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Investigation of Isomerization of 2-Seleno-1, 3, 2-diazaphospholidine Derivatives

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Abstract: 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. The structures of isomerized products were determined by IR, ^{1}H NMR, ^{31}P NMR, elemental analysis and X-ray crystallography. The mechanism of isomerization was also proposed.

Keywords: Isomerization, 2-seleno-1, 3, 2-diazaphospholidine derivatives, crystal structure, mechanism.

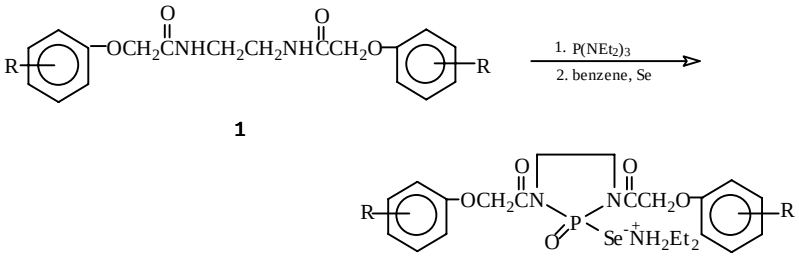
The thiono-thiolo rearrangement has been widely reported in the phosphorus chemistry, likewise, the isomerization of P=Se to P-Se in phosphorus compounds has been also found in literature[1~4]. Nuretdinov[2] early found selenone-selenol isomerization of β,ν-unsaturated esters of selenophosphoric acids, and the converse isomerization of selenol-selenone of the compounds containing a selenium bridge between two phosphoryl centers was also reported by Dembinski[4]. However, the isomerization of phosphoroheterocycles 1, 3, 2-diazaphospholidine-2-selenide derivatives has not been reported. This paper focuses on the rearrangement of P=Se to P-Se in 1, 3, 2-diazaphospholidine derivatives, resulting in the formation of corresponding organic ammonium salts (**Scheme 1**). The pathway of the isomerization is suggested to involve three-step reactions as shown in **Scheme 2**.

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 as outside standard). Melting Point was determined by Thomashoover 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. The intermidiates **1** were routinely prepared by treatment of ethylenediamine with 2 equivalent of phenoxyacetyl chloride in the presence of Et_3N in anhydrous benzene. **1**a : R= *p*-Me, mp: 173-175°C, yield: 80%; **1**b: R= 3, 5-Me_2, mp:

198-199°C, yield: 73%.

Scheme 1



A1: R= *p*-Me

A2: R= 3, 5-Me_2

Isomerization reaction

A suspension of compounds **1** (1.5 mmol) and tris(diethylamino) phosphine (2 mmol) kept in a two-necked flask were heated directly in the range of 180°C -190°C for 5 h under N_2. Then the mixture was cooled to room temperature. After addition of benzene (15 mL), water (0.05 mL) and selenium (0.3 g) to the reaction, the mixture was subsequently warmed up to 80°C and stirred for another 2.5 h. The crude product was obtained by flash chromatography using a mixture of equal volume of ethyl acetate and petroleum ether as eluent, and further recrystallization from a mixture of chloroform and petroleum ether afforded final colorless crystal.

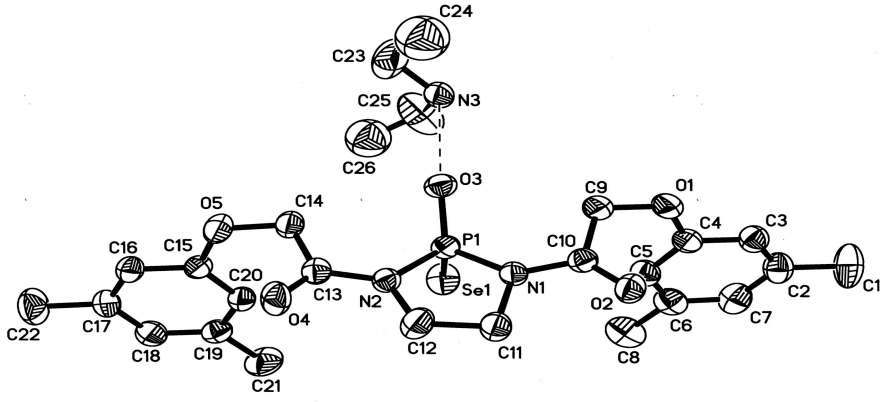
*Experimental data for **A1** and **A2***

