Journal of Chemical Crystallography, Vol. 31, Nos. 9–10, October 2001 (© 2002)

Isomerization of 2-seleno-1,3,2-diazaphospholidine derivatives

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Received April 20, 2001

For the first time the isomerization of 1,3,2-diazaphospholidine-2-selenide derivatives in refluxing benzene in the presence of trace water was observed, and the structure of isomerized product was determined by X-ray diffraction, IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis. The mechanism of isomerization was also proposed. The isomerized phosphoroheterocycle ($C_{26}H_{38}N_3O_5PSe$, Mr = 582.52) is orthorhombic with space group *Pbca*, $a = 17.1010(9)$ Å, $b = 16.6404(9)$ Å, $c = 20.7517(11)$ Å, $V = 5905.3(5)$ Å^3, $Z = 8$, $Dr = 1.310$ g/cm^3, $\lambda = 0.71073$ Å, μ (Mo Kα) $= 1.363$ mm^{-1}, $F(000) = 2432$. The structure was refined to $R1 = 0.0482$, $wR2 = 0.1204$ for 5214 unique reflections with $I > 2\sigma(I)$. Intramolecular and intermolecular hydrogen bonds are observed in the crystal packing.

KEY WORDS: Isomerization; 2-seleno-1,3,2-diazaphospholidine derivatives; crystal structure; mechanism.

Introduction

The thiono–thiolo rearrangement has attracted considerable interest in the past decades,[1–4] which proved to be an important and efficient method for the synthesis of phosphorothioates and their analogs from P═S containing precursors. Likewise, the selenone–selenol rearrangement of P═Se to P—Se in phosphorus compounds has also been reported in the literature.[5] Nuretdinov early reported the isomerization of β, γ-unsaturated esters of selenophosphoric acids,[6] and Dembinski also found the converse isomerization of selenol–selenone of the compounds containing a selenium bridge between two phosphoryl centers.[7] Predvoditelev has investigated the isomerization of dioxaphosphorinane derivatives, which when treated with $PhCH_2P^+Ph_3Br^-$ gives 84% isomerized product,[8] but, to our knowledge, the isomerization of phosphoroheterocycles 1,3,2-diazaphospholidine 2-selenide derivatives which show highly selective herbicidal activity[9] has not been reported. This paper describes the rearrangement of P═Se to P—Se in 1,3,2-diazaphospholidine derivatives resulting in the formation of the corresponding organic ammonium salts. The pathway of the isomerization is suggested to involve a three-step reaction. The structure of the product was determined by X-ray diffraction and characterized by microanalysis and other spectroscopic methods.

Experimental

^{1}H NMR and ^{31}P NMR spectra were recorded with a BRUKER AC-P 200 Spectrometer ($CDCl_3$ as solvent, TMS as internal, 85% H_3PO_4

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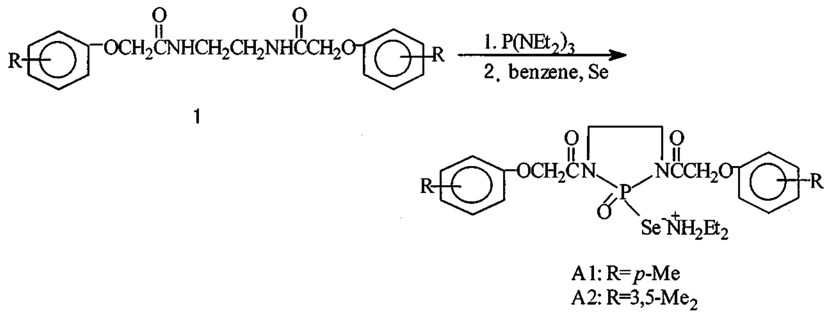


Scheme 1.

as outside standard). Melting point was determined on THOMSHOOVER melting point apparatus and the thermometer was uncorrected. Elemental analysis was carried out with Yanaco CHN CORDER MT-3 autoanalysis apparatus. IR spectrum was performed on a SHIMADZU-435 spectrometer, and band positions were reported in wave numbers (cm^{-1}).

