Reaction of Trichloro(*o*-phenylenedioxy)phosphorane with 1,2-Alkadienylphosphonates

N. G. Khusainova, G. R. Garipova, T. A. Zyablikova, R. A. Cherkasov, and A. N. Pudovik

Kazan State University, Kazan, Tatarstan, Russia

Received October 4, 2000

Abstract — Trichloro(*o*-phenylenedioxy)phosphorane reacts with 1,2-alkadienylphosphonates with selective replacement of the alkoxy group in the phosphinoyl moiety, yielding the corresponding 1,2-alkadienylchlorophosphonates and *o*-phenylene chlorophosphate.

Trichloro(*o*-phenylenedioxy)phosphorane (\mathbf{I}) is an efficient chlorinating agent which have found application in organic synthesis. Gloede [1] studied in detail reactions of phosphorane I with alcohols, amines, carbonyl compounds, and compounds containing an imino group [1]. Mironov et al. [2, 3] recently reported on reactions of I with alkynes, which resulted in formation of unsaturated heterocycles containing phosphorus and chlorine atoms. It was found that phosphorane I reacts with arylacetylenes at the triple bond of the latter. The reaction is accompanied by opening of the 1,3,2-dioxaphosphole ring and migration of chlorine atom to afford 4-chloro-2H-1,2-benzoxaphosphinines [2]. According to our data [4, 5], phosphorane I does not add at the multiple bond of propynyl- and vinylphosphonates, and the reaction results in selective replacement of one alkoxy group in the phosphonate by chlorine, the unsaturated moiety remaining intact.

Reactions of phosphorane I with allene systems were not studied previously. Phosphorylated propadienes are known to readily take up chlorine and other electrophilic reagents at the 2,3-double bond, and 3,3-disubstituted propadienylphosphonates react with electrophiles to give oxaphospholes [6, 7].

In the present communication we report on the reaction of phosphorane **I** with propadienylphosphonates **IIa–IIc** in carbon tetrachloride or benzene at room temperature. The IR spectra of the reaction mixtures, recorded in 24 h and in a week after mixing the reactants, showed the presence of absorption at 1955–1960 cm⁻¹, which corresponds to stretching vibrations of the cumulene moiety. The ¹H NMR spectrum of the reaction mixture formed by compounds **I** and **IIb** contained a multiplet at δ 5.2 ppm, belonging to terminal CH₂= protons. According to

the ¹H signal intensities, the product had only one ethoxy group. These data indicate formation of ethyl propadienylchlorophosphonate (**IIIb**). The ³¹P signal of **I** (δ_P 26 ppm) completely disappears from the ³¹P NMR spectrum of an equimolar mixture of phosphorane **I** and phosphonate **IIb** in 24 h after mixing the reactants. Instead, two new signals appear at δ_P 20 (phosphate **IV**) and 32 ppm (chlorophosphonate **IIIb**). Chlorophosphonate **IIIb** is selectively formed in the presence of a two- or even threefold excess of **I**. Similar reactions were observed between phosphorane **I** and dimethyl and diethyl propadienylphosphonates **IIa** and **IIc**.



IIa, IIIa, $R = CH_3O$, R' = H; **IIb, IIIb**, $R = C_2H_5O$, R' = H; **IIc, IIIc**, $R = C_3H_7O$, R' = H; **Va, VIa**, $R = CH_3O$, $R' = CH_3$; **Vb, VIb**, $R = C_2H_5O$, $R' = CH_3$.

The process is very sensitive to moisture. When insufficiently dry argon was passed through the reaction mixture, partial hydrolysis of phosphorane **I** occurred, and liberated hydrogen chloride [1] added at the multiple bonds of propadienylphosphonate **II**. In the ¹H NMR spectrum of the mixture formed by compounds **I** and **IIa** a signal appears at δ 3.1 ppm (²J_{PH} = 22 Hz), which belongs to the methylene protons of the hydrochlorination product, dimethyl 2-chloro-2-propenylphosphonate (**VII**). Also, 2,3-addition product is formed, dimethyl 2-chloro-1-propenylphosphonate (**VIII**); it gives a signal at δ 2.3 ppm from the methyl group attached to the *sp*²-hybridized carbon atom [=C(Cl)CH₃]. In keeping with the signal intensity ratio, hydrochlorination at the 1,2-bond prevails over HCl addition at the 2,3-bond, which is consistent with earlier data [8]. A complex multiplet in the region 5–5.5 ppm belongs to olefinic protons in 1,2-propadienylchlorophosphonate **IIIa** and hydrochlorination products **VII** and **VIII**.

