# ISOMERIZATION OF 1-OXO-1-CHLOROPHOSPHOLENES IN THE PRESENCE OF PHOSPHORUS TRICHLORIDE

B. A. Arbuzov, A. O. Vizel',
R. S. Giniyatullin, and L. I. Shchukina

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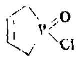
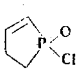
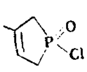
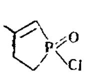
The isomerizing action of phosphorus trichloride on phospholene derivatives was observed. It was shown that mixtures of isomers, with predominance of 2-phospholene, are formed when isomerically pure 1-oxo-1-chlorophospholenes are heated in the presence of phosphorus trichloride.

In [1, 2] it was noted that mixtures of isomers that differ with respect to the position of the ring double bond are formed in the synthesis of phospholene derivatives when phosphorus trichloride is used as one of the starting reagents. The reaction of dienes with alkyl dichlorophosphites leads to 3-phospholene [3, 4]. The introduction of phosphorus trichloride into the reaction mixture induces the formation of a mixture

TABLE 1. Results of Experiments on the Catalytic Isomerization of 1-Oxo-1-chlorophospholenes

| Expt. | Starting compounds: structure | $d_4^{20}$ | $n_D^{20}$ | No. of moles of $PCl_3$ per mole of phospholene | Reaction product: yield, % | bp, °C (mm) | $d_4^{20}$ | $n_D^{20}$ | Cl, %* | percentage of the isomerization product, % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 |  | mp 53—54° | 1,5200 | 1 | 52,5 | 70—74 (0,04) | 1,3323 | 1,5238 | 26,3<br>26,0 | 76 |
| 2 | | | | 0 | 80 | 60—62 (0,02) | mp 53° | 1,5200 | 26,3<br>26,0 | 7 |
| 3 |  | 1,3304 | 1,5245 | 1 | 45 | 70—75 (0,02) | 1,3322 | 1,5230 | 26,0<br>26,0 | 24 |
| 4 | | | | 0 | 79 | 80—85 (0,02) | 1,3310 | 1,5247 | 26,4<br>26,0 | 5 |
| 5 |  | 1,2538 | 1,5122 | 1 | 70 | 80—85 (0,02) | 1,2603 | 1,5218 | 23,6<br>23,5 | 85 |
| 6 | | | | 0 | 80 | 75—76 (0,04) | 1,2564 | 1,5123 | 23,7<br>23,5 | 4 |
| 7 |  | 1,2618 | 1,5235 | 1 | 51 | 80—82 (0,02) | 1,2592 | 1,5223 | 23,6<br>23,5 | 11 |
| 8 | | | | 0 | 73 | 93—95 (0,07) | 1,2590 | 1,5222 | 23,5<br>23,5 | 12 |

*The upper numbers are the experimentally found values, while the lower numbers are the calculated values.

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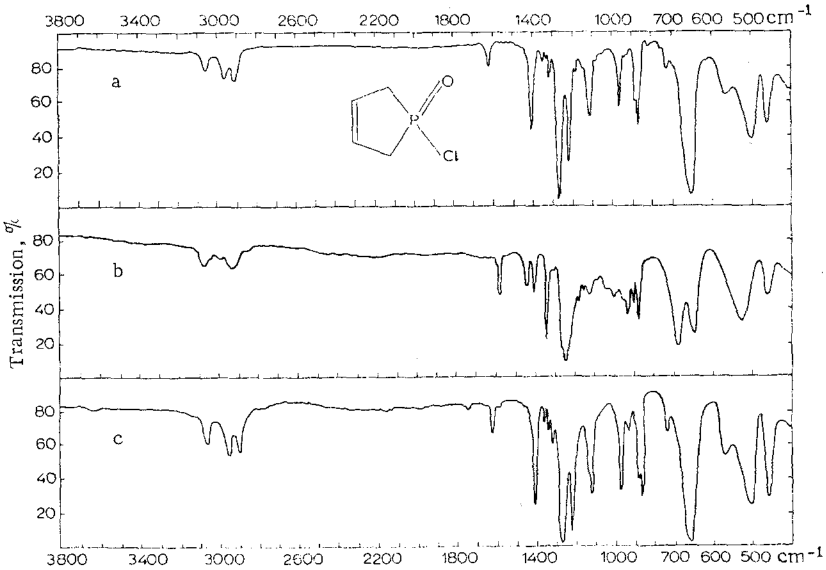

Fig. 1. IR spectra for experiments 1 and 2: a) Starting 1-oxo-1-chloro-3-phospholene; b) product of thermal treatment in the presence of phosphorus trichloride (experiment 1); c) product of thermal treatment (experiment 2).