A1: R= *p*-Me，colorless crystal. mp: 120-122°C, yield: 38%. Elemental analysis for $C_{24}H_{34}N_3O_5PSe$ (553.96) Calcd (%) C: 51.99, H: 6.14, N: 7.58. Found (%) C: 51.56, H: 5.90, N: 7.77. ^{1}H NMR ($CDCl_3$ as solvent, TMS as internal, δ ppm): 9.56 (br, 2H, NH_2), 6.92 (dd, 8H, $^3J_{H\text{-}H}$= 7.46 Hz, $H_{arom.}$, AA'BB' system), 5.02-4.82 (m, 4H, 2×OCH_2), 4.12-3.78 (dm, 4H, CH_2CH_2), 3.05-2.89 (m, 4H, $N(C\underline{H}_2CH_3)_2$), 2.26 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.45 (t, 6H, $^3J_{H\text{-}H}$= 7.26 Hz, $N(CH_2C\underline{H}_3)_2$). ^{31}P NMR ($CDCl_3$ as solvent, 85% H_3PO_4 as external standard, δ ppm): 8.29. IR (KBr, cm^{-1}): 3060 ($\upsilon_{Ar\text{-}H}$), 2513 (υ_{+NH}), 1989 (δ_{+NH}), 1683, 1652 ($\upsilon_{C=O}$), 1610, 1510, 1435, 1388 ($\upsilon_{C=C}$), 1216 ($\upsilon_{P=O}$), 1079 ($\upsilon_{Ar\text{-}O\text{-}C}$).

A2: R=3, 5-Me_2, colorless crystal. mp: 145-147°C, yield: 33%. Elemental analysis for $C_{26}H_{38}N_3O_5PSe$ (581.96) Calcd (%) C: 53.61, H: 6.53, N: 7.22. Found (%) C: 53.15, H: 6.35, N: 7.08. ^{1}H NMR ($CDCl_3$ as solvent, TMS as internal, δ ppm): 9.52 (br, 2H,

NH_2), 6.61(s, 2H, $H_{arom.}$), 6.52 (s, 4H, $H_{arom.}$), 5.04-4.87 (m, 4H, 2×OCH_2), 4.10-3.78 (dm, 4H, CH_2CH_2), 3.15-2.95 (m, 4H, $N(C\underline{H}_2CH_3)_2$), 2.23 (s, 12H, 4×$CH_3$), 1.44 (t, 6H, $^3J_{H\text{-}H}$= 7.12 Hz, $N(CH_2C\underline{H}_3)_2$).

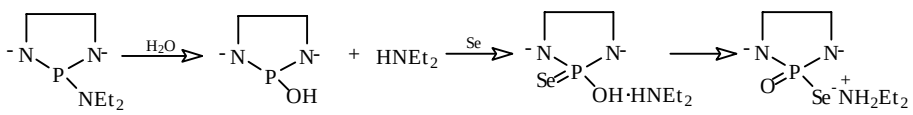
Figure 1 Molecular structure of compound **A2** in X-ray crystal analysis



Results and Discussion

The phosphoroheterocycle 1, 3, 2-diazaphospholidine can readily isomerize into the selenolic compounds in refluxing benzene in the presence of selenium and trace water. The reaction possibly proceeded *via* hydrolysis, oxidation and rearrangement (**Scheme 2**). On reaction, the tervalent phosphoroheterocycle was susceptible to hydrolysis, simultaneously 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 thermally stable P-Se bond. Besides the general spectroscopic methods, the product was directly identified by X-ray diffraction (**Figure 1**). The crystal analysis indicates that the bond distance of P (1)-O (3) is 1.486 Å, shorter than that of the normal P-O bond, while P (1)-Se (1) longer than that of normal P=Se bond, it reveals that the bond P (1)-O (3) exists in the form of double bond and the atoms P (1), Se (1) are combined only by single δ bond, which just accounted for the isomerization of P=Se to P-Se. Furthermore, the bond distance of Se (1)-N (3) is 4.654 Å, which reveals that the two atoms interact only by electrostatic effect.

Scheme 2



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