Sulfur Phosphorus Heterocycles $RP(S)S_n$ and $[RP(S)S_m]_2$, Synthesis and Dynamic Properties

Josef Hahn[a]; Anno Borkowsky[a]; Tina Nataniel[a]

[a] Institut für Anorganische Chemie der Universität, Köln, FRG

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SULFUR PHOSPHORUS HETEROCYCLES $RP(S)S_n$ AND $[RP(S)S_m]_2$, SYNTHESIS AND DYNAMIC PROPERTIES

JOSEF HAHN, ANNO BORKOWSKY, TINA NATANIEL
Institut für Anorganische Chemie der Universität Köln, FRG.

Abstract   Sulfur   phosphorus   heterocycles   of   general composition $RP(S)S_n$ and $[RP(S)S_m]_2$ have been synthesized from silyl   and   stannyl   esters   of   trithiophosphonic   acids $RP(S)(SEMe_3)_2$ (E = Si, Sn). The phosphorus-31 nucleus has been used as an NMR probe for the study of ring reversal and related dynamic processes. The results obtained, provide insight into the mechanism and energy barrier of the crown reversal of cyclo-octasulfur. Moreover, some of the heterocycles show configurational changes at the P atoms as well as reversible oligomerization reactions.

INTRODUCTION

In contrast to the high standard of knowledge of the structure of sulfur rings S_n in crystalline state, very little information is available   concerning   the   conformation   and   the   conformational changes of these compounds in solution. This is a consequence of the lack of appropriate spectroscopic methods for studying the corresponding dynamic processes. An indirect way of getting the desired   information   is   to   investigate sulfur   rings   containing heteroatoms which can serve as a probe for dynamic NMR measurements. Because of the small difference between the S-S and S-P bond length, S-P heterocycles showing an S_nP or $(S_mP)_2$ ring skeleton represent especially useful model compounds for this purpose.

SYNTHESIS OF THE S-P HETEROCYCLES

In contrast to S-P heterocycles of composition $RP(S)S_n$, which are not known from earlier work, a great number of diphosphacyclo-

sulfanes $[RP(S)S_m]_2$ of ring size four have been   described.   They
are, however, not of interest in this context,   because   ring size
four is quite unfavourable for sulfur rings.   The only representa-
tive of ring size six, $[BrP(S)S_2]_2$, is known to be frozen   in   the
twist-boat   conformation[1] and was synthesized by an obscure   reac-
tion[2]. For that reason, it cannot be used for the study of confor-
mational changes,   nor can the way of formation contribute to   the
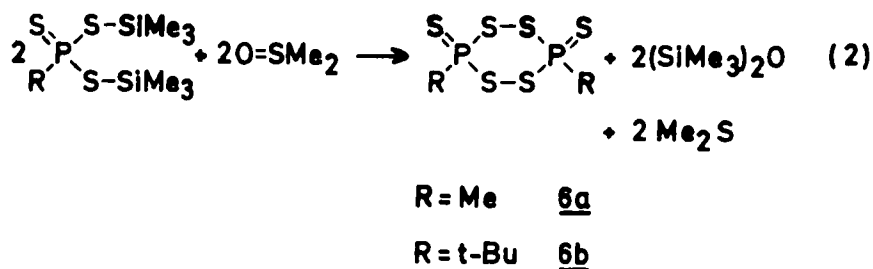development of a general synthetic route for S-P heterocycles.

The   latter   problem could be solved by   the   preparation   of
silyl   and stannyl esters of trithiophosphonic acid $RP(S)(SEMe_3)_2$
(E = Si,   Sn)[3],   which react smoothly with halogens and   dichloro-
sulfanes, yielding the S-P heterocycles of interest[4]. Molecules of
composition $RP(S)S_n$ are   obtained with chlorosulfanes S_xCl_2 of
chainlength   x > 2.   The primary yield of the reaction varies   be-

$$\begin{array}{c} S \\ \diagdown \\ P \\ \diagup \diagdown \\ R \end{array} \begin{array}{c} S-EMe_3 \\ \\ S-EMe_3 \end{array} + S_{n-2}Cl_2 \longrightarrow \begin{array}{c} S \\ \diagdown \\ P \\ \diagup \end{array} \begin{array}{c} \\ S_n \\ \end{array} + 2EMe_3Cl \qquad (1)$$

