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THIOPHENE RING FORMATION DURING THE INTERACTION OF ALKYLSULFENYL CHLORIDES WITH ESTERS OF 3-METHYL-1,2,4-PENTATRIENEPHOSPHONIC ACID

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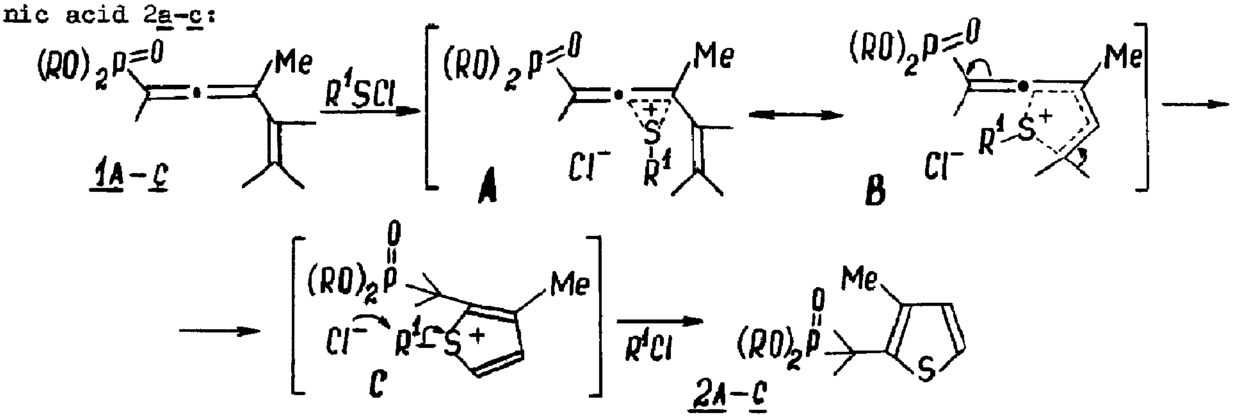
Summary: Dialkyl esters of 3-methyl-1,2,4-pentatrienephosphonic acid react with alkylsulfenyl chlorides to produce dialkyl esters of 2-thienylphosphonic acid.

It was shown recently[1,2] that sulfenyl chlorides are good electrophilic reagents for interaction with esters of substituted 1,2-alkadienephosphonic acids, leading to five-membered P-containing heterocycles. Continuing the studies in this field, we found that the treatment of dialkyl esters of 3-methyl-1,2,4-pentatriene phosphonic acid 1a-c with these reagents does not yield the expected vinyl-substituted 1,2-oxaphosphol-3-enes, as obtaind during the halogenation[3] of the same alkatrienephosphonates. Instead, a new type of thiophene ring cyclization reaction takes place, resulting in formation of esters of 2-thienylphosphonic acid 2a-c:



R = CH_3(a), C_2H_5(b), i-C_3H_7(c) ; R^1 = CH_3, C_2H_5, i-C_3H_7

The reaction is carried out in inert solvents (CCl_4, $CHCl_3$, $C_2H_4Cl_2$, etc.) at a temperature of -12° to -8°C. The structure of the compounds obtained was established on the basis of their IR, ^{1}H- and ^{31}P-NMR spectra. Thus, the ^{1}H-NMR sp tra of all esters 2a-c exhibit signals for H^4 (δ 6.75 d, $^3J_{HH}$ = 5.0 Hz) and H (δ 7.05 dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{HP}$ = 2.6 Hz)[4], as well as for CH$_3$-C (δ 2.15 - 2. $^5J_{CH_3,P}$ = 3.4 Hz) and CH$_2$-P (δ 3.19 - 3.24 d, $^2J_{CH_2,P}$ = 20.4 - 21.0 Hz). The chemical shifts (-23.2 to -24.3 p.p.m. with respect to trimethylphosphate) responds to tetracoordinated phosphorus compounds. The ^{1}H-NMR spectra of the reaction mixtures indicate aiso the presence of R^{1}Cl protons. The IR spectra 2a-c contain bands for P=O (1260 cm^{-1}), P-O-R (1050 cm^{-1}) and =C-H (720 cm^{-1}).

All known methods for preparation of 2-thienylphosphonic acid derivatives[5- are based on 2-substituted thiophenes as starting materials. The new method d loped by us involves a thiophene ring formation during the reaction.

The cyclization observed could be attributed to a transannular effect[8,9] the sulfur atom from the intermediate episulfonium ion A upon the neighbourin vinyl group, apparently present in a s-cis conformation (see scheme). This c formation allows a transannular overlap of sulfur and π-bond orbitals leadin the formation of a five-membered sulfonium ion B. The latter is further isome zad to the S-alkylthiofenium chloride C which can easily lose alkylchloride t give 2a-c.

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