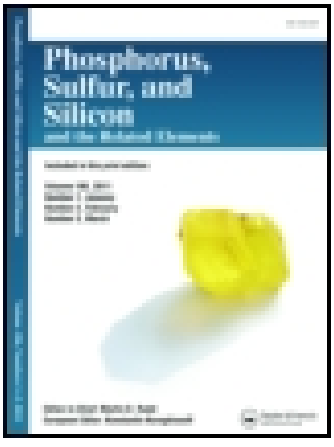

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RING-CHAIN HALOGENOTROPIC TAUTOMERISM. 2,2-DIPHENYL-1,2λ⁴-THIAPHOSPHOLANIUM BROMIDE ⇋ 3-BROMOPROPYLDIPHENYLPHOSPHINE SULFIDE

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RING-CHAIN HALOGENOTROPIC TAUTOMERISM. 2,2-DIPHENYL-1,2λ^4-THIAPHOSPHOLANIUM BROMIDE ⇋ 3-BROMOPROPYLDIPHENYLPHOSPHINE SULFIDE

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A new type of ring-chain anionotropic tautomerism for cyclic thiaphospholanium bromide **2A** and isomeric phosphine sulfide **2B** was investigated. Both of the tautomers were isolated in crystalline form. Their structures were proved by IR, Raman, ^{1}H, ^{31}P NMR spectroscopy and X-ray analysis. In solution the equilibrium position doesn't depend on the kind of dissolved tautomer. The effect of the solvent, concentration and temperature on the equilibrium **2A** ⇋ **2B** was studied as well as kinetics of interconversion of tautomers.

Keywords: 3-bromopropyldiphenylphosphine sulfide; 2,2-diphenyl-1,2λ^4-thiaphospholanium bromide; ring-chain halogenotropic tautomerism; kinetics of tautomers interconversion

INTRODUCTION

The ring-chain anionotropic tautomerism occurs more rarely in organic chemistry than the prototropic one. In most cases the conclusion about ring-chain anionotropic tautomerism was based either on irreversible rearrangements or dual reactivity of the isomers.[1] By now only few examples of true tautomeric equilibrium are known. The interesting covalent system belongs to them.[2,3]

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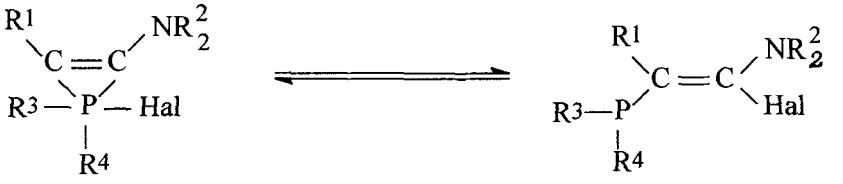


In solution either equilibrium between two forms or its shift to one of them were observed depending on the substituents R and the halogen nature. Recently[4,5] we synthesized 2,2-diphenyl-1,2λ⁴-thiaphospholanium and thiaphosphorinanium iodides **1A** (n = 1,2) by intramolecular S-alkylation. These compounds were found to exist in solution in equilibrium with the corresponding 3- and 4-iodoalkyldiphenylphosphine sulfides **1B**. The equilibrium depends on the solvent nature and the ring size.

1A **1B**

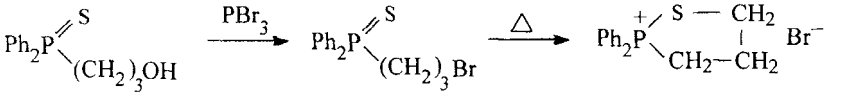
In the present work the bromo analogues of **1A** and **1B**—2,2-diphenyl-1,2λ⁴-thiaphospholanium bromide **2A** and 3-bromopropyldiphenylphosphine sulfide **2B** were studied.

2A **2B**

RESULTS AND DISCUSSION

Synthesis and structure of 2A and 2B

Crystalline 3-bromopropyldiphenylphosphine sulfide **2B** was obtained by heating of 3-hydroxypropyldiphenylphosphine sulfide with phosphorus tribromide.



2B **2A**

On fast heating sulfide **2B** has a m.p. 82–83°C. On slow heating it begins to melt at 82°C, but doesn't melt completely and crystallizes again. On heating of **2B** at 100°C for 30 min. bromide **2A** with m.p. 163–164°C was obtained. The structures of **2A** as cyclic thiaphospholanium salt and **2B** as open isomer were confirmed by IR, Raman, ^{1}H, ^{31}P NMR spectroscopy and X-ray analysis data.