E = Si, Sn

|	n =7	n =6	n =5
R = Me	**1a**	**2a**	**3a**
R = t-Bu	**1b**	**2b**	**3b**
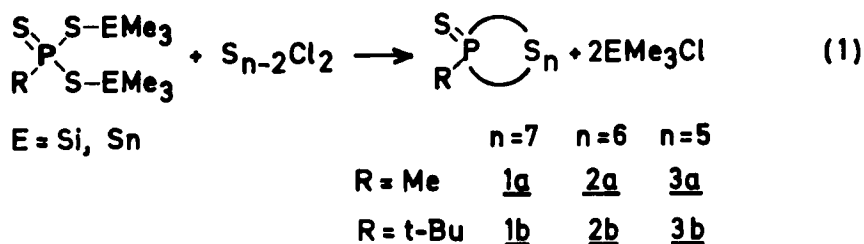
tween 70 and 50 %.   However,   because of the low crystallizability
of the heterocycles in presence of polymeric byproducts,   the pure
compounds could only be isolated in yields of 30 to 5%.

On reacting the esters with the clorosulfanes SCl_2 and S_2Cl_2,
instead   of the four- and five-membered rings,   the   corresponding
dimers $[RP(S)S_m]_2$, m = 3, 4; R = Me, t-Bu (4a,b, 5a,b) are formed.
Up to now   these compounds could only be identified by mass   spec-
trometry.   The   ^{31}P NMR spectra   are   quite complex, indicating   a
large number of isomers and possibly also oligomeric forms.

As may be expected,   the tetrathiadiphosphorinanes $RP(S)S_2{}_2$
(6a,b) are formed in the reaction of the esters with the   halogens
Cl_2 and Br_2. In better yields (ca. 70%)   these heterocycles can be
obtained by reacting the silyl esters with dimethylsulfoxide[5].

$$2 \underset{R}{\overset{S}{\underset{}{\diagdown}}}P \overset{S-SiMe_3}{\underset{S-SiMe_3}{\diagup}} + 2O=SMe_2 \longrightarrow \underset{R}{\overset{S}{\underset{}{\diagup}}}P \overset{S-S}{\underset{S-S}{\diagup}} P \overset{S}{\underset{R}{\diagup}} + 2(SiMe_3)_2O \quad (2)$$

$$+ 2 Me_2 S$$

R = Me   6a

R = t-Bu   6b

Although the tetrathiadiphosphorinanes 6a,b are stable in crystalline state, in solution sulfur elimination occurs, which in the case of 6b leads to the formation of the dithiadiphosphetane [t-BuP(S)S]$_2$. By contrast, 6a loses only one S atom producing the trithiadiphospholan 7. Obviously, the Me substituent stabilizes
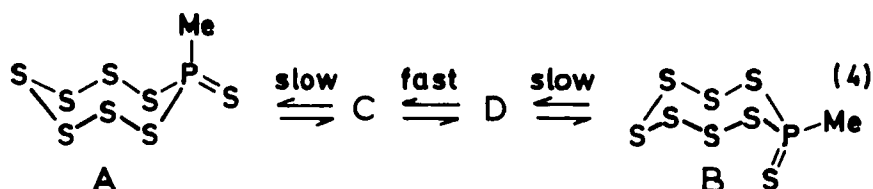
$$(3)$$
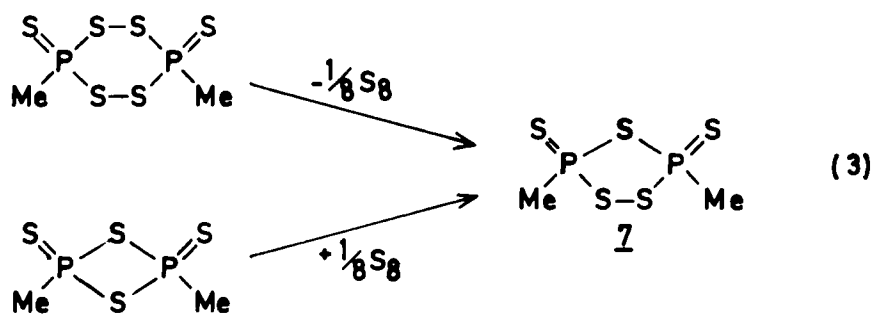
ring size five. This was confirmed by demonstrating that the four-membered ring [MeP(S)S]$_2$ disproportionates on heating in dioxane into 7 and compounds of lower S-content. In the presence of an excess of sulfur, 7 can be obtained in 50 % yield from the sulfurination reaction of MeP(S)S $_2$.