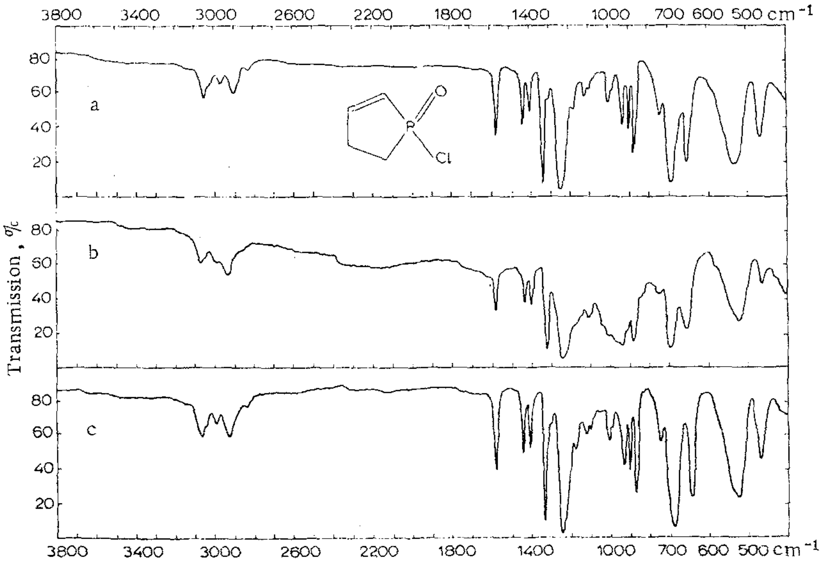

Fig. 2. IR spectra for experiments 3 and 4: a) Starting 1-oxo-1-chloro-2-phospholene; b) product of thermal treatment in the presence of phosphorus trichloride (experiment 3); c) product of thermal treatment (experiment 4).

of 2- and 3-phospholenes [4]. It is known that some phospholene derivatives undergo prototropic isomerization under the influence of bases [1, 5] and acids [5]. The concept of the isomerizing action of phosphorus trichloride on the phospholene derivatives formed during the reactions has not previously been expressed, and this possibility has not been experimentally investigated.

We have studied the effect of phosphorus trichloride on two pairs of isomers of 1-oxo-1-chlorophospholenes. The experimental results (Table 1 and Figs. 1-4) demonstrate that heating the phospholenes to 130-160°C in the presence of phosphorus trichloride brings about migration of the double bond. The degree of conversion of 3-phospholenes to 2-phospholene derivatives is high. The reverse process takes place with greater difficulty. The thermal isomerization noted at and above 200° [1, 5] proceeds only to a small degree under the conditions that we used. It is interesting to note that 1-oxo-1-chloro-4-methyl-2-phospholene cannot be detected after isomerizing action on 3-methyl derivatives. Evidence for this is the ab-

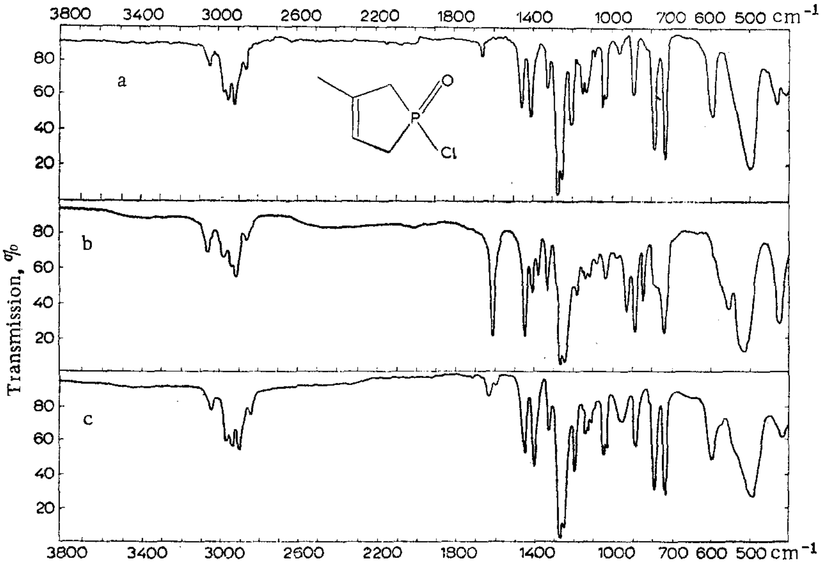

Fig. 3. IR spectra for experiments 5 and 6: a) Starting 1-oxo-1-chloro-3-methyl-3-phospholene; b) product of thermal treatment in the presence of phosphorus trichloride (experiment 5); c) product of thermal treatment (experiment 6).