The vibration spectra of crystalline **2A** contain the bands 570 cm^{-1} (IR) and 572 cm^{-1} (Raman) corresponding to P-S-CH_2 group. The open isomer **2B** has two bands in the region 600 cm^{-1}: 612, 622 cm^{-1} (IR) and 613, 623 cm^{-1} (Raman). Two bands of P=S vibrations are known in this region: 615, 639 cm^{-1} (IR), 614, 635 cm^{-1} (Raman) for $Ph_3P(S)$[6] and 615, 630 cm^{-1} (IR), 613, 623 cm^{-1} (Raman) for $Ph_2P(S)CH_2C(O)NEt_2$.[7]

After dissolving in CH_2Cl_2 the ^{31}P-{^{1}H} spectrum of bromide **2A** contains the singlet signal at δ 72.6 ppm†. This is in close agreement with the signal at 72.2 ppm of cyclic iodide **1A** (n = 1) with well-established structure.[4]

In the ^{31}P-{^{1}H} NMR spectrum of sulfide **2B** the signal at 42.0 ppm corresponds to the signal of open isomer **1B** (n = 1) at 42.2 ppm and the signal of 3-chloropropyldiphenylphosphine sulfide at 42.1 ppm.[8]

X-ray Analysis Data

It was found that salt **2A** (Figure 1) is isostructural with the earlier investigated 2,2-diphenyl-1,2λ^4-thiaphospholanium iodide **1A** (n = 1) with bond lengths and angles (Table I) close to the corresponding values in the **1A** (n = 1).[4] The five-membered thiaphospholanium ring in the crystal structure of **2A** has an envelope conformation, its central carbon atom is disordered over two positions C(2′) and C(2″) which are displaced from the plane of other atoms of the ring by 0.57 and −0.37Å. The phosphorus atom is characterized by a slightly distorted tetrahedral environment with the endocyclic angle as small as 100.3(1)°. The opposite C(4)PC(10) angle in the phosphorus tetrahedron (108.3(2)°) as well as the angles involving the P-S bond (C(4)PS 110.9(2)° and C(10)PS 110.8(2)°) are close to the ideal tetrahedral value whereas the C(4)PC(1) and C(4)PC(10) angles (113.5(3)° and 113.0(3)°) are considerably widened. The P-S and S-C(3) bond lengths (2.062(2)Å and 1.842(7)Å, respectively) are similar to the corresponding values in the structure **1A** (n = 1) (2.068(1)Å and 1.850(3)Å). Slight decrease of the P-S and S-C(3) bond lengths in the structure **2A** in comparison with **1A** (n = 1), probably results from the libration shortening (X-ray inves-

†Because the spectrum is recorded within minutes after dissolving, the second signal at 42.0 ppm associated with isomer **2B** (3–5%) is also observed.

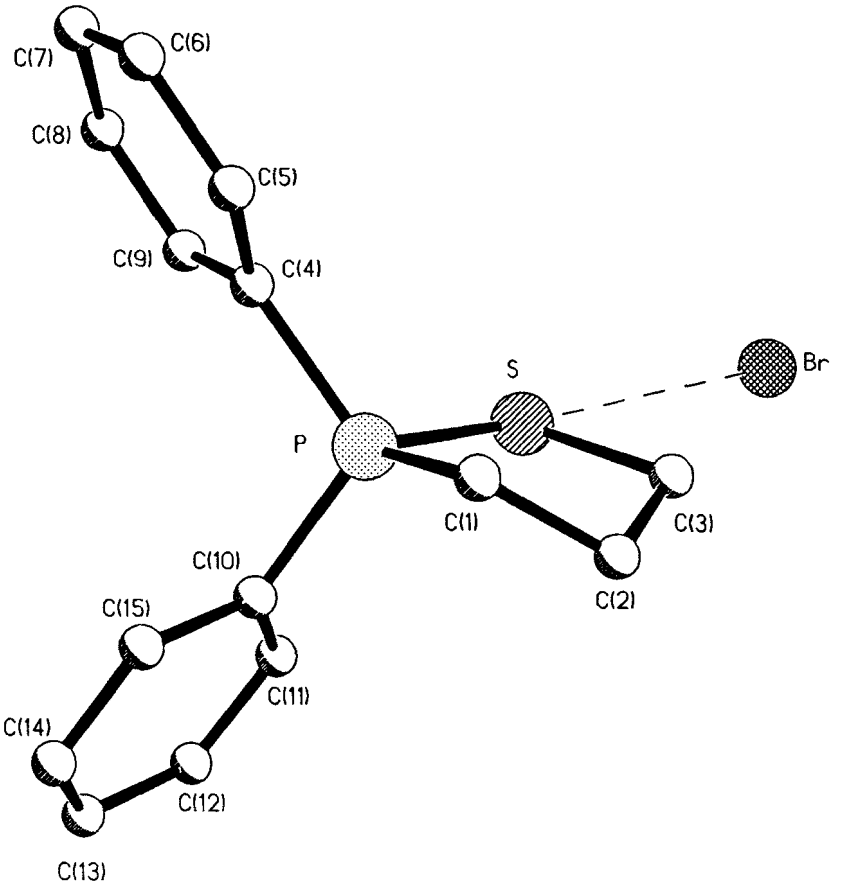


FIGURE 1 The general view of the cation and anion in structure **2A** showing the atomic numbering scheme. One of the positions of the disordered carbon atoms is omitted for clarity.