$$\begin{array}{rcl} R_2P(O)CH=C=CR'_2 &+ &HCl\\ \mathbf{IIa, V, Xb}\\ &\longrightarrow & R_2P(O)CH_2CCl=CR_2 &+ & R_2P(O)CH=CClCHR'_2,\\ & & \mathbf{VII, IXa, IXb, XI} & & \mathbf{VIII} \end{array}$$

IIa, **VII**, **VIII**, $R = CH_3O$, R'= H; **Va**, **IXa**, $R = CH_3O$, $R' = CH_3$; **Vb**, **IXb**, $R = C_2H_5O$, $R' = CH_3$; **Xb**, **XI**, R = CI, $R' = CH_3$.

By reactions of phosphorane I with 3-methyl-1,2butadienylphosphonates Va and Vb we obtained alkyl 1,2-alkadienylchlorophosphonates VIa and VIb, respectively. The IR spectra of the reaction mixtures contained an absorption band at 1955 cm⁻¹ (C=C=C). In the ¹H NMR spectra we observed a characteristic multiplet signal at δ 5.2 ppm from the α -olefinic proton (PCH=) and a signal from the methyl groups [=C(CH₃)₂] on the terminal carbon atom of phosphorylated alkadiene. The intensity ratio of these signals and those from the alkoxy group is consistent with the proposed structures. In addition, doublets at δ 3.0–3.2 ppm (²J_{PH} = 22 Hz) appeared due to methylene group protons, indicating formation of 1,2-adducts with hydrogen chloride, dialkyl 2-chloro-3-methyl-2-butenylphosphonates **IXa** and **IXb**.

The ¹H NMR spectrum of the reaction mixture obtained from phosphorane **I** and phosphonate **Vb** lacked signals at δ 5.95 ppm (² $J_{PH} = 33$, ³ $J_{HH} = 8.5$ Hz) and δ 7.13 ppm (³ $J_{PH} = 48$, ³ $J_{HH} = 8.5$ Hz), which are typical of olefinic protons in the oxaphosphole structure [8, 9], although its formation could be expected as a result of attack by hydrogen chloride on the C²=C³ bond of **Va** and **Vb**. The ³¹P NMR spectrum of the same reaction mixture contained signals at δ_P 18 (**IV**), 34 (**IXb**), and 39 ppm (**VIb**).

In the ³¹P NMR spectrum of the mixture of reactants I and Va signals were observed at δ_p 19 (IV), 28 (IXa), and 37 ppm (VIa). The presence of signals at δ_p 37 and 39 ppm suggests that we cannon rule out formation of 2-alkoxy-5,5-dimethyl-1,2 λ^5 -oxaphosphole 2-oxides [8, 9] in reactions of phosphorane I with phosphonates Va and Vb: In this case, ¹H NMR signals from olefinic protons of the oxaphospholes are likely to be obscured by the multiplet signal from the =CHP proton of chlorophosphonates VI and aromatic proton signals of chlorophosphate IV. On the other hand, the absence of products having an oxaphosphole structure is consistent with the data of [10], according to which the yield of 1,2-addition products attains 80% when an aprotic ionizing species (e.g., dimethyl sulfoxide) is added to the reaction mixture in a nonpolar solvent (assuming that phosphorane I plays the role of such species). Compounds VIa, VIb, IXa, and IXb were identified only on the basis of the NMR and IR spectra, for we failed to isolate these products by distillation.

