

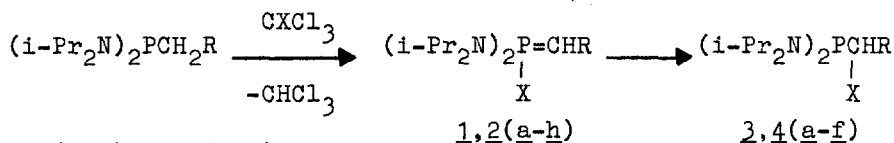
### HALOGENOTROPY IN PHOSPHORUS-CARBON DIAD

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ABSTRACT: Phosphorus-carbon diad halogenotropic transformations of P-halogenoylids 1,2 and  $\alpha$ -halogenoalkylphosphines 3,4 are described. Kinetic studies reveal the monomolecular mechanism of 1a  $\rightarrow$  3a chlorotropic rearrangement.

In previous papers we have described irreversible 1,2(P  $\rightarrow$  C) and 1,2(C  $\rightarrow$  P) halogenotropic rearrangements which attracted considerable attention.<sup>1</sup> These transformations accompanied by the change of the coordination number of the phosphorus atom are very interesting from the theoretical point of view /spontaneous transition from P(IV) to P(III) is unusual for the phosphororganic compounds/. This prompted us to describe here the results of our studies on the kinetics and mechanism of the 1,2(P  $\rightarrow$  C) halogenotropic rearrangement of P-halogenoylids to  $\alpha$ -halogenoalkylphosphines as well as to report our preliminary results concerning the reversible 1,2(P  $\rightleftharpoons$  C) halogenotropy



X = Cl (1,3), Br (2,4)

R = H (a), Me (b), Pr (c), i-Pr (d), Cl (e), Br (f), Ph (g), SiMe<sub>3</sub> (h)

P-Halogenoylids 1,2 were obtained by the reaction of bis(diisopropylamino) alkylphosphines with CXCl<sub>3</sub> (X=Cl, Br) in toluene, diethyl ether or pentane at the temperature below 0°C.<sup>2,3</sup> At 0°C or higher P-halogenoylids 1,2(a-f) readily rearrange to  $\alpha$ -halogenoalkylphosphines 3,4(a-f) isolated in high yields from the reaction mixture and purified by the low-temperature crystallisation from pentane.<sup>4</sup> The P-halogenoylids 1a,2a (R=H) are relatively stable in solution at low temperature and could be detected by use of high-field <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy.<sup>3</sup> The ability to observe ylids 1a,2a directly allowed us to perform the detailed rate studies on their conversion into halogenomethylphosphines 3a,4a.<sup>5</sup> Kinetic analysis of 1a  $\rightarrow$  3a rearrangement has shown that reaction rate strictly obeys the first-order equation at different initial concentrations of ylid 1a (C<sub>0</sub> 0.05-0.5 mol/l) and at various temperatures (Figure 1). For 1a  $\rightarrow$  3a rearrangement in Et<sub>2</sub>O-CHCl<sub>3</sub> (95:5) the values of the rate constant K<sub>I</sub> · 10<sup>-4</sup>, s<sup>-1</sup> = 2.2 (0°C), 3.7 (10°), 4.6 (15°), 7.3 (20°), 12.1 (25°)

were determined. From the temperature dependence of  $K_I$  the activation parameters  $E_a$   $11.4 \pm 1$  kcal/mol and  $\Delta S^\ddagger$   $-27.5 \pm 3$  e.u. ( $+20^\circ\text{C}$ ) were calculated. It should be noted that the variations of the initial concentration  $C_0$  does not affect the rate constant  $K_I$ . However, the rate constant  $K_I$  depends strongly on the solvent polarity. Thus, the rearrangement rate increases very much with increasing the solvent polarity in the sequence:  $\text{C}_5\text{H}_{12} < \text{Et}_2\text{O} < \text{C}_6\text{H}_6 < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CH}_3\text{CN}$ . As shown in figure 2, the rate constant  $K_I$  almost linearly increases when the chloroform content in  $\text{Et}_2\text{O}-\text{CHCl}_3$  and, consequently, the polarity of the medium rise

