## Properties of Onium Salts of Phosphorus and Nitrogen

M. Zh. Ovakimyan, S. K. Barsegyan, N. M. Kikoyan, and M. G. Indzhikyan

Institute of Organic Chemistry, National Academy of Sciences of Armenia, Erevan, Armenia

Received March 11, 2004

**Abstract**—Ammonium and phosphonium halides when heated with excess dimethyl or diethyl phosphite can undergo anion exchange as a result of alkylation of halide ions with dialkyl phosphites. Experimental data were obtained, that cast some doubt in the commonly accepted opinion that reactions of tertiary amines and phosphines with dihalides in apolar media result in exclusive formation of monosalts.

It was previously shown that (1-alkoxy-2-bromoethyl)phosphonium salts, unlike other phosphonium salts, undergo thermolysis at low temperatures to form triphenylphosphine oxide as a phosphorus-containing product [1]. It was proposed that these reactions are driven by coordination of the alkoxyl oxygen with onium phosphorus atoms and by the presence of the readily leaving bromine atom  $\beta$  to phosphorus.

Proceeding with this research, we made an attempt to prepare a 2-phosphorylated analog of (1-alkoxy-2bromoethyl)phosphonium salts from a (1-butoxyvinyl)- triphenylphosphonium salt and dimethyl phosphite. However, heating of (1-alkoxyvinyl)triphenylphosphonium salts with excess dimethyl phosphite unexpectedly gave a phosphorus-containing nonhalogenated salt whose <sup>1</sup>H NMR spectrum diplayed, along with characteristic signals of the phosphonium cation of the starting salt, a doublet at 3.50 ppm, assignable to the POCH<sub>3</sub> group, and a PH doublet with a coupling constant of 650 Hz. These results led us to conclude that bromine had exchanged for a methyl hydrogen phosphite anion.

$$\begin{array}{c} Ph_{3}P^{+}-C=CH_{2}+(CH_{3}O)_{2}P \swarrow P & \xrightarrow{O} Ph_{3}P^{+}-C=CH_{2}\\ Br^{-} & OR & CH_{3}O & \xrightarrow{O^{-}} & OR \\ H \swarrow P & O & OR \end{array}$$

 $R = C_2H_5, C_4H_9.$ 

Similar halide exchange we also observed with methyltriphenylphosphonium bromide that was used as an example of a compound containing no double bonds. However, we failed to obtain a diphosphonium salt with two methyl hydrogen phosphite anions. When heated with a fourfold excess of dimethyl phosphite, ethylenebis(triphenylphosphonium) dibromide completely decomposed, and dimethyl phosphite converted into an acid. After treatment of the reaction mixture with alkali we isolated triphenylphosphine oxide. Probably, the decomposition of the salt with a loss of the ethylene bridge had been preceded by anion exchange by the following scheme.

$$\begin{array}{cccc} & & & & & & & \\ Ph_{3}P^{+}-CH_{2}CH_{2}-P^{+}Ph_{3} & & & \\ Br^{-} & & Br^{-} \end{array} \xrightarrow{(CH_{3}O)_{2}P^{+}_{H}} & \xrightarrow{-O}{} & P^{+}OCH_{3} & \xrightarrow{-O}{} & P^{+}OCH_{3} \\ & & & & Ph_{3}P^{+}-CH_{2}CH_{2} & -P^{+}Ph_{3} \end{array} \xrightarrow{} & Ph_{3}P=O+Ph_{3}P+CH_{2}=CH_{2} \\ \end{array}$$

To elucidate the mechanism of the observed reaction, we have studied the reaction of an ammonium salt, acetyltrimethylammonium bromide, with diethyl phosphite and found that halide ions can be alkylated with trialkyl phosphite only in the presence of at least fourfold excess of the alkylating agent.

