INTRAMOLECULAR P=S 
AND P=N ALKYLATION. GENERAL 
METHOD FOR SYNTHESIZING 
1,2-HETERAPHOSPHACYCLANES*

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Results have been generalized for investigations on the synthesis of 1,2-thiaphosphacyclanes by 
intramolecular P=S alkylation of ω-haloalkyl substituted compounds of four-coordinated phosphorus 
with a P=S bond. The method has been extended to nitrogen-containing analogs with a P=N bond. A 
new general method is proposed for the synthesis of 1,2-thia- and 1,2-azaphosphacyclanes.

Keywords: 1,2-azaphosphacyclanes, 1,2-thiaphosphacyclanes, intramolecular alkylation, ring–chain 
halotropism tautomerism.

Interest in the chemistry of phosphorus-containing heterocyclic compounds is linked with their 
participation in many biochemical processes, with their use as therapeutic preparations and agents for plant 
protection, with use in organic synthesis, metal-complex catalysis, and other areas. Unlike the 
1,3,2-diheteraphosphacyclanes, which have been well investigated, the 1,2-heteraphosphacyclanes have been 
little studied due to their lower availability. A most part of them were obtained by multistage syntheses, 
frequently under rigid conditions [1-4].

In recent years we have developed a new general approach to the synthesis of 
1,2-heteraphosphacyclanes based on the intramolecular alkylation of ω-haloalkyl substituted compounds of four-coordinated phosphorus with a P=E bond (E = S, N). The aim of the present work was to correlate our 
investigations on the synthesis and study of the properties of 1,2-thiaphosphacyclanes [5-10] and to supplement 
them with new data on the development of methods of synthesizing 1,2-azaphosphacyclanes.

Intramolecular P=E alkylation (E=S) was used for the first time for the synthesis of 2,2-diphenyl-1,2κ₄-thiaphospholanium iodide and 2,2-diphenyl-1,2λ₄-thiaphosphorinanium iodide (1), which were obtained on refluxing ω-chloroalkyldiphenylphosphine sulfides 2 with NaI in acetone [5] (Scheme 1). Reaction occurs 
through the intermediate formation of the ω-iodoalkyl-substituted derivatives 3, revealed on the base of 31P and 
1H NMR spectra. The ω-bromoalkyl-substituted phosphine sulfides 4 are smoothly converted on short-term 
heating at 100°C in the absence of solvent into the cyclic bromides 5 [6,8], from which the perchlorates 6 
and tetrafluoroborate 7b are obtained by anion exchange reaction [7].

* Dear Mikhail Grigorievich! Accept our congratulations on your anniversary. We acknowledge profoundly 
your enormous creative powers.

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The 1,2-thiaphosphacyclanium salts 1, 5-7 are stable crystalline compounds, which structures were confirmed by data of IR, and $^{31}$P and $^1$H NMR spectra (Table 1), and also by data of X-ray structural investigations for iodides 1a,b, bromides 5a,b, and for perchlorate 6a. An intense absorption band was observed in the IR spectra of the cyclic salts at 570 cm$^{-1}$, assigned to the vibrations of the P–S–CH$_2$ ring fragment. The position of the $\delta$$_P$ signal in the $^{31}$P NMR spectra depends on the ring size. It was shifted by 35 ppm towards low field in 1,2-thiaphospholanium salts compared with 1,2-thiaphosphorinanium salts, which is in agreement with the data of [11].

According to the data of X-ray structural investigations [5-7] the five-membered phosphorus-containing rings in compounds 1a, 5a, and 6a are characterized by an envelope conformation with the average deviation of one of the carbon atoms from the plane of the remaining coplanar atoms by 0.6 Å. The six-membered phosphorus-containing rings in 1,2-thiaphosphorinanium salts 1b and 5b have the conformation of a slightly distorted chair. In all the structures investigated the phosphorus atom is characterized by a slightly distorted tetrahedral configuration with a reduction in the endocyclic angle to 100.3(2)$^\circ$ and 108.1(2)$^\circ$ in the 1,2-thiaphospholanium and 1,2-thiaphosphorinanium rings respectively. Unexpectedly shortened P’S···Hal interionic contacts were detected for the halide salts. 1,2-Thiaphosphacyclanes have not been investigated by X-ray structural analysis previously.

TABLE 1. Physicochemical and Spectral Characteristics of Compounds 1, 5-7

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp, °C (solvent)</th>
<th>IR spectrum (KBr), $\nu$ (P–S–CH$_2$), cm$^{-1}$</th>
<th>$^{31}$P NMR spectrum (in CH$_2$Cl$_2$), $\delta$, ppm</th>
<th>Yield, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>203-204 (CH$_3$CN–EtOAc)</td>
<td>572</td>
<td>72.2</td>
<td>77</td>
<td>[5]</td>
</tr>
<tr>
<td>1b</td>
<td>204-205 (CH$_3$CN–EtOAc)</td>
<td>565</td>
<td>37.6</td>
<td>65</td>
<td>[5]</td>
</tr>
<tr>
<td>5a</td>
<td>163-164 (CHCl$_3$–EtOAc)</td>
<td>572</td>
<td>72.6</td>
<td>77</td>
<td>[6]</td>
</tr>
<tr>
<td>5b</td>
<td>161-162 (CHCl$_3$–EtOAc)</td>
<td>567</td>
<td>38.0</td>
<td>78</td>
<td>[8]</td>
</tr>
<tr>
<td>6a</td>
<td>152-153.5 (CHCl$_3$–ether)</td>
<td>570</td>
<td>72.6</td>
<td>81</td>
<td>[7]</td>
</tr>
<tr>
<td>6b</td>
<td>182-184 (CH$_2$Cl$_2$–ether)</td>
<td>570</td>
<td>37.6</td>
<td>67</td>
<td>[7]</td>
</tr>
<tr>
<td>7b</td>
<td>186-188 (CH$_2$Cl$_2$–ether)</td>
<td>572</td>
<td>37.4</td>
<td>Quant.</td>
<td>[7]</td>
</tr>
</tbody>
</table>