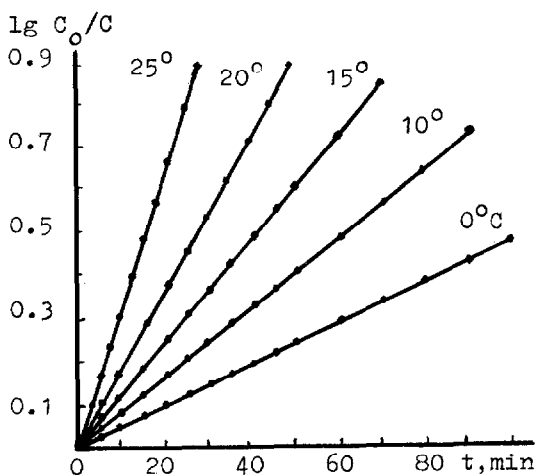


Figure 1. Semilogarithmic plots for  $1a \rightarrow 3a$  rearrangement at different temperatures

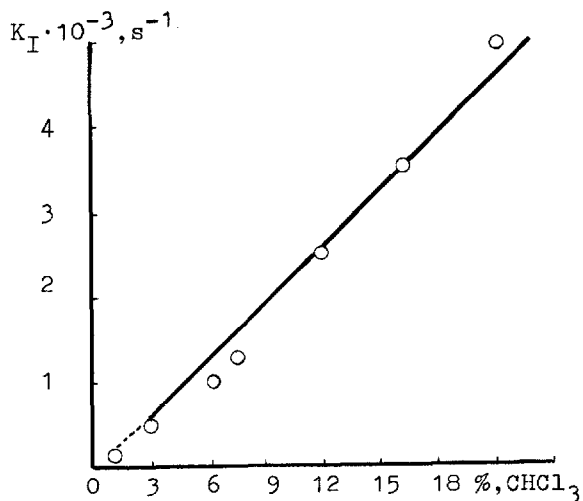
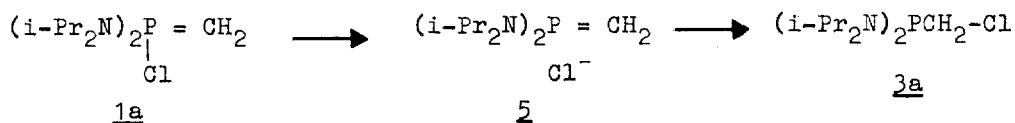


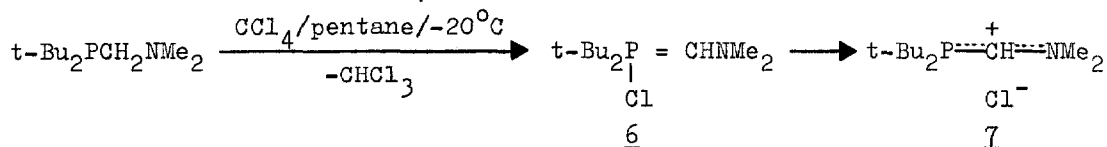
Figure 2. Dependence of the I-st order rate constant  $K_I$  of  $1a \rightarrow 3a$  rearrangement on the chloroform content in  $\text{Et}_2\text{O}-\text{CHCl}_3$  solvent

These results allow us to conclude that the chlorotropic rearrangement proceeds via the monomolecular mechanism. The dissociation of P-chloroylid with the P-Cl bond cleavage gives a mesomeric phosphinium cation  $\underline{5}$  which transforms into the chloromethylphosphine  $\underline{3a}$  as a result of a nucleophilic attack of chlorid-ion on the electronically deficient carbon atom. The stabilisation of the cation  $\underline{5}$  resulting from the positive charge delocalisation in four-centered system  $\begin{matrix} & \text{N} & \\ & \diagdown & \\ & \text{P} & \\ & \diagup & \\ & \text{N} & \end{matrix} \text{---} \text{C} <$  is apparently sufficient to ensure its formation during the P-Cl bond cleavage.<sup>6</sup> The latter process is promoted by increasing of dissociating power of the solvent ( $\text{CH}_3\text{CN} > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{C}_6\text{H}_6 > \text{C}_5\text{H}_{12}$ )

