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Conversions of 2-Phenyl-1,3,2-dioxaphospholane Under the Action of Hydrogen Chloride

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Abstract — The reaction of 2-phenyl-1,3,2-dioxaphospholane with HCl gives a mixture of phenylphosphinic acid, bis(2-chloroethyl) phenylphosphonate, and phenylphosphine; therewith, intermediate oligomeric phosphonites, hydrophosphoryl compounds, and phosphoranes were detected. Thermal treatment of the reaction mixture results in formation of ethylene phenylphosphonate and (2-chloroethyl)phenylphosphinate.

Together with other heterophosphacyclanes, 1,3,2-dioxaphospholanes are widely used in organic synthesis [1]. Recently we proposed a method for preparing 4-chloromethyl-substituted 1,3,2-dioxaphosphacyclanes by reaction of geminal phosphorus dichlorides $RP(X)Cl_2$ (X = lone electron pair, R = Cl; X = O, R = Me, Ph, OEt, OMent, NEt_2, Cl) with glycidol [2–4]. At the same time, it was found that 2-methyl- and 2-phenyl-4-chloromethyl-1,3,2-dioxaphospholanes (X = lone electron pair; R = Me, Ph) immediately they form undergo further transformations leading to hydrophosphoryl compounds, cyclic and acyclic phosphonates, and primary phosphines [4]. We presumed that all further transformations of primary cyclic phosphonites are induced by the free HCl present in the reaction mixture.

1,3,2-Dioxaphospholanes are commonly prepared by reaction of geminal disubstituted phosphorus derivatives $RP(X)Y_2$ (X = lone electron pair, O, S, etc.; Y = Cl, $NAlk_2$, OMe, etc.) with vicinal diols. Richter [5] reported the formation in similar reactions with dichlorophosphines of 1,3,2-dioxaphospholan-2-ones and primary phosphines along with 1,2,3-dioxaphospholanes [5]. The resulting product ratios were strongly dependent on the amount of base in the reaction mixture. However, no explanation of the reasons for and ways of formation of these products was gives in that work. In our opinion, the "unexpected" products are formed under the action of HCl on the starting cyclic phosponites.

At the same time, Mukaiyama *et al.* [6], who studied direct reaction of HCl with 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite) (**I**), stated that the single reaction product is (2-chloroethyl)phenylphosphinate (**II**). The fairly high (>49%) yield of hydrophosphoryl compound **II** gave the referees grounds to include this reaction into the list of promising methods of synthesis of alkylene phosphonohaloidites [7]. The controversy in the available data prompted us to study in more detail the reaction of phosphonite **I** with HCl by ^{31}P and ^{13}C NMR spectroscopy.

We reacted compound **I** with excess HCl by the procedure described in [6]. The ^{31}P NMR spectrum of the crude reaction mixture contained four signals: a triplet at δ_P –123.36 ppm , $^1J_{PH}$ 198 Hz ($PhPH_2$, ~26% of the total integral intensity), a broadened singlet at δ_P 20.09 ppm without direct P–H coupling constants [~50%, bis(2-chloroethyl) phenylphosphonate (**III**); the assignement was conformed by the independent synthesis of this compound from $PhP(O)Cl_2$ and 2-chloroethanol], and a doublet at δ_P 28.33 ppm of PhPH(O)OR ($^1J_{PH}$ ~570 Hz, ~22%), and a signal of 2-phenyl-1,3,2-dioxaphospholan-2-one (**IV**) at δ_P 37.14 ppm (2%). This spectrum always reproduced on repeated experiments (see figure, spectrum *d*).

The ^{31}P NMR spectrum of the reaction mixture shortly after HCl had began to pass through the solution of the starting compound (see figure, spectrum a) contained only two signals of roughly equal intensity (δ_P 162.4 and 157.5 ppm) and a weak signal at δ_P 160.3 ppm (see figure, spectrum b). The first and third signals belong respectively compound **I** and its dimmer (the tendency of phosphonites for dimerization is well known [8]). The second signal probably belongs to a cyclic oligomer of dioxaphospholane **I**. Evidence for this assumption comes from the observation of Mukaiyama *et al.* [6] that after addition to the cyclic phosphonite of a catalytic amount of sulfuric acid produces thickening of the mixture.