According to [2, 3], tertiary amines and phosphines react with equimolar amounts of dihalides in apolar media (ether, benzene) with exclusive formation of monoammonium salts on account of the fact that they are only soluble in polar media. As shown in the present work, heating of triphenylphosphine in ether or benzene with equimolar amount of 1,4-dichlorobut-2-ene results in exclusive formation of a diphosphonium salt. The reactions of 1,4-dichlorobut-2-ene with trimethylamine or *N*-methylmorpholine under the same conditions provide the corresponding monosalts as major products, as well as small amounts (10%) of disalts.

Diphosphonium salts were also formed in the reactions of triphenyl- and tributylphosphines with 1,2-dibromoethane under conditions applied for monosalt formation.

The resulting data suggest that the reactions simultaneously involve in part two reaction centers. An alternative explanation relying on partial solubility of monosalts in ether or benzene seems unlikely.

## **EXPERIMENTAL**

The <sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained on a Varian Mercuri-300 spectrometer (300 MHz) in  $CDCl_3$  and  $CD_3OD$ .

**Reaction of (1-butoxyvinyl)triphenylphosphonium bromide with dimethyl phosphite.** A mixture of (1-butoxyvinyl)triphenylphosphonium bromide and 2 g of dimethyl phosphite was heated in 7 ml of toluene at 100°C for 10 h. The solvent was then removed by distillation, and the residue was thoroughly washed with dry ether and dried in a vacuum to obtain 2 g (98%) of (1-butoxyvinyl)triphenylphosphonium methyl hydrogen phosphite. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD),  $\delta$ , ppm (*J*, Hz): 0.90 t [3H, O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, *J*<sub>HH</sub> 6.2], 1.25 m [2H, O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>], 1.70 m (2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.70 d (3H, POCH<sub>3</sub>, <sup>3</sup>*J*<sub>PH</sub> 12.3), 4.05 t (2H, OCH<sub>2</sub>, *J*<sub>HH</sub> 6.2), 5.00 d.d (H<sup>b</sup>, PCCHaH<sup>b</sup>, <sup>3</sup>*J*<sub>PH</sub> 14.3, *J*<sub>HH</sub> 4.5), 5.80 d.d (H<sup>a</sup>, PCCH<sup>a</sup>H<sup>b</sup>, <sup>3</sup>*J*<sub>PH</sub> 39.0, *J*<sub>HH</sub> 4.5), 7.60–7.90 m [15H, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]. Found, %: C 65.56; H 6.35; P 13.13. C<sub>25</sub>H<sub>30</sub>O<sub>4</sub>P<sub>2</sub>. Calculated, %: C 65.79; H 6.58; P 13.59.

**Reaction of methyltriphenylphosphonium bromide with dimethyl phosphite.** A mixture of 1 g of methyltriphenylphosphonium bromide and 1.3 g of dimethyl phosphite was heated in 6 ml of toluene at 100°C for 8 h and then treated as described above to obtain 1 g (96%) of methyltriphenylphosphonium hydrogen phosphite. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (*J*, Hz): 2.40 d (3H, PCH<sub>3</sub>, <sup>2</sup>J<sub>PH</sub> 14.0), 3.50 d (3H, OCH<sub>3</sub>, <sup>3</sup>J<sub>PH</sub> 12.3), 7.70–8.10 m [15H, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]. Found, %: C 64.37; H 5.15; P 15.22. C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>P<sub>2</sub>. Calculated, %: C 64.52; H 5.91; P 16.67.

**Reaction of ethylenebis(triphenylphosphonium) dibromide with dimethyl phosphite.** A mixture of 2 g of ethylenebis(triphenylphosphonium) dibromide and 1.3 g of dimethyl phosphite was heated at 100°C for 8 h. Excess dimethyl phosphite was distilled off, and the residue was dried to obtain 1.8 g of a material whose treatment with aqueous NaOH to isolate 0.3 g of triphenylphosphine oxide, mp 154°C. Mixed sample with an authentic sample gave no melting point depression.

