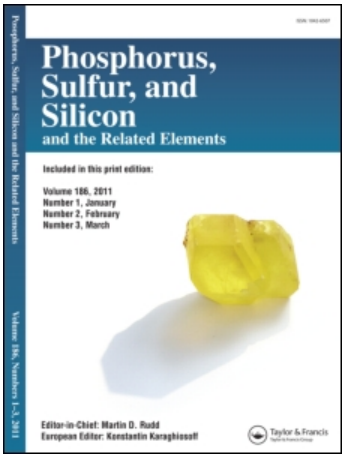

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Sulfur-Phosphorus and Selenium-Phosphorus Heterocycles -Synthesis and Structure Elucidation by Modern NMR -Techniques

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SULFUR-PHOSPHORUS AND SELENIUM-PHOSPHORUS HETEROCYCLES - SYNTHESIS AND STRUCTURE ELUCIDATION BY MODERN NMR-TECHNIQUES

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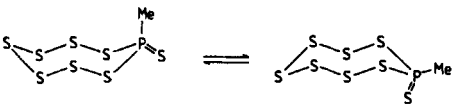
Abstract The cis-trans isomerization of the four-membered heterocycle $(MeP(S)S)_2$ (1), well known as methylperthiophosphonic acid anhydride, has been found to proceed via its eight-membered dimer. This can be concluded from the order of the reaction, the activation parameters, and three intermediates, which were found by DNMR methods to take part in the isomerization process. A new synthetic route to selenium phosphorus heterocycles is offered by the oxidative ring closing reaction of the trimethylsilyl esters of triselenophosphonic acids (6) with bromine or dimethylsulfoxide. The silyl esters have been obtained from the reaction of bis(trimethylsilyl)-organophosphanes with elemental selenium. The structures of the tetraselenadiphosphorinane $(MeP(Se)Se_2)_2$ (7) and the triselenadiphospholane $MeP(Se)Se_2MeP(Se)Se$ (8) have been elucidated by homonuclear ^{31}P double quantum spectra.

INTRODUCTION

Heterocycles of the general composition $RP(S)S_n$ (n = 5-7) and $(RP(S)S_2)_2$ undergo different dynamic processes: ring reversal (eq. (1)), inversion of configuration (eq. (2)), and reversible dimerization reactions (eq. (3))[1,2]. The inver-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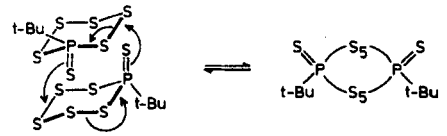
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sion as well as the dimerization reaction are assumed to proceed via related electrocyclic mechanisms involving the exchange of endo- and exocyclic sulfur atoms[1-3]. Considering the variety of dynamic processes of these novel heterocycles, the well known dithiadiphosphetanes $(RP(S)S)_2$ are expected to undergo similar processes, although they are commonly believed to exist only in a trans conformation. This assumption probably is a consequence of the results of crystal structure analysis. Meanwhile, Ohms, Großmann, Buchta, and Treichler found that in solution many of these compounds show cis-trans isomerization[4,5]. However, as their approach was different from ours, important additional aspects of the reaction are presented in this contribution. Moreover, we report on the synthesis and structure of new selenium phosphorus heterocycles, which would allow to observe the exchange of endo- and exocyclic chalcogen atoms by dynamic NMR methods, provided that they undergo similar dynamic processes as the analogous sulfur compounds.

DYNAMIC PROCESSES of 2,4-DIMETHYL-2,4-DITHIO-1,3,2,4-DITHIADIPHOSPHETANE

At room temperature the $^{31}P\{^1H\}$ NMR spectrum of $(MeP(S)S)_2$ (1) (saturated solution in 1,2-dichlorobenzene/toluene-d8 = 3/1) shows two broad singlets at 23.2 and 13.1 ppm of relative intensities 5:1, which were assigned to the trans and cis isomer, respectively. The assignment of the high-field signal to the cis isomer is based on the following facts.

a) On dissolving 1 at -30°C under NMR spectroscopic control (solvent = CS_2) only the low-field signal appears in the spectrum. As the dynamic process is slow at that temperature, the isomer in solution must be identical with the trans form of the solid state.