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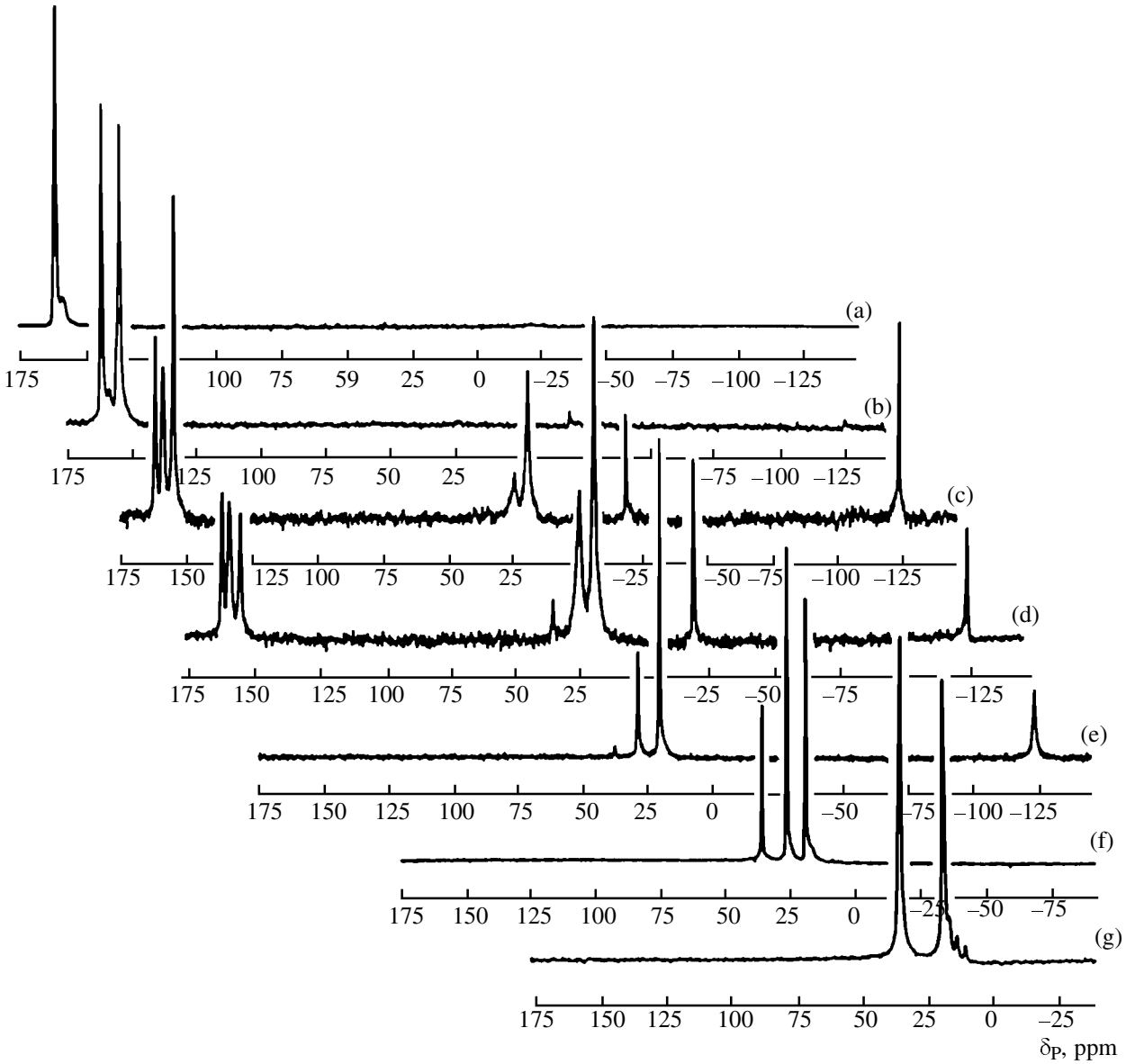
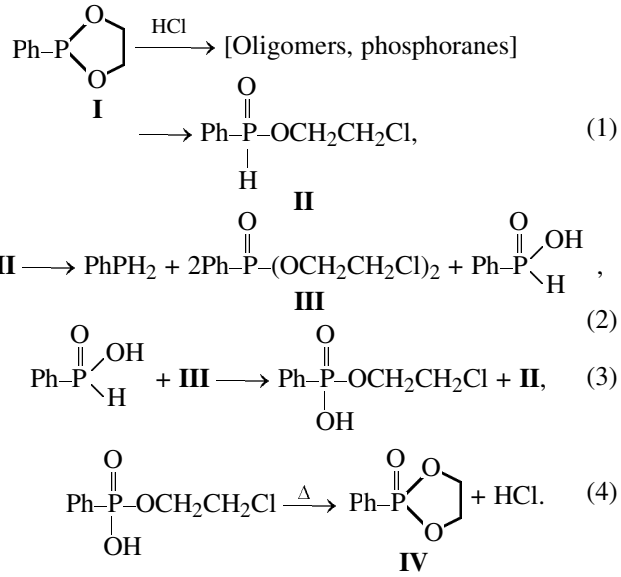


