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Synthesis and X-Ray Study of Cis and Trans Isomers of 6-Cyano-2-oxa-10-thia-1-phosphabicyclo[4.4.0]decane-1-oxide

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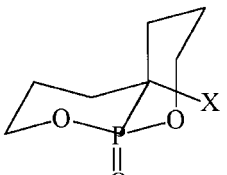
ABSTRACT: *Intramolecular cyclization of bis(3-chloropropyl)-diethoxythiophosphorylacetonitrile* **7**, *taking place under distillation in vacuo, yields 6-cyano-2-oxa-10-thia-1-phosphabicyclo[4.4.0]decane-1-oxide* **10** *as a mixture of cis and trans isomers in a 2.3:1 ratio. The isomers were separated chromatographically. For both isomers, single crystals with nonequivalent enantiomeric ratios were obtained under crystallization. The structures of both isomers of bicyclophostone* **10** *are confirmed by X-ray study of single crystals.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:163–170, 2000

INTRODUCTION

2,10-Dioxa-1-phosphabicyclo[4.4.0]decane-1-oxides **1a,b** obtained by multistep procedures from the corresponding 1,2-oxaphosphinanes (phostones) are recognized in the published literature [1,2]. We have obtained the 6-cyano derivative **1c** as the result of thermal *bis*-dealkylation of the *bis*(3-chloropropyl)dialkoxyphosphorylacetonitriles [3].

Dioxaphosphabicyclodecanes **1a–c,** including those having a substituent in the 6-position, were found to form solely as stable *cis* isomers [1–4], unlike the corresponding nonphosphorus analogs: decalin and 2,10-dioxabicyclo[4.4.0]-decane, which are formed and exist in solutions as an equilibrium mixture of cis and trans isomers [6,7].



1 a-c

a , X = H
b , X = CO_2Me
c , X = CN

According to calculation by the molecular mechanics method, using the MMX force field carried out for **1c,** the *cis* isomer is preferable thermodynamically (ΔE = 7.84 kcal/mol) [3]. Also, it was reported that the reaction between **1a** and the Lawesson reagent leads to the corresponding thio analog **2,** that also exists in the form of the *cis* isomer only [5]. Furthermore, on exhaustive exchange of oxygen for sulfur atoms in **1a** under severe conditions (P_4S_{10}, Py), 2,10-dithia-1-phosphabicyclo[4.4.0]-decane-1-sulphide **3** is formed as a mixture of *cis* and *trans* isomers in a 1.5:1 ratio [5].

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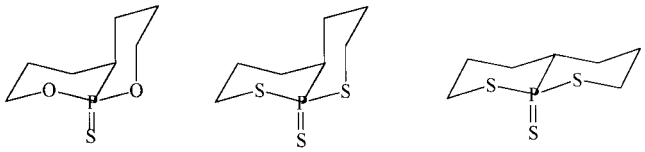


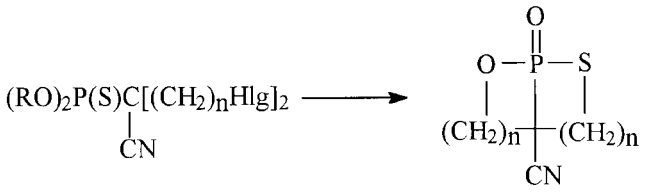
2 **3a (cis)** **3b (trans)**

The introduction of the large sulfur atom appears to decrease steric strain in the trans-isomer due to the increase of the *H…H* distance resulting from the elongation of the ordinary P–X (X = O, S) bond. It should be noted that the intermediate products of the exhaustive exchange of oxygen for sulfur cascade reaction having only one cyclic sulfur atom were not obtained, although the investigation of the stereochemistry of such type unsymmetric compounds would be of particular interest.

One would expect that intramolecular condensation of C,C-*bis*(ω-haloalkyl)dialkoxythiophosphorylacetonitriles **4** would allow us to obtain compounds **5** containing different cyclic fragments in the molecule (Scheme 1).