*Preparation of compound **1***

A total of 0.3 g (5 mmol) of ethylenediamine and 1.5 mL Et_3N were dropped into a 100 mL three-necked flask containing 30 mL anhydrous benzene, and there a solution of 10.5 mmol of phenoxy acetyl chloride in 10 mL anhydrous benzene was added dropwise within 15 min in ice bath. The mixture was stirred for 1 h, subsequently warmed to room temperature, and stirred for another 2 h. The solid formed was filtered and washed with water several times. A colorless product was obtained by recrystallization of the solid from ethanol. **1a**: R = *p*-Me, mp: 173–175°C, yield: 79.6%; **1b**: R = 3,5-Me, mp: 198–199°C, yield: 72.5%.

Isomerization reaction

A total of 1.5 mmol of the dried compound **1** was added to a two-necked flask and heated directly with 2 mmol of tris(diethylamino)phosphine at 180–190°C for 5 h under nitrogen, then the mixture was cooled to room temperature. After addition of 15 mL of benzene, 0.3 g of selenium was added and the mixture was warmed to 80°C for another 2.5 h. The product was obtained by flash chromatography (with equal volumes of ethyl acetate and petroleum ether as eluant) and recrystallized from a mixture of chloroform and petroleum ether (Scheme 1).

A1: R = *p*-Me, colorless crystal, mp: 120–122°C, yield: 37.6%, FM: $C_{24}H_{34}N_3O_5PSe$, FW= 553.96. Elemental Analysis. Calcd. (%) C: 51.98, H: 6.13, N: 7.58. Found (%) C: 51.56, H: 5.90, N: 7.77. ^1H NMR ($CDCL_3$ as solvent, TMS as internal) δ (ppm): 1.45 (t, 6H, $J_{H-H} = 7.26$ Hz, $N(CH_2CH_3)_2$), 2.24 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.89–3.05 (m, 4H, $N(CH_2CH_3)_2$), 3.78–4.12 (dm, 4H, 2 × CH_2), 4.82–5.02 (m, 4H, 2 × OCH_2), 6.92 (dd, 8H, $J_{H-H} = 7.46$ Hz, Ar—H, AA′BB′system), 9.56 (br, 2H, NH_2). ^{31}P NMR ($CDCL_3$ as solvent, 85% H_3PO_4 as out standard) δ (ppm): 8.29. IR (KBr, cm^{-1}): 3060 ν (Ar—H), 2979–2783 ν (CH_2), ν (CH_3), 2513, 1989 ν ($^+NH_2$), δ ($^+NH_2$), 1683, 1652 ν (C═O), 1610, 1510, 1435, 1388 ν (C═C), 1216 ν (P═O), 1079 ν (Ar—O—C).

A2: R = 3,5-Me_2, colorless crystal, mp:145–147°C, yield: 32.8%. FM = $C_{26}H_{38}N_3O_5Pse$, FW = 581.96. Elemental Analysis. Calcd. (%) C: 53.61, H: 6.52, N: 7.21. Found (%) C: 53.15, H: 6.35, N: 7.08. ^1H NMR ($CDCl_3$ as solvent, TMS as internal) δ (ppm): 1.44 (t, 6H, $J_{H-H} = 7.12$ Hz, $N(CH_2CH_3)_2$), 2.23 (s, 12H, 4 × CH_3), 2.95–3.15 (m, 4H, $N(CH_2CH_3)_2$), 3.78–4.10 (dm, 4H, 2 × CH_2), 4.87–5.04 (m, 4H, 2 × OCH_2), 6.52 (s, 4H, Ar—H), 6.61 (s, 2H, Ar—H), 9.52 (br, 2H, $^+NH_2$).