^{31}P NMR spectra of 2-phenyl-1,3,2-dioxaphospholane (**I**), its reaction mixtures with HCl, and reaction products. (a) Compound **I**, (b) reaction mixture after passing of the first portion of HCl, (c) reaction mixture after passing of 0.9 equiv of HCl, (d) the latter mixture kept for 1.5 days at room temperature, (e) final reaction mixture after passing of excess HCl, (f) first fraction obtained by distillation of the final reaction mixture, and (g) second fraction obtained by distillation of the final reaction mixture.

On further passing of HCl, the signals at δ_P 162.4 and 157.5 ppm decreased, at first the former signal faster. At the same time, signals of a hydrophosphoryl compound (δ_P ~24.5 ppm, $^1J_{PH}$ 557 Hz), acyclic phosphonate **III**, and $PhPH_2$, as well as signal at δ_P ~ –19 ppm, belonging to 5-phenyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (δ_P –20 ppm [9]) appeared (see figure, spectrum c). With deficient HCl, the ^{31}P NMR spectrum of the reaction mixture kept for 1.5 days at room temperature preserved all the above signals and, in addition, a weak singlet appeared belonging to cyclic phosphonate **IV**. Therewith, the signal at δ_P 157.5 ppm appreciably decreased, whereas those of the hydrophosphoryl compounds and acyclic phosphonate **III** slightly increased (see figure, spectrum d). Barboting into the intermediate mixture of excess hydrogen chloride at room temperature led to the above-described ^{31}P NMR spectrum (see figure, spectrum e).

Distillation of the final crude mixture gave two liquid fractions (the volatile phenylphosphine was collected separately into a special cooled trap). The first contained 33% of linear phosphonate **III**, 42% of the hydrophosphoryl compound [δ_P 27.13 ppm ($^1J_{PH}$ 554 Hz)], and 25% of dioxaphospholane **IV** (see figure, spectrum *f*). The second contained ~37% of phosphonate **III** and 42% of phosphonate **IV** (see figure, spectrum g). Thus, the content of cyclic phosphonate **IV** much increased during distillation.

We suggest that the reaction of dioxaphospholane **I** with HCl may occur by a way depicted by the following schemes. Therewith, reactions (1) and (2) proceed fast at room temperature, whereas reactions (3) and (4) require thermal activation. Phenylphosphine, phosphonate **III**, and phenylphosphonous acid are probably formed by transformation of intermediate phosphinate **II**. We did not isolate phenylphospohnous acid, but the published ^{31}P NMR data [10] correspond to characteristics of the hydrophosphoryl compound detected in the crude mixture. At the same time, the stoichiometry of the final reaction products, presented in scheme (2), corresponds to the intensity ratio of their signals in the final reaction mixture before thermal treatment.



Thus, scheme (2) formally reflects disproportionation of hydrogen phosphonite **II**. However, it is unclear why this reaction which even with free phosphonous (phosphinous) acids RPO_2H_2 requires rigid conditions to occur and has not yet described for their esters [7], in our case occurs rather fast at room temperature. We suggest that the transformations illustrated by the schemes are induced by fast exchange processes catalyzed by hydrogen chloride, rather than redox reactions.