RESULTS AND DISCUSSION

We considered it possible to synthesize **4** by the alkylation of the thiophosphorylacetonitrile **6** by unsymmetric α,ω-dihaloalkanes under phase-transfer catalysis conditions using an excess of 50% aqueous NaOH as a base and without solvent, by analogy with the method of synthesis of the phosphoryl analog of compound **4b,** having two 3-chloropropyl groups, which we described earlier [3]. However, it turned out that the result of such interaction is defined by the alkylene chain length in the electrophilic component. When $n = 3$, the desired acyclic compound **7** is formed in high yield, whereas when $n = 2$ and $n = 4$, the cycloalkanes **8** and **9** (Scheme 2) are the only reaction products. It should be noted that similar results to those we have observed earlier [8] when studying the alkylation of thiophosphorylacetonitriles **6** by unsymmetric α,ω-dihaloalkanes in other interphasic systems. Such results testify that the formation of the corresponding P-substituted cyclopropanes and cyclopentanes is thermodynamically beneficial.



4 a-c

a, n=2
b, n=3
c, n=4

5

SCHEME 1

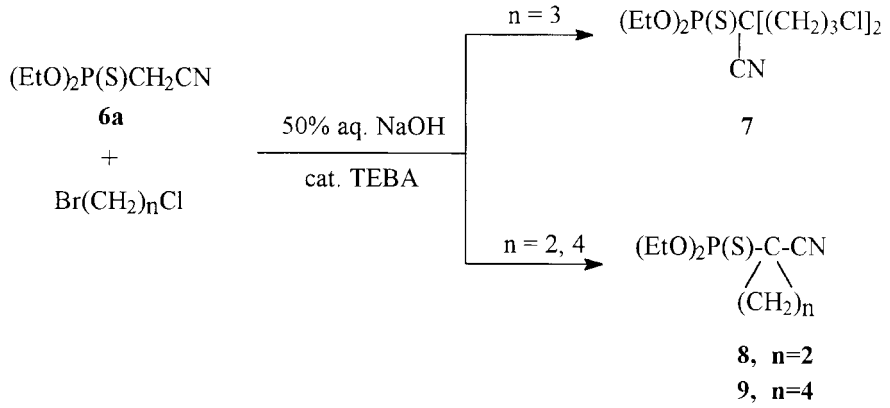
It was found that, under distillation in vacuo, *bis*(3-chloropropyl)-diethoxythiophosphorylacetonitrile **7** undergoes intramolecular cyclization, like its phosphoryl analog [3], and is transformed nearly completely to the bicyclic compound **10** (Scheme 3).

According to the aforementioned proposal concerning the increase in stability of the trans isomer when passing from phosphabibyclodecanes with 1,2-oxaphosphinane rings **1a–c** to the similar compounds having the 1,2-thiaphosphinane structure, bicyclothiolphostone **10** is actually formed as a result of such cyclization as a mixture of *cis*-**10a** and *trans*-**10b** isomers in a 2.3:1 ratio. It should be noted that, in this case, the proportion of the trans isomer is less than that for compound **3** having two thiaphosphinane rings [5], thus serving as an additional argument in favor of our proposal.

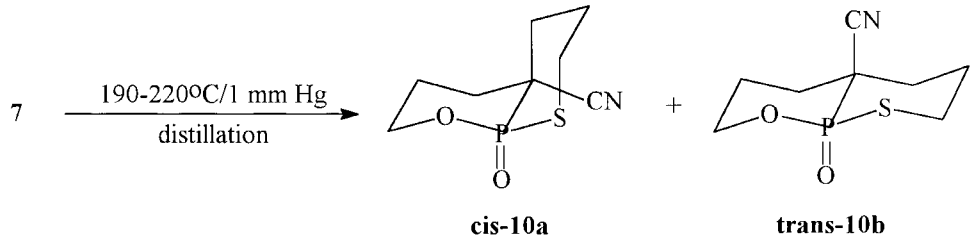
Phosphabicyclodecane **10** is likely formed as a result of a multistep process. Firstly, the intramolecular S-alkylation with subsequent dealkylation leads to the intermediate **11** as a mixture of two diastereomers (**A** and **B**). This stage is similar to the intramolecular cyclization among ω-haloalkylsubstituted phosphonates and phosphinates, including those that are cyano-substituted [9,10]. Further intramolecular alkylation appears to proceed on the oxygen atom of the P = O group, analogously [11] followed by the dealkylation resulting in the closure of the second, 1,2-oxaphosphinane moiety of the bicycle **10**. As this takes place, *cis*-**10a** is formed from the diastereomer **A,** whereas the corresponding trans isomer **10b** is formed from the diastereomer **B** (Scheme 4).