tigations of the **1A** (n = 1) salt was carried out at 153K and for **2A** at 293K). The Ph rings exhibit different orientations relative to the C(1)PSC(3) plane, the torsion angles SPC(4)C(5) and SPC(10)C(11) being equal to 117.6° and 9.5°, respectively. In the crystal structure of **2A** as well as in the earlier studied structures **1A** (n = 1,2), short interionic contacts P^+-S...Hal^- are observed. These contacts in both thiaphospholanium salts **2A** and **1A** (n = 1) (3.471(1) and 3.633(2)Å, respectively) are equally shortened as compared to the sums of the Van der Waals radii of corresponding atoms (the Van der Waals radii for S, Br and I are 1.81Å, 1.97Å and 2.11Å, respectively).[9] However in case of the thiaphosphorinanium ring **1A** (n = 2) the corresponding S...I^- was shown to be considerably longer (3.825(1)Å).[4] It is noteworthy, that the difference be-

TABLE I Important bond lengths (Å) and angles (deg) for **2A**

Bond lengths			
S-C(3)	1.842(7)	C(1)-C(2″)	1.45(2)
S-P	2.062(2)	C(1)-C(2′)	1.487(11)
P-C(4)	1.780(5)	C(2′)-C(3)	1.541(12)
P-C(10)	1.801(5)	C(2″)-C(3)	1.45(2)
P-C(1)	1.818(5)		
Bond angles			
C(3)-S-P	93.3(2)	C(2′)-C(1)-P	104.6(5)
C(4)-P-C(10)	108.3(2)	C(1)-C(2′)-C(3)	112.0(7)
C(4)-P-C(1)	113.5(3)	C(3)-C(2″)-C(1)	120.0(11)
C(10)-P-C(1)	113.0(3)	C(2″)-C(3)-S	110.1(7)
C(4)-P-S	110.9(2)	C-(2′)-C(3)-S	110.6(5)
C(10)-P-S	110.8(2)	C(9)-C(4)-P	119.3(4)
C(1)-P-S	100.3(2)	C(5)-C(4)-P	122.1(4)
C(2B)-C(1)-P	107.2(7)	C(11)-C(10)-P	120.4(4)
C(15)-C(10)-P	118.5(4)		

tween the S...Hal$^-$ distances in the thiaphosphorinanium (**1A** (n = 2)) and thiaphospholanium (**2A** and **1A** (n = 1)) salts correlates with the significant difference in the P-S bond lengths, the latter being noticeably shorter in **1A** (n = 2) (2.048(1)Å) as compared to those in **2A** (2.062(2)Å) and **1A** (n = 1) (2.068(1)Å). In all investigated structures P$^+$-S...Hal$^-$ angles are close to 180° (the average value is 174°). Taking into account the specific direction of the S...Hal$^-$ contact (see P$^+$-S...Hal$^-$ angles) and the correlation between the P-S bond lengths and the S...Hal$^-$ distances, one can assume that this interionic contacts are due to the interaction of the halogen lone electron pair with the antibonding orbital of the P-S bond (n $\rightarrow$ σ^* interaction).

Bond lengths and angles in the open form **2B** (Figure 2) are quite typical of this sort of compounds[10] (Table II). The P=S bond length in **2B** is equal to 1.933(2)Å and close to the corresponding bond in the $Ph_3P{=}S$ (1.950Å).[11] The phosphorus atom has a slightly distorted tetrahedral environment: bond angles at the phosphorus atom vary in the range 102.9(2)°–114.2(3)°. The bromopropyl fragment adopts the synclinal conformation, the torsion angle SPC(1)C(2) is equal to 46°. The analysis of the crystal packing in **2B** shows that all intermolecular distances have the expected values.

Hence, the structures of bromides were unambiguously established as the cyclic isomer for bromide **2A** and the open isomer for bromide **2B**.