Compound **A2** in a mixture of chloroform and petroleum ether (1/3, v/v) was allowed to

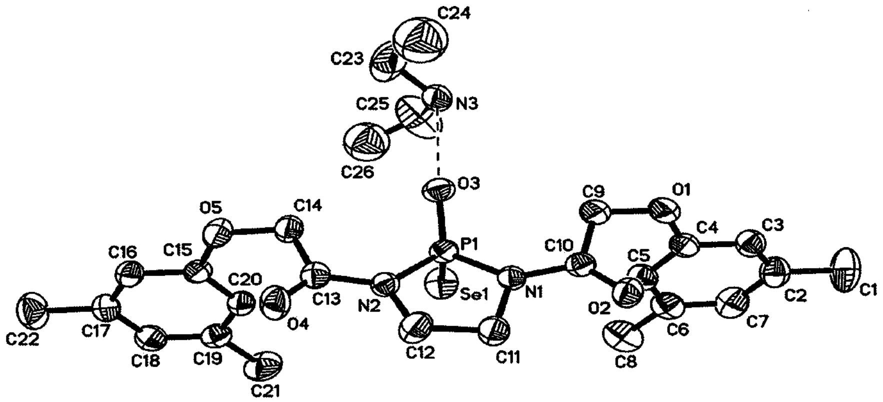


Fig. 1. Molecule structure of compound **A2** with 50% probability for ellipsoids.

stand at room temperature until colorless crystals separated out gradually.

Structure determination by X-ray diffraction

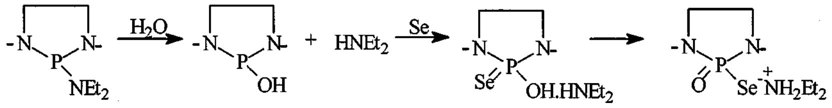
A colorless crystal of the compound having approximate dimensions of 0.20 mm × 0.25 mm × 0.3 mm was mounted on a glass fiber in a random orientation. The determination of the unit cell dimensions and the data collection were performed with Mo $K\sigma$ radiation ($\lambda = 0.71073$ Å) on a BRUKER SMART 1000 diffractometer using ω scan mode. A total of 23,560 reflections were collected in the range of $1.96° < \theta < 25.02°$ at room temperature, of which 5214 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the successive refinements. The correction for LP factors was applied.

The structure was determined by direct method (SHELX97). Most of the non-hydrogen atoms were located from an E-map, the others were determined with successive differential Fourier syntheses. Then, the structure was refined by full-matrix least-squares method with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were located theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. A full-matrix least-squares refinement gave final $R1 = 0.0482$ and $wR2 = 0.1204$. The maximum peak in the final difference Fourier maps was 0.303 e Å^{-3} and the minimum peak was −0.401 e Å^{-3}.

All calculations were carried out using SHELXS97. The molecular structure of compound **A2** is shown in Fig. 1, together with the packing of the molecules in a unit cell in Fig. 2.

Results and discussion

The isomerism of 2-seleno-1,3,2-diazaphosphoroheterocycles was discovered quite accidentally when we worked on the synthesis of some diazaphosphoroheterocycles. It was found that such phosphoroheterocycle could readily isomerize into the selenolic compounds in refluxing benzene in the presence of trace water. The isomerization reaction starting from compound **1** possibly consisted of three steps: hydrolysis, oxidation, and rearrangement (Scheme 2). On reaction, the tervalent phosphoroheterocycle was susceptible to hydrolysis, simultaneously



Scheme 2.

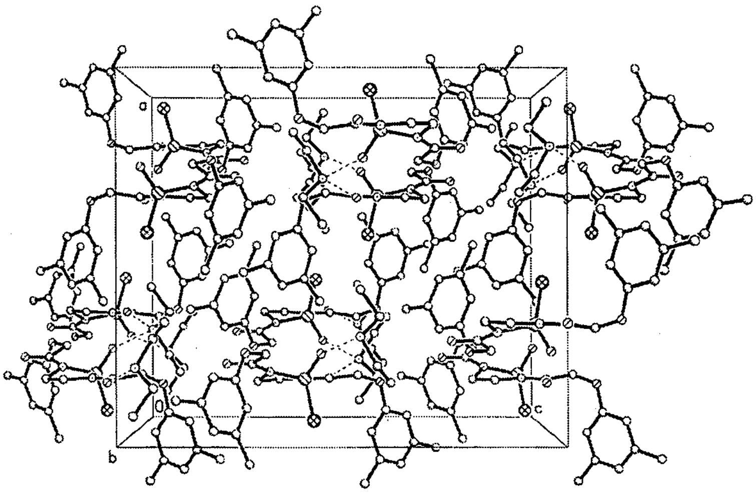


Fig. 2. Packing of the molecules in a unit cell.