Thus, we believe that the *cis*-**10a**:*trans*-**10b** ratio depends mainly on the ratio between diastereomers **A** and **B** at the first stage of the formation of the corresponding intermediate **11** [12]. It should be mentioned that the cyclization of *C*-alkyl-*C*-halopropylthiophosphorylacetonitriles leading to 2-oxo-3-cyano-3-alkyl-1,2-thiaphosphinanes under distillation *in vacuo* usually does result in the preferable formation of the diastereomers of the type **A.**

As by-products in this reaction, nonsulfur bicyclophostone **1c** (δ_P 8.5 ppm) and 6-cyano-2,10-dithia-1-phosphabicyclo[4.4.0]decane-1-oxide **14** (δ_P, 46.2 ppm) are formed in small amounts. Intermediate **11** is likely capable of reacting with the starting compound **7** under severe thermal conditions, resulting in the formation of thio compound **12** with a 1,2-



SCHEME 2

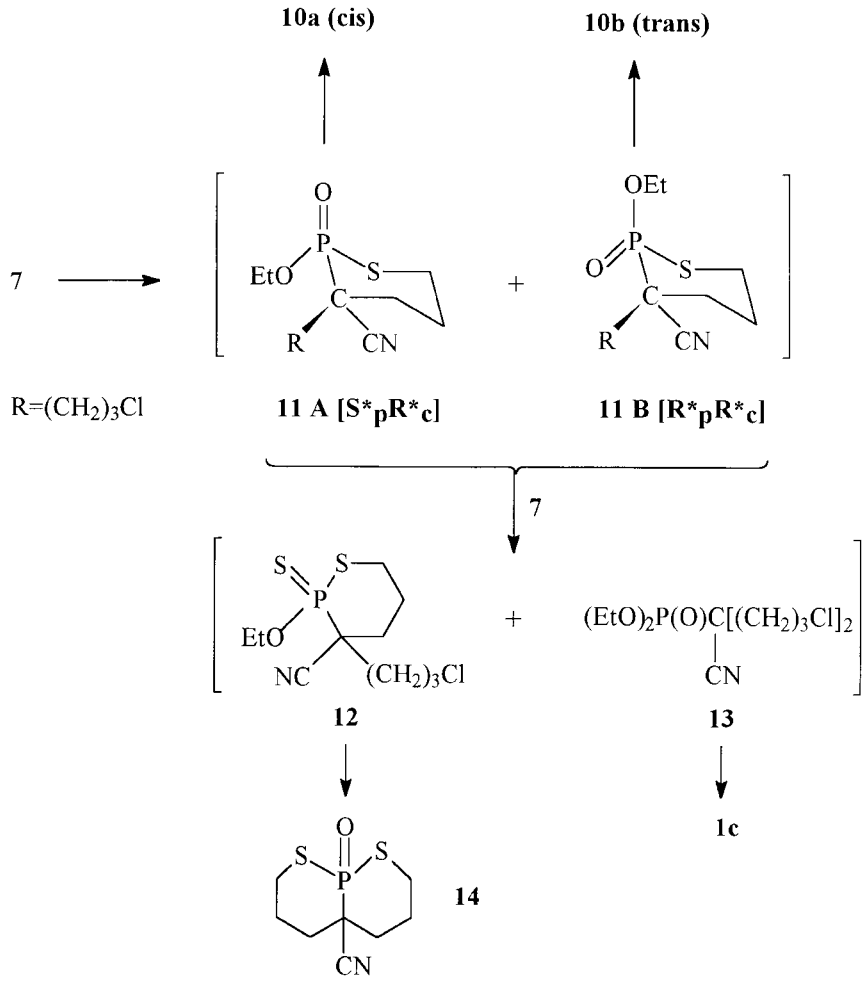


SCHEME 3

thiaphosphinane fragment and the phosphorylacetonitrile **13.** The further cyclization of these compounds yields the aforementioned by-products.

Upon addition of ether to the distillate containing phosphabicyclodecane **10,** the latter precipitates as a mixture of **10a:10b** in a 3.4:1 ratio. We have managed to separate *cis* and *trans* isomers **10** by column chromatography. Their composition and structure were confirmed by elemental analysis data and IR and NMR (^{1}H, ^{13}C, ^{31}P) spectra (Tables 1, 2). In the ^{31}P NMR spectra, signals of **10a,b** are located at δ = 36–45 ppm, characteristic of the 2-oxo-3-cyano-1,2-thiaphosphinanes [10], the signal of the *trans* isomer being shifted downfield. In the ^{13}C NMR spectra *cis*-**10a** and *trans*-**10b** have similar systems of signals (Table 1), and the signals of the tertiary carbon atom bearing the cyano-group for these compounds are shifted downfield compared to the same signals both for the monocyclic cyanosubstituted 1,2-thiaphosphinanes [10] and the bicyclophostone **1c** [3]. In