Tautomerism 2A $\leftrightharpoons$ 2B. The Dependence on the Solvent Nature and Temperature

As it was cited above by dissolving of isomers **2A** and **2B** the ^{31}P NMR spectra are in agreement with the structures of the isomers used. On keeping, the signals of the second isomer increase in the spectrum, and the spectrum corresponding

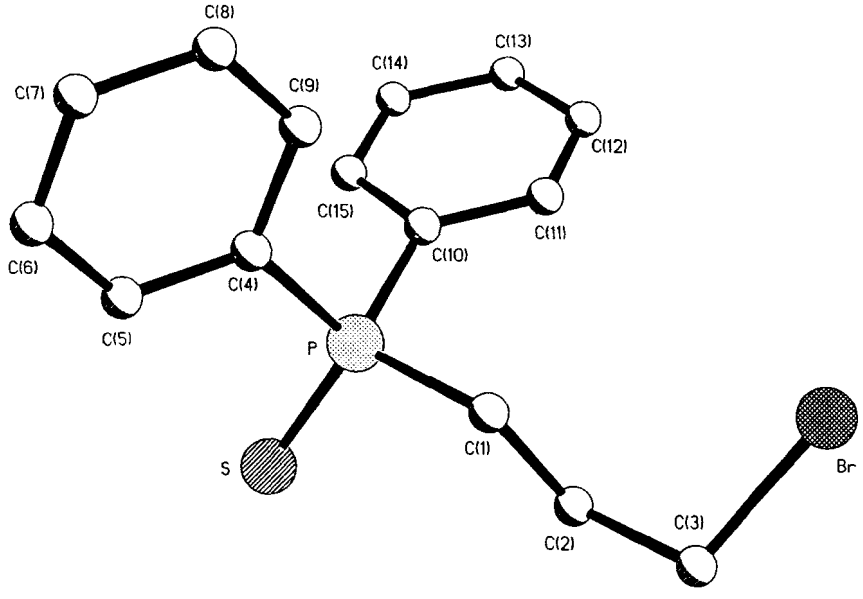


FIGURE 2 The general view of molecule **2B** and atomic numbering scheme.

to the equilibrium **2A** ⇋ **2B** is finally registered. The equilibrium position does not depend on which isomer was taken for the preparation of the solution. It is also remarkable that the ^{1}H NMR spectrum of the acyclic bromide **2B** in $CDCl_3$ (after dissolution or in the state of equilibrium) contains a triplet signal typical of the protons of the methylene group $(CH_2)C\underline{H}_2Br$ with δ 3.46 ppm ($^3J_{HH}$6.4 Hz). The equilibrium position depends to a significant extent on the solvent nature. The constants of the tautomeric equilibrium **2A** ⇋ **2B** in various sol-

TABLE II Important bond lengths (Å) and angles (deg) for **2B**.

Bond lengths			
Br-C(3)	1.964(6)	P-C(10)	1.816(5)
P-C(4)	1.813(5)	P-S	1.933(2)
P-C(1)	1.816(6)		
Bond angles			
C(4)-P-C(1)	102.9(3)	C(1)-C(2)-C(3)	113.8(5)
C(4)-P-C(10)	105.6(2)	C(2)-C(3)-Br	110.6(4)
C(1)-P-C(10)	107.3(3)	C(5)-C(4)-P	120.6(5)
C(4)-P-S	114.2(2)	C(9)-C(4)-P	119.9(4)
C(1)-P-S	113.0(2)	C(11)-C(10)-P	123.7(4)
C(10)-P-S	112.9(2)	C(15)-C(10)-P	117.9(4)
C(2)-C(1)-P	114.6(4)		

TABLE III The dependence of the equilibrium position **2A** ⇋ **2B** on the solvent nature, K_T = [**2B**]/[**2A**], (20°C), c = 0,1 mol/l

Solvents	*Content of 2A* %	K_T
CH_2Cl_2	38	1.63
$CHCl_3$	65	0.54
CH_3CN	82	0.22
CH_3COCH_3	2	49.0
$(CH_3)_2NCHO$	42	1.38

vents are listed in Table III. The content of the cyclic form **2A** is larger in more polar acetonitrile as well as in iodides **1A** (n = 1,2) as compared to that in methylene chloride and chloroform. However, a low content of the cyclic form in acetone and dimethylformamide does not correlate with the polarity of solvents. A sharply increased content of the acyclic form is, probably, associated with specific solvation of the P=S groups in these solvents. The temperature dependence of the position of tautomeric equilibrium **2A** ⇋ **2B** in methylene chloride is presented in Table IV. As the temperature increases, the content of the open form **2B**‡ in the equilibrium mixture increases. The ΔH value for the tautomeric equilibrium **2A** ⇋ **2B** was calculated from the dependence of $\ln K_T$ on 1000/T (Figure 3), for which an excellent linear correlation with a correlation coefficient 0.995 is observed. As in other ring-chain tautomeric systems, the transformation of the cyclic form to the open one is an endothermal process. In Table IV are also listed other thermodynamical parameters.

