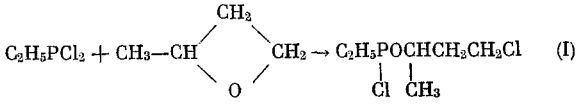
REACTION OF ETHYLDICHLOROPHOSPHINE WITH 2-METHYLOXETANE

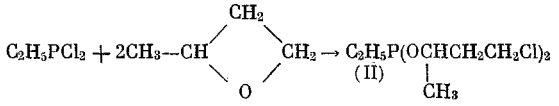
O. N. Nuretdinova, L. Z. Nikonova, and B. A. Arbuzov

UDC 542.91:547.1'118

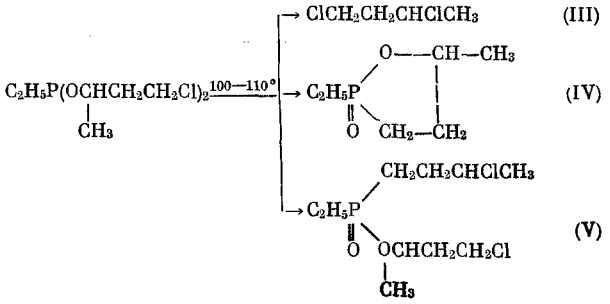
While the reaction of ethyldichlorophosphine with oxiranes was studied in [1, 2], the analogous reaction with oxetanes was unknown. It turned out that while trivalent phosphorus derivatives with both one and two β-chloroethyl groups can be readily isolated from the reaction with ethylene oxide [1], we were able to isolate only O-(1-methyl-3-chloropropyl)ethylchlorophosphonite (I) from the reaction with 2-methyloxetane by distillation



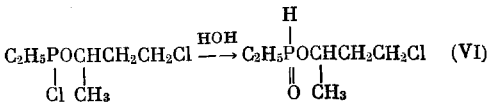
Moreover, if equimolar amounts of the reagents are used in the reaction, the yield of (I) is 30-40%. In this case, in addition to (I) another series of substances which boil above and below (I) is obtained. The yield of (I) increases considerably with excess ethyldichlorophosphine. The reaction of 2 mole of 2-methyloxetane with 1 mole of ethyldichlorophosphine yields O,O-bis(1-methyl-3-chloropropyl)ethylphosphonite (II)



When (II) was distilled in vacuo (0.1 mm) it began to boil violently with the liberation of low-boiling products. We therefore heated (II) at 100-110° for 20-30 min and then distilled it. The following products were isolated by distillation:

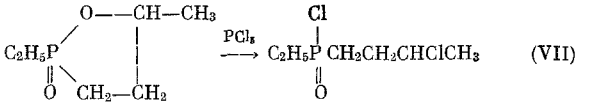


whereas (III) and (V) are pure compounds according to elemental analysis, (IV) is contaminated with O-(1-methyl-3-chloropropyl)ethylphosphonite (VI) (ν_{P-H} 2350-2370 cm^{-1}). The appearance of (VI) in the reaction mixture is possible as a result of two reactions: 1) partial hydrolysis of (I) and 2) reaction of HCl with (II). We obtained phosphonite (VI) by controlled hydrolysis of (I):



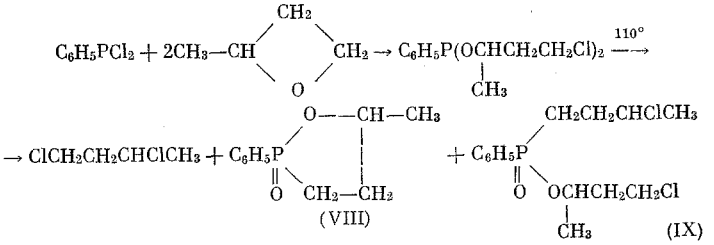
A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 548-550, March, 1972. Original article submitted February 19, 1971.

Treatment of (IV) containing (VI), which were isolated from the reaction of ethyldichlorophosphine with 2-methyloxetane, with PCl_5 gave 50% of 3-chlorobutylethylphosphinyl chloride (VII). This indicates that phostone (IV) is the chief product in this mixture



A great deal of undistilled brown residue remains in the flask after distillation of (VII). Dichlorobutane is obtained in insignificant quantities in this reaction [due to contamination by (VI)]. Pure (IV) ($\sigma_{P^{31}}$ – 70 ppm) is obtained by heating (IV) containing (VI) with sodium metal in toluene. Compounds similar to (IV) were previously obtained in [3]. Workup of (V) yields (VII) (70%), $POCl_3$, and dichlorobutane. Little residue is obtained in the distillation flask. It turns out that the reason that a large amount of residue is obtained in the reaction of PCl_5 with (IV) is the energetic reaction of (IV) with the $POCl_3$ that forms. In the process, compounds which do not yield to distillation are obtained. (IV) is obtained in 40% yield when (V) is heated at 200-215° for 40 min.

