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New Synthetic Approach to Phosphonium Salts Derived from 4,5-Bis(diphenylphosphino)-1-phenylpyridazin-6-one and Quantum-Chemical Calculations of Their Formation

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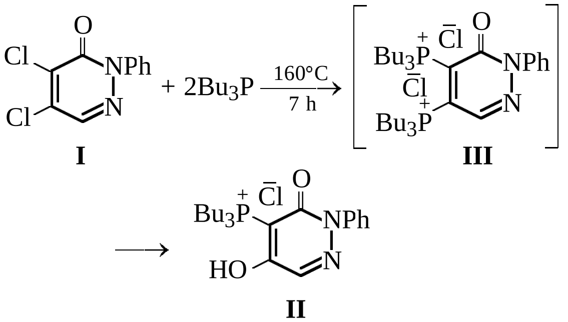
Abstract—4,5-Bis(diphenylphosphino)-1-phenylpyridazin-6-one reacts with ethyl iodide, 1,2-dichloroethane, 1,2-dibromomehtane, and *o*-dibromobenzene to give the corresponding bis-phosphonium salts which, depending on the halogen derivative, can undergo further transformations involving cleavage of the P–C bond in the β-position with respect to the carbonyl group.

By reaction of 4,5-dichloro-1-phenylpyridazin-6-one (**I**) with tributylphosphine we recently synthesized the first representative of C-phosphorylated pyridazinones, tributyl(4-hydroxy-6-oxo-1-phenylpyridazin-5-yl)phosphonium chloride (**II**). The product was studied by the X-ray diffraction, spectroscopic, and quantum-chemical methods [1].

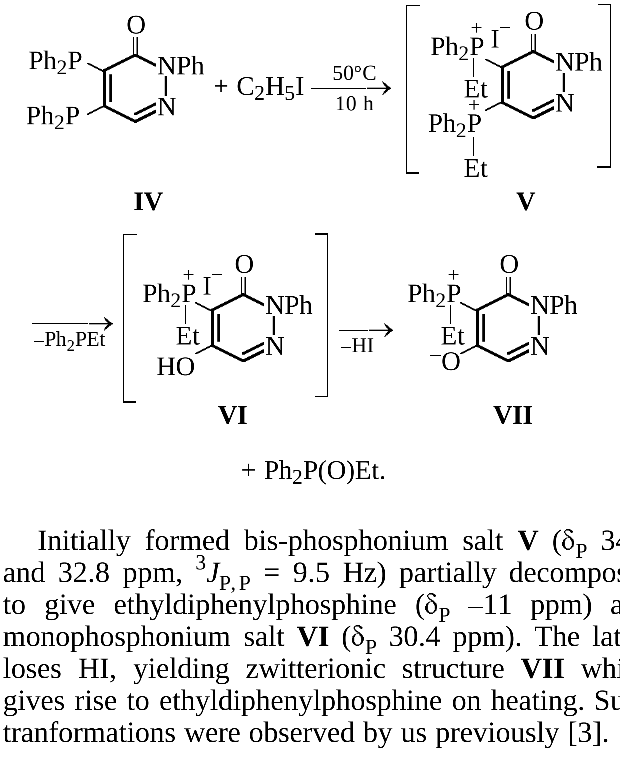


I **III** **II**

(1)

However, we failed to obtain bis-phosphonium salt **III** by reaction of **I** with 2 mol of tributylphosphine. Probably, fairly severe reaction conditions and subsequent treatment of the reaction mixture promoted decomposition of salt **III**, so that the only identified product was compound **II**. In the present work we made an ettempt to synthesize bis-phosphonium salts from pyridazinone **I** by another procedure, namely by reaction of 4,5-bis(diphenylphosphino)-1-phenylpyridazin-6-one (**IV**), which was obtained by us previously [2], with mono- and dihaloalkanes and *o*-dibromobenzene.

