



A phosphoryl to spiro-bicyclophosphorane transformation via β -amidic proton elimination in phosphorylated hydrazides

Khodayar Gholivand*, Hamid R. Mahzouni, Forough Molaei, Ali A. Kalateh

Department of Chemistry, Faculty of Basic Sciences, Tarbiat Modares University, PO Box 14115-175, Tehran, Iran

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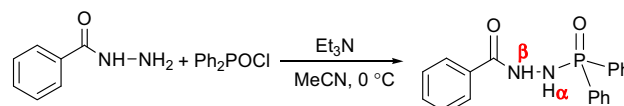
Spiro-bicyclophosphorane

ABSTRACT

The reaction between phosphoryl-containing reagents and hydrazides has been studied. The tetrahedral phosphoryl structure is transformed into a spiro-bicyclophosphorane system with trigonal bipyramidal geometry by the elimination of a β -amidic proton in the reaction between a hydrazide and phosphoryl reagents with at least two leaving groups (Cl) bound to the phosphorus atom, such as POCl_3 or PhPOCl_2 . In the spiro-bicyclophosphorane structure, the C=N imine bond is formed upon β -amidic proton elimination, leading to the conversion of the C=O into a C–O bond and the formation of a P–O bond. All of these structural rearrangements are supported by X-ray crystallography data, and NMR and IR experiments.

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The structures of cyclic pentacoordinate phosphoranes have attracted significant interest because they serve as models for biologically active compounds and intermediates.^{1–4} Heterocyclic phosphoranes with a P–N–N=C–O unit have been previously prepared via the redox coupling of a trialkyl- or triarylphosphine (PR_3) and a dialkyl azodicarboxylate ($\text{ROOCN}=\text{NCOOR}$).^{5,6} Such N- and O-cycloadditions also occur in the reaction of a simple hydrazide (RCONHNH_2) with phosphorus(III) mono- or triamides to form cyclophosphorane systems.^{7,8} Moreover, there are reports on the synthesis and reactivities of phosphorus hydrazides [$\text{P}(\text{X})(\text{NRNH}_2)_2$, X = O and S],^{9–16} although these compounds do not transform into products with the phosphorane structure. To the best of our knowledge, phosphoryl-containing reagents have never been used for the formation of spiro-bicyclophosphoranes. Here, we present the synthesis of such compounds based on the reaction of simple hydrazides (benzhydrazide and 4-pyridinecarboxylic acid hydrazide) with phosphoryl-containing reagents (POCl_3 , PhPOCl_2 and Ph_2POCl). The molecular geometry of the products depends on the number of appropriate leaving groups (Cl) bound to the phosphoryl functional group in the reactant. A simple acid-base reaction between benzhydrazide and a phosphoryl-containing reactant with only one chlorine atom (Ph_2POCl) produces a product with tetrahedral structure at the phosphorus atom. On the other hand, products with a trigonal bipyramidal structure (spiro-bicyclophosphorane) are formed, when phosphoryl reagents with at least two chlorine atoms (PhPOCl_2 or POCl_3) are used.



Scheme 1. Synthesis of **1**.

Compound **1** was prepared by the reaction between a mixture of benzhydrazide, Ph_2POCl , and triethylamine in acetonitrile¹⁷ (Scheme 1). Figure 1 shows the X-ray crystal structure of **1**. The P=O (1.489(2) Å), P1–N2 (1.659(2) Å), and C=O (1.235(2) Å) distances are similar to those in other well-known phosphoramides¹⁸ and carbacylamidophosphates¹⁹ with tetrahedral configurations at the phosphorus atom. The chemical shift of the β -amidic proton in the ^1H NMR spectrum of **1** appeared at 10.17 ppm (Table 1), implying its high acidity and ability to undergo elimination in basic media. The chemical shifts of 21.80 and 166.93 ppm in the ^{31}P and ^{13}C NMR spectra, respectively, and the bands at 1198 (P=O) and 1655 (C=O) cm^{-1} in the IR spectrum confirm the presence of P=O and C=O functional groups in **1**. We have recently shown that the $^2J_{\text{PNH}}$ coupling constant increases when the P–N distance is shortened.²⁰ Here, the $^2J_{\text{PNH}}$ value (21.9 Hz) in **1** is relatively high in magnitude compared with other phosphoramide compounds previously reported,^{18,20} although the P1–N2 distance is not too short.