The appearance of cyclic phosponate **IV** in the crude reaction mixture might be assigned to oxidation of phosphonite **I** with atmospheric oxygen, since the ability of the latter to oxidize acyclic esters arylphosphonous acids is well known [11]. However, this process is unlikely to contribute much into the overall scheme of the reaction in hand. Thus, the mixture obtained by barboting dry air free of HCl for half an hour through a solution of phosphonite **I** in benzene contained, by ^{31}P NMR data, no more than 1% of phosphonate **IV**. The formation of additional amount of cyclic phosphonate IV in the course of distillation of the reaction product may well be represented by schemes (3) and (4), since the intramolecular cyclization of phosphonates and monoesters of orthophosphoric acid, containing 2-haloalkyl radicals in the ester has been described [12]. In principle, compound **IV** might be formed by direct cyclization of compound **III** with elimination of a 1,2-dichloroethane molecule. However, such process did not observed on distillation of pure acyclic phosphonate **III**.

This process might be studied in more detail with an individual compound **II**. It might be prepared by partial hydrolysis of bis(2-chloroethyl) phenylphosphonite (**V**) in the presence of HCl. We tried to prepare compound **V** by reaction of $PhPCl_2$ with 2-chloroethane in the presence of triethylamine. However, the fraction obtained by distillation of the crude reaction mixture contained, by ^{13}C and ^{31}P NMR data, 50% of the isomeric 2-chloroethyl (2-chloroethyl)phenylphosphinate. This result might well be expected, since the tendency of dialkyl phenylphosphonites for thermal rearrangement with formation of the second P–C bond is a known fact [13]. At the same time, Mukaiyama *et al.* [6] described the polymerization of cyclic phosphonites in rigid conditions (>150°C in the presence of catalysts or prolonged heating at 200°C without catalysts), leading to phosphoryl compounds with two P–C bonds. Detailed inspection of the ^{31}P and ^{13}C NMR spectra of crude reaction mixtures gives us grounds to state that the above-described processes produce no compounds containing a PhP(O)C fragment.

Thus, the reaction of phosphonite **I** with HCl occurs in an intricate fashion and always gives a mixture of products from the very beginning. The facility of exchange processes accompanying this reaction makes it unsuitable from a preparative standpoint. The fact that the reaction studied gives the same products as reactions of dichlorophosphines with vicinal diols and glycidol suggests a common mechanism of these two types of processes.

EXPERIMENTAL

The NMR spectra were obtained on Bruker WM-250 (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz) and Bruker CXP-100 (^{31}P, 36.5 MHz) instruments relative to internal TMS (^{1}H, ^{13}C) and external H_3PO_4 (^{31}P) in $CDCl_3$ (^{1}H, ^{13}C), C_6H_6 (^{31}P).

2-Phenyl-1,3,2-dioxaphospholane (I). A solution of 8.28 g of dichloro(phenyl)phosphine in 50 ml of dry benzene was added dropwise with stirring under nitrogen to a solution of 2.87 g of ethylene glycol and 14.51 g of triethylamine in 50 ml of dry benzene, maintaining the temperature at ~5°C using an ice bath. The reaction mixture was refluxed for 1 h and cooled to room temperature. The precipitate was filtered off, the filtrate was concentrated at reduced pressure and distilled in a vacuum to obtain 5.2 g (67%) of compound **I**, bp 82°C (0.8 mm) {bp 79–80°C (0.8 mm) [6]}. ^{31}P NMR spectrum: δ_P 162.40 ppm.

Reaction of dioxaphospholane I with HCl was performed by the procedure described in [6]. Hydrogen chloride dried with sulfuric acid was barboted over the course of 2 h through a solution of 4.4 g of compound **I** in 10 ml of dry benzene. Heat release was observed first 10 min. After barboting of HCl had been complete, the ^{31}P NMR spectrum of the reaction mixture was measured, and then the solvent and volatile phenylphosphine were removed in a vacuum. The residue was distilled in a vacuum to obtain 0.7 g of a fraction [bp 147°C (0.8 mm)] containing 33% of phosphonate **III**, 42% of hydrophosphoryl compound (δ_P 27.13 ppm, $^1J_{PH}$ 554 Hz), and 25% of 2-phenyl-1,3,2-dioxaphospholan-2-one (**IV**) [^{13}C NMR spectrum, δ_C, ppm (*J*, Hz)]: 65.95 s (OCH_2), 126.42 d, 127.91 d, 130.80 d, 132.30 d (Ph, $^1J_{PC}$ 185.6, $^3J_{PC}$ 15.1, $^2J_{PC}$ 10.3, $^4J_{PC}$ 2.6); ^{31}P NMR spectrum: δ_P 37.14 ppm] and 2 g of a fraction [bp 190–215°C (0.8 mm)] containing, according to the ^{31}P NMR spectrum, ~37% of phosphonate **III** and 41% of phosphonate **IV**; 22% falled at three signals (δ_P 11, 14, and 17 ppm).