**Reaction of acetyltrimethylammonium bromide** with diethyl phosphite. A mixture of 1 g of acetyltrimethylammonium bromide and 1.5 g of diethyl phosphite was refluxed in toluene for 7 h and then treated to obtain 1 g (93%) of acetyltrimethylammonium ethyl hydrogen phosphite. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (*J*, Hz): 0.90 t [3H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N<sup>+</sup>, *J*<sub>HH</sub> 6.5], 1.30 m [29H, POCH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>2</sub> · CH<sub>2</sub>N<sup>+</sup>], 1.70 m [2H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>], 3.30 s [9H, (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>], 4.10 m [4H, POCH<sub>2</sub>CH<sub>3</sub>, N<sup>+</sup>CH<sub>2</sub> · (CH<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>]. Found, %: C 63.92; H 11.81; P 7.11. C<sub>21</sub>H<sub>48</sub>NO<sub>3</sub>P. Calculated, %: C 64.12; H 12.21; P 7.89.

**Reaction of triphenylphosphine with 1,4-dichlorobut-2-ene.** 1,4-Dichlorobut-2-ene, 3.5 g, was added dropwise to 7.3 g of triphenylphosphine in dry benzene, and the reaction mixture was refluxed on a water bath for 16 h. The precipitate that formed was filtered off, washed with two portions of dry ether, and dried to obtain 8.2 g (93%) of but-2-ene-1,4-diylbis(triphenylphosphonium) dichloride. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD),  $\delta$ , ppm (*J*, Hz): 4.20 d.d (4H, PCH<sub>2</sub>, <sup>2</sup>*J*<sub>PH</sub> 14.5, *J*<sub>HH</sub> 6.5), 5.90 t (2H, CH=CH, *J*<sub>HH</sub> 6.9), 7.80–7.90 m (30H, PC<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P NMR spectrum (CD<sub>3</sub>OD),  $\delta_{\rm p}$ , ppm: 24.64. Found Cl<sup>-</sup>, %: 10.90. C<sub>40</sub>H<sub>36</sub>Cl<sub>2</sub>P<sub>2</sub>. Calculated Cl<sup>-</sup>, %: 10.94.

**Reaction of N-methylmorpholine with 1,4-dichlorobut-2-ene.** 1,4-Dichlorobut-2-ene, 20.2 g, was added dropwise to 16.2 g of N-methylmorpholine in dry ether, and the reaction mixture was left to stand at room temperature for 7 days. The precipitate was then filtered off, washed with dry ether, and dried to obtain 27.5 g of a mixture of salts, whose recrystallization from isopropanol gave 5.5 g (11%) of but-2-ene-

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 75 No. 7 2005

1,4-diylbis(*N*-methylmorpholinium) dichloride. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD), δ, ppm (*J*, Hz): 3.20 s [6H, (CH<sub>3</sub>)<sub>2</sub>N], 3.50 m [8H, N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>], 4.00 m [8H, O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>], 4.25 d (4H, NCH2,  $J_{\rm HH}$  6.9), 6.50 t (2H, CH=CH,  $J_{\rm HH}$  6.9). Found Cl<sup>-</sup>, %: 21.25. C<sub>14</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>. Calculated Cl<sup>-</sup>, %: 21.71.

The filtrate was evaporated to obtain 22 g of a mixture of but-2-ene-1,4-diylbis(*N*-methylmorpholinium) dichloride and 1-(*N*-methylmorpholinio)-4-chlorobut-2-enyl chloride (1:14). <sup>1</sup>H NMR spectrum of 1-(*N*methylmorpholinio)-4-chlorobut-2-enyl chloride,  $\delta$ , ppm: 3.10 and 3.15 s (3H, CH<sub>3</sub>N<sup>+</sup>), 3.50 m (4H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>), 4.00 m (6H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>Cl), 4.15 m (2H, N<sup>+</sup>CH<sub>2</sub>), 5.80–6.40 m (2H, *cis*- and *trans*-CH=CH).

