BRIEF COMMUNICATIONS

REACTIONS OF β-CHLOROETHYL DERIVATIVES OF TRICOORDINATED PHOSPHORUS ACIDS WITH 1-NITRO-1-PROPENE

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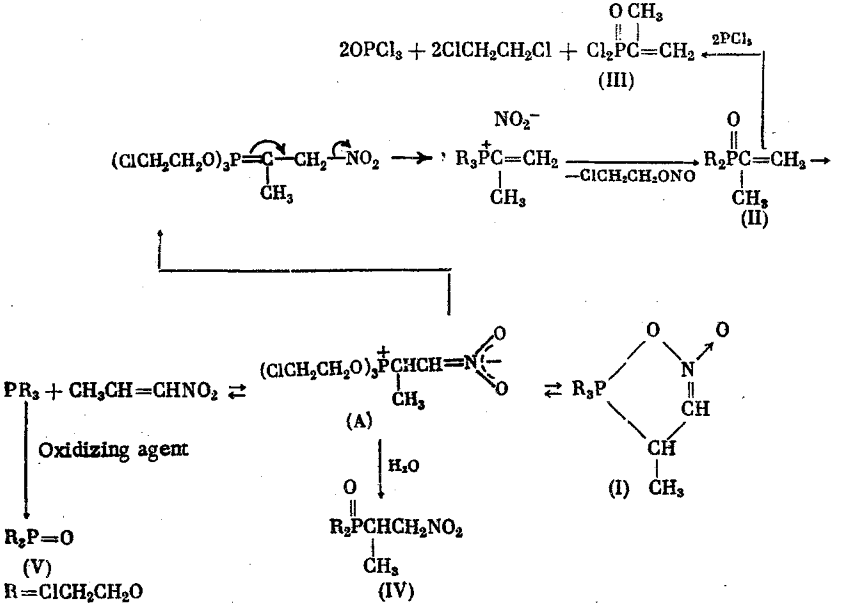
UDC 542.91:547.1'118

The reaction of tris(β-chloroethyl) phosphite with 1-nitro-1-propene proceeds in several competing directions, whose realization depends on a number of factors (temperature, order of mixing the reactants, presence of trace amounts of water). Thus, four resonance signals at 30, 2.5, −21, and −29 ppm were detected in the $^{31}P-\{^1H\}$ NMDR spectrum of a reaction mixture, which was obtained by adding 1-nitro-1-propene to tris(β-chloroethyl) phosphite at 30-35°C under the conditions of exposure to atmospheric moisture. The signal at 30 ppm was assigned to the corresponding adduct (I) with a pentacoordinated P atom, which under more drastic conditions decomposes to give bis(β-chloroethyl) isopropenylphosphonate (II) with δ −21 ppm. This is confirmed by a symbatic increase in the integral intensity of the latter with decrease in the intensity of the signal at 30 ppm when the reaction mixture is kept at 70-80° for 30 min. Compound (II) easily reacts with PCl_5 to give dichloroisopropenylphosphonate (III), whose constants, as well as the IR and PMR spectra, coincide completely with those of the specimen obtained by the method given in [1] (see Scheme):



The fact that the IR spectrum of the reaction mixture had the ν_s and ν_{as} absorptions of the nitro group enabled us to assign the signal at −29 ppm to bis(β-chloroethyl) (α-methyl-β-nitroethyl)phosphonate (IV), which was obtained by the counter reaction of bis(β-chloroethyl) trimethylsilyl phosphite (−125 ppm) with 1-nitro-1-propene [2].

It should be mentioned that the formation of small amounts of (IV) cannot be avoided even when tris(β-chloroethyl) phosphite is reacted with 1-nitro-1-propene under conditions that exclude the admittance of atmospheric moisture. This cannot be avoided even when the starting 1-nitro-1-propene is dried well.

