Reaction of *O*-phenylchloromethylthiophosphonyl isothiocyanate with dicyanomethane

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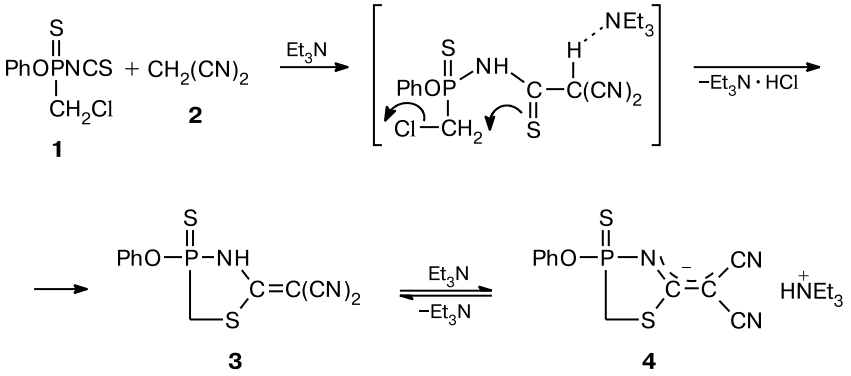
Chloromethylphosphonyl isothiocyanates add primary and secondary amines to give the corresponding phosphorylated thioureas, which easily undergo base-catalyzed cyclization into 1,3,4-thiazaphospholines.[1] When comparing experimental and calculated (*ab initio* and semiempirical) data for intramolecular cyclization of the simplest chloromethylphosphonylated thioureas, we arrived at the conclusion that the most probable reaction pathway involves initial complex formation between the base and thiourea, which weakens the N—H bond. A subsequent nucleophilic attack of the thione S atom on the C atom of the chloromethyl group results in replacement of the Cl atom, yielding 1,3,4-thiazaphospholine ring and the base hydrochloride.[2]

To progress along this line, it was expedient to synthesize a compound structurally close to chloromethylphosphonylated thiourea but containing a more acidic (compared to the amino group) proton. In this situation, the formation of an H complex followed by cyclization into a saturated ring system could be expected. Dicyanomethane (**2**) was used as a proton nucleophile in the addition reaction with *O*-phenylchloromethylthiophosphonyl isothiocyanate (**1**). The reaction product was 1,3,4-thiazaphospholidine **3**; its structure was confirmed by IR and ^{1}H and ^{31}P NMR spectroscopic data. For instance, its IR spectrum contains absorption bands of the C=C (1535 cm^{-1}) and NH groups (3155 cm^{-1}). When an equimolar amount of triethylamine is added to compound **3**, its ^{31}P NMR spectrum no longer shows the signal at δ 89.9; instead, a peak appears at δ 121.1. Attempted purification of the product recovered thiazaphospholine **3**; apparently, the ^{31}P chemical shift δ 121.1 can be assigned to unstable salt **4**.

Semiempirical PM3 quantum-chemical calculations with the MOPAC 6 program package[3] and DFT/PBE/3z calculations with the Priroda program[4] also provide evidence for the formation of structure **3** and the thermodynamic favorability of cyclization (**1** + **2** → **3** + HCl). The differences in enthalpies of formation and total energies with consideration of the zero-point vibration energy, and Gibbs energies between structure **3** and an alternative cyclic structure with an endocyclic N=C bond (2.8, 12.8, and 12.6 kcal mol^{-1}, respectively) indicate that 1,3,4-thiazaphospholidine **3** is thermodynamically more stable. The reaction of its formation is characterized by $\Delta H_f^0 = -12.8$ kcal mol^{-1}, $\Delta E_0 = -15.4$ kcal mol^{-1}, and $\Delta G_{298} = -10.9$ kcal mol^{-1}, where ΔH_f^0 is the enthalpy of formation of the molecule under the standard conditions,



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E_0 is the total energy with consideration of the zero-point vibration energy, and G_{298} is the Gibbs energy. For the reaction

1 + **2** + Et_3N ⟶ **3** + $Et_3N \cdot HCl$,

the following thermodynamic parameters were determined: $\Delta H_f^0 = -21.3$ kcal mol^{-1}, $\Delta E_0 = -29.1$ kcal mol^{-1}, and $\Delta G_{298} = -15.9$ kcal mol^{-1}.

The ^{1}H NMR spectrum was recorded on a Bruker WM-250 spectrometer (250.13 MHz) with Me_4Si as the external standard. ^{31}P NMR spectra were recorded on a CXP-90 instrument (36.47 MHz) with 85% H_3PO_4 as the external standard. IR spectrum was recorded on a UR-20 instrument in the 400—3600 cm^{-1} range.

2-Dicyanomethylene-4-phenoxy-4-thioxo-1,3,4-thiazaphospholidine (3). A solution of dicyanomethane **2** (2.54 g, 38.4 mmol) in 25 mL of anhydrous dichloromethane was added dropwise under argon at −5 °C to a stirred solution of isothiocyanate **1** (10.15 g, 38.5 mmol) and triethylamine (5.07 g, 50.1 mmol) in 100 mL of anhydrous dichloromethane. The reaction mixture was kept at 20 °C for two days, washed with water, and dried with magnesium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized from chloroform to give compound **3** (4.6 g, 41%), m.p. 196—198 °C. ^{1}H NMR (DMSO), δ: 3.70 (m, 2 H, CH_2); 7.16 (m, 5 H, Ph); 11.93 (br.s, 1 H, NH). ^{31}P NMR (CD_3CN), δ: 89.9. IR, ν/cm^{-1}: 660 (P=S); 1190 (P—O—C); 1490, 1590 (Ph); 1535 (C=C); 2230 (C≡N), 3155 (NH). Found (%): C, 45.16; H, 2.42; N, 14.65; P, 10.91; S, 21.80. $C_{11}H_8N_3OPS_2$. Calculated (%): C, 45.04; H, 2.75; N, 14.33; P, 10.56; S, 21.86.

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