With 3-methyl-1,2-butadienylphosphonic dichloride (Xb) as an example, we examined reactions of I with phosphorylated 1,2-alkadienes having no alkoxy groups on the phosphorus. No exothermic effect was observed on mixing I and Xb at room temperature. According to the ³¹P NMR data, after 2–3 weeks, as well as after a month, the reaction mixture in CCl_4 or C_6H_6 contained only the initial compounds. When an equimolar mixture of phosphorane I and dichloride Xb in benzene was heated for 15 h at 80–90°C, a signal appeared in the ¹H NMR spectrum at δ 3.8 ppm (²J_{PH} = 16 Hz), which was assigned to the methylene protons of 2-chloro-3-methyl-2-butenylphosphonic dichloride (XI). The ³¹P NMR spectrum of the mixture contained signals at $\delta_{\rm p}$ 23 (I), 17 (IV), 26 (Xb), and 37 ppm (XI). In the IR spectrum of product XI we observed a medium-intensity band at 1960 cm⁻¹, typical of stretching vibrations of the cumulated double bond system. These data led us to conclude that some amount of hydrogen chloride is released in the reaction of I with Xb in benzene on heating; and it selectively adds at the $C^1 = C^2$ bond of the diene. According to the NMR data, no cyclic 2,2,2-trichloro-5,5-dimethyl-1, $2\lambda^5$ -oxaphosphole was detected in the reaction mixture (Macomber and Kennedy [11] observed formation of such product when hydrogen chloride was passed through a solution of **Xb** in methylene chloride over a period of at least 25 days). Mikhailova et al. [12] presumed that hydrochlorination of 1,2-alkadienylphosphonic dichlorides in an inert solvent (CCl₄, C₆H₆) containing aprotic ionizing species involves nucleophilic addition of HCl at the $C^1 = C^2$ bond via attack by chloride ion on the central carbon atom; no protophilic cyclization occurs under these conditions.

Thus the cumulated double bond system in 1,2alkadienylphosphonates and 1,2-alkadienylphosphonic chlorides is inactive toward trichloro(o-phenylenedioxy)phosphorane at room temperature. 1,2-Alkadienylphosphonic esters react with phosphorane **I** via replacement of one alkoxy group by chlorine, and this reaction can be regarded as a new selective procedure for preparation of alkyl 1,2-alkadienylchlorophosphonates.

EXPERIMENTAL

The IR spectra (films) were recorded on a UR-20 spectrometer. The NMR spectra were obtained on Varian-60 (¹H, 60 MHz) and Bruker CXP instruments (³¹P, 36.47 MHz) using CCl₄ or C₆H₆ as solvent. The chemical shifts were measured relative to TMS (¹H) or H₃PO₄ (³¹P). All operations were performed under argon.

Reaction of trichloro(*o*-phenylenedioxy)phosphorane (I) with dialkyl 1,2-propadienyl- and 3-methyl-1,2-butadienylphosphonates IIa–IIc, Va, and Vb. Dialkyl 1,2-alkadienylphosphonate IIa– IIc, Va, or Vb, 0.01 mol, was added dropwise to a solution of 0.01 mol of phosphorane I in 10 ml of carbon tetrachloride or benzene; the mixture warmed up by 14–15°C. After a day, the mixture was distilled in vacuo, a fraction boiling in the range 58–80°C (0.4 mm) being collected. Colorless needles of *o*-phenylene chlorophosphate (IV) separated from the distillate on storage. Yield 1.2–1.3 g (64–70%), mp 59–61°C. ³¹P NMR spectrum: $\delta_{\rm P}$ 18–19 ppm. Published data [13]: mp 61–63°C, $\delta_{\rm P}$ 19 ppm.

Fractional distillation of the liquid part of the distillate gave alkyl propadienylchlorophosphonates **IIIa–IIIc**.

Methyl propadienylchlorophosphonate (IIIa). Yield 0.76 g (50%), bp 67–70°C (0.03 mm). ³¹P NMR spectrum: δ_P 34 ppm. Found, %: C 31.58; H 3.85; P 20.49. C₄H₆ClO₂P. Calculated, %: C 31.47; H 3.93; P 20.32.

Ethyl propadienylchlorophosphonate (IIIb). Yield 1 g (61%), bp 63–65°C (0.5 mm), n_D^{20} 1.4760; published data [14]: bp 72–74°C (2 mm), n_D^{20} 1.4781. ³¹P NMR spectrum: δ_P 32 ppm. Found, %: C 36.14; H 4.94; P 18.47. C₅H₈ClO₂P. Calculated, %: C 36.03; H 4.80; P 18.62.