Reaction of trimethylamine with 1,4-dichlorobut-2-ene. 1,4-Dichlorobut-2-ene, 11.5 g, was added with cooling to a solution of 5.4 g of trimethylamine in dry ether, and the reaction mixture was left to stand for 3 days. The precipitate was filtered off, thoroughly dried with ether, and dried to obtain 11.1 g of a mixture of (4-chlorobut-2-enyl)trimethylammonium chloride and but-2-ene-1,4-diylbis(trimethylammonium) dichloride (5:1, <sup>1</sup>H NMR data). <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD),  $\delta$ , ppm (*J*, Hz): monosalt: 3.10 s and 3.20 s [9H, (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>], 3.95 m (2H, CH<sub>2</sub>Cl), 4.10 m (2H, NCH<sub>2</sub>), 5.95–6.40 m (2H, *cis*- and *trans*-CH=CH); disalt: 3.05 s and 3.15 s {18H, *cis*- and *trans*-[(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>]2}, 4.15 and 4.30 m [4H, *cis*- and *trans*-(N<sup>+</sup>CH<sub>2</sub>)<sub>2</sub>], 6.40 m (2H, *cis*- and *trans*-CH=CH).

**Reaction of triphenylphosphine with 1,2-dibromoethane.** A mixture of 6 g of triphenylphosphine and 4.4 g of 1,2-dibromoethane was refluxed in toluene for 7 days. The solvent was then distilled off, and the residue was thoroughly washed with dry ether to obtain 6.2 g of a mixture of salts, whose recrystallization from ethyl acetate–ethanol gave 3.1 g (37%) of ethylenebis(triphenylphosphonium) dibromide, mp 196°C. <sup>1</sup>H NMR spectrum (DMSO),  $\delta$ , ppm (*J*, Hz): 4.20 d (4H, P<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>P<sup>+</sup>, <sup>2</sup>J<sub>PH</sub> 5.5), 7.80–7.90 m {30H, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>}. Found Br<sup>-</sup>, %: 22.10. C<sub>38</sub>H<sub>34</sub>. Br<sub>2</sub>P<sub>2</sub>. Calculated Br<sup>-</sup>, %: 22.47.

Reaction of tributylphosphine with 1,2-dibromoethane. A mixture of 5.3 g of tributylphosphine and 4.9 g of 1,2-dibromoethane in toluene was heated under argon on a water bath for 2 days. The solvent was then removed, and the residue was thoroughly washed with dry ether to obtain 8.8 g of a mixture of (2-bromoethyl)tributylphosphonium bromide and ethylenebis(tributylphosphonium) dibromide (4:1, 1H NMR data). The mixture was recrystallized from ether-ethyl acetate to isolate 1 g of ethylenebis(tributylphosphonium) dibromide. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm (*J*, Hz): 0.90–1.00 m {18H,  $[P^{+}(CH_{2}(CH_{2})_{2}CH_{3})_{3}]_{2}\}, 1.40-1.60 \text{ m} \{24\text{H},$  $[P^+(CH_2(CH_2)_2CH_3)_3]_2$ , 2.50–2.60 m {12H,  $[P^+(CH_2(CH_2)_2CH_3)_3]_2\}$ , 3.30 d (4H,  $P^+CH_2CH_2P^+$ ,  $^{2}J_{PH}$  6.3). Found Br<sup>-</sup>, %: 26.60. C<sub>26</sub>H<sub>58</sub>Br<sub>2</sub>P<sub>2</sub>. Calculated Br<sup>-</sup>, %: 27.03.

## REFERENCES

- Torgomyan, A.M., Ovakimyan, M.Zh., and Indzhikyan, M.G., *Arm. Khim. Zh.*, 1977, vol. 30, no. 5, p. 439.
- Babayan, A.T., Indzhikyan, M.G., and Gegelyan, Zh.G., Zh. Org. Khim., 1966, vol. 2, no. 12, p. 2117.
- Babayan, A.T., Martirosyan, G.T., Gyul'nazaryan, A.H., and Arakelyan, N.M., Arm. Khim. Zh., 1972, vol. 25, no. 2, p. 123.