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MECHANISM OF THE REACTIONS OF TRIALKYL PHOSPHITES WITH α-HALOCARBONYL COMPOUNDS

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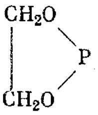
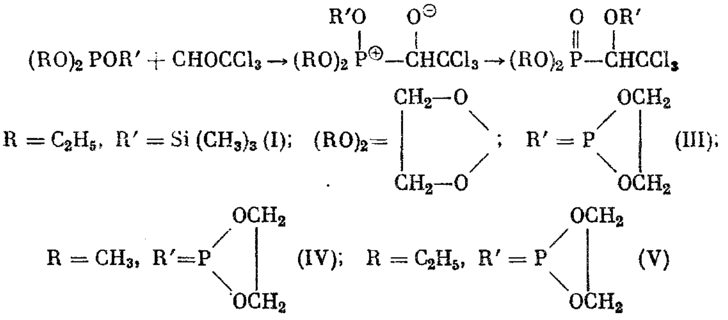
A number of mechanisms have been proposed for the reactions of trialkyl phosphites with α-halocarbonyl compounds. It has been postulated that the reaction begins with the nucleophilic attack of the P atom at the carbonyl carbon, the carbonyl oxygen, the α carbon atom, or the positively polarized halogen atom of the halocarbonyl compound [1]. Therefore, in considering the mechanism of these reactions the determination of the reaction center of the molecule of the α-halocarbonyl compound is of great importance.

We have previously studied the reactions of diethyl trimethylsilyl phosphite [2] and of pyrophosphites [3] containing the  group with chloral. As a result we obtained diethyl α-trimethylsiloxy-β,β,β-trichloroethylphosphonate (I) with a 92% yield and α-dialkylphosphono-β,β,β-trichloroethylethylene phosphites with a yield >90%:



$$(RO)_2POR' + CHOCCl_3 \rightarrow (RO)_2\overset{R'O}{\overset{|}{P}}{}^{\oplus}\!-\!\overset{O^{\ominus}}{\overset{|}{C}}HCCl_3 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}\!-\!\overset{OR'}{\overset{|}{C}}HCCl_3$$

The reaction of diethyl trimethylsilyl phosphite with trichloroacetaldehyde resulted in the formation of diethyl α-trimethylsiloxy-β-chloroethylphosphonate (II) with a 59% yield. Dialkyl acyl phosphites reacted similarly with mono-, di-, and trichloroacetaldehyde in [4]. The occurrence of these reactions in only one direction to form products with a P—C bond indicated that the reactions of P(III) derivatives with chloral begin with the nucleophilic attack of the P atom on the carbonyl C atom of chloral.

We have recently shown that at −70°C trialkyl phosphites react with chloral to form 2,2,2-trialkoxy-3,5-bis(trichloromethyl)-1,4,2-dioxaphospholanes (E) [5], which are stable at < −40°C:

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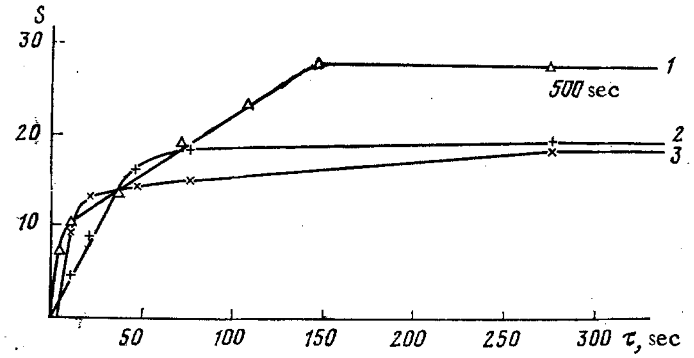
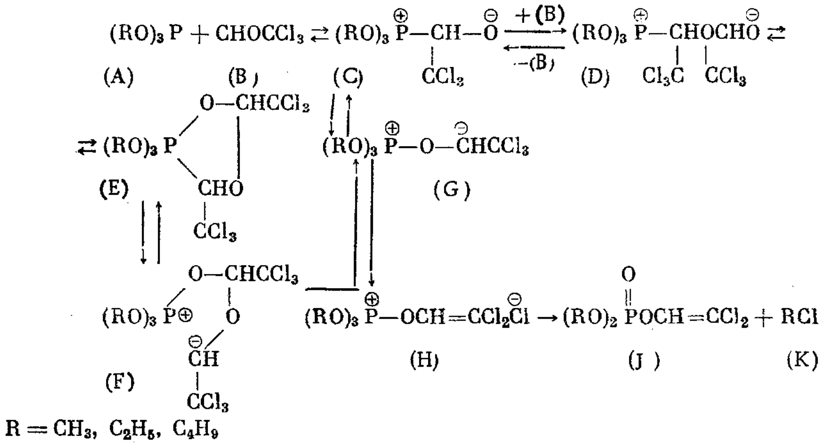
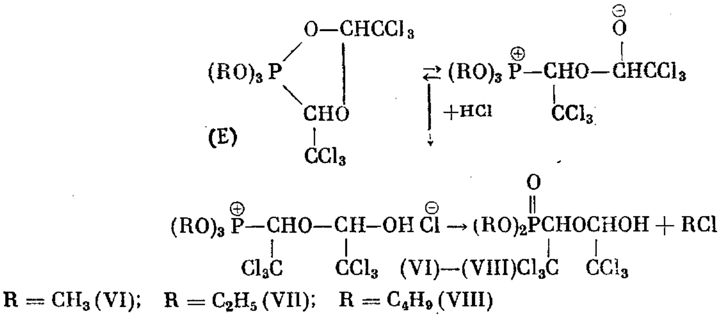


Fig. 1. Kinetic curves of the reaction of triethyl phosphite with chloral in CH_2Cl_2 (1 mole/liter) with the ratios between the reactants: 1) 1:1 (according to $\nu_{C=C}$ of diethyl dichlorovinyl phosphate); 2, 3) 1:2 (according to $\nu_{C=C}$ of diethyl β,β-dichlorovinyl phosphate and $\nu_{C=O}$ of chloral, respectively).



R = CH_3, C_2H_5, C_4H_9

Recalling that the reactions of trialkyl phosphites with carbonyl compounds which have strong electron-acceptor substituents result in the formation of 1,3,2-dioxaphospholanes [6, 7], we investigated the structure of E in greater detail. As a result of the treatment of E at −70°C with dry HCl, we obtained the corresponding dialkyl α-(1-hydroxy-2,2,2-trichloroethoxy)-β,β,β-trichloroethylphosphonates:



R = CH_3 (VI); R = C_2H_5 (VII); R = C_4H_9 (VIII)

The data obtained confirm the 1,4,2-dioxaphospholane structure of E.

Since the pentacovalent product E is thermally unstable, it could be postulated that it forms only at low temperatures as a result of the sequence of reactions A + B → C → D → E. Under ordinary conditions (without cooling) the sequence of reactions is as follows: A + B → C → G → H → J + K.

In order to resolve this question, we studied the kinetics of the reaction of triethyl phosphite (TEP) with chloral by the method of high-speed Raman spectroscopy. The course of the reaction was monitored according to the changes in the intensities of the lines of the

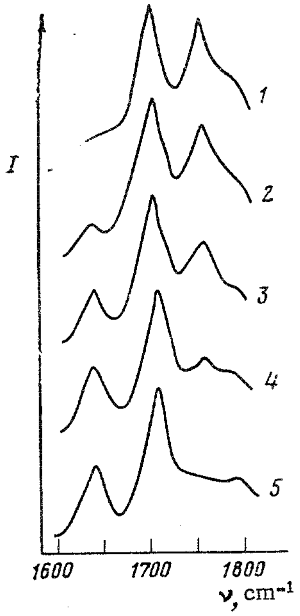


Fig. 2. Raman spectra of the reaction of triethyl phosphite with chloral in the presence of acetone (1:1:3 ratio between the reactants): 1) after 10 sec; 2) 30 sec; 3) 3 min; 4) 47 min; 5) 78 min.