Dynamic Properties

Like cyclo-octasulfur, MeP(S)S$_7$ clearly prefers the crown confor-mation. Of the two different isomers A and B with axial and equa-torial position of the Me group, respectively, only A is present in crystalline state[6]. According to ^{1}H and ^{31}P dynamic NMR (DNMR) studies in the temperature range between +80 and -90°C, in solu-tion, both isomers exist in a thermodynamic equilibrium, which may

be described by equation (4). Magnetization is not directly trans-

$$
\text{A} \quad \underset{\text{slow}}{\rightleftharpoons} \quad \text{C} \quad \underset{\text{fast}}{\rightleftharpoons} \quad \text{D} \quad \underset{\text{slow}}{\rightleftharpoons} \quad \text{B} \tag{4}
$$

fered from A (B) to B (A) but only via the intermediates C and D, which were found to be present in very low concentrations.

From molecular model inspections and MNDO[7] calculations it becomes clear that the most likely intermediates of the crown-to-crown interconversion are chair-boat conformations. Although cyclooctane is known to prefer the chair-boat form, the latter is not favourable for eight-membered sulfur rings, because two pairs of neighbouring dihedral angles largely deviate from the value of 90°, which is prefered by S-S bonds. Since in the PS_7 heterocycle two of the strained dihedral angles can be formed by P-S bonds, two favourable conformations become possible, which have been as-signed to the isomers C and D. This assignment is consistent with
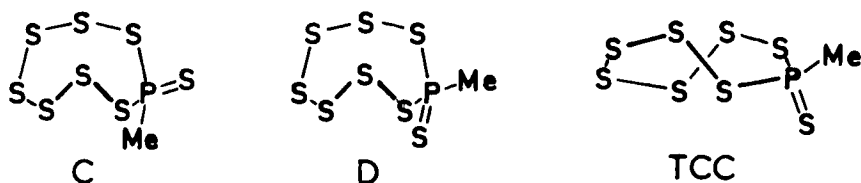
the results of MNDO calculations. Theoretical calculations were also used to determine the transition state for the crown-to-chair-boat conversion. This process includes a sign reversal of two neighbouring dihedral angles. Minimum strain energy occurs, if this is not a synchronous but rather a step by step process, and if essential rotation about P-S bonds is involved. The geometry of the transition state resembles the twist-chair-chair form (TCC), and its energy lies 62.4 kJ/mol above that of the crown conforma-tion. This value is in reasonable agreement with the activation energy of the crown-to-chair-boat conversion of 75.9 kJ/mol ob-

tained experimentally from DNMR kinetic data. On the basis of an
analog mechanism, a barrier of 81.7 kJ/mol was calculated for
cyclo-S_8 crown-to-crown interconversion. On the assumption that
the MNDO method underestimates the energy of the transition state
by about the same factor as in the case of the model compound
MeP(S)S_7, the barrier to cyclo-S_8 ring reversal should be as high
as 95 kJ/mol.

The seven-membered heterocycle MeP(S)S_6 (<u>2a</u>) most probably
shows rapid interconversion between two chair conformations with
axial and equatorial orientation of the Me group, respectively.
The investigation of this process has, however, not yet been con-
cluded.