The reaction of **IV** with excess ethyl iodide was carried out at 50°C (reaction time 10 h). Removal of excess alkyl halide under reduced pressure gave an orange solid with mp 200°C, which was poorly soluble in common organic solvents. We succeeded in recording the ^{31}P NMR spectrum of **IV** in CD_3OD only on heating; therefore, partial decomposition of salt **IV** with formation of a mixture of products cannot be excluded. Several signals were observed in the ^{31}P NMR spectrum: two doublets with equal intensities at δ_P 34.3 and 32.8 ppm ($^3J_{P,P}$ = 9.5 Hz) and two singlets at δ_P 30.4 and –11 ppm. These data allowed us to assume the following reaction scheme:



IV **V** **VI** **VII**

(2)

Initially formed bis-phosphonium salt **V** (δ_P 34.3 and 32.8 ppm, $^3J_{P,P}$ = 9.5 Hz) partially decomposes to give ethyldiphenylphosphine (δ_P –11 ppm) and monophosphonium salt **VI** (δ_P 30.4 ppm). The latter loses HI, yielding zwitterionic structure **VII** which gives rise to ethyldiphenylphosphine on heating. Such tranformations were observed by us previously [3].

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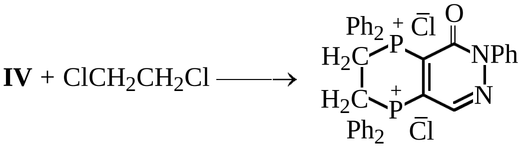
Unfortunately, the mass spectrum of the product contained no molecular ion peaks from phosphonium salts **V** and **VI**, and we observed only the following peaks, *m*/*z*: 540 (**IV**), 214 (Ph_2PEt), 185 (Ph_2P), etc., in agreement with the proposed scheme. An analogous fragmentation pattern of cyclic phosphonium salts was described in [4]; it was also noted that high-melting salts undergo partial decomposition, so that no molecular ion peaks can be found (only fragment ion peaks were present in the spectrum).

It was of specific interest to examine reactions of pyridazinone **IV** with dihaloalkanes and *o*-dibromobenzene, which were expected to result in formation of heterocyclic bis-phosphonium salts. Up to now, only bisphosphoniocycloalkanes have been reported [4–6]. The reaction of **IV** with excess 1,2-dichloroethane (the latter was also the solvent) afforded stable bisphosphonium salt **VIII**.

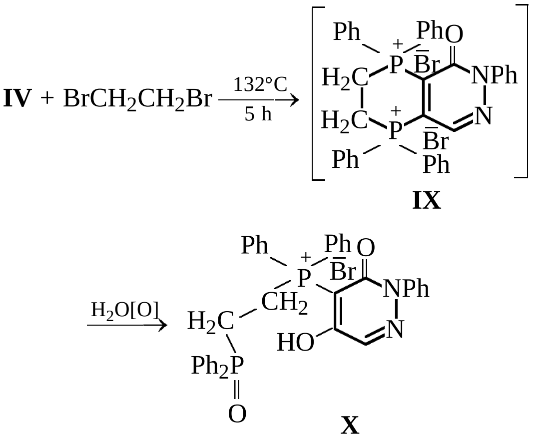


VIII

(3)

After removal of excess dichloroethane, we isolated crystals with mp 165°C. The ^{31}P NMR spectrum of the product contained two doublets with equal intensities at δ_P 32.1 and 29.0 ppm ($^3J_{P,P}$ = 9.5 Hz). In the IR spectrum we observed bands belonging to vibrations of the pyridazine ring at 1650 (C=O) and 1610 cm^{-1} (C=C) and of the benzene ring, whereas absorption assignable to P=O, OH, and other groups typical of decomposition products of **VIII** was absent.

A similar result was expected for the reaction of pyridazine **IV** with 1,2-dibromoethane, which was carried out by heating compound **IV** in excess reagent under reflux for 5 h. By removal of excess 1,2-dibromoethane we obtained crystals with mp 137°C (from ethanol). The product showed in the ^{31}P NMR spectrum two doublets of equal intensities at δ_P 34.4 and 25.3 ppm ($^3J_{P,P}$ = 9.5 Hz). The IR spectrum contained bands at 1650 (C=O) and 1610 cm^{-1} (C=C) and also OH and P=O absorption bands at 3100 and 1175 cm^{-1}, respectively. Presumably, the product was monophosphonium salt **X** which was formed from the primary product, bisphosphonium salt **IX**.