Kinetics of Tautomeric Transformations

The rate of tautomeric transformations **2A** ⇋ **2B** was studied in methylene chloride solutions at 20°C by the $^{31}P\text{-}\{^1H\}$ NMR method. Both cyclic and open isomers were used as starting substances. The data obtained are listed in Table

TABLE IV The temperature dependence of the tautomeric equilibrium constants and some thermodinamic parameters for the system **2A** ⇋ **2B** in CH_2Cl_2, c = 0.1 mol/l

T(K)	K_T	*ΔG (kcal/mol)*	*ΔH (kcal/mol)*	*ΔS (e.u.)*
278	0.88	0.071		
293	1.63	−0.284	6.92	24.6
308	2.85	−0.641		
318	4.32	−0.924		

‡Earlier[112] the studies of the mechanism of polymerization of deoxothiolphostones Ph-P-S$(CH_2)_nCH_2$ (n = 2,3) in the presence of MeI, $PhCH_2Br$ in modelling experiments performed directly in ampoules for measuring ^{31}P NMR spectra showed that, along with the signals of the thiaphosphonium salt, the signals, which were presumably assigned to the isomeric acyclic sulfide, appeared in the spectra of solutions at 80°C. These signals disappeared on lowering the temperature to 35°C.

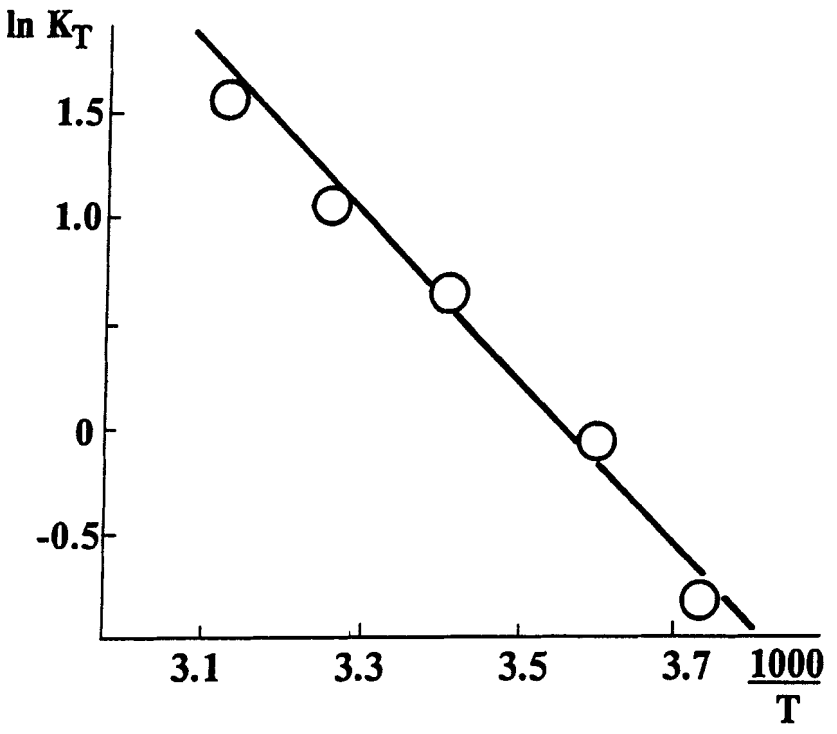


FIGURE 3 The temperature dependence of the tautomeric equilibrium constants **2A** ⇋ **2B** in CH_2Cl_2, c = 0.1 mol/l.

V. The curves of the transformation of **2A** and **2B** to the equilibrium mixture **2A** ⇋ **2B** are presented in Figure 4 and Figure 5.

In both cases, the equilibrium is achieved in about 15 h, and the ratio between the two forms in the equilibrium mixture does not depend on the starting com-

TABLE V The time dependence of the tautomers **2B** and **2A** content during the equilibrium establishment (20°C, c = 0.1 mol/l)

Starting isomer ***2A***		*Starting isomer* ***2B***	
Time (h)	*% **B***	*Time (h)*	*% **A***
0	0	0	0
0.25	3.9	0.08	1.6
0.58	10.3	0.42	4.6
1.00	21.1	0.83	9.8
1.67	30.4	1.5	15.1
3.00	42.7	2.83	19.4
4.75	45.2	4.58	27.3
23.00	62.0	22.83	38.0