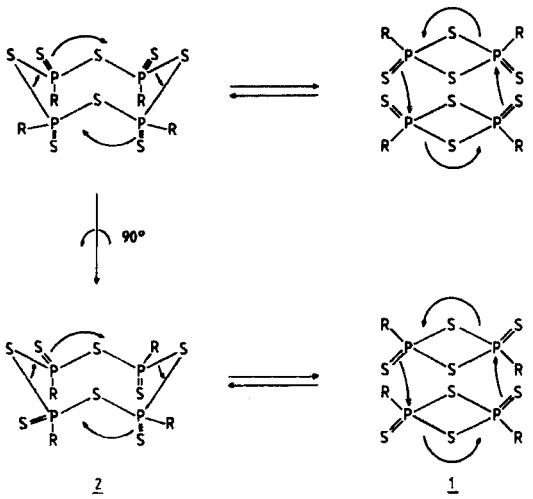
b) The intensities of the two signals do not depend on concentration. Thus, the second signal cannot be assigned to a dimeric form.

c) The ^{31}P NMR spectrum of the asymmetric substituted dithiadiphosphetanes, which form at room temperature shortly after mixing the two symmetric molecules $(MeP(S)S)_2$ (1) and $(EtP(S)S)_2$, shows AX-patterns, clearly indicating the presence of two P atoms in each isomer.

d) The high-field signal becomes more intensive with increasing polarity of the solvent used (in tetrahydrofuran it is nearly as intensive as the low-field signal). Consequently it belongs to the isomer with the more polar structure.

The observed linebroadening of both NMR signals caused by an exchange process between the two isomers increases with temperature, indicating that the cis-trans isomerization becomes faster. Since the reaction rate was also found to depend on concentration, the isomerization must be an intermolecular process. From a plot of $\ln(c \cdot t^{-1})$ versus $\ln c$ (the lifetime t of an isomer results from lineshape analysis of spectra measured at different concentrations c and constant temperature) the order of the reaction has been determined to be 1.8. The activation parameters ΔH^*(trans, cis) = 35.5 (±1.1) $kJmol^{-1}$ and ΔS^*(trans, cis) = -100.1 (±2.9) $Jmol^{-1}K^{-1}$ have been obtained from the effect of temperature on the reaction rate at constant concentration.

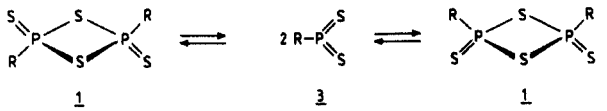
The large negative activation entropy indicates a highly-ordered transition state, which according to the order of the reaction is formed by two molecules of 1. This conclusion leads directly to the proposed reaction mechanism



(4)

2 1

with an eight-membered dimer 2 as intermediate. An alternative mechanism suggested by Ohms et al.[4] assumes an organodithiophosphorane (3) as intermediate, which in the case of R = 2,4,6-t-butylphenyl was found to be more stable



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than its four-membered dimer[6]. Of course, the cleavage of the dithiadiphosphetane must be connected with a positive activation entropy, which does not correspond with the experimental results. Nevertheless, the phosphorane intermediate can not completely be excluded if dithiadiphosphetanes with bulky substituents are involved. Unfortunately, an experimental proof is difficult as the cis conformation is destabilized for sterical reasons in these cases.

Additional evidence for the mechanism involving the eight-membered heterocycle could be gained from saturation transfer experiments. These experiments indicate that the three very weak signals ($\delta(^{31}P)$ = 59.4, 65.5, and 69.3), are due to intermediates which take part in the exchange process and are not caused by impurities. Our assignment of these resonances to eight-membered intermediates is based on the following facts.

a) The signals are shifted down-field from the resonances of the four-membered rings into the range expected for tetrathiatetraphosphocanes.

b) The identification of three isomers with similar chemical shifts corresponds with ring size eight, allowing four configurational isomers (tttt, ttcc, tctc, cccc; t = trans, c = cis) discernible by NMR spectroscopy (in comparison with two isomers of ring size six and eight isomers of ring size twelve).