stretching vibrations of the C=O group of chloral and of the C=C bond in the final diethyl β,β-dichlorovinyl phosphate (J). As a result of the reaction of TEP with chloral with a 1:1 ratio between the reactants the chloral was completely consumed during the recording of the first Raman spectrum, since the line of the C=O group at 1760 cm^{-1} was absent. From 5 to 10 sec after the beginning of the reaction, its rate (according to the appearance and increase in the intensity of the line of the corresponding C=C bond of J at 1652 cm^{-1}) slowed. The reaction was completed after 145 sec (Fig. 1 curve 1). When the ratio between the reactants was 1:2, at the time of the recording of the first spectrum the line corresponding to the C=O group of chloral was also absent. The appearance and increase in intensity of the lines of the C=O group of chloral and of the C=C bond in J were next observed. The rate of the reaction after approximately 15-20 sec (according to $\nu_{C=O}$) and 40-60 sec (according to $\nu_{C=C}$) was slowed (curves 2 and 3). The process was not completed even after 300 sec. Thus, the reaction of TEP with chloral with an excess of the latter proceeds significantly more slowly.

The results obtained show that the first step of the reaction of TEP with chloral proceeds rapidly and is not the rate-determining step of the reaction. As a result, the rapid formation of 2,2,2-triethoxy-3,5-bistrichloromethyl-1,4,2-dioxaphospholane and its slow decomposition take place at ∿20°C, as at −70°C [5]. The slowing of the reaction rate with increasing chloral concentrations is apparently due to the displacement of the equilibrium $A + B \rightleftarrows C \rightleftarrows D \rightleftarrows E$ in favor of E. If the reaction had proceeded according to the scheme $A + B \rightleftarrows C \rightleftarrows D \rightleftarrows E \rightarrow F \rightarrow G \rightarrow H \rightarrow J \rightarrow K$, on the other hand, an increase in the concentration of E in the reaction mixture should have resulted in an increase in the rate. Nevertheless, since examples of the cleavage of a phosphorus—carbon bond in analogous cyclic phosphoranes are known [8], the possibility of the occurrence of the reaction along the path E → F → G should not be ruled out.

The reaction of TEP with chloral in the presence of acetone (1:1:3 reactant ratio) proceeds differently. In this case the Raman spectrum showed a gradual decrease in the intensity of the line corresponding to the $\nu_{C=O}$ vibration of chloral, as well as the appearance and increase in intensity of the $\nu_{C=C}$ line of the final vinyl phosphate (Fig. 2). The reaction was completed in 78 min and apparently followed the scheme $A + B \rightarrow C \rightarrow G \rightarrow H \rightarrow J \rightarrow K$.

2,2,2-Triethoxy-3,5-bis(chloromethyl)-1,4,2-dioxaphospholane ($\delta_{^{31}P}$ + 41 ppm), which is formed by the reaction of TEP with chloral in CH_2Cl_2 at ∿20°C, is fairly stable. In the absence of a solvent it readily decomposes to form diethyl vinyl phosphate. The relative thermal stability in comparison to 2,2,2-trialkoxy-3,5-bis(trichloromethyl)-1,4,2-dioxaphospholanes, which are stable in CH_2Cl_2 at temperatures below −40°C [5], is obviously attributable to the nature of the substituents in positions 3 and 5 of the dioxaphospholane ring. In the cases in which these substituents are unsubstituted alkyls, dioxaphospholanes of similar structure can be distilled without decomposition [9]. Thus, it may be assumed that the decomposition of the 1,4,2-dioxaphospholanes with electron-acceptor substituents in positions 3 and 5 is due to the ease of the ionization of the P—O phospholane ring and the ability of the dipolar ion (C), which forms as a result of the equilibrium reaction $E \rightleftarrows D \rightleftarrows C$, to undergo the phosphonate—phosphate rearrangement $C \rightleftarrows G$.