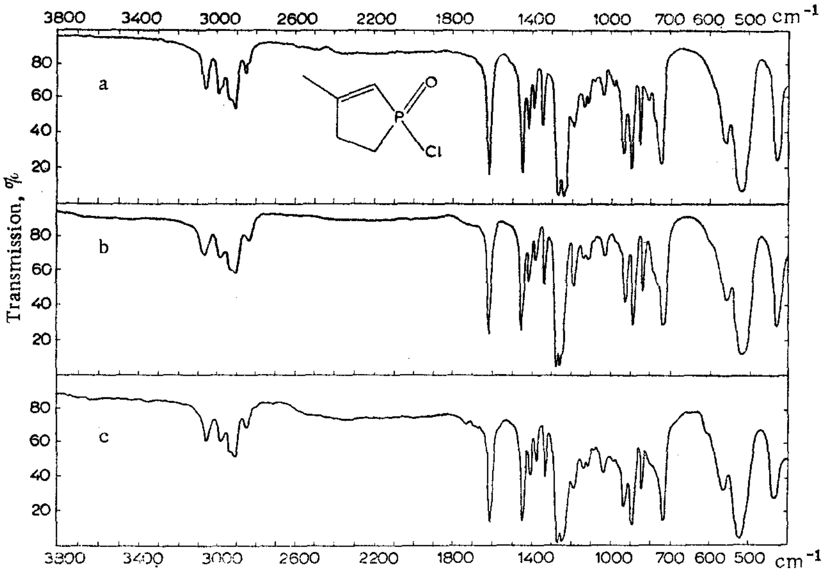

Fig. 4. IR spectra for experiments 7 and 8: a) Starting 1-oxo-1-chloro-3-methyl-2-phospholene; b) product of thermal treatment in the presence of phosphorus trichloride (experiment 7); c) product of thermal treatment (experiment 8).

sence of absorption bands at 1580-1590 cm$^{-1}$ in the IR spectra (Figs. 3 and 4). The possibility of the formation of 4-methyl-2-phospholene and a number of other reaction products of isoprene with phosphorus trichloride was discussed in [6]. However, the indicated phospholene was not detected by NMR spectroscopy in that investigation either.

In working with the phosphorus acid chlorides it is difficult to avoid contact of the reaction products with hydrogen chloride. It has been reported [5] that hydrochloric acid does not cause isomerization of 1-oxo-1-methyl-3-phospholene. Our experiments have shown that dry hydrogen chloride at elevated temperatures and pressures does not cause shifting of the double bond of 1-oxo-1-chloro-3-phospholene.

The above results make it possible to assert that the formation of mixtures of isomers can occur by isomerization of the final or intermediate products in the syntheses of phospholene derivatives using phosphorus trichloride. The isomerizing agent may be phosphorus trichloride itself.

## EXPERIMENTAL

The starting 1-oxo-1-chloro-2-phospholene and 1-oxo-1-chloro-3-phospholene [7], as well as 1-oxo-1-chloro-3-methyl-2-phospholene and 1-oxo-1-chloro-3-methyl-3-phospholene [8], were obtained and purified by known methods.

Catalytic and Thermal Isomerization. Ten-gram samples of the pure isomers (experiments 2, 4, 6, and 8) and mixtures of 20 g of the pure isomers with equimolar amounts of phosphorus trichloride (experiments 1, 3, 5, and 7) were sealed in glass tubes. The tubes containing 1-oxo-1-chlorophospholenes (experiments 1-4) were heated at 130° for 5.5 h. The tubes with 1-oxo-1-chloro-3-methylphospholenes (experiments 5-8) were heated at 160° for 4 h. The products were distilled twice, and the isomeric composition of the products was determined by the method in [7] for the unsubstituted phospholenes (experiments 1-4) and by the method in [8] for the 3-methyl derivatives (experiments 5-8).

Experiment with Hydrogen Chloride. 1-Oxo-1-chloro-3-phospholene was dissolved in an equal volume of dry liquid hydrogen chloride, and the mixture was allowed to stand in a sealed tube at 20° for 18 h. The tube was opened, the undissolved gaseous hydrogen chloride was set free, and the tube was again sealed and held at 100° for 6 h. Fractional distillation gave a preparation with bp 68-70° (0.05 mm), mp 53°, $d_4^{20}$ 1.3344, and $n_D^{20}$ 1.5208. Found: C 35.2; H 4.4; Cl 26.0; P 22.6%; $MR_D$ 31.1. $C_4H_6ClOP$. Calculated: C 35.2; H 4.4; Cl 26.0; P 22.7%; $MR_D$ 31.3.

All of the IR spectra were recorded with a UR-10 spectrometer (droplets between KBr plates). The authors thank L. Kh. Ashrafullin and S. A. Samartsev for recording the spectra.

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