the IR spectrum of *cis*-**10a,** the absorption band of the P=O group is close to that of the corresponding non-sulfur-containing analog *cis*-**1c** (1250 and 1260 cm^{-1}, correspondingly). At the same time, it is shifted up to 1225 cm^{-1} for *trans*-**10b**. The location of the absorption band of the cyano group is practically constant, not only for all the phosphabicyclodecanes (**1c, 10a,b**), but also for the starting *bis*(3-chloropropyl)thiophosphorylacetonitrile **7**. It should be noted also that the absorption of the P–S-bond of the 1,2-thiaphosphinane ring in *cis*-**10a** is shifted bathochromically compared to that of *trans*-**10b** (Table 2).

Both *cis* and *trans* isomers are formed in the reaction as a statistical mixture of enantiomers. The enantiomeric composition has been investigated by ^{31}P NMR spectroscopy. Thus, in the ^{31}P NMR spectra of **10a,b** in the racemic phenylethylamine/C_6D_6 (1:1) mixture, a single signal is observed for each racemic isomer and in the optically active l-phenyethylamine/C_6D_6 (1:1), these signals are split into two signals of equal intensity ($\Delta\delta$ 0.039 ppm, **10a**; 0.007 ppm, **10b**). After chromatographic separation, the enantiomer ratio remains equal to 1:1 for the individual *trans* isomer. Also, for the *cis* isomer, the enantiomer ratio varies from 1.5:1 to 1:1.5 in three fractions (3 $\times$ 50 mL) eluted from the column. On crystallization of the solid from the first fraction from benzene, the resulting single crystals contain enantiomers in the ratio of approximately 85:15 (according to NMR data in 1-PhCH(NH_2)CH_3/C_6D_6), with the enantiomer with the downfield shift prevailing. According to the X-ray study of such a single crystal, the major enantiomer has the R-configuration of both the phosphorus and carbon atoms (Figure 1). The additional crystallization of *trans* **10b** from benzene



SCHEME 4

gives the single crystals with the enantiomeric ratio of about 70:30.