It should be noted that the reaction of TEP with chloroacetone does not result in the formation of a product with a 1,4,2-dioxaphospholane structure like E. The monitoring of the reaction by ^{31}P NMR at ∿20°C in a CH_2Cl_2 solution revealed a gradual decrease in the signal of the original TEP ($\delta_{^{31}P}$ −140 ppm), as well as the appearance and growth of the signal of the final reaction product, viz., diethyl α-methylvinyl phosphate ($\delta_{^{31}P}$ + 10 ppm). At the same time, the signal with $\delta_{^{31}P}$ + 40 ppm, which characterizes the pentavalent compound, was not detected. Because of the spatial hindrances and the weak electrophilic character of the carbonyl carbon of chloroacetone, the reaction apparently follows the path $A + B \rightarrow C \rightarrow G \rightarrow H \rightarrow J + K$, skipping the formation of 2,2,2-triethoxy-3,5-dimethyl-3,5-bis(chloromethyl)-1,4,2-dioxaphospholane.

EXPERIMENTAL

The spectra were recorded over the course of the reaction on a high-speed spectrograph with a premonochromator, which was built at the Institute of Spectroscopy of the Academy of Sciences of the USSR. The time resolution of the system for the recording of the Raman spectra was 0.2 sec. The reaction mixtures were prepared in CH_2Cl_2 solutions (1 mole/liter with respect to triethyl phosphite) and were admitted to cuvettes from the mixing vessel under the pressure of the air at ∿20°C. The supply of a reaction mixture to a cuvette and the recording of the first spectrum took ∿1 sec.

The premonochromator made it possible to isolate the portion of the spectrum needed for the investigation (100 Å) and to weaken by a factor of 10^6 the noise from the scattered parasite laser line. The Raman spectrum generated by the spectrograph was enhanced with respect to the brightness by an electrooptic converter, and then with the aid of a pair of objectives it was projected onto the target of a vidicon and stored on it. The signal from the vidicon was recorded on the screen of a storage oscillograph. The excitation of the Raman spectra was effected by an argon laser ($\lambda = 488$ nm, power equal to 200 MW). When a pulsed laser was used for the excitation of the Raman scattering, a time resolution of 10^{-3} to 10^{-8} sec could be realized on the spectrometer. The change in the concentration of the reactants was determined from the area S under the contour of the respective line in the spectrum.

The ^{31}P NMR spectra were recorded on a YaMR KGU-4 instrument (10.2 MHz) relative to 85% H_3PO_4, and the PMR spectra were recorded on a Varian T-60 instrument relative to TMS.

Diethyl α-Trimethylsiloxy-β,β,β-trichloroethylphosphonate (I). A solution of 22 g of chloral in 30 ml of ether was added at −60°C with stirring to 31.5 g of diethyl trimethylsilyl phosphite in 50 ml of absolute ether, the cooling was removed, and after 12 h the ether was driven off, and the mixture was distilled in an apparatus for film distillation [the unreacted compounds were released at a temperature of 75°C (0.2 mm), and the distillation of I was carried out at 125°C (0.2 mm)]. The yield of I was 49.2 g (92%), d_4^{20} 1.2474, n_D^{20} 1.4610, $\delta_{^{31}P}$ −13 ppm. Found: C 30.34; H 5.78; P 8.74; Si 7.88%. Calculated for $C_9H_{20}Cl_3OPSi$: C 30.23; H 5.59; P 8.66; Si 7.86%.

Diethyl α-Trimethylsiloxy-β-chloroethylphosphonate (II). In a similar manner the reaction of 22.8 g of diethyl trimethylsilyl phosphite with 8.5 g of trichloroacetaldehyde,yielded 18.5 g (59%) of II with bp 75-77°C (0.08 mm), d_4^{20} 1.1018, n_D^{20} 1.4400, $\delta_{^{31}P}$ −18 ppm. Found: C 36.98; H 7.62; Cl 12.63; P 10.43; Si 9.41%. Calculated for $C_9H_{22}ClO_4PSi$: C 37.43; H 7.62; C 12.30; P 10.74; Si 9.73%.

Ethylene Glycol α-(Ethylene glycol)phosphono-β,β,β-trichloroethyl Phosphite (III). A solution of 8.3 g of chloral in 30 ml of ether was added at −30°C with stirring to 11.2 g of diethylene glycol pyrophosphite in 50 ml of absolute ether. The cooling was removed, the mixture was filtered, and the precipitate was washed with absolute ether. This yielded 19.1 g (98%) of III with mp 166-168°C. Found: C 21.14; H 2.75; Cl 30.76; P 17.28%. Calculated for $C_6H_9Cl_3O_6P_2$: C 20.83; H 2.60; Cl 30.82; P 16.76%.