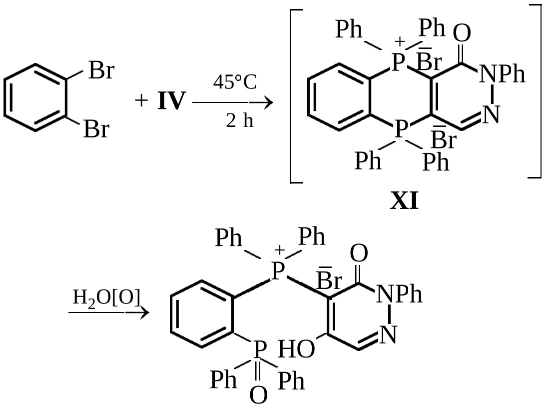


IX

X

(4)

o-Dibromobenzene reacted with **IV** in a way similar to 1,2-dibromoethane:



XI

XII

(5)

After cooling, a yellow solid precipitated from the mixture. It melted at 380°C with decomposition. In the ^{31}P NMR spectrum we observed two doublets at δ_P 32.1 and 31.0 ppm ($^3J_{P,P}$ = 2 Hz). The product displayed IR bands at 1650 (C=O), 1610 (C=C), 1180 (P=O), and 3400 cm^{-1} (OH). These spectral data and the behavior of the other phosphonium salts derived from **IV** led us to conclude that the primary product of the reaction of **IV** with *o*-dibromobenzene is also cyclic bis-phosphonium salt **XI** which then decomposes by the above scheme, yielding compound **XII**.

The mass spectra of the products obtained by reactions of **IV** with dihalogen derivatives, as well as of the product obtained with ethyl iodide, contained only fragment ion peaks. The ease of decomposition of cyclic phosphonium salts and their high sensitivity to atmospheric moisture and oxygen were noted in [7–9].

An additional support to formation of bis-phosphonium salts in reactions of pyridazine **IV** with mono- and dihalogen derivatives was obtained by quantum-chemical calculations. Using the PM3 procedure (this method was used by us previously to estimate the stability of some structures, to reveal factors responsible for reactivity, etc. [1, 2]), we calculated the heats of formation of bis-phosphonium salts in the above reactions. The data given below show that in all cases the formation of bisphosphonium salts from dihalogen derivatives is favorable from the viewpoint of thermodynamics; the enthalpy of the reaction with ethyl iodide is positive but small in absolute value. Therefore, the reaction with ethyl iodide can be a reversible process. In fact, unchanged initial compound **IV** was isolated together with the other products only in the reaction with ethyl iodide.

				$\Delta\Delta H_f^0$, kcal/mol
	IV +	$ClCH_2CH_2Cl \longrightarrow$	**VIII**	–59.9
ΔH_f, kcal/mol	197.8	23.3	161.2	
	IV +	$BrCH_2CH_2Br \longrightarrow$	**IX**	–28.4
ΔH_f, kcal/mol		–3.4	166.0	
	IV +	$o\text{-}Br_2C_6H_4 \longrightarrow$	**XI**	–24.4
ΔH_f, kcal/mol		39.5	212.9	
	IV +	$C_2H_5I \longrightarrow$	**V**	1.7
ΔH_f, kcal/mol		2.1	203.7	

Naturally, in all the cases the entropy constituent of the Gibbs energy is unfavorable; however, taking into account relatively low reaction temperature, its contribution should not be crucial. Polar medium (polar reagents and solvents) should facilitate the reaction, as compared to the gas phase for which the calculations were performed.

Both experimental results and calculation data suggest a common scheme for reactions of the tertiary phosphines under study with halogen derivatives. Initially, regardless of the substituents on the phosphorus atom and halogen nature, phosphonium (or bis-phosphonium) salts are formed. They can undergo partial or complete decomposition, depending on the reaction conditions and procedure for treatment of the reaction mixture. The available data indicate that decomposition of bisphosphonium salts derived from pyridazine **IV** involves mainly cleavage of the P–C bond in the β-position with respect to the carbonyl group.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrophotometer from samples dispersed in mineral oil. The ^{31}P NMR spectra were obtained on a Varian Unity-300 spectrometer (120.4 MHz) from 10–15% solutions in CD_3OD, using 85% H_3PO_4 as external reference. The ^{31}P chemical shifts were determined with an accuracy of ±0.2 ppm. The mass spectra were run on a Hitachi M-80V GC–MS system (70 eV, cathode emission current 100 mA, ion source temperature 140°C). Quantum-chemical calculations were performed on a Pentium 166MMX computer using MOPAC 6 software [10].