Propyl propadienylchlorophosphonate (IIIc). Yield 1.2 g (66%), bp 74–77°C (0.6 mm), n_D^{20} 1.4772; published data [14]: bp 96–97°C (1.5 mm), n_D^{20} 1.4790. ³¹P NMR spectrum: δ_P 31 ppm. Found, %: C 40.03; H 5.64; P 17.32. C₆H₁₀ClO₂P. Calculated, %: C 39.89; H 5.53; P 17.17.

In the reactions of phosphorane I with 1,2-butadienylphosphonates Va and Vb, products VIa, VIb, IXa, and IXb were identified by NMR and IR spectroscopy in the liquid part of the distillate obtained after separation of crystalline chlorophosphate IV. We failed to separate mixtures **VI/IX** by vacuum distillation.

Reaction of phosphorane I with 3-methyl-1,2butadienylphosphonic dichloride (Xb). Dichloride **Xb**, 0.01 mol, was added to a solution of 0.01 mol of phosphorane I in 15 ml of benzene, and the mixture was heated for 15 h at 80–90°C. Subsequent vacuum distillation gave colorless needles of chlorophosphate **IV**, yield 0.6 g (32%), mp 62°C. Fractional distilation of the residue gave 0.45 g (20%) of phosphonic dichloride **XI**, bp 51–53°C (0.5 mm), n_D^{20} 1.5160; published data [12]: bp 65–67°C (1 mm), n_D^{20} 1.5179.

ACKNOWLEDGMENTS

This study was performed in the framework of the Program "Universities of Russia–Fundamental Research" and the Program for financial support of leading scientific schools of the Russian Federation (project no. 00-15-97424).

REFERENCES

- Gloede, J., Z. Chem., 1982, vol. 22, no. 4, pp. 126– 134.
- Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 9, pp. 1482–1509.
- Mironov, V.F., Shtyrlina, A.A., Azancheev, N.M., and Konovalov, A.I., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 1, pp. 160–161.
- Khusainova, N.G., Mironov, V.F., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 9, pp. 1578–1579.
- Khusainova, N.G., Reshetkova, G.R., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 3, pp. 396–398.
- Khusainova, N.G. and Pudovik, A.N., Usp. Khim., 1987, vol. 56, no. 6, pp. 975–1003.
- Mikhailova, T.S., Angelov, Kh.M., Ignat'ev, V.M., Dogadina, A.V., Zakharov, V.I., Ionin, B.I., and Petrov, A.A., *Zh. Obshch. Khim.*, 1977, vol. 47, no. 12, pp. 2701–2707.
- Mikhailova, T.S., Zakharov, V.I., Ignat'ev, V.M., Ionin, B.I., and Petrov, A.A., *Zh. Obshch. Khim.*, 1980, vol. 50, no. 8, pp. 1690–1702.
- Mikhailova, T.S., Ignat'ev, V.M., Ionin, B.I., and Petrov, A.A., *Zh. Obshch. Khim.*, 1978, vol. 48, no. 3, p. 701.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 71 No. 3 2001

- Mikhailova, T.S., Chunin, E.D., Skvortsov, N.K., Ignat'ev, V.M., Ionin, B.I., and Petrov, A.A., *Zh. Obshch. Khim.*, 1979, vol. 49, no. 8, pp. 1752– 1756.
- 11. Macomber, R.S. and Kennedy, E.R., J. Org. Chem., 1976, vol. 41, no. 14, pp. 3191–3196.
- 12. Mikhailova, T.S., Ignat'ev, V.M., Ionin, B.I., and

Petrov, A.A., Zh. Obshch. Khim., 1980, vol. 50, no. 4, pp. 762–770.

- 13. Gloede, J., J. Prakt. Chem., 1981, vol. 323, no. 4, pp. 621–629.
- Kondrat'ev, Yu.A., Tarasov, V.V., Vasil'eva, A.S., Ivakina, N.M., and Ivin, S.Z., *Zh. Obshch. Khim.*, 1968, vol. 38, no. 9, pp. 1791–1793.