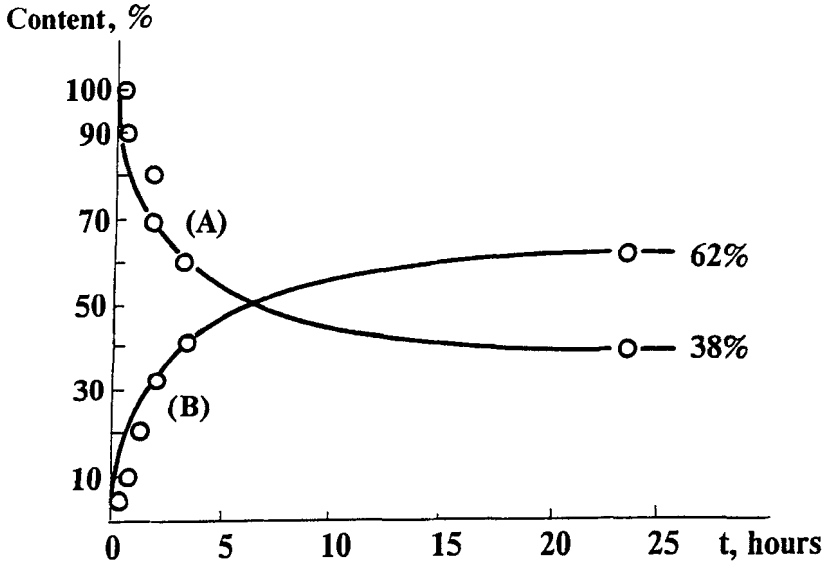


FIGURE 4 The kinetic curves of **2A** transformation to the equilibrium mixture **2A** + **2B**.

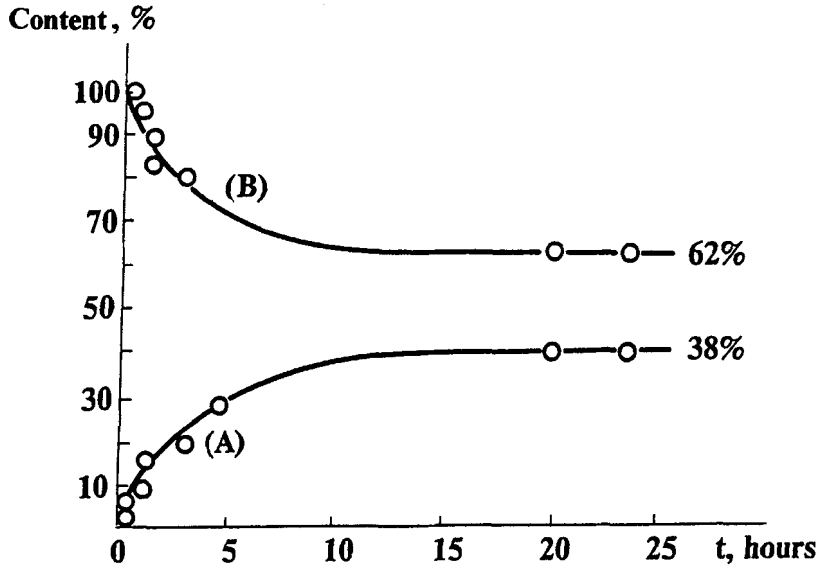


FIGURE 5 The kinetic curves of **2B** transformation to the equilibrium mixture **2B** + **2A**.

TABLE VI The kinetic constants of interconversion **2A** and **2B** (k min^{-1}; CH_2Cl_2, 20°C, c = 0.1 mol/l)

2A ⇋ *2B*	*2B* ⇋ *2A*
$k_1 = 2.97 \times 10^{-3}$	$k'_1 = 1.67 \times 10^{-3}$
$k_2 = 1.80 \times 10^{-3}$	$k'_2 = 2.72 \times 10^{-3}$

pounds. The rate constants k_1 and k_2 for the interconvertions **2A** ⇋ **2B** and **2B** ⇋ **2A** were calculated from the experimental data using the equations for reversible monomolecular reactions and the tautomeric equilibrium constants (Table VI)[¶]. The k_1 and k_2 constants were, naturally, cross-equal: $k_1 = k'_2$ and $k_2 = k'_1$ (within the experiment accuracy). It is noticeable that the cation and anion in bromide **2A** behave, in the kinetics sense, as one particle forming, probably, a tight ion pair in CH_2Cl_2 solution. It follows from the fact that the ratio [**2B**]/[**2A**] is constant at different initial concentrations (Table VII). If the thiaphospholanium salt dissociated to ions (two particles), the ratio between the tautomeric forms [**2B**]/[**2A**] would decrease on dilution, as it was the case for dimethylformamide, for which ionic dissociation is possible.