Initial 4,5-bis(diphenylphosphino)-1-phenylpyridazin-6-one (**IV**) was synthesized by the procedure reported in [2].

Reaction of 4,5-bis(diphenylphosphino)-1-phenylpyridazin-6-one (IV) with ethyl iodide. A mixture of 1 g of bis-phosphine **IV** and excess ethyl iodide was refluxed for 10 h. After removal of ethyl iodide under reduced pressure, an orange solid precipitated with mp 200°C. Yield 0.44 g. IR spectrum, ν, cm^{-1}: 1748 (C=O); 1640, 1607, 1594 (C=C, C=N); 700–1250 (C–C, P–C); 400–700 (P–C–C). ^{31}P NMR spectrum, δ_P, ppm: 32.8 d and 34.3 d ($^3J_{P,P}$ = 9.5 Hz); 30.4 s, –11 s.

Reaction of 4,5-bis(diphenylphosphino)-1-phenylpyridazin-6-one (IV) with 1,2-dichloroethane. Bis-phosphine **IV**, 1 g, was heated in excess 1,2-dichloroethane for 10 h under reflux. Removal of the solvent under reduced pressure gave pink crystals with mp 165°C. Yield 0.88 g. IR spectrum, ν, cm^{-1}: 1650 (C=O); 1610, 1607, 1594 (C=C, C=N); 700–1250 (C–C, P–C); 400–700 (P–C–C). ^{31}P NMR spectrum, δ_P, ppm: 32.1 d and 29.0 d ($^3J_{P,P}$ = 9.5 Hz). Found, %: C 75.22; H 4.62; P 10.76. $C_{36}H_{30}Cl_2N_2OP_2$. Calculated, %: C 67.6; H 4.7; P 11.1.

Reaction of 4,5-bis(diphenylphosphino)-1-phenylpyridazin-6-one (IV) with 1,2-dibromoethane. Bis-phosphine **IV**, 0.225 g, was heated in excess 1,2-dibromoethane for 5 h under reflux. Removal of the solvent gave yellow crystals with mp 137°C. Yield 0.157 g. IR spectrum, ν, cm^{-1}: 1650 (C=O); 1610, 1607, 1594 (C=C, C=N); 3100 (OH); 1175 (P=O); 700–1250 (C–C, P–C); 400–700 (P–C–C). ^{31}P NMR spectrum, δ_P, ppm: 34.4 d and 25.3 d ($^3J_{P,P}$ = 9.5 Hz). Found, %: C 63.4; H 4.55; N 4.11; P 9.1. $C_{36}H_{31}BrN_2O_3P_2$. Calculated, %: C 59.35; H 4.12; N 3.85; P 8.52.

Reaction of 4,5-bis(diphenylphosphino)-1-phenylpyridazin-6-one (IV) with *o*-dibromobenzene. A mixture of 0.5 g of bis-phosphine **IV** in 20 ml of THF was heated to the boiling point, and 0.11 g of *o*-dibromobenzene in 20 ml of THF was added dropwise over a period of 2 h under vigorous stirring. Light yellow crystals separated. Yield 0.33 g, mp 380°C (decomp.). IR spectrum, ν, cm^{-1}: 1650 (C=O); 1610, 1607, 1594 (C=C, C=N); 3400 (OH); 1180 (P=O); 700–1250 (C–C, P–C); 400–700 (P–C–C). ^{31}P NMR spectrum, δ_P, ppm: 32.1 d and 31.0 d ($^3J_{P,P}$ = 2 Hz). Found, %: C 59.29; H 4.31; N 2.85; P 8.73. $C_{40}H_{31}BrN_2O_3P_2$. Calculated, %: C 61.8; H 3.8; N 3.6; P 7.9.

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