releasing diethylamine. In the presence of selenium oxidation subsequently occured leading to the formation of P═Se bond. With the help of diethylamine the P═Se bond smoothly isomerized to P—Se bond resulting in organoammonium salts. Besides the general spectroscopic methods, the product was directly identified by X-ray diffraction study.

X-ray diffraction analysis was employed for the confirmation of the isomerization of these phosphoroheterocycles. X-ray data and refinement are given in Table 1. The coordinates and equivalent isotropic displacement factors of the non-hydrogen atoms are given in Table 2. Selected bond lengths and bond angles are listed in Table 3.

The bond distance of 1.486 Å for P(1)—O(3) is shorter than that of a normal P—O bond, while the bond distance of P(1)—Se(1) is longer than that of a normal P═Se bond. From this we conclude that the bond P(1)—O(3) exists in the form of a double bond and the P(1), Se(1) atoms are joined only by a single σ bond, which supports the isomerization of P═Se to P—Se in the diazaphosphoroheterocycle. On the other hand, the bond distance of Se(1)—N(3) is 4.654 Å, which reveals that the two atoms interact by electrostatic effect and also lead to the conclusion that the isomerized product is organic ammonium salt.

Table 1. Crystal Data and Structure Refinement for **A2**

Empirical formula	$C_{26}H_{38}N_3O_5PSe$
CCDC deposit no.	CCDC-1003/6077
Color	Colorless
Crystal size, mm^3	$0.20 \times 0.25 \times 0.30$
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	$a = 17.1010(9)$ Å $b = 16.6404(9)$ Å $c = 20.7517(11)$ Å
Volume, Å^3	5905.3(5)
Z	8
Formula weight	582.52
Density (calculated), Mg mm^{-3}	1.310
Absorption coefficient, mm^{-1}	1.363
$F(000)$	2432
Diffractometer used	SMART CCD 1000
Radiation/wavelength	Mo Kα(graphite mono chrom.)/0.71073 Å
Temperature, K	298(2)
θ range for data collection, deg	1.96–25.02
Scan type	ω
Index ranges	$-20 \leq h \leq 20, -19 \leq k \leq 19, -24 \leq l \leq 17$
Reflections collected	23560
Independent reflections	5214 [$R_{\text{int}} = 0.0658$] ($I \geq 2\sigma(I)$)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Goodness of fit on F^2	1.005
R, wR [$I > 2\sigma(I)$]	$R1 = 0.0482$, $wR2 = 0.1204$
Largest diff. peak and hole, e Å^{-3}	0.303 and −0.401
Data/restraints/parameters	5214/0/323

Table 2. Atomic Coordinates (10^4) and Isotropic Displacement (10^3 Å^2)