1,3-Dichlorobutane and a mixture of phostone (VIII) and (IX) are formed as a result of the reaction of phenyldichlorophosphine with 2 mole of 2-methyloxetane and heating of the reaction mixture without preliminary distillation. Since the boiling points of (VIII) and (IX) are close, distillation yields only a mixture of them in which (VIII) predominates (Cl 6.42%)



EXPERIMENTAL METHOD

The reaction of ethyldichlorophosphine with 2-methyloxetane was carried out according to the method described in [4] (under an inert gas). A reagent ratio of 1:1 or excess ethyldichlorophosphine yielded 30-60% of O-(1-methyl-3-chloropropyl)ethylchlorophosphonite (I) with bp 90° (10 mm); d_4^{20} 1.1404, n_D^{20} 1.4779. Found: C 35.42; H 6.37; Cl 34.94; P 15.64%. $C_6H_{13}Cl_2OP$. Calculated: C 35.46; H 6.40; Cl 34.97; P 15.27%. (II) was not isolated by the reaction of ethyldichlorophosphine with 2 mole of 2-methyloxetane but was heated at 100-110° for 30 min and then distilled. A mixture of 9.5 g of ethyldichlorophosphine and 10.5 g of 2-methyloxetane yielded: 1) ~4 g of 1,3-dichlorobutane with bp 33-34° (13 mm); d_4^{20} 1.1158, n_D^{20} 1.4423. Found: C 37.83; H 6.34; Cl 55.54%. $C_4H_8C_{12}$. Calculated: C 37.80; H 6.30; Cl 55.90%. 2) 6.5 g of phostone (IV) containing phosphonite (VI) with bp 70° (0.1 mm); d_4^{20} 1.1002, n_D^{20} 1.4638. Found: C 45.98; H 8.56; P 19.34%. $C_6H_{13}\cdot O_2P$. Calculated: C 48.64; H 8.78; P 20.94%. 3) 5 g of (V) with bp 109-110° (0.1 mm); d_4^{20} 1.1464, n_D^{20} 1.4745. Found: C 43.65; H 7.54; Cl 25.38; P 11.35%. $C_{10}H_{21}PCl_2O_2$. Calculated: C 43.63; H 7.63; Cl 25.81; P 11.27% ($\delta_{P^{31}}$ – 56 ppm). When 6 g of (IV) containing (VI) was refluxed with 0.15 g of Na in toluene for 3 h, 3 g of pure (IV) with bp 72-73° (0.2 mm); d_4^{20} 1.0905, n_D^{20} 1.4656 was obtained. Found: C 48.55; H 8.70; P 21.06%. $C_6H_{13}O_2P$. Calculated: C 48.64; H 8.78; P 20.94% ($\delta_{P^{31}}$ – 70 ppm).

Reaction of (IV) with PCl_5. A total of 12.4 g of (IV) (not freed from Na) was added to 17.5 g of powdered PCl_5 in 50 ml of ether. The temperature was held at no higher than 30°. After the PCl_5 disappeared, the mixture was held at room temperature for ~1 h and then distilled to give 8.7 g (51%) of 3-chlorobutylethylphosphinyl chloride (VII) with bp 86-87° (0.15 mm); d_4^{20} 1.2051; n_D^{20} 1.4861. Found: C 35.50; H 6.45; Cl 34.55; P 15.44%. $C_6H_{13}Cl_2OP$. Calculated: C 35.46; H 6.40; Cl 34.97; P 15.27%. The first fraction was $POCl_3$ with bp 107-109°, and a large amount of residue remained in the distillation flask.

Reaction of (V) with PCl_5. Similarly, 11 g of (V) yielded 5.6 g of (VII) with bp 91-92° (0.15 mm); d_4^{20} 1.2051; n_D^{20} 1.4864. Found: P 15.44%. $C_6H_{13}Cl_2OP$. Calculated: P 15.27%. The first fraction contained a mixture of dichlorobutane and $POCl_3$. The dichlorobutane was isolated by washing this mixture with water and extraction with ether.

Reaction of (IV) with $POCl_3$. The addition of 3 g of (IV) to 33 g of $POCl_3$ in ether raised the temperature to the boiling point of ether. The resulting substances could not be distilled [only 0.3 g of a substance with bp 91° (0.2 mm); d_4^{20} 1.2128, n_D^{20} 1.4800 was isolated. Found: Cl 29.73; P 17.52%].

Hydrolysis of O-(1-Methyl-3-chloropropyl)ethylchlorophosphonite (I). Water (0.72 g) was added with stirring to 8.2 g of (I) in 50 ml of $CHCl_3$. The mixture was refluxed for 1 h and distilled to give 4.9 g (65%) of (VI) with bp 79-81° (0.2 mm); d_4^{20} 1.1256, n_D^{20} 1.4561. Found: Cl 19.01; P 16.51%. $C_6H_{14}ClO_2P$. Calculated: Cl 19.24; P 16.80%.

CONCLUSIONS

The reaction of ethyldichlorophosphine with 2-methyloxetane was studied.

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