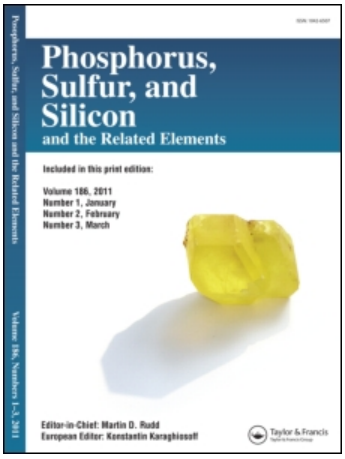

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Synthesis of 1,2-Azaphosphacyclanes; Generality of the Mechanism of P=N Alkylation and Arbuzov Reaction

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SYNTHESIS OF 1,2-AZAPHOSPHACYCLANES; GENERALITY OF THE MECHANISM OF P=N ALKYLATION AND ARBUZOV REACTION

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*A novel convenient "one-pot" synthesis of 2-oxo-1,2λ^5-azaphosphacyclanes **1** and 1,2λ^4-azaphosphacyclanium salts **2** via intramolecular N-alkylation of ω-halogenalkyl-substituted iminophosphoryl compounds **3** has been developed. The common nature of the reaction of intramolecular cyclization of iminophosphoryl compounds having an alkoxy group at the phosphorus atom and the Arbuzov reaction has been established.*

Keywords: 1,2-Azaphosphacyclanes; intramolecular alkylation

For a few years we have been studying the methods for the synthesis and properties of 2-oxo-1,2λ^5-thiaphosphacyclanes and 1,2λ^4-thiaphosphocyclanium salts.[1–4] The general pathway to the synthesis of these compounds was elaborated. In solutions of 1,2-thiaphosphocyclanium salts, the rare ring-chain halogenotropic tautomerism was observed and investigated in detail.

It seemed very attractive to extend the method of intramolecular alkylation to preparation of 2-oxo-1,2λ^5-azaphosphacyclanes **1** and 1,2λ^4-azaphosphacyclanium salts **2**, since these compounds have been little studied due to their low availability.

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RESULTS AND DISCUSSION

Synthesis of 1-Phenyl-2-oxo-1,2λ^5-azaphosphacyclanes

As far as is known, the nitrogen atom in the P=N–R group is more inclined to reactions of nucleophilic substitution than the sulfur atom in the P=S group. That is why we had reason to suppose that intramolecular alkylation running like the imide–amide rearrangement should lead to the formation of 1-phenyl-2-oxo-1,2λ^5-azaphosphacyclanes **1**. In this case, diethylanilidophosphites **3** were used as initial compounds. For the preparation of chloroalkyliminophosphonate **4**, buthyllithium was used; the stage of cyclization of the type of imide–amide rearrangement was carried out on heating. For this purpose, ω-chloroalkyl-substituted derivatives of phosphorus imidoacids **4** were transformed to corresponding iodides **4′** by heating with sodium iodide in acetonitrile solution. Simultaneously with the exchange of the chlorine atom for iodine the cyclization takes place to form phosphonium salt **5**. Then after the splitting RI azaphosphocyclane **1** is formed. In this case intermediates **4**, **4′**, and **5** were not isolated, which was an advantage of this procedure. The compounds **1** were prepared under sufficiently mild conditions in a yield of about 60% (Figure 1).

The spectral data fully confirm the cyclic structure. For example, if chloroalkyliminophosphonates (**4**, R = EtO, R′ = Et) had δ_p equal to 20.9 ($n = 3$) and 21.7 ppm ($n = 4$), cyclic compounds have δ_p 43.4 and 27.8 ppm, correspondingly. As a rule, chemical shifts of six-membered cycles are located in a stronger field than those of five-membered cycles ($\Delta\delta_p$ 16 ppm). It should be noted that azaphospholane **1** ($n = 3$, R = EtO) is not stable to air moisture and hydrolyzes gradually to form the betaine $EtOP(O)(O^-)(CH_2)_nN^+H_2Ph$ **6**. Azaphosphorinane **1** ($n = 4$) is considerably more stable. Betaine **6** is also caused by hydrolysis, but it requires boiling in a water–acetone solution for 1.5 h.