Atom	x	y	z	$U_{eq}{}^a$
Se(1)	5649(1)	5753(1)	5625(1)	82(1)
P(1)	6726(1)	6296(1)	5826(1)	54(1)
O(1)	7516(2)	4314(2)	7126(2)	78(1)
O(2)	7163(2)	5767(2)	7605(2)	80(1)
O(3)	7425(2)	6029(2)	5460(1)	64(1)
O(4)	6614(2)	8546(2)	5341(2)	82(1)
O(5)	6547(2)	7925(2)	4131(2)	75(1)
N(1)	6920(2)	6325(2)	6633(2)	54(1)
N(2)	6666(2)	7330(2)	5815(2)	55(1)
C(1)	6427(4)	2275(4)	8515(3)	135(3)
C(2)	6328(4)	2925(3)	8020(3)	83(2)
C(3)	6938(3)	3362(3)	7787(2)	72(1)
C(4)	6838(3)	3948(3)	7328(2)	66(1)
C(5)	6101(3)	4116(3)	7090(2)	70(1)
C(6)	5462(3)	3676(3)	7309(3)	79(2)
C(7)	5594(4)	3094(3)	7772(3)	90(2)
C(8)	4668(3)	3848(3)	7022(3)	105(2)
C(9)	7457(3)	4955(3)	6690(2)	72(1)
C(10)	7158(2)	5709(3)	7025(2)	57(1)
C(11)	6617(3)	7049(2)	6941(2)	77(2)
C(12)	6640(3)	7707(3)	6453(2)	83(2)
C(13)	6663(2)	7814(3)	5291(2)	59(1)
C(14)	6772(3)	7418(3)	4640(2)	68(1)
C(15)	5757(2)	7994(3)	4004(2)	56(1)
C(16)	5565(3)	8497(3)	3501(2)	61(1)
C(17)	4806(3)	8608(3)	3325(2)	75(1)
C(18)	4229(3)	8184(3)	3648(3)	82(2)
C(19)	4408(3)	7671(3)	4144(2)	70(1)
C(20)	5183(3)	7587(3)	4332(2)	64(1)
C(21)	3790(3)	7183(4)	4493(3)	109(2)
C(22)	4599(4)	9171(4)	2776(3)	121(2)
C(23)	8435(7)	5315(5)	4171(4)	183(5)
C(24)	9145(6)	5516(6)	4590(5)	190(4)
N(3)	7921(3)	4900(3)	4597(2)	79(1)
C(25)	7168(6)	4530(5)	4238(4)	170(4)
C(26)	6706(5)	5021(5)	3943(4)	164(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Angles (deg) and Bond Lengths (Å)

Bond	Angle (deg)	Bond	Length
O(3)—P(1)—N(1)	110.76(18)	Se(1)—P(1)	2.0931(12)
O(3)—P(1)—N(2)	109.89(17)	P(1)—O(3)	1.483(3)
N(1)—P(1)—N(2)	89.73(17)	P(1)—N(1)	1.708(3)
O(3)—P(1)—Se(1)	118.52(13)	P(1)—N(2)	1.724(3)
N(1)—P(1)—Se(1)	112.22(13)	O(1)—C(4)	1.374(6)
N(2)—P(1)—Se(1)	112.08(13)	O(1)—C(9)	1.404(5)
C(4)—O(1)—C(9)	118.3(4)	O(2)—C(10)	1.206(5)
C(15)—O(5)—C(14)	117.5(3)	O(4)—C(13)	1.225(5)
C(10)—N(1)—C(11)	117.6(3)	O(5)—C(15)	1.381(5)
C(10)—N(1)—P(1)	128.2(3)	O(5)—C(14)	1.406(5)
C(11)—N(1)—P(1)	112.6(3)	N(1)—C(10)	1.372(5)
C(13)—N(2)—C(12)	118.1(3)	N(1)—C(11)	1.457(5)
C(13)—N(2)—P(1)	127.2(3)	N(2)—C(13)	1.353(5)
C(12)—N(2)—P(1)	114.7(3)	N(2)—C(12)	1.465(5)
C(6)—C(7)—C(2)	123.2(5)	C(9)—C(10)	1.523(6)
C(23)—N(3)—C(25)	113.0(6)	C(11)—C(12)	1.492(6)
N(1)—C(11)—C(12)	107.4(4)	C(13)—C(14)	1.515(6)
N(2)—C(12)—C(11)	107.4(4)	C(23)—N(3)	1.425(9)
N(2)—C(13)—C(14)	117.2(4)	C(23)—C(24)	1.530(12)
O(5)—C(14)—C(13)	112.1(4)	N(3)—C(25)	1.609(9)
O(1)—C(9)—C(10)	110.8(4)	C(25)—C(26)	1.291(9)