EXPERIMENTAL

All experiments were carried out in argon atmosphere; solvents were distilled in argon also. IR spectra were determined on UR-20 infrared spectrophotometer (KBr). Raman spectra of **2A** and **2B** crystals were recorded on U-1000 instrument with laser-excited atomic fluorescence (ν = 514 nm) in Spectroscopic Center RAS. NMR spectra were recorded on a Bruker WP-200SY spectrometer at 200.13 MHz (^1H) using HMDS as internal standart, and 80.01 MHz (^{31}P) using 85% H_3PO_4 as external standart. The solution concentrations were 0.1

TABLE VII The concentration influence on the ratio [**2B**]/[**2A**]* in two solvents (20°C).

Initial concentration c mol/l	*[2B]/[2A]*	
	CH_2Cl_2	*DMFA*
0.3	1.2	1.7
0.2	1.2	1.5
0.1	1.6	1.4
0.05	1.5	1.2
0.02	1.3	0.9

*) Calculated from the integral intensity ratio of ^{31}P NMR spectra

[¶]The straight line in the coordinates lnQ/(Q-x) and t, where $Q = K_T/(K_T + 1)$, have correlation coefficients r = 0.963 (transformation of **2A** to the equilibrium mixture) and r = 0.994 (transformation of **2B** to the equilibrium mixture).

mol/l. The kinetic investigations were carried out in sealed NMR tubes. The transformation were monitored by ^{31}P NMR spectra.

X-ray experimental data for **2A** and **2B** were obtained at 293K using a four-circle "Siemens P3/PC" diffractometer (monochromated MoKα radiation, $\theta/2\theta$-scan, $2\theta < 60°$). The crystals of **2A** and **2B** are monoclinic at 293K. Important crystallographic parameters for **2A** are: a = 12.034(4)Å, b = 11.788(3)Å, c = 11.462(4)Å, β = 115.66(2)°, V = 1465Å^3, Z = 4, space group $P2_1/c$, μ = 3.036 mm^{-1}, F(000) = 688, d_{calc} = 1.537 gcm^{-3}; and for **2B**: a = 23.735(8)Å, b = 10.536(3)Å, c = 14.469(5)Å, β = 123.34(2)° V = 3023(2) Å^3, Z = 8, space group $C2/c$, μ = 2.944 mm^{-1}, F(000) = 1376, d_{calc} = 1.491 gcm^{-3}. The total number of the measured reflections for **2A** and **2B** structures were 2850 and 3489.

Both structures were solved by direct method and refined by full-matrix least squares against F^2 in the anisotropic (H-atoms isotropic) approximation. All hydrogen atoms were located from the electron density difference synthesis and were included in the refinement using the riding motion model. The difference Fourier synthesis for **2A** revealed additional peaks which were interpreted as a disorder of the central carbon atom of the thiaphospholane ring. The occupancies of the two positions labelled C(2′) and C(2″) refined to 0.6 and 0.4, respectively.

The refinement for **2A** and **2B** converged to R1 = 0.0736, 0.0620 for the 2487 and 1978 independent reflections with $I > 2\sigma(I)$; wR2 = 0.1735, 0.1527 and GOF = 1.01, 1.078 for all 3077 and 2706 independent reflections, respectively. All calculations were performed using an IBM PC computer and SHELXTL PLUS 5 (gamma version) program package. The final atomic parameters for structures **2A** and **2B** are listed in the Tables VIII and IX.

3-Bromopropyldiphenylphosphine Sulfide 2B

To a stirring suspension of 1.1 g (4.10^{-3}mol) 3-oxypropyldiphenylphosphine sulfide[14] in 15 ml of dry benzene solution was added dropwise over 20 min 0.6 g (2.2.10^{-3} mol) of PBr_3 in 5 ml of benzene. The mixture was refluxed for 3h, cooled and 5 ml of water and 25 ml of $CHCl_3$ were added. The organic layer was washed with a concentrated solution of $NaHCO_3$ (5 ml) and with water (5 ml) and dried over Na_2SO_4. The solvents were evaporated under reduced pressure and the residue was extracted with boiling heptane. The white crystals **2B** were obtained from heptane solution by cooling. Yield 1.1 g (81%), m.p. 81–83°C; after recrystallization from ethanol m.p. 82–83°C, $\nu_{P=S}$ 612, 622 cm^{-1} (IR); 613, 623 cm^{-1} (RS); ^{31}P-{^1H} NMR CH_2Cl_2: δ 42.0 ppm; ^1H NMR ($CDCl_3$): δ 2.17–2.23 (m, 2H, $CH_2\underline{CH_2}CH_2$); 2.611, 2.623 (dt, $^3J_{HH}$ 11.4 Hz; $^2J_{PH}$ 4.8 Hz, 2H, $PC\underline{H_2}$ CH_2); 3.46 (t, $^3J_{HH}$ 6.4 Hz, 2H, CH_2Br); 7.25–7.85 (m,

TABLE VIII Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for **2A**.