Ethylene Glycol α-Dimethylphosphono-β,β,β-trichloroethyl Phosphite (IV). The reaction of 5.2 g of dimethyl ethylene glycol pyrophosphite with 3.8 g of chloral yielded 5.6 g (62%) of IV with mp 138°C. Found: C 20.70; H 3.25; P 17.36%. Calculated for $C_6H_{11}Cl_3O_6P_2$: C 20.74; H 3.18; P 17.84%.

Ethylene Glycol α-Diethylphosphono-β,β,β-trichloroethyl Phosphite (V). The reaction of 5.8 g of diethyl ethylene glycol pyrophosphite with 3.7 g of chloral yielded 3.6 g (38%) of V with mp 163-165°C. Found: C 28.66; P 16.82%. Calculated for $C_8H_{15}Cl_3O_6P_2$: C 28.34; P 16.82%.

Dimethyl α-(1-Hydroxy-2,2,2-trichloroethoxy)-β,β,β-trichloroethylphosphonate (VI). A solution of 2.42 g of HCl in 15 ml of absolute ether was added to 2,2,2-trimethoxy-3,5-bis-(trichloromethyl)-1,4,2-dioxaphospholane, which was obtained from 19.63 g of chloral in 200 ml of CH_2Cl_2 and 8.25 g of trimethyl phosphite at −80°C. Removal of the solvent yielded 23 g (85.3%) of VI with mp 109-110°C (from ether). Found: C 17.87; H 2.36; P 7.70%. Calculated for $C_6H_9Cl_6O_5P$: C 17.77; H 2.22; P 7.65%. $\delta_{^{31}P}$ −16 ppm.

Diethyl α-(1-Hydroxy-2,2,2-trichloroethoxy)-β,β,β-trichloroethylphosphonate (VII). In a similar manner 15.1 g of chloral, 8.48 g of TEP, and 1.96 g of HCl yielded 14 g (62.70%) of VII with mp 97-98°C. Found: C 22.37; H 3.07; P 7.17%. Calculated for $C_8H_{13}Cl_6O_5P$: C 22.17; H 3.00; P 7.15%. $\delta_{^{31}P}$ −16 ppm.

Dibutyl α-(1-Hydroxy-2,2,2-trichloroethoxy)-β,β,β-trichloroethylphosphonate (VIII). The reaction of 30.2 g of chloral, 25.58 g of tributyl phosphite, and 3.72 g of HCl yielded 30 g (60.1%) of VIII with mp 68-70°C. Found: C 30.15; H 4.35; Cl 43.41; P 6.51%. Calculated for $C_{12}H_{21}Cl_6O_5P$: C 29.44; H 4.29; Cl 43.55; P 6.33%. PMR spectrum (δ, ppm): 5.10 (d, J_{PCH} = 11 Hz), 5.57 (s, OCH), 6.50 (s, OH).

CONCLUSIONS

1. Trialkyl phosphites react with chloral at low temperatures (from −40 to −70°C) in a 1:2 ratio to form 1,4,2-dioxaphospholanes, which are converted under the action of HCl into dialkyl α-(1-hydroxy-2,2,2-trichloroethoxy)-β,β,β-trichloroethylphosphonates.

2. The kinetics of the reaction of triethyl phosphite with chloral have been studied by high-speed Raman spectroscopy, and it has been shown that the formation of 2,2,2-triethoxy-3,5-bis(trichloromethyl)-1,4,2-dioxaphospholane is observed at room temperature and that the latter compound slowly decomposes into diethyl β,β-dichlorovinyl phosphate and ethyl chloride with the accompanying splitting off of chloral.

3. It has been postulated that the reaction of trialkyl phosphites with chloral begins with the attack of the phosphite phosphorus atom on the carbonyl carbon atom of chloral. The first step in the process is rapid and is not the rate-determining step of the reaction.

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