The amount of tris(β-chloroethyl) phosphate (V) (δ = 2.5 ppm) that is formed relative to the other reaction products is considerably higher than that expected, for only a small amount of trimethyl phosphate is formed

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0568-5230/78/2706-1217$07.50

when trimethyl phosphite is reacted with 1-nitro-1-propene under analogous conditions. In this connection the question of the nature of the oxidizing agent arose. It is logical to assume that the starting 1-nitro-1-propene can be the oxidizing agent. Then the ratio of (II) to (V) would be independent of the order of mixing the starting reactants, but with the reverse order of mixing the reactants the amount of (V) relative to (II) decreases substantially. Consequently, if 1-nitro-1-propene takes part in the oxidation of tris(β-chloroethyl) phosphite, then it does this but slightly. Further, β-chloroethyl nitrite which could be expected during the formation of (II), cannot be isolated from the reaction mixture. The experiment with pure β-chloroethyl nitrite, obtained by counter synthesis, made it possible to show that β-chloroethyl nitrite is the oxidizing agent of the tris(β-chloroethyl) phosphite in the above discussed reaction (checked by the $^{31}P-\{^1H\}$ NMDR method). Also in agreement with this conclusion is the fact that, irrespective of the order of mixing the starting reactants, the amount of tris(β-chloroethyl) phosphite consumed is somewhat greater than that required by theory if we start with an equimolar mixture of the reactants. It should also be added that the bipolar intermediate (A), which is formed in the first step as the result of the nucleophilic addition of tris(β-chloroethyl) phosphite to the β-C atom of 1-nitro-1-propene [3], can also substantially function as the oxidizing agent on the background of β-chloroethyl nitrite.

As was to be expected, the reaction of bis(β-chloroethyl) methylphosphonite with 1-nitro-1-propene proceeds more vigorously and by a similar scheme. As a result, a reaction mixture was obtained, in whose $^{31}P-\{^1H\}$ NMDR spectrum were detected signals at −31, −44, and −58 ppm. The β-chloroethyl ester of methylisopropenylphosphinic acid (VI) ($\delta = -44$ ppm) was isolated by distilling this mixture, in whose PMR spectrum were detected all of the corresponding proton-containing functional groups. The reaction of (VI) with PCl_5 gave methylisopropenylphosphinyl chloride (VII), whose structure was rigorously proved by the IR and PMR spectra. This result opens up wide possibilities for the synthesis of various derivatives of methylisopropenylphosphinic acid. Thus, the reaction of (VI) with isopropanol gave the isopropyl ester of methylisopropenylphosphinic acid (VIII), which cannot be obtained by the reaction of O,O-diisopropyl methylphosphonite with 1-nitro-1-propene in ether [3, 4]. In the spectrum of the reaction mixture the signal at −31 ppm was assigned to bis(β-chloroethyl) methylphosphonate (IX), the oxidation product of the starting phosphonite. The validity of such an assignment was confirmed by the counter synthesis of (IX) via the reaction of dichloromethylphosphonate with ethylene chlorohydrin. A small amount of impurity with δ −58 ppm also indicates the formation of β-chloroethyl methyl (α-methyl-β-nitroethyl)phosphinate (X), which was also obtained by counter synthesis from O-β-chloroethyl-O-trimethylsilyl methylphosphonite (−161 ppm) and 1-nitro-1-propene [2]. A detailed examination of the PMR spectrum of (X) makes it possible to note the formation of practically only one of the possible diastereomers, which is the consequence of the stereospecificity of the reaction.

The reaction of 1-nitro-1-propene with bis(β-chloroethyl) phenylphosphonite also proceeds in a similar manner. According to the data of the $^{31}P-\{^1H\}$ NMDR spectrum, the reaction mixture contains three phosphorus-containing compounds with $\delta = -19$, −35, and −44 ppm. All of the formed compounds were identified by the portrait method employing the corresponding pure specimens, which were obtained by counter synthesis. The compounds that are formed here are bis(β-chloroethyl) phenylphosphonate (XI) (−19 ppm), β-chloroethyl phenylisopropenylphosphinate (XII) (−35 ppm), and traces of β-chloroethyl phenyl(α-methyl-β-nitroethyl)phosphinate (XIII) (−44 ppm). Compound (XIII) was obtained by reacting O-β-chloroethyl-O-trimethylsilyl phenylphosphonite with 1-nitro-1-propene and represents a mixture of two diastereomers in a 38 : 62 ratio, which corresponds to a very low degree of stereospecificity.

EXPERIMENTAL

The $^{31}P-\{^1H\}$ NMDR spectra were obtained on a spectrometer with a frequency of 10.2 MHz relative to 85% H_3PO_4.