Atom	*x*	*y*	*z*	*U*
Br	1534(1)	−10870(1)	−2446(1)	47(1)
S	2234(1)	−8478(1)	−490(1)	40(1)
P	2497(1)	−7003(1)	564(1)	30(1)
C(1)	1159(6)	−7044(6)	908(6)	43(1)
C(2′)	923(10)	−8272(8)	993(11)	40(2)
C(2″)	393(14)	−7985(14)	178(20)	48(4)
C(3)	946(7)	−8949(7)	−146(8)	62(2)
C(4)	2521(4)	−5804(4)	−369(5)	31(1)
C(5)	1644(5)	−4935(5)	−688(5)	42(1)
C(6)	1665(6)	−4033(6)	−1417(6)	51(1)
C(7)	2563(6)	−3963(6)	−1879(6)	50(1)
C(8)	3435(6)	−4819(6)	−1562(7)	53(2)
C(9)	3432(6)	−5725(5)	−810(7)	47(1)
C(10)	3934(4)	−7047(4)	2002(4)	31(1)
C(11)	4776(5)	−7911(5)	2178(5)	43(1)
C(12)	5903(6)	−7893(6)	3301(6)	52(2)
C(13)	6168(6)	−7046(6)	4185(6)	48(1)
C(14)	5318(5)	−6197(6)	4010(6)	45(1)
C(15)	4194(5)	−6178(5)	2911(5)	37(1)

10 H,C_6H_5); Anal. Found: C 52.90; H 4.63; P 9.42%. Calcd. for $C_{15}H_{16}BrPS$: C 53.11; H 4.75; P 9.13%.

2,2-Diphenyl-1,2λ^4-thiaphospholanium Bromide 2A

0.2 g bromide **2B** was heated slowly without solvent. The compound melted at 85°C and began to crystallize at once. After heating at 100°C during 30 min. the reaction mixture was solid. Recrystallization from $CHCl_3$-$CH_3COOC_2H_5$

TABLE IX Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for **2B**.

Atom	*x*	*y*	*z*	*U*
Br	531(1)	6285(1)	1833(1)	84(1)
P	1673(1)	9658(1)	4627(1)	35(1)
S	2580(1)	10211(2)	5162(1)	57(1)
C(1)	1254(3)	8913(6)	3275(5)	43(1)
C(2)	1668(3)	7921(6)	3158(5)	45(1)
C(3)	1298(3)	7263(7)	2044(6)	58(2)
C(4)	1101(3)	10932(5)	4417(4)	41(1)
C(5)	1263(3)	12171(6)	4378(5)	50(1)
C(6)	793(5)	13125(8)	4125(7)	66(2)
C(7)	190(4)	12846(8)	3955(6)	66(2)
C(8)	20(4)	11615(8)	3989(7)	67(2)
C(9)	464(3)	10647(7)	4220(5)	55(2)
C(10)	1640(3)	8545(5)	5555(4)	38(1)
C(11)	1344(3)	7364(6)	5234(6)	49(1)
C(12)	1364(4)	6548(7)	5992(7)	62(2)
C(13)	1667(4)	6882(8)	7056(6)	66(2)

mixture gave 0.15 g (75%) of pure compound **2A** m.p. 163–164°C. ν_{P-S} 570 cm^{-1} (IR); 572 cm^{-1} (RS); $^{31}P-\{^1H\}$ NMR (CH_2Cl_2): δ 72.6 ppm; ^1H NMR ($CDCl_3$): δ 2.509; 2.634 (dpent, $^3J_{HH}$ 6.4 Hz $^3J_{PH}$ 25.3 Hz, 2H, $P^+CH_2C\underline{H}_2$); 3.379, 3.412 (dt, $^3J_{HH}$ 6.4 Hz, $^3J_{PH}$ 6.4 Hz; 2H,$CH_2C\underline{H}_2SP^+$); 3.710, 3.757 (dt, $^3J_{HH}$ 6.4 Hz, $^2J_{PH}$ 9.0 Hz, 2H, $P^+C\underline{H}_2CH_2$); 7.46–7.91 (m, 10 H,C_6H_5). Anal. Found: C 52.78; H 4.59; P 9.19%. Calcd. for $C_{15}H_{16}BrPS$: C 53.11; H 4.75; P 9.13%.

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