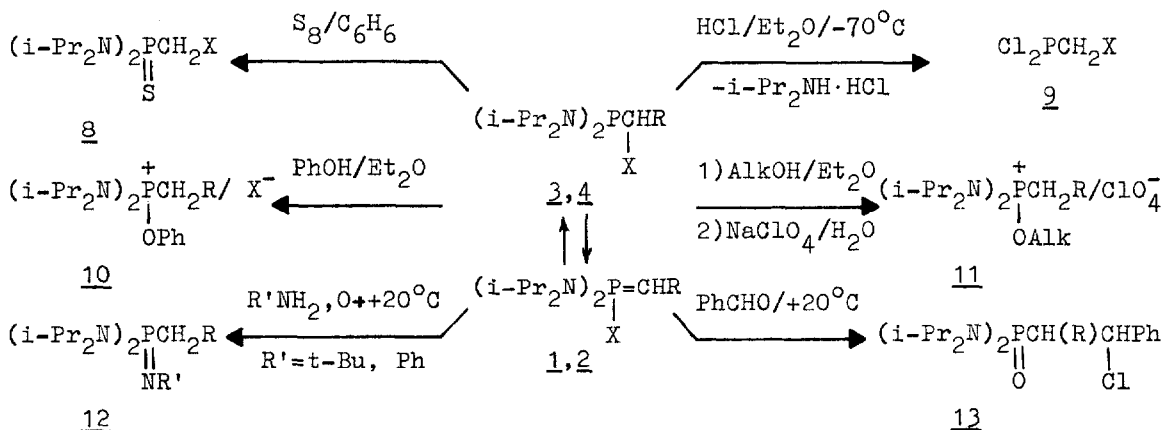


The transformation of P-chloroylid  $\underline{6}$  containing a dimethylamino group at the  $\alpha$ -carbon atom into a stable salt-like compound  $\underline{7}$  (m.p.  $151^\circ\text{C}$ ) can be regarded as an additional evidence for the proposed mechanism. The stabilization of the phosphinium cation  $\underline{7}$  is achieved by the effective delocalization of the

positive charge in the  $\text{>P}^{\oplus}\text{---C}^{\ominus}\text{---N}$  triad <sup>7</sup>



NMR and chemical study of the compounds 1,2 have shown that the rearrangement  $1 \rightleftharpoons 2$  is reversible and its direction depends on the nature of substituents R at the  $\alpha$ -carbon atom. The equilibrium is strongly shifted toward the chlorotropic form with tervalent phosphorus atom in the case of compounds 3a-d containing electron-donating group (R = H, Me, Pr, i-Pr). <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra of these compounds reveal only signals related to the phosphine form. On the other hand, the equilibrium  $1 \rightleftharpoons 2$  shifts towards the ylid form if the substituents at the  $\alpha$ -carbon atom are electron-withdrawing (compounds 1g,h, R = Ph, SiMe<sub>3</sub>). Compounds 3e (R = Cl) existing in non-polar solvents (ether, hexane, benzene) only in the phosphine form (<sup>1</sup>H, <sup>13</sup>C NMR; <sup>31</sup>P NMR spectra shows a single signal at +56 ppm) in chloroform appears in two forms 1e and 3e (signals at  $\delta_{\text{P}}$  +60 and +56 ppm in a 1:4 ratio). In chlorobenzene at +20°C this compound exists mainly in the phosphine form but at temperature higher than +60°C the phosphine form partially rearranges into the ylid form to give the equilibrium mixture of two chlorotropic forms 1e and 3e ( $\delta_{\text{P}}$  +60 and +56 ppm).  $\alpha$ -Halogenoalkylphosphines 3,4(a-f) undergo reactions typical both for tervalent phosphorus compounds and P-halogenoylids. Being tervalent phosphorus compounds, the  $\alpha$ -halogenoalkylphosphines 3,4 add sulfur and react with anhydrous HCl with the P-N bond cleavage. Like the P-halogenoylids, they add alcohols and phenols forming the phosphonium salts 10,11, react with primary amines and aniline to afford the iminophosphonates 12. They also form the 2-chloroalkylphosphonates 13 on interaction with aldehydes <sup>8</sup>



Apparently, the products 10-13 are formed via the reactions of alcohols, phenols, amines and benzaldehyde with the ylid halogenotropic forms 1,2 which exist in the tautomeric equilibrium with the phosphine forms 3,4.

Compounds 8-13 were obtained in good yields, isolated, and investigated by spectroscopic methods (IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR).<sup>9</sup>

## NOTES AND REFERENCES

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  - 1a: Yield 98%. NMR ( $\delta$ , ppm, J, Hz,  $\text{C}_6\text{D}_5\text{CD}_3$ ,  $-20^\circ\text{C}$ ):  $\delta_{\text{C}}$  23.13 d, J(CP) 41 (CCN); 33.29 d, J(CP) 145.6 (P=C); 47.82 d, J(CP) 4.5 (CN).  $\delta_{\text{P}}$  +61.