The bulky t-Bu substituent of t-BuP(S)S_5 (<u>3b</u>) destabilizes
the chair form of the molecule in favour of the twist-boat confor-
mation. This leads to a thermal equilibrium between these isomers,
thereby offering a model for the cyclo-S_6 chair-to-chair reversal,
which also proceeds via the twist-boat form as an intermediate.

(5)

(6)
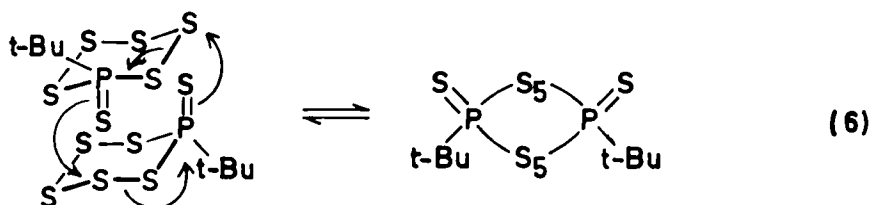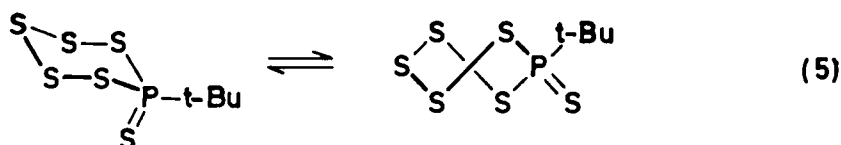
Moreover, <u>3b</u> undergoes a second dynamic process. From its depen-
dence on concentration and the negative reaction entropie (S ◻
-83 J/mol), it was assigned to the dimerization of <u>3b</u>.

The dimerization of t-BuP(S)S_5 (<u>3b</u>) by a mechanism involving
an exchange between exo- and endo-cyclic S atoms is supported by a
related rearrangement reaction of [MeP(S)S_2]$_2$ (<u>6a</u>). In solution,

this six-membered heterocycle exists in four isomers:

(7)
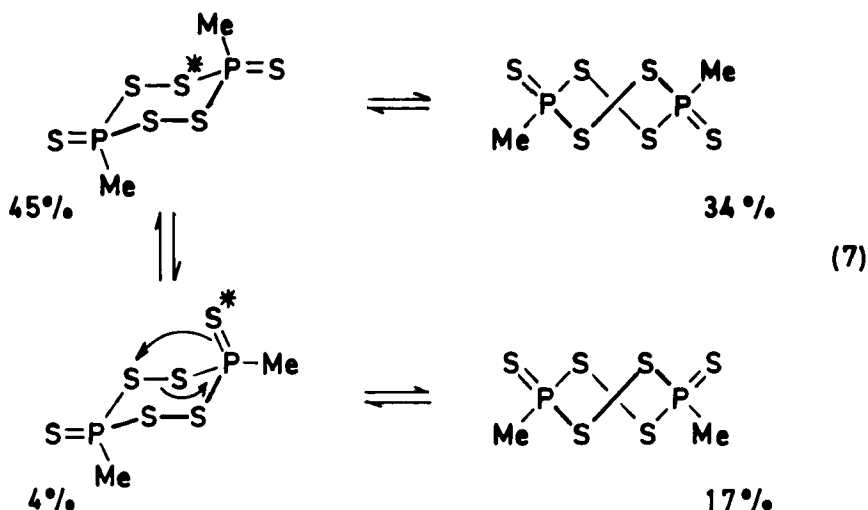
two chair and two twist-boat conformations differing in the orientation of their substituents - cis and trans, respectively. Besides the expected chair-to-twist-boat conversions, a third dynamic process could be detected. It is characterized by a magnetization transfer between the coalescence signal of the cis isomers and the trans-chair conformation. This process suggests pyramidal inversion at the P atom, which can, however, be excluded in the present case, as the P atom is pentavalent. It is therefore most likely that the inversion proceeds via the mutual exchange of an exo- and an endo-cyclic S atom, as described by equation (7).

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