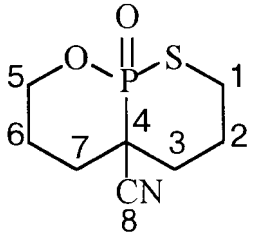
The independent determination of the structures of the compounds synthesized was carried out by X-ray investigation of the corresponding single crystals, which demonstrated that **10a** and **10b** have the *cis* and *trans* configuration, respectively. The analysis of geometry, anisotropic thermomotion parameters, as well as difference Fourier synthesis, indicated the superposition of two R_P and S_P enantiomers in both crystals (Figures 1, 2). In general, the geometry of the isomers obtained is close to those for previously described phosphabicyclodecane-1-oxides **1a–c** [1–3]. The torsion angles O(2)P(1)C(4)C(8) featuring the mutual arrangement of phosphoryl and cyano groups are equal to −48.4° and 179° in *cis*-**10a** and *trans*-**10b,** respectively. In spite of small errors in bond lengths and valence angles for *cis*-**10a** (cf. Figure 1), the systematic errors introduced for both isomers by superposition of enantiomers do not allow us neither to give a reliable estimation of the differences in interactions of phosphoryl oxygen with lone electron pairs of the cyclic heteroatoms, nor to discuss subtle differences in crystal structures. The acentric structures suffer from the fact that they were only measured centrosymmetrically.

EXPERIMENTAL

General

The NMR spectra were recorded on a Bruker WP-200SY and AMX-400 in $CDCl_3$, using tetramethylsilane (TMS) (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. ^{31}P NMR spectra of the isomers **10a** and **10b** were also recordered in *d*,-l-$PhCH(NH_2)CH_3$/C_6H_6 (1:1) and 1-$PhCH(NH_2)CH_3$/C_6H_6 (1:1) solutions at the concentration 0.1 mol/L.

TABLE 1 31_P, 13_C and ^1H NMR Data of *cis*-**10a** and *trans*-**10b** isomers of 6-cyano-2-oxa-10-thia-1-phosphabicyclo [4.4.0]decane-1-oxide in $CDCl_3$



		δ ^{13}C (*J Hz*)								
Compound	δ ^{31}P	*C1* ($^2J_{PC}$)	*C2* ($^3J_{PC}$)	*C3* ($^2J_{PC}$)	*C4* ($^1J_{PC}$)	*C5* ($^2J_{PC}$)	*C6* ($^3J_{PC}$)	*C7* ($^2J_{PC}$)	C8 ($^2J_{PC}$)	δ ^1H (*multiplicity, integral*)
10a	35.6	33.58 (3.6)	23.13 (5.4)	29.89 (3.4)	39.08 (83.4)	70.09 (7.9)	22.02 (4.5)	30.57 (4.5)	118.2 (7.2)	2.02–2.16 (m, 4H), 2.20–2.60 (m, 4H), 2.91–3.18 (m, 2H, SCH_2), 4.21–4.48, 4.5–4.68 (2m, 1H + 1H OCH_AH_B)
10b	44.8	33.30 (4.9)	24.88 (5.6)	29.56 (7.1)	41.80 (86.8)	68.78 (5.9)	25.41 (6.0)	30.72 (2.2)	119.28 (2.6)	1.82–1.89 (m, 1H), 1.94–2.08 (m, 1H), 2.09–2.22 (m, 2H), 2.25–2.37 (m, 3H), 2.52–2.64 (m, 1H) 3.05–3.18, 3.41–3.50 (2m, 1H + 1H, SCH_AH_B), 4.33–4.43, 4.70–4.78 (2m, 1H + 1H, OCH_AH_B)

TABLE 2 IR Spectral Data for Compounds **7** and **10a,b** in KBr

	ν, cm^{-1}				
Compound	P=S	P=O	P–O–C	P–S–C	CN
7	647	—	1040	—	2235
10a	—	1250	1015, 1035	464, 566	2233
10b	—	1225	1015, 1035	487, 578	2235

Bis(*3-chloropropyl*)*diethoxythiophosphorylacetonitrile* (**7**)

