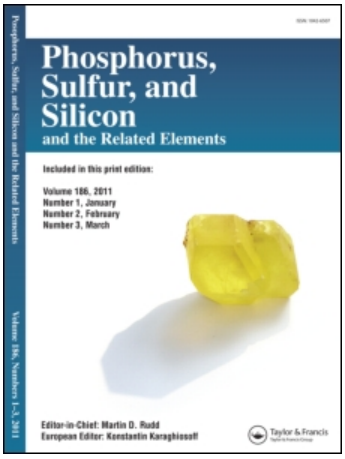


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Some Transformations of 1,2-Heterophosphacyclanes

Tatyana A. Mastryukova; Inga M. Aladzheva; Dmitrii I. Lobanov; Olga V. Bykhovskaya; Pavel V. Petrovskii; Konstantin A. Lyssenko; Martin I. Kabachnik

To cite this Article Mastryukova, Tatyana A. , Aladzheva, Inga M. , Lobanov, Dmitrii I. , Bykhovskaya, Olga V. , Petrovskii, Pavel V. , Lyssenko, Konstantin A. and Kabachnik, Martin I.(1999) 'Synthesis and Some Transformations of 1,2-Heterophosphacyclanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 569 — 572
To link to this Article: DOI: 10.1080/10426509908546308
URL: http://dx.doi.org/10.1080/10426509908546308

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 569-572
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Some Transformations of 1,2-Heterophosphacyclanes

TATYANA A. MASTRYUKOVA, INGA M. ALADZHEVA, DMITRII I. LOBANOV, OLGA V. BYKHOVSKAYA, PAVEL V. PETROVSKII, KONSTANTIN A. LYSSENKO and MARTIN I. KABACHNIK

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova, 28, 117813 Moscow, Russia

The general pathway to 1,2-monoheterophosphacyclanes via intramolecular S-and N-alkylation of ω-halogenoalkylsubstituted thiophosphoryl and iminophosphoryl compounds has been developed. Intramolecular alkylation of 3-and 4-halogenoalkyldiphenylphosphine sulfides results in 1,2λ^4-thiaphospholanium and thiaphosphorinanium halogenides. In solution of these compounds the rare ring-chain halogenotropic tautomerism has been observed and investigated in detail. Intramolecular Pishchimuka rearrangement of the esters of ω-halogenoalkylsubstituted thiophosphorus acids was found to be a synthetic route to 2-oxo-1,2λ^5-thiaphospholanes and thiaphosphorinanes.

Keywords: intramolecular alkylation; 1,2-thiaphosphacyclanes; ring-chain halogenotropic tautomerism; 1,2-azaphosphacyclanes

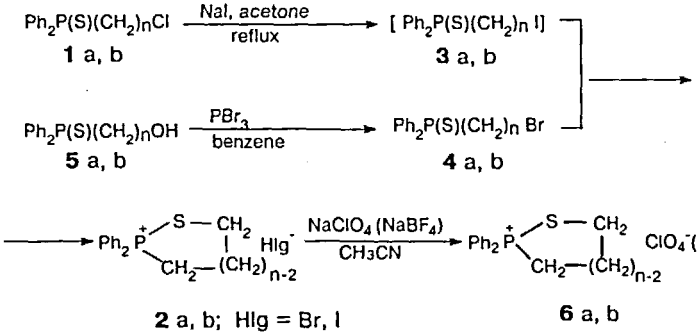
INTRODUCTION

Although the heterocyclic organophosphorus compounds are known for decades 1,2-monoheterophosphacyclanes with C-P-S and C-P-N fragments are poorly investigated. Contrary to 1,3,2-diheterophophacyclanes, there were no facile synthetic routes for their preparation. We elaborated the general method of 1,2-heterophosphacyclanes synthesis by intramolecular alkylation of ω-halogenoalkylsubstituted compounds with P=S and P=N groups.

RESULTS AND DISCUSSION

Intramolecular Alkylation Of ω- Halogenoalkyldiphenylphosphine Sulfides

Recently[1] we have found that refluxing of 3- and 4- chloroalkyldiphenylphosphine sulfides **1a,b** (throughout this paper a: n=3; b: n=4) with sodium iodide in acetone leads to 2,2-diphenyl-1,2λ⁴-thiaphospholanium and thiaphosphorinanium iodides **2a,b** (Hlg = I).

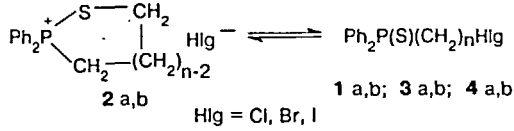


The reaction proceeds initially by replacing chlorine atom in **1** by iodine to give **3**. The intramolecular alkylation of **3** produces cyclic thiaphosphonium iodides **2** with high yields. We failed to cyclicyze 3-chloropropylphosphine sulfide **1a** even under heating without solvent at 140°C during 2 hours. Contrary to iodides **3**, ω-bromoalkyldiphenylphosphine sulfides **4a,b** are rather stable substances. Nevertheless both crystalline bromide **4a**[2] and liquid bromide **4b** turn completely to cyclic bromides **2a,b** on heating at 100°C within 0.5 hour. Perchlorates and tetrafluoroborates **6** were prepared by anion exchange. The structures of compounds **1,2,4,6** were determined by IR, Raman, ^1H and ^{31}P spectroscopy and confirmed by X-ray crystal analysis. Hydrolysis of the salts **2a,b** at 100°C under argon proceeds as a cleavage of the P-S bond yielding phosphinyl substituted mercaptanes $Ph_2P(O)(CH_2)_nSH$ (**7a,b**); the reaction with sodium ethylate in ethanol-benzene in air leads to disulfides $[(Ph_2P(O)(CH_2)_nS]_2$ (**8a,b**).