1g: Yield 90%. NMR ( $\delta$ , ppm, J, Hz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}}$  22.62 d, J(CP) 24.4 (CCN); 47.46 d, J(CP) 5 (CN); 49.01 d, J(CP) 192 (P=C); 117.65; 122.41 d, J(CP) 19.5; 126.7 d, J(CP) 24; 142.2 d, J(CP) 5 ( $\text{C}_6\text{H}_5$ ).  $\delta_{\text{P}}$  +54.08.

2a: Yield 90%.  $^{31}\text{P}$  NMR (ether,  $-30^\circ\text{C}$ ):  $\delta_{\text{P}}$  +58.4 ppm.
  - 3a: Yield 80%, m.p.  $31^\circ\text{C}$ . NMR ( $\delta$ , ppm, J, Hz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  0.98 d, J(HH) 6.6; 1.02 d, J(HH) 6.6 ( $\text{CH}_3\text{C}$ ); 3.06 m (CHN); 3.40 d, J(HP) 9.96 ( $\text{PCH}_2$ ).  $\delta_{\text{C}}$  24.17 d, J(CP) 6; 24.55 d, J(CP) 6 (CCN); 39.95 d, J(CP) 19 (PC); 47.02 d, J(CP) 11.8 (CN).  $\delta_{\text{P}}$  +46.3.

4a: Yield 60%, m.p.  $56-58^\circ\text{C}$ . NMR ( $\delta$ , ppm, J, Hz,  $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  0.98 d, J(HH) 8; 0.99 d, J(HH) 8 ( $\text{CH}_3\text{C}$ ); 3.01 m (CHN); 3.22 d, J(HP) 9.7 ( $\text{CH}_2\text{Br}$ ).  $\delta_{\text{C}}$  22.04 d, J(CP) 7; 22.44 d, J(CP) 8 (CCN); 26.52 d, J(CP) 27.6 (PCBr); 44.83 d, J(CP) 11.8 (CN).  $\delta_{\text{P}}$  +48.2.

Compound, yield, m.p.: 3b, 70%,  $52-54^\circ\text{C}$ ; 3c, 70%,  $45-47^\circ$ ; 3d, 75%,  $83^\circ$ ; 3e, 75%,  $57-59^\circ$ ; 4b, 45%,  $60-61^\circ$ ; 4f, 45%,  $94-95.5^\circ$ .

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR spectra of compounds 3,4(b-f) are described in:

      - Kolodiazhnyi O.I., Golokhov D.B.- Zh. Obshch. Khim., in press.
      - Kolodiazhnyi O.I., Golokhov D.B., Ustenko S.N.- Zh. Obshch. Khim., in press.
  - The kinetic measurements were performed by means of the  $^{31}\text{P}$  NMR method in thermostatic tubes. Changes in the intensity of signals at  $\delta_{\text{P}}$  +61 ppm (1a) and  $\delta_{\text{P}}$  +46 ppm (3a) were observed. NMR spectral measurements were obtained with a Bruker WP-200 (200 MHz) nuclear magnetic resonance spectrometer.
  - Kolodiazhnyi O.I.- Zh. Obshch. Khim., in press.
  - Kolodiazhnyi O.I., Kalibabtschuk N.N.- Zh. Obshch. Khim., 1985, 55, 2782.
  - Kolodiazhnyi O.I.- Tetrahedron Lett., 1981, 22, 1231.
  - Compound (substituents), yield, m.p., b.p. (mmHg): 8 (X=Cl), 85%,  $64^\circ\text{C}$ , -; 8 (X=Br), 90%,  $56.5^\circ$ , -; 9 (X=Cl),  $50^\circ$ , -,  $130^\circ$  (760); 10 (R=H, X=Br), 90%,  $174^\circ$ , -; 11 (R=H, Alk=Me), 85%,  $215^\circ$ , -; 11 (R=Alk=Me), 75%,  $210^\circ$ , -; 12 (R=H, R'=t-Bu), 50%, -,  $100^\circ$  (0.05); 12 (R=H, R'=Ph), 88%, -,  $145^\circ$  (0.05); 13 (R=H), 75%,  $88.5^\circ$ , -; 13 (R=Me), 60%,  $111^\circ$ , -.
- NMR spectra of compounds 8-13 are described in 4b,c.

10. All new compounds gave satisfactory analytical and spectral data.