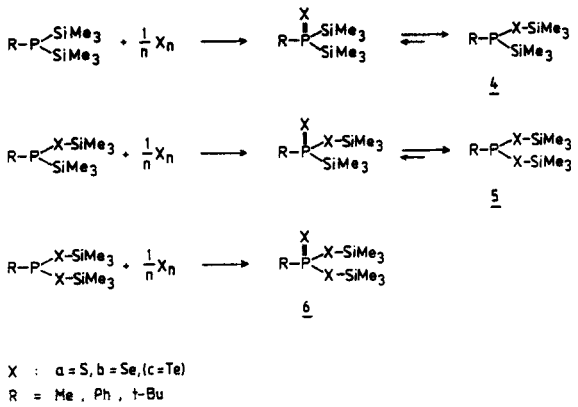
c) As the exchange between different conformational isomers should be fast, one A_2B_2 (cctt) and three A_4 systems are expected in the ^{31}P NMR spectrum which is also in agreement with the three singlets found experimentally.

SYNTHESIS OF THE SELENIUM-PHOSPHORUS HETEROCYCLES

Many of the reaction mechanisms mentioned above involve the exchange between endo- and exocyclic sulfur atoms. In contrast to the sulfur compounds, selenium-phosphorus heterocycles would offer the possibility to observe this process

NMR spectroscopically. Moreover, the synthesis of the corresponding heterocycles appeared to be a challenging task as none of the few preparative routes to Se-P heterocycles so far known could be applied. We found that the silyl esters of the triselenophosphonic acids 6b represent useful starting compounds for heterocycles containing selenium and phosphorus.

By analogy with the sulfur compounds a general access to the silyl esters of triselenophosphonic acids is offered by the reaction of elemental selenium with bis(trimethylsilyl)-phosphanes. The reaction is best carried out in toluene solution. Depending on the reactivity of the starting compounds, the temperature is kept between -25 and +20°C.



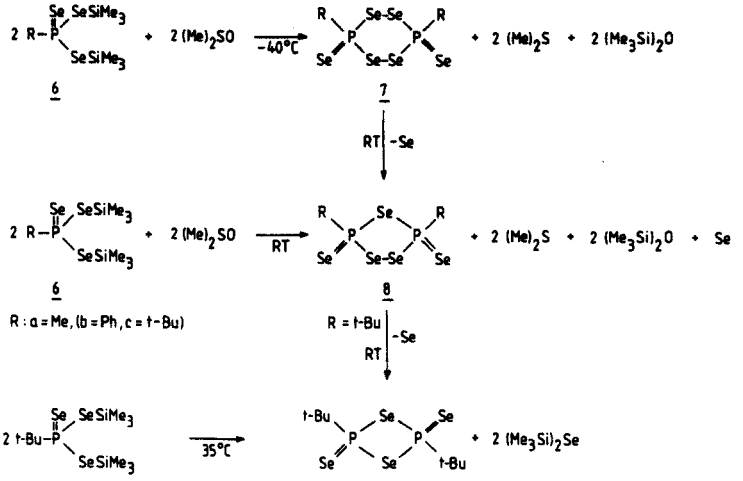
(6)

Whereas sulfur should be added in stoichiometric amounts, selenium must be present in a bimolar surplus. During the sulfur and selenium addition the two intermediates 4 and 5 can be identified by ^{31}P NMR spectroscopy. The addition reaction starts with a nucleophilic attack at the chalcogen chain. The subsequent equilibrium, involving the migration of a silyl group, is completely shifted to the side of the phosphinous acid ester allowing a second and third nucleophilic attack. At -25°C the addition of selenium stops at the stage of the diselenophosphonous acid esters 5b, which can be isolated in a pure state at that temperature. The isolation of the corresponding dithioester is only possible for the t-butyl-substituted compound[7].

The reaction of tellurium with the silylphosphanes differs considerably from that of its lower homologues. Only

the t-butyl-substituted phosphane forms the monotellurium adduct 4c. Even a large surplus of tellurium does not lead to higher adducts. In all other cases organocyclophosphanes and bis(trimethylsilyl)monotellane are obtained. It is assumed that the monoadduct is formed as an intermediate, which immediately reacts with a P-$SiMe_3$ group forming a P-P bond and the silyltellane.