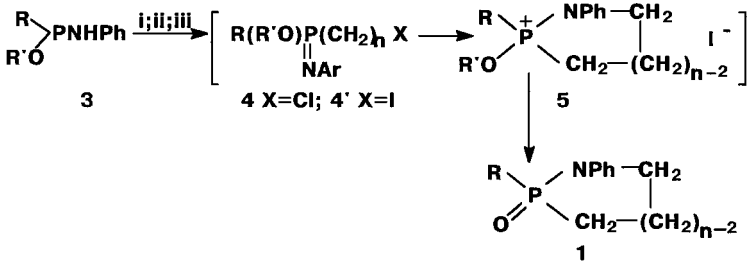
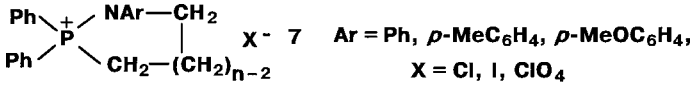


FIGURE 1 i, BuLi, THF, −60°C; ii, $Cl(CH_2)_nBr$; iii, NaI, MeCN, Δ; R = MeO, EtO, Ph; R′ = Me, Et; $n = 3, 4$.

Some Consideration About the Mechanism of the Reaction

The results obtained provided reason to believe that the reaction of intramolecular alkylation proceeds via intermediate phosphonium salts **5**. In some cases the phosphonium salts were registered by ^{31}P-NMR; in some cases we failed in fixing them. Because ionic mechanism was of no doubt, it should be supposed that the formation of phosphonium intermediates is the rate-controlling stage for this reaction sequence.

We managed to obtain stable phosphonium salts of azaphosphacyclanes **7** in the case of diphenyl derivatives, wherein the formation of rearrangement products with phosphoryl group was excluded.



The data of infrared (IR), ^{1}H-NMR, and ^{31}P-NMR spectra and x-ray analysis undoubtedly prove cyclic structure of these compounds.

While searching for synthetic routes to phosphonium salts, an interesting fact was observed. The structures of these salts are identical to those of phosphonium intermediates forming at the first stage of the Arbuzov rearrangement. As is well known, under ionic mechanism, phosphites and amido- and thiophosphites, subjected to haloalkanes action, transform to the corresponding phosphonates via the stage of intermediate phosphonium salts. These two processes are presented in Figure 2.

That is why the next step in our research was the synthesis of cyclic derivatives on the basis of three-coordinated phosphorus compounds via the Arbuzov reaction. This might provide a possibility to prove the common nature of the Arbuzov reaction and the reaction of intramolecular alkylation. This proof has been demonstrated using derivatives containing the ω-chloroalkyl radical in the amide group. The synthesis

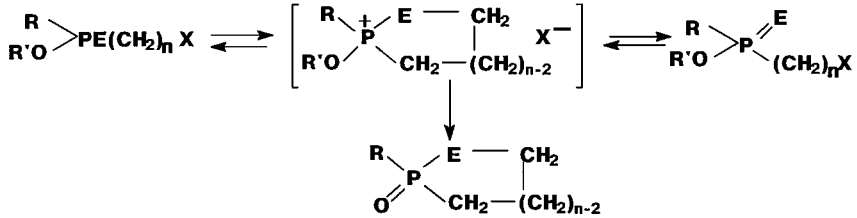


FIGURE 2 E = N, S, O; n = 3, 4.

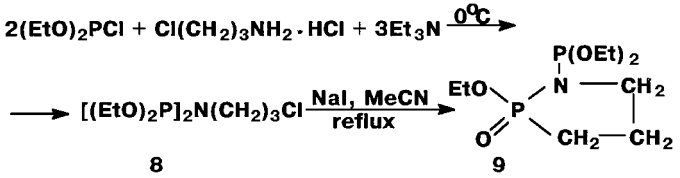


FIGURE 3

of the corresponding salt **7** (Ar = H, X = I) was carried out from diphenylchlorophosphine and the hydrochloride of an amine containing a ω-chloroalkyl substituent. It was isolated and fully characterized (mp decomp. 220–225°C, δ_p 53.8 ppm). Then practically the same reaction was performed with $(EtO)_2PCl$. Here 2 mol chlorophosphite was used in order to phosphorylate the nitrogen in the cycle. The reaction runs with yield of 69%. Oxo-1,2-azaphospholane **9** was characterized by ^{31}P-NMR spectra: δ_p 50.0 d, 137.0 d ppm, J_{pp} 41.6 Hz (Figure 3).

Then compound **9** with N—P(III) group was transformed to the corresponding sulfide **10** by refluxing with sulfur in C_6H_6 for 1.5 h. Compound **10** was purified by column chromotography and fully characterized by IR and ^{1}H- and ^{31}P-NMR spectra and elemental alalysis. The results obtained point unambiguously to the common nature of intramolecular alkylation and the Arbuzov reaction.

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