The phosphoryl structure is transformed into a spiro-bicyclophosphorane system by a dehydration–cyclization rearrangement, when at least two Cl leaving groups are bound to the P=O functional group in the starting material. The reaction between benzhydrazide and POCl_3 (2:1), in acetonitrile under reflux conditions,

* Corresponding author. Tel.: +98 21 82883443.

E-mail address: gholi_kh@modares.ac.ir (K. Gholivand).

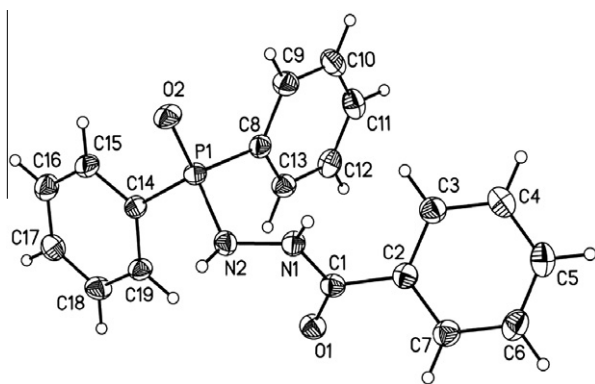
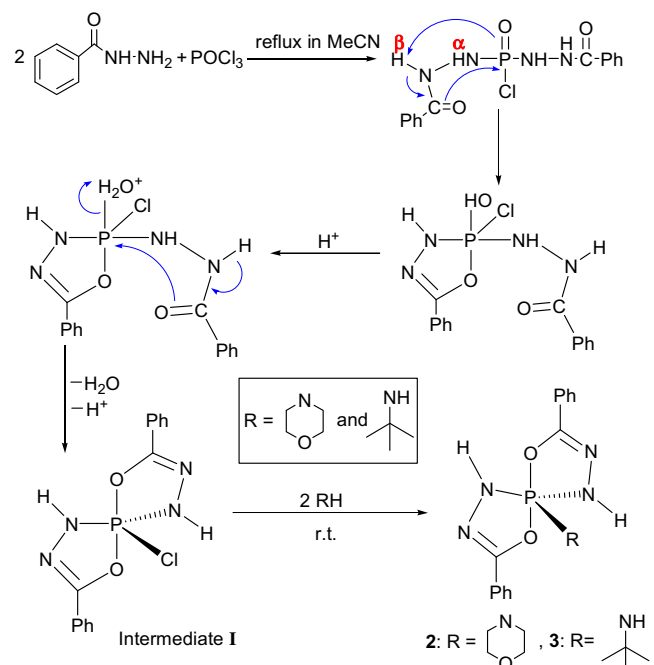


Figure 1. ORTEP representation of compound **1**. Selected bond lengths (Å) and bond angles (°): P1–N2, 1.6587(15); P1–O2, 1.4886(12); P1–C8, 1.7981(18); P1–C14, 1.7941(17); N1–N2, 1.4048(19); C1–N1, 1.346(2); C1–O1, 1.235(2); O1–P1–O2, 170.12(8); O2–P1–N2, 118.55(7); O2–P1–C14, 110.93(7); O2–P1–C8, 111.42(8); C8–P1–C14, 108.41(8); N2–P1–C14, 103.67(7); N2–P1–C8, 103.10(8).

leads to intermediate **1**. Compounds **2** and **3** were prepared by treatment of the appropriate amines (morpholine and *tert*-butylamine) with intermediate **1** (2:1),²¹ Scheme 2. The proposed synthetic pathway for products **2** and **3** (Scheme 2) indicates that cyclization of the initial phosphorylated hydrazide is started by elimination of the β -amidic proton followed by dehydration. Compound **2** was recrystallized from a mixture of methanol and acetonitrile (4:1) at room temperature to obtain crystals suitable for X-ray analysis.

