SUMMARY

Ferrocenyl boric and 1,1'-ferrocenylene diboric acids react with copper phthalimide with formation of N-ferrocenylphthalimide. In an analogous way N-styryl-, N-phenyl-, and N-p-methoxyphenylphthalimides were obtained from styryl, phenyl, and p-anisyl boric acids.

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THE REACTION OF 2,3-DIMETHYLBUTADIENE WITH ETHYLENE- AND PROPYLENE CHLOROPHOSPHITES

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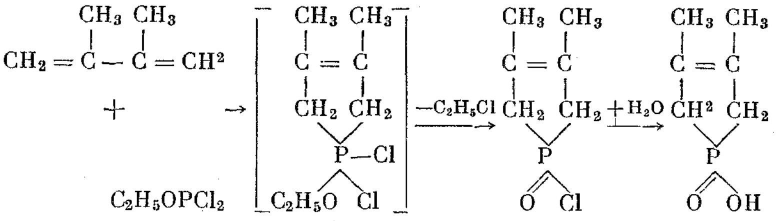
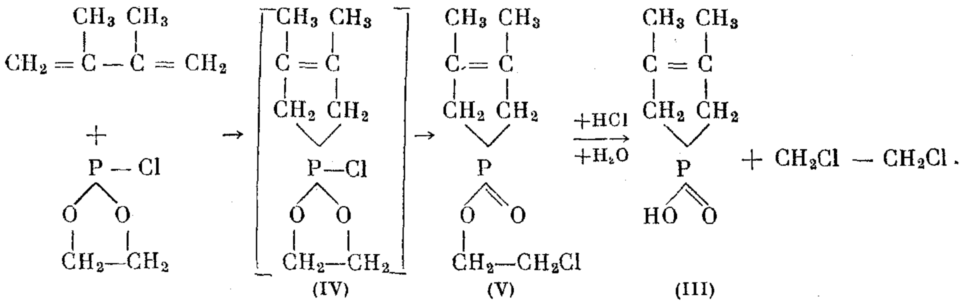
Recently Petrov and Razumova [1] published a preliminary report on the reaction of propylene chlorophosphite with butadiene and other dienes in the presence of zinc chloride. The authors drew the conclusion of the addition of the chlorophosphite to the diene in the 1,2-position on the basis of the infrared spectrum of the addition product and the absence of a reaction for chlorine bound to the primary carbon. We have shown [2] that ethoxydichlorophosphine adds to dienes (2, 3-dimethylbutadiene) in the presence of copper stearate with formation of a ring compound (I). On distillation, the latter splits out ethyl chloride and gives the acid chloride (II) which on saponification passes into the acid (III) with m.p. 121-123°.



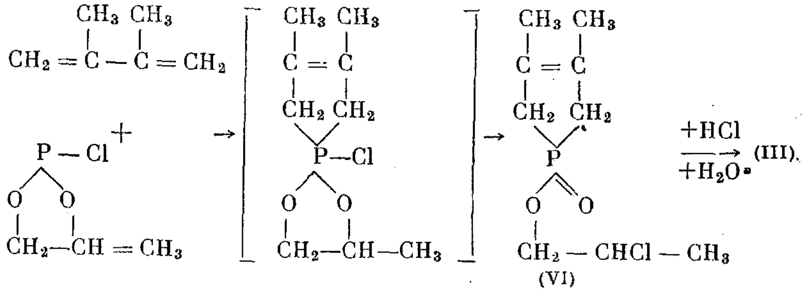
(I) (II) (III)

It would seem very probable that ring chlorophosphites would react with dienes by the same type of reaction, and the products obtained by Petrov and Razumova would have a ring structure.

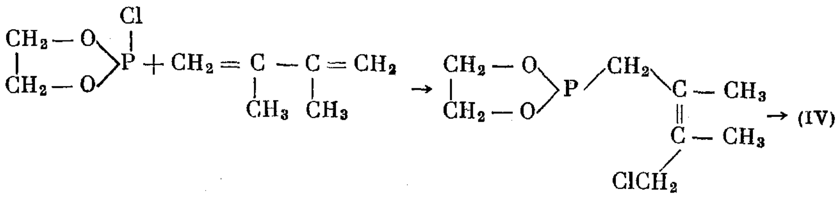
Our experiments have confirmed this suggestion. By heating 2,3-dimethylbutadiene with ethylene chlorophosphite to 100-110° in the presence of zinc chloride we have obtained an addition product with b.p. 120-121° (1 mm); n_D^{20} 1.5020; d_4^{20} 1.2021; found: MR 51.19; for $C_8H_{14}O_2PCl$, calculated: MR 51.12, which does not react with cuprous chloride and appears to be a derivative of pentavalent phosphorus. When it is saponified with hydrochloric acid it gives acid (III) with m.p. 119-121° (mixed sample shows no change in m.p.). The reaction between ethylenechlorophosphite and 2,3-dimethylbutadiene follows the scheme



The intermediate product (IV) passes into (V) with ring closure. In the case of propylene chlorophosphite and 2,3-dimethylbutadiene under analogous conditions we obtained the addition product (VI) with b.p. 135-136° (3.5 mm), n_D^{20} 1.4960; d_4^{20} 1.1598; found: MR 56.03; for $C_9H_{16}O_2PCl$ |= calculated: MR 55.74. When this was saponified with hydrochloric acid it gave acid (III) with m.p. 119-121°. The reaction could be expressed by the following scheme



The formation of the ring compounds in the reaction of compounds with trivalent phosphorus and dienes can be represented either by direct addition of the diene in position 1,4 to the trivalent phosphorus, or by addition of a derivative with trivalent phosphorus to the diene in the 1,4-position followed by addition of allyl chloride to the trivalent phosphorus with formation of an intermediate product of type (IV)



We will study the mechanism of this reaction.