The silyl esters of the triselenophosphonic acids 6b react in an oxidative ring closing reaction with bromine or dimethylsulfoxide (eq. (7)) to form novel 1,2,4,5,3,6-tetra-



selenadiphosphorinanes 7 as primary products. Even at low temperatures, these six-membered rings are quite unstable. At ambient temperature they quickly loose one or two selenium atoms. For the methyl- or t-butyl-substituted compounds the five- and four-membered rings, respectively, result as final products. In the case of the phenyl substituent both ring sizes may be obtained. The equilibrium of the t-butyltriselenophosphonic acid bis(trimethylsilyl) ester with the corresponding diselenodiphosphetane and $Se(SiMe_3)_2$ (eq. (9)) is completely shifted to the side of the four-membered ring. The condensation reaction becomes fast above 35°C. Therefore, the ester can be synthesized at room temperature and is quite stable at -20°C.

The five-membered ring 3,5-dimethyl-3,5-diseleno-1,2,4,3,5-triselenadiphospholane (8a) has been isolated as a light-orange crystalline powder. Its structure has been characterized by elemental analysis, IR, and mass spectroscopy. The most convincing structural proof was achieved by the analysis of the ^{77}Se satellite lines of the ^{31}P NMR spectrum ($\delta(^{31}P) = 47.6$). The satellite spectrum consists of the AB parts of two ABX type spectra, which are caused by molecules containing the ^{77}Se atom (X atom) in the position of one of the double-bonded Se atoms or in the endocyclic Se_2 linkage, respectively. As expected, the direct coupling of a P atom, ($^1J(PSe)$), to a double-bonded Se atom (-778 Hz) is significantly larger than the coupling to a single-bonded Se atom (-369 Hz). Most surprisingly the ^2J coupling constant (^{77}Se-Se-P) and the ^3J coupling constant (^{77}Se=P-Se-P) have the same values (-12.5 Hz). The P-P coupling constant ($^2J(PP) = 34$ Hz) is, of course, not influenced by the different positions of the ^{77}Se atom and is therefore identical in either spin system. Furthermore, there is no significant isotopic effect on the chemical shift so that the spin systems may be assumed to be of the AA'X type. The two P atoms of the molecule containing the ^{77}Se isotope in the symmetrical ring position are magnetically equivalent. The corresponding A_2X spin system shows a doublet ($^1J(PSe)$ = -381 Hz), which nearly coincides with the outer lines of one of the AB type subspectra.

The interpretation of the satellite spectrum was unambiguously confirmed by a homonuclear double quantum spectrum. The pulse sequence used is identical with the well known INADEQUATE sequence[8], but has so far not yet been applied to analyse satellite spectra. As a consequence of the double quantum filter all spin systems without P-P coupling vanish from the spectrum. Especially important is the suppression of the central line, which hides or perturbes all other signals close to the center. The doublet of the A_2X system disappears as well, giving additional proof for the correct assignment of these lines. When a non-refocussing sequence is applied, the signals are in antiphase with respect to the P-P coupling. This offers the possibility to resolve very small couplings.

This type of resolution enhancement and the very effective suppression of the central line were needed to analyse the satellite spectrum of 3,6-dimethyl-3,6-diseleno-1,2,4,5,3,6-tetraselenadiphosphorinane (7a), which was identified as primary product in the ring closing reaction ($\delta(^{31}P)$ = -33.1). Depending on whether the ^{77}Se atom is in endo- or exocyclic position, two different types of isotopic substituted molecules result. The inner lines of the corresponding ABX type subspectra (rel. intensities 1:2) lie very close to the center ($^{3}J(Se-Se-P)$ = 3.2 Hz, $^{4}J(Se=P-Se-Se-P)$ = 0.9 Hz) and are therefore completely hidden in the normal spectrum. The small P-P long-range coupling ($^{3}J(PP)$ = 3.2 Hz) can also be resolved only in the DQF spectrum.

The six-membered heterocycle is in equilibrium with a second isomer of very low concentration ($\delta(^{31}P)$ = 33.3). Furthermore it slowly undergoes an irreversible rearrangement into a heterocycle, which according to the NMR spectrum ($\delta(^{31})P$ = -27.5) may be assigned to a third isomer of the tetraselenadiphosphorinane (7a). The nature of these dynamic processes and the question whether they are connected with the exchange of endo- and exocyclic selenium atoms are under study now.

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