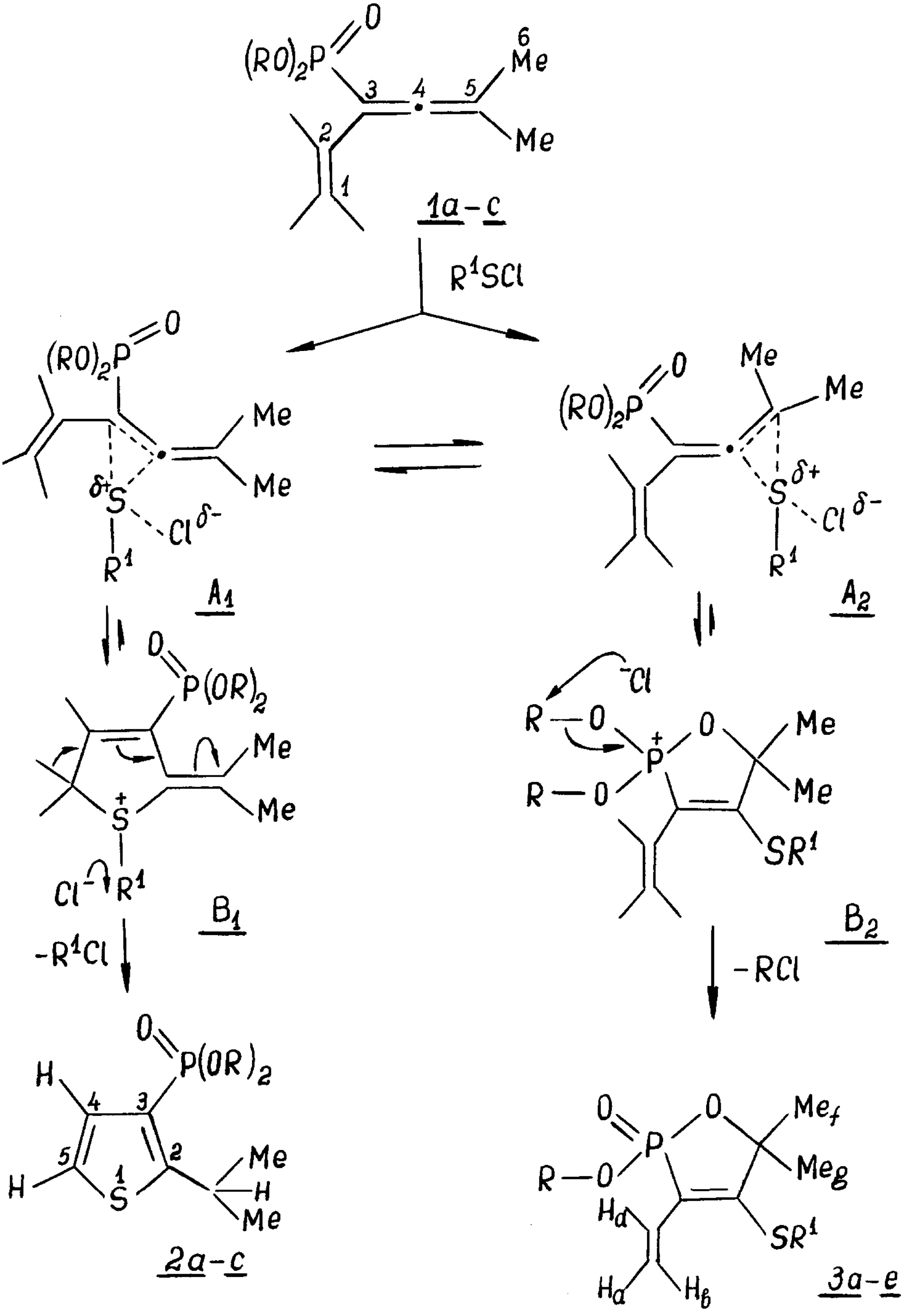
Table 2

		Chemical shifts, δ				J Hz	
№	R (R^1)	Ha (Hb)	R^1S (Hd)	Hf (Hg)	^{31}P	Ha-Hd (Hb-Hd)	Hd-P
3a	CH_3 (CH_3)	5.50d (5.82d)	2.45s (6.63qq)	1.59s (1.48s)	-30.5	10.8 (16.4)	28.0
b	CH_3 (i-C_3H_7)	5.48d (5.76d)	CH_3 1.42d CH 3.56q (6.61qq)	1.56s (1.46s)	-29.8	10.6 (16.2)	28.4
c	C_2H_5 (CH_3)	5.40d (5.74d)	2.35s (6.57qq)	1.47s (1.39s)	-28.2	10.4 (17.6)	28.8
d	C_2H_5 (C_2H_5)	5.42d (5.74d)	CH_3 1.36t CH_2 2.97q (6.58qq)	1.50s (1.41s)	-28.6	10.6 (16.8)	28.4
e	i-C_3H_7 (CH_3)	5.41d (5.74d)	2.37s (6.56qq)	1.48s (1.40s)	-27.8	11.0 (17.2)	28.2

weak field (δ 5.40 - 6.63) a multiplet signal for protons of the vinyl group is found characteristic for the spin system ABCX. The chemical shifts of ^{31}P of all compounds (Tabl. 1 and 2) determined with 85% H_3PO_4 as external standard are typical for such structures[3,4]. In the ^1H-NMR spectrum of the crude reaction products, containing 2b and 3c, we observed signals for the protons of CH_3Cl (δ 3.03) and C_2H_5Cl (δ CH_3 1.68, CH_2 3.60) together with the signals for the protons of 2b and 3c. It was found that the ratio of the two phosphonates depends on temperature. At 0°C in the reaction mixture of 2a and 3a, the 1,2-oxaphosphol-3-ene predominates (2a:3a = 1.00 : 1.33), while at -40°C the 3-thienylphosphonic ester is present in larger amounts (2a:3a = 1.25 : 1.00).

The chemical transformations thus observed (see the Scheme) are in

Scheme



accordance with the following reaction mechanism. The initial reaction act is the attack of electrophilic sulfur on the most nucleophilic atom of the trienic system of π-bonds (C^4) with the formation of two episulfonium ions A_1 and A_2. The ion A_1 is in the plane of the π-bond of the vinyl group (s-cis conformation), and for this reason A_1 is easily transformed in the more stable five-membered cyclic sulfonium ion B_1. The both methyl groups at C^5 stabilized A_2 which facilitates its interaction with the phosphorilic group. As a result the ion B_2 with a quaziphosphonic structure is formed. Further the ion B_1 reacts through protonic isomerization and elimination of R^1Cl to 2a-c, while B_2 through Arbusov's rearrangement gives 3a-e.

The change in the 2a-c to 3a-e yields ratio with temperature is probably depending on the stability of the episulfonium ions. At higher temperature A_2 favours the oxaphospholenic cyclization. At low temperature B_1 is formed faster shifting the equilibrium to the thiophenic derivatives. The simultaneous realization of the both cyclization processes is connected with introduction of 1,2- and 1,3-dienic parts of the π-electronic system into the reaction course. This fact is obviosly due to the ability of the sulfur atom to form cyclic ions[5,6], which are further transformed into stable five-membered heterocyclic compounds.

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