EXPERIMENTAL

Reaction of ethylene chlorophosphite [3] with 2,3-dimethyl-1,3-butadiene. In a thick-walled, tightly closed vessel we placed 85 g of ethylene chlorophosphite [b.p. 53-54° (22 mm), n_D^{20} 1.4900]; 100 ml of dimethylbutadiene, 1.4 g of freshly fused zinc chloride, and 0.05 g of hydroquinone. The vessel was kept for 20 hours at 100° and then opened. The oily, little mobile liquid was distilled in a vacuum. After two successive distillations we isolated a fraction with the following constants: b.p. 120-121° (1 mm), n_D^{20} 1.5020; d_4^{20} 1.2021; found: MR 51.19; for $C_8H_{14}O_2PCl$; calculated: MR 51.12; yield of product 77.6 g or 54.5%, calculated on the ethylene chlorophosphite. Found: C 42.66; H 7.14; Cl 16.99; P 14.92%. $C_8H_{14}O_2PCl$. Calculated: C 46.05; H 6.76; Cl 16.99; P 14.84%. The product did not react with cuprous chloride; was stable in air, it was 3,4-dimethyl-(1-β-chloroethoxy)-3-phospholine-1-oxide (V).

Saponification of 3,4-dimethyl-(β-chloroethoxy)-3-phospholine-1-oxide. Four g of this oxide and 12 ml of 20% hydrochloric acid were heated in a sealed tube at 120-130° for 12 hours. Then the contents of the tube were removed to a porcelain dish, strongly diluted with water, and evaporated on a water bath to full removal of hydrogen chloride. The residue was made alkaline with 30% sodium hydroxide solution; the alkaline solution was extracted with ether to remove neutral substances. The aqueous alkali solution was again made acid (Congo) and evaporated dry. The organic acid was removed from the dry residue with absolute alcohol. The alcohol was evaporated and the acid was recrystallized from water in the presence of activated charcoal. The resulting acid (III), 1.8 g or 64% of the theory, had m.p. 119-121°. A mixed sample with acid (III) obtained previously [2] gave no melting point depression.

Reaction of propylene chlorophosphite [3] with 2,3-dimethyl-1,3-butadiene. In a thick-walled, tightly closed vessel we placed 57 g of propylene chlorophosphite [b.p. 41° (9 mm); n_D^{20} 1.4730], 48 ml of dimethylbutadiene, 0.85 g of freshly fused zinc chloride, and 0.05 g of hydroquinone. The vessel was kept for 25 hours at 100-110°. Then the reaction products were distilled in a vacuum. After two repeated redistillations we obtained a fraction with b.p. 135-136° (3.5 mm), n_D^{20} 1.4960; d_4^{20} 1.1598; found: MR 56.03; calculated for $C_9H_{16}O_2PCl\,|\!=$ MR 55.74; yield of product 46.3 g or 51.30% of the theory, calculated on the propylene chlorophosphite. Found: C 48.63; H 7.41; Cl 15.78; P 13.95%. $C_9H_{16}O_2PCl$. Calculated: C 48.54; H 7.24; Cl 15.92; P 13.91%. The product did not react with cuprous chloride, was stable in air; it was 3,4-dimethyl-1-(β-chloropropoxy)-3-phospholine-1-oxide.

Saponification of 3,4-dimethyl-1-(β-chloropropoxy)-3-phospholine-1-oxide. Six g of the compound obtained in the previous experiment was heated in a sealed tube with four times the volume of 20% hydrochloric acid for 14 hours at 125°. The product which separated was submitted to the above treatment. We obtained acid (III), 0.9 g or 29.7% of the theory, with m.p. 119-121°. A sample mixed with the acid obtained in the above experiment gave no melting point depression. Found: C 49.40; H 7.50; P 21.32%. $C_6H_{11}O_2P$. Calculated: C 49.31; H 7.53; P 21.23%.

SUMMARY

2,3-Dimethyl-1,3-butadiene reacts in the diene synthesis with ethylene and propylene chlorophosphites with simultaneous occurrence of the Arbuzov rearrangement to form 3,4-dimethyl-1-(β-chloroalkoxy)-3-phospholine-1-oxides.

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SOME CHARACTERISTICS OF EQUILIBRIUM TRANSFORMATIONS OF SUBSTITUTED CYCLOPENTADIENES*

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In previous communications [1-3] we showed that for substituted cyclopentadienes there is a characteristic slowing of the thermodynamic equilibrium between the isomers with double bonds in the ring. Establishment of equilibrium occurs under comparatively mild conditions (20-60°); at lower temperatures we can isolate and keep practically individual isomers which have not yet proceeded to equilibrium [1, 3] or have been separated artificially [2]. When equilibrium is established the concentration of 1-(I), 2-(II), and 5-(III) methylcyclopentadienes in the mixtures is ($I:II:III \simeq 17:15:1$) from diene (III), and in the intermediate stages of the transformation there is almost entire formation of diene (I) [3].

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* Communication 9 in the series "Substituted Cyclopentadienes and Related Compounds."