Figure 2 shows the molecular structure of compound **2**. The phosphorus atom adopts a distorted trigonal bipyramidal geometry in spiro-bicyclic phosphorane **2** with the oxygen atoms in axial and nitrogen atoms in equatorial positions. The C1–N2 distance (1.282(3) Å) in **2** is considerably shorter than a typical C–N single bond, while the C1–O1 distance (1.351(2) Å) in **2** is longer than the C=O bond in **1**. This is in good agreement with the β -amidic proton elimination and the changes in the C1–N2 and C1–O1 bond lengths upon cyclization. In the ³¹P NMR spectrum of **2**, a triplet of triplets appeared at –37.72 ppm. This splitting pattern arises from the spin couplings between the phosphorus nucleus and two NH_{α} (²J_{PNH} = 40.4 Hz) and two axial N–CH_{morpholine} (³J_{PCH} = 8.9 Hz) protons. The spin couplings between the phosphorus nucleus and two



Scheme 2. Synthesis of compounds **2** and **3** and the proposed reaction mechanism.

NH_{α} protons (²J_{PNH} = 45.2 Hz) and one $NH_{tert\text{-butylamine}}$ (²J_{PNH} = 12.1 Hz) proton lead to a doublet of triplets for the ³¹P NMR signal in compound **3**. The ²J_{PNH} coupling constants in compounds **2** and **3** are larger than the corresponding values in **1**. The decrease in δ (¹³C) values, from 166.93 ppm in **1** to 152.54 and 151.68 ppm, respectively, in compounds **2** and **3** (Table 1), confirms the formation of a CO–P connection between the carbonyl oxygen atom and the phosphorus atom upon cyclization. The CO–P bond leads to spin couplings for the phosphorus and carbon nuclei with ²J_{POC} values in the range of 14.1–14.6 Hz. The sharp bands at ~1330 cm⁻¹ in the IR spectra of compounds **2** and **3** confirm the decrease in the bond order from C=O to C–O on cyclization and that the oxygen atom is bound to the phosphorus atom.

Compounds **4–6** were synthesized by the reaction of a mixture of triethylamine and benzhydrazide or 4-pyridinecarboxylic acid

Table 1
Selected spectroscopic data of products **1–8**

Product	δ^a (³¹ P) in ppm	¹ H: $\delta^{b,c}$ (ppm)/ ² J _{PNH} (Hz)	¹³ C: $\delta^{b,c}$ (ppm)/ ² J _{POC} (Hz)	ν (C=O) in cm ⁻¹
1	21.80	H ^a : 7.76/21.9 H ^b : 10.17/– ¹ H: $\delta^{b,c}$ / ² J _{PNH} (Hz)	166.93/–	1655
2	–37.72	8.57/40.4	152.54/14.1	–/1330
3	–43.31	3.69/12.1 8.17/45.2	151.68/14.6	–/1328
4	–36.19	8.85/36.9	154.20/10.9	–/1324
5	–47.40	7.15/13.4 8.58/39.9	152.52/15.1	–/1324
6	–46.92	7.32/13.3 8.99/40.9	150.71/15.4	–/1326
7	–45.23	6.75/36.6 8.48/39.6 9.88/–	152.06/14.6 166.39/–	1669/1329
8	–45.31	7.12/37.3 8.98/41.1 10.38/–	150.41/15.4 164.91/–	1686/1323

^a The ³¹P NMR spectra were recorded for DMSO-*d*₆ solutions at 202.45 MHz.

^b The ³¹H and ¹³C NMR spectra were recorded for DMSO-*d*₆ solutions at 500.13 and 125.77 MHz, respectively.

^c The chemical shifts for the amidic protons and carbonyl (or imine) carbon atoms are provided.

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