A mixture of diethoxythiophosphorylacetonitrile **6a** (5.0 g, 25.91 mmol), triethylbenzylammonium chloride (0.6 g, 2.59 mmol, 10 mol. %), and NaOH (8.3 g, 103.64 mmol) as a 50% aqueous solution was stirred for 5 minutes. Then 1,3-bromochloropropane (12.2 g, 77.72 mmol) was added in small portions. After the reaction mixture had been stirred for 2 hours at room temperature, 1.0 g of 1,3-bromochloropropane was added additionally, and stirring was continued for 0.5 hour. The reaction mixture was diluted with water (15 mL) and extracted with benzene (4 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (40-100 mesh; eluent, hexane-acetone gradiently from 100:0 up to 100:2). The fraction eluted with hexane-acetone 100:2 was concentrated in vacuo yielding 7.0 g (80%) of the target compound as an oil, which transformed to the white solid over time. Tm.p. 35°C. ^{31}P NMR δ ($CDCl_3$) 90.74; ^1H NMR δ ($CDCl_3$) 2.05 (t, CH_3, 6H, $^3J_{HH}$ 6.8 Hz), 1.91–2.18 (m, $C\underline{H}_2C\underline{H}_2CH_2Cl$, 8H), 3.57 (t, CH_2Cl, 2H, $^3J_{HH}$ 5.2 Hz), 3.58 (t, CH_2Cl, 2H, $^3J_{HH}$ 6.0 Hz), 4.16–4.31 (m, OCH_2, 4H); ^{13}C NMR δ ($CDCl_3$) 15.45 (d, CH_3, $^3J_{PC}$ 6.2 Hz), 27.48 (d, $CH_2CH_2\underline{C}H_2Cl$, $^3J_{PC}$ 6.6 Hz), 29.82 (s, $\underline{C}H_2CH_2CH_2Cl$), 37.52 (d, P*C*(CN), $^1J_{PC}$ 119.5 Hz), 43.76 (s, CH_2Cl), 63.81 (d, OCH_2, $^2J_{PC}$ 7.4 Hz), 117.53 (d, CN, $^2J_{PC}$ 6.9 Hz). Anal. Calcd for $C_{12}H_{16}NO_2PS$: C, 41.62; H, 6.40; N, 4.12; P, 8.95. Found: C, 41.17; H, 6.77; N, 3.96; P, 8.98.

Diethoxythiophosphorylcycloalkanecarbonitriles (**8,9**)

From **6a** (2.0 g, 10.36 mmol) and 1,2-bromochloroethane (3.3 g, 41.44 mmol), under the previously described conditions, 1.1 g (49%) of hem-disubstituted cyclopropane **8** was obtained by distillation. b.p. 126–128°C/10 mm Hg, n^{20}_D 1.4892, ^{31}P NMR δ (C_6H_6) 92.0; ^1H NMR corresponds to the data published in the literature [13].

In the same manner, from **6a** (2.0 g, 10.36 mmol) and 1,4-bromochlorobutane (5.33 g, 31.08 mmol), after distillation in vacuo, 1.8 g (70%) of hem-disubstituted cyclopentane **9** was obtained. b.p. 122–