Monitoring of the reaction of phosphonite I with HCl by ^{31}P NMR spectroscopy. Concentrated H_2SO_4 was added in portions of 5–10 drops to 0.92 g of NH_4Cl. The HCl formed was barboted with a stream of dry nitrogen through a drying flask with H_2SO_4 into a solution of 2.9 g of phosphonite **I** in 8 ml of benzene until HCl no longer evolved (~20 min). After that, a sample was taken to measure the ^{31}P NMR spectrum. When ammonium chloride had completely reacted, the mixture was left to stand in a closed system for 1.5 day, after which excess HCl was barboted into it, and the ^{31}P NMR spectrum was measured.

Bis(2-chloroethyl) phenylphosphonate (III). A solution of 3.14 g of 2-chloroethanol in 20 ml of dry benzene was added dropwise with stirring under argon to a solution of 3.8 g dichloro(phenyl)phosphine and 3.94 g of triethylamine in 20 ml of the same solvent, maintaining the temperature at ~5°C using an ice bath. The mixture was stirred for 1 h at 40°C and cooled to room temperature. The precipitate was filtered off, the filtrate was evaporated at reduced pressure, and the residue was distilled in a vacuum to obtain 4.78 g (87%) of phosphonate **III**, bp 134°C (0.8 mm), n_D^{20} 1.5251. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.69 t.d (2H, CH_2Cl, $^4J_{PH}$ 1.6, $^3J_{HH}$ 5.8), 4.17–4.38 m (2H, OCH_2), 7.41–7.60 m (3H, Ph), 7.77–7.89 m (2H, Ph). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 42.34 d (CH_2Cl, $^3J_{PC}$ 5.5), 64.96 d (OCH_2, $^2J_{PC}$ 4.7), 126.44 d, 127.94 d, 130.99 d and 132.27 d (Ph, $^1J_{PC}$ 189.8, $^3J_{PC}$ 14.8, $^2J_{PC}$ 10.0 and $^4J_{PC}$ 2.9). ^{31}P NMR spectrum: δ_P 20.09 ppm.

Reaction of $PhPCl_2$ with 2-chloroethanol. A solution of 2.58 g of $PhPCl_2$ in 20 ml benzene was added dropwise under argon at ~5°C to a stirred solution of 3.23 g of 2-chloroethanol and 6.14 ml of triethylamine in 25 ml of the same solvent. The mixture was stirred for 1 h at 40°C and then cooled. The precipitate was filtered off, the solvent was removed at reduced pressure, and the residue was distilled in a vacuum to obtain a single fraction [4.8 g, bp 118–120°C (0.8 mm)] containing **bis(2-chloroethyl) phenylphosphonite (V)** {bp 138–140°C (3 mm) [14]} [^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 42.68 d (CH_2Cl, $^3J_{PC}$ 7.00), 66.22 d (OCH_2, $^2J_{PC}$ 8.7), 128.0 d, 129.35 d, 129.93 s and 139.35 d (Ph, $^3J_{PC}$ 5.2, $^2J_{PC}$ 19.2 and $^1J_{PC}$ 20.1); ^{31}P NMR spectrum: δ_P 161.38 ppm] and its isomer **(2-chloroethyl) (2-chloroethyl)phenylphosphinate** [^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 33.78 d (PCH_2, $^1J_{PC}$ 94.2), 36.76 s (CH_2Cl), 43.70 d (CH_2Cl, $^3J_{PC}$ 5.2), 63.80 d (OCH_2, $^2J_{PC}$ 6.1), 128.56 d, 129.15 d, 131.16 d and 132.65 d (Ph, $^3J_{PC}$ 13.1, $^1J_{PC}$ 126.4, $^2J_{PC}$ 10.6 and $^4J_{PC}$ 2.4); ^{31}P NMR spectrum: δ_P 40.44 ppm].

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