Ring-Chain Halogenotropic Tautomerism

The behaviour of the cyclic salts **2** and bromides **4** in solution was unexpected. Two tautomeric forms were found to exist in solution: the ring 1,2λ⁴-thiaphos-

pholanium **2a** (or thiaphosphorinanium **2b**) form and the isomeric open phosphine sulfide form **1,3** or **4**.



It is a new type of scantily investigated ring-chain anionotropic tautomerism. The equilibrium for bromides **2** and **4** does not depend on which isomer is taken for the preparation of the solution. The equilibrium position is influenced by the ring size, the solvent used and the anion nature (Table 1). The cyclic form content in equilibrium increases when passing from five-membered 1,2-thiaphosholanium ring to the less strained six-membered 1,2-thiaphosphorinanium one. The equilibrium shifts to the cyclic form in more polar acetonitrile as compared with chloroform and methylene chloride. In passing from iodides to bromides and further to chlorides the content of the open form increases.

TABLE 1. THE CONTENT OF THE CYCLIC FORM 2 AND 6 (%)[a]

Solvent	Chlorides		Bromides		Iodides		Perchlorates	
	n=3	n=4	n=3	n=4	n=3	n=4	n=3	n=4
CH_2Cl_2	0	0	38	48	70	85	100	100
$CHCl_3$	0	0	65	85	87	92	100	100
CH_3CN	9[b]	3[c]	82	82	100	100	-	-

a) ^{31}P NMR data; b) after 6 months; c) after 6 months the equilibrium position didn't achieve.

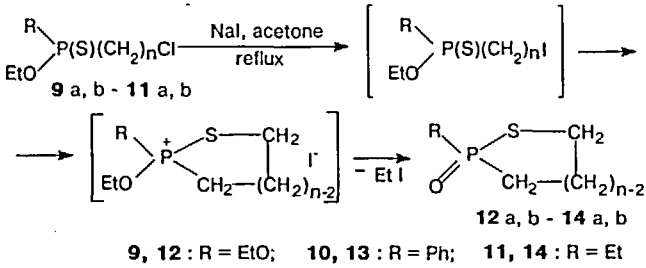
The temperature dependence of equilibrium in methylene chloride was investigated using bromide **4a** as an example. An elevation of the temperature was found to result in increasing of the open form. Some thermodynamical parameters of tautomeric equilibrium were calculated. By ^{31}P NMR method the kinetics of tautomeric transformations of bromides **2,4** was studied in methylene chloride at 20°C. Both cyclic and open isomers were used as starting substances. In the case of bromides **2a**, **4a** the equilibrium was reached after about 25 hours while for bromides **2b**, **4b** - after about 25 days. The rate constants k_1 and k_2 of the direct and reverse reaction were obtained from the experimental data.

Intramolecular Pishchimuka Rearrangement

To elaborate the synthetic routes to new types of 1,2-thiaphosphacyclanes we extended intramolecular alkylation over another classes of organothiophosphorus

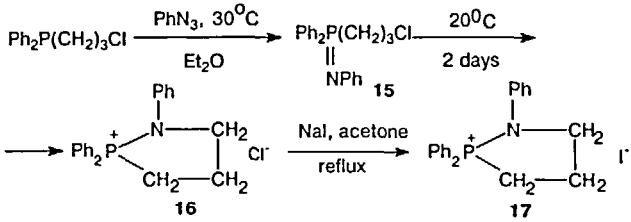
compounds. It was found that the esters of thiophsphorus acids **9-11** underwent the intramolecular rearrangement on refluxing with sodium iodide producing 2-oxo-1,2λ⁵-thiaphosphacyclanes (thiolphostones) **12-14.**

The idea can be successfully used for synthesis of 1,3,2-dithiolphostones.



9, 12 : R = EtO; **10, 13** : R = Ph; **11, 14** : R = Et

The method of intramolecular alkylation has been advantageously extended also to the synthesis of 1,2-azaphosphocyclanes. The reaction of 3-chloropropyldiphenylphosphine with phenyl azide resulted in phosphine imine **15** which turned into cyclic 1-2λ⁴-azaphospholanium chloride **16** at 20°C. By refluxing of **16** with sodium iodide in acetone iodide **17** was produced. Its structure was confirmed by X-ray analysis.



Acknowledgements

This work was supported by the Russian Fundamental Research Foundation (grants No 96-03-32992, No 96-15-97298).

References

[1] I.M. Aladzheva, O.V. Bykhovskaya, D.I. Lobanov et al, Mendeleev Commun., 48 (1996).

[2] D.I. Lobanov, I.M. Aladzheva, O.V. Bykhovskaya et al, Phosphorus, Sulfur and Silicon, **128**, 145 (1997).