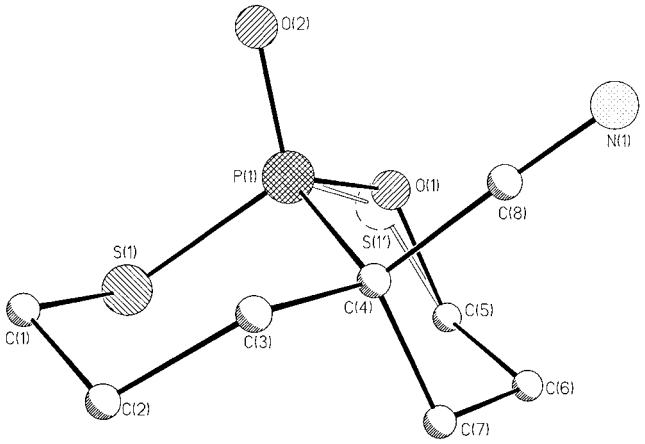


FIGURE 1 General view of the major R_P enantiomer in *cis*-**10a** crystal structure and scheme illustrating the superposition of the enantiomers. The position of the sulfur atom is shown for the minor enantiomer only. The main bond lengths (A) and valent angles (deg): P(1)–O(2) 1.463(2), P(1)–O(1) 1.575(4), P(1)–C(4) 1.823(2), P(1)–S(1) 2.020(1), S(1)–C(1) 1.821(4), O(2)–P(1)–O(1) 111.4(2), O(2)–P(1)–C(4) 113.46(12), O(1)–P(1)–C(4) 105.3(2), O(2)–P(1)–S(1) 114.97(10), O(1)–P(1)–S(1) 105.5(2), C(4)–P(1)–S(1) 105.46(8), C(5)–O(1)–P(1) 120.3(3), C(1)–S(1)–P(1) 96.17(12)

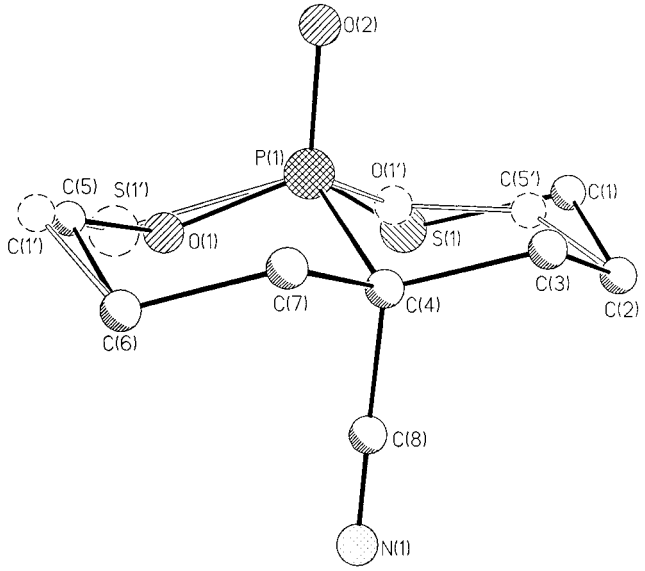


FIGURE 2 General view of *trans*-**10b** and scheme illustrating superposition of S_p and R_p enantiomers. Only the positions of sulfur and oxygen atoms and the methylene carbon atoms bonded with them are indicated for the minor enantiomer S_P.

134°C/1 mm Hg, n^{20}_D 1.4891, ^{31}P NMR δ (C_6H_6) 93.2; ^{1}H NMR corresponds to the data published in the literature [13].

6-Cyano-2-oxa-10-thia-1-phosphabicyclo[4.4.0]decane-1-oxide (**10**)

The reaction mixture from the synthesis of **7,** before the chromatographic purification, was distilled in vacuo with collection of a fraction having a b.p. of 190–230°C/1 mm Hg, which contained cis(**a**)- and trans(**b**)-isomers in a 2.3:1 ratio based on the NMR ^{31}P data. The same result was achieved under the distillation of the isolated target compound **7** (7.0 g, 20.70 mmol) with a catalytic amount of Et_3NCH_2PhCl. After addition of cold ether to this fraction, it was maintained for 2 hours at 0°C, and the resulting solid was filtered off, yielding 1.95 g of white solid with a cis:trans ratio of 3.4:1, m.p. 71–75°C. The isomers were separated by column chromatography on silica gel (40–100 mesh; eluent, hexane-acetone gradiently from 10:0 up to 10:3), yielding **10b** (0.25 g, hexane-acetone 10:2), and **10a** (0.8 g, hexane-acetone 10:3).

For the *cis*-**10a:** R_f 0.23 (hexane-acetone 1:1), m.p. 115–118°C. Anal. Calcd. for $C_8H_{12}NO_2PS$: C, 44.23; H, 5.57; N, 6.45. Found: C, 43.72; H, 5.58; N, 6.02.