Hydrogen bonds between atoms N(3)—O(3) (2.730 Å) and O(4)—N(3) (2.845 Å) (O(4)—N(3)—O(3) (106°) link organoammonium cations and the anions. Atom N(3) simultaneously interacts with the atom O(3) in one molecule and the atom O(4) in another molecule, related by hydrogen bond N_3—$H_{31} \cdots O_4$ (N_3—H_{31} (1.077 Å), $H_{31} \cdots O_4$ (2.845 Å), $\angle N_3H_{31}O_4 = 165.80^\circ$, $(-x + 3/2, y - 1/2, z)$) and hydrogen bond N_3—$H_{32} \cdots O_3$ (N_3—H_{32} (0.913 Å), $H_{32} \cdots O_3$ (1.836 Å), $\angle N_3H_{32}O_3 = 165.89^\circ$). Figure 1 illustrates moderate intramolecular hydrogen bond, and Fig. 2 shows intramolecular and intermolecular hydrogen bonds.

Based on the least-squares equation and coplanar theory by Nordman,[10] the five atoms P(1), N(2), C(11), C(12), and N(1) deviate from the least-squares plane by 0.0119 (0.0016), −0.0217 (0.0029), −0.0130 (0.0017), 0.0229 (0.0031), 0.4243 (0.0060), respectively, indicating that the atom N(1) deviates far from the ring plane and the five-membered ring exists in an envelope configuration. This accounts for the observation that the protons attached to C(11), C(12) in ^{1}H NMR spectrum appeared to be not magnetically equivalent. In addition, according to Paxton's study on d–p π bond of pentavalent phosphorus compounds,[11] it can be stated that there are no d–p π bond properties between atom P and the other two nitrogen atoms because the bond lengths (P(1)—N(1) (1.708 Å), P(1)—N(2) (1.724 Å)) are close to that of a normal P—N bond (1.76 Å), while its analogs such as 1,3,2-diazaphospholidine-4-thione (one) 2-sulfide have strong d–p π bonds between atom P and the other two nitrogen atoms in the molecules, which is of fundamental importance for their planar structures.[12,13]

Acknowledgments

We thank Dr Linhong Weng and her assistant Xuebing Leng for X-ray diffraction performance.

References

1. Bruzik, K.; Stec, W.J. *J. Org. Chem.* **1981**, *46*(8), 1625. Bruzik, K.; Stec, W.J. *Phosphorus Sulfur* **1988**, *35*(3/4), 229.
2. Pudovik, A.N.; Konovalova, I.V.; Zimin, M.G.; Dvoinishnikova, T.A. *Zh. Obshch. Khim*. **1978**, *48*(3), 490.
3. Poulter, C.D.; Mautz, D.S. *J. Am. Chem. Soc*. **1991**, *113*(13), 4895.
4. Sasaki, M.; Itoh, Y.; Yamamoto, N.; Yamada, Y. *Chem. Lett.* **1993**, *11*, 1835.
5. Mikolajczyk, M.; Kielbasinski, P.; Goszczynska, Z. *J. Org. Chem.* **1977**, *42*(22), 3629.
6. Nuretdinov, I.A.; Buina, N.A. *Zh. Obshch. Khim.* **1969**, *39*(4), 930.
7. Dembinski, R.; Kaminski, R.; Michalski, J.; Skowronska, A. *J. Chem. Soc., Chem. Commun.* **1986**, *24*, 1770.
8. Predvoditelev, D.A.; Rosadkina, E.N.; Bekker, A.R.; Nifantev, E.E. *Zh. Obshch. Khim.* **1988**, *58*(7), 1504.
9. Deng, S.L.; Chen, Y.R.; Yang, X.F. *Chem. J. Chinese Univ.* **2001**, *22*(11), 1833.
10. Prade, M.D.; Nordman, C.E. *Inorg. Chem.* **1969**, *8*, 1669.
11. Paxton, K.; Hamor, T.A. *J. Chem. Soc., Dalton Trans.* **1978**, 647.
12. He, L.N.; Chen, R.Y.; Zhuo, J. *Chin. J. Struct. Chem.* **1997**, *16*(3), 215.
13. Deng, S.L.; Chen, R.Y. *Chin. J. Struct. Chem.* **2000**, *19*(4), 271.