Bis(β-chloroethyl) isopropenylphosphonate (II), yield 46.3%; bp 117-118° (1 mm); n_D^{20} 1.4760; d_4^{20} 1.2823. Found: C 34.20; H 5.40; P 12.31; Cl 29.00%. $C_7H_{13}O_3PCl_2$. Calculated: C 34.01; H 5.26; P 12.55; Cl 28.75%.

Bis(β-chloroethyl) trimethylsilyl phosphite, yield 70.1%; bp 82° (0.08 mm); n_D^{20} 1.4560; d_4^{20} 1.1507. Found: P 11.37; Si 9.80; Cl 25.73%. $C_7H_{17}O_3PSiCl_2$. Calculated: P 11.11; Si 10.04; Cl 25.45%.

Bis(β-chloroethyl)(α-methyl-β-nitroethyl)phosphonate (IV), yield ~100%; n_D^{20} 1.4858. Found: N 4.60; P 10.70; Cl 24.37%. $C_7H_{14}NO_5PCl_2$. Calculated: N 4.76; P 10.55; 24.15%.

O-β-Chloroethyl methylisopropenylphosphinate (VI), yield 47.4%; bp 85-87° (0.1 mm); n_D^{20} 1.4740, d_4^{20} 1.1741. Found: C 39.37; H 6.47; P 16.70%. $C_6H_{12}O_2PCl$. Calculated: C 39.45; H 6.58; P 16.99%.

Methylisopropenylphosphinyl Chloride (VII), yield 71.3%; bp 93-95° (11 mm); n_D^{20} 1.4819; d_4^{20} 1.1955. Found: C 34.60; H 5.89; P 22.50; Cl 25.47%. C_4H_8OPCl. Calculated: C 34.66; H 5.77; P 22.38; Cl 25.63%.

O-Isopropyl methylisopropenylphosphinate (VIII), yield 82.5%, bp 35-36° (0.05 mm); n_D^{20} 1.4460; d_4^{20} 0.9897. Found: C 51.80; H 9.32; P 19.00%. $C_7H_{15}O_2P$. Calculated: C 51.85; H 9.26; P 19.14%.

O-β-Chloroethyl O-trimethylsilyl methylphosphonite, yield 63.0%; bp 76° (10 mm); n_D^{20} 1.4423. Found: P 14.67; Si 12.83%. $C_6H_{16}O_2PSiCl$. Calculated: P 14.45; Si 13.05%.

β-Chloroethyl methyl(α-methyl-β-nitroethyl)phosphinate (X), yield ~100%; n_D^{20} 1.4853. Found: N 5.90; P 13.77%. $C_6H_{13}NO_4PCl$. Calculated: N 6.10; P 13.51%.

Phenylisopropenylphosphonyl chloride, yield 71.6%; bp 89-91° (0.08 mm); n_D^{20} 1.5596. Found: C 53.96; H 5.20; P 15.69; Cl 17.63%. $C_9H_{10}OPCl$. Calculated: C 53.87; H 4.99; P 15.46; Cl 17.71%.

O-β-Chloroethyl phenylisopropenylphosphinate (XII), yield 73.3%; bp 124-125° (0.08 mm); n_D^{20} 1.5370. Found: C 53.87; H 5.70; P 12.53; Cl 14.41%. $C_{11}H_{14}O_2PCl$. Calculated: C 53.99; H 5.73; P 12.68; Cl 14.52%.

β-Chloroethyl phenyl(α-methyl-β-nitroethyl)phosphinate (XIII), yield ~100%; n_D^{20} 1.5370. Found: N 4.61; P 10.89%. $C_{11}H_{15}NO_4PCl$. Calculated: N 4.80; P 10.63%.

The authors thank É. I. Gol'dfarb for taking the $^{31}P-\{^1H\}$ NMDR spectra.

CONCLUSIONS

The reactions of the β-chloroethyl derivatives of trivalent phosphorus acids proceed via an ionic intermediate, which, depending on the experimental conditions, is stabilized in the direction of ring closure to give an adduct with a pentacovalent phosphorus atom and the formation of the corresponding unsaturated and (α-methyl-β-nitroethyl)phosphoryl compounds. The liberated β-chloroethyl nitrite functions as an oxidizing agent of the starting β-chloroethyl derivatives of trivalent phosphorus acids.

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