For the *trans*-**10b:** R_f 0.34 (hexane-acetone 1:1), m.p. 170–172°C. Anal. Calcd. for $C_8H_{12}NO_2PS$: C, 44.23; H, 5.57; N, 6.45. Found: C, 43.91; H, 5.47; N, 6.43.

X-Ray Structure Determination of cis-**10a** *and trans*-**10b**

Single crystals for *cis*-**10a** and *trans*-**10b** were slowly produced from benzene solutions. Accurate unit-cell parameters and orientation matrices were obtained by least-squares refinement of carefully centered 24 reflections in the $23° \le \theta \le 27°$ ranges. Two standard reflections were monitored every 98 reflections for *cis*-**10a** and *trans*-**10b** and showed no significant variations in both cases. Data were corrected for Lorentz and polarization effects. Carefully chosen, rather small, well-formed, and essentially isometric single-crystal samples, the quality of the obtained results, and the relatively low-absorption-coefficient values justified no necessity for absorption corrections.

The structures were solved by direct methods and subsequent difference Fourier maps. The positions for all H-atoms in both molecules were calculated geometrically and refined in the "riding" ap-

TABLE 3 Crystal Data and Details of the X-Ray Experiments for *cis*-**10a** and *trans*-**10b**

	Compound	
	cis-**10a**	*trans*-**10b**
Formula	$C_8H_{12}NO_2PS$	$C_8H_{12}NO_2PS$
Mol Wt	217.22	217.22
Cryst Size (mm)	0.15 × 0.20 × 0.25	0.10 × 0.20 × 0.20
Cryst System	Orthorombic	Monoclinic
Space Group	$P2_12_12_1$	$P2_1$
Cell Constants		
a, Å	7.810(3)	6.208(3)
b, Å	11.254(4)	11.960(7)
c, Å	11.671(3)	6.963(4)
β, °		104.07(4)
V, Å^3	1025.9(6)	501.5(5)
Z	4	4
D_{calc} (g cm^{-3})	1.406	1.439
diffractometer	Siemens P3/PC	Siemens P3/PC
temp (K)	298	153
radiation (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
scan mode	θ-2θ	ω
$2\theta_{max}$ (deg)	60	52
range of h, k, l	$0 \le h \le 11$	$0 \le h \le 6$
	$0 \le k \le 20$	$0 \le k \le 15$
	$0 \le l \le 21$	$-9 \le l \le 8$
Number of Parameters used in refinement	129	156
Total Unique Refls Collected	3267	1127
Abs Coeff, μ(Mo Kα), (mm^{-1})	0.439	0.439
R1 (on F for refls with $I > 2\sigma(I)$)	0.0491(1679 refls)	0.0788 (1039 refls)
wR2 (on F^2 for all refls)	0.1545(3217 refls)	0.2112 (1106refls)
Largest Difference Peak and Hole, eÅ^{-3}	0.502 and −0.302	0.981 and −0.606

proximation. The analysis of the difference Fourier synthesis for *cis*-**10a** and *trans*-**10b** revealed additional peaks, which were interpreted as the disordering caused by the superposition of two enantiomers R_p and S_p. The ratios of the two enantiomers in the crystal structures of *cis*-**10a** and *trans*-**10b** were approximately equal to 85:15 and 70:30, respectively. The absolute configuration of the phosphorus atom in the dominant enantiomer in the crystal structure of *cis*-**10a** was determined with the help of the Flack parameter, which, in the case of the R_p configuration, was equal to 0.15(15). Unfortunately, in the case of *trans*-**10b**, the absolute configuration was not determined reliably because of the extremely high deviation (0.9) of the Flack parameter [14]. On the basis that the occupancies of the sulfur in the minor S_p enantiomer of *cis*-**10a** was refined to 0.15, the positions of carbon, oxygen, and nitrogen atoms of this enantiomer were impossible to locate. All calculations were carried out on an IBM PC with SHELXTL PLUS 5 programs. Crystal data and details of the X-ray experiments are given in Table 3. A complete description of X-ray crystallographic structure determinations have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2, 1EW, UK.

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