REACTIONS OF CYCLIC PHOSPHOROCHLORIDOUS ESTERS

WITH DIENIC HYDROCARBONS

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In a previous paper [1] we have shown that cyclic ethylene and propylene phosphorochloridites undergo 1,4addition with 2,3-dimethyl-1,3-butadiene. The addition products undergo intramolecular Arbuzov rearrangement with formation of substituted dihydrophosphole oxides. In the further development and extension of this investigation we have studied the reactions of cyclic phosphorochloridous esters with linear and cyclic conjugated dienes. We have carried out the addition of 1,2-dimethylethylene and (chloromethyl)ethylene phosphorochloridites to 2,3dimethyl-1,3-butadiene and of ethylene and (chloromethyl)ethylene phosphorochloridites to 2,4-hexadine and to alloocimene. All the reactions go by the same mechanism and lead to substituted dihydrophosphole oxides:



- 1. R_2 and $R_5 = H$; R, R_1 , R_3 , and $R_4 = CH_3 c_3$.
- 2. R, R₂, and R₅ = H; R₁ = CH_2C1^- ; R₃ and R₄ = CH_3^- ;
- 3. R, R₁, and R₃ = H; R₂ = $\frac{CH_3}{CH_3}$ >C = CH-; R₄ and R₅ = CH₃;
- 4. R and $R_3 = H$; $R_1 = CH_2Cl-$; $R = \frac{CH_3}{CH_3} > C = CH-$; R_4 and $R_5 = CH_3-$;
- 5. R, R₃, and R₄ = H; R₁ = CH₂Cl-; R₂ and R₅ = CH₃-.

The characteristics of the substituted 2,5-dihydrophosphole-1-oxides obtained are given in Table 1. They are thick colorless (greenish in the case of alloocimene) liquids with a pleasant smell. The structures of the products were confirmed by their hydrolysis and their infrared spectra.

The infrared spectra of all the compounds obtained contained a strong absorption band at 1248-1250 cm⁻¹ characteristic for the stretching vibrations of the P = O group, a band at 1665 cm⁻¹ characteristic for the stretching vibrations of a disubstituted C = C bond in a five-membered ring, and a band at 1647 cm⁻¹ for alloocimene derivatives (C = C in side chain). For the P-O-C group we found characteristic absorption bands at 1047 and 1025 cm⁻¹.

Also, to confirm the structure of the products of the reaction of alloocimene with cyclic phosphorochloridites we attempted to add ethylene phosphorochloridite to 1,1,3-trimethyl-1,3-butadiene. The fact that cyclic phosphorochloridites do not add to 1,1,3-trimethyl-1,3-butadiene under analogous conditions indicates that the linkage

NO	C*************************************	B. P., °C	20.	,20	554	ound,	9/0	Cal	culate	1, %	Reaction	Yield	-
NO.	structure of product	(b, mm)	<i>a</i> "	7n	C	н	P	υ	н	Ъ	time, h	alo	Formula
-	CH ₃ O CHCl P CH ₃	144—145(3)	1,4914	1,1383	50,81	66'2	13, 29	50,74	19,7	13,10	52	65,2	CıeH1aO2PCI
24	CH ₃ CH ₃ Cl 0 CH ₃ CHCl P CH	154—156(5)	1,5083	1,2692			11,95			12,06	27	53,3	C ₅ H ₁₅ O ₂ PCl ₂
с С	$\begin{array}{c} \operatorname{CH}_{3} \\ \operatorname{CH}_{3} \operatorname{CH} & \operatorname{O} \\ \operatorname{CH}_{3} - \operatorname{O} \\ \operatorname{CH}_{3} - \operatorname{O} \\ \operatorname{CH}_{3} \\ \end{array} \right) \operatorname{P} \left(\operatorname{CH}_{3} \\ \operatorname{CH}_{3} \\ \operatorname{CH}_{3} \\ \end{array} \right)$	154—156(3)	1,5026	1,1234			11,64			11,81	22	53,2	C ₁₂ H ₂₀ O ₂ PCI
4	CH _s Cl O CH _s CH _a CHcl O CH _s CH _a CHcl P CH _a	164165(3)	1,5120	1,1666	49,82	6,88	9,72	50,16	6,76	96,96	50	55,48	C ₁₃ H ₂₁ O ₂ PCl ₂
			-		් ට්	ystalli2	zes on	standin	2; m.	p. 86-6	87°		-
<u>م</u>	CH ₃ CI O CH ₃ CH ₂ CI O CH ₃ CHCI P CH ₃	134—136(6)	1,4850	1,1912	42,13	5,78	12,03	42,02	5,84	12,06	58	20,3	C ₉ H ₁₅ O ₂ PCl ₂
* Th	: orientation in the ring closure of the	s cyclic pho	phite v	vas not	detern	nined, é	and for	compc	A spund	io. 2, 4	, and 5 th	e ester gi	ouping may have

the structure $(ClCH_2)_2CH-O-$. For compounds No. 3 and 4 it is possible that the double bond in the dihydrophosphole ring may be in the 2,3- or 4,5-position.

TABLE 1

of phosphorochloridites to alloocimene occurs at the less highly substituted dienic system of double bonds. This is in good accord with data in the literature on diene synthesis with alloocimene [2]. As cyclic phosphorochloridites were found to be fairly reactive, it was important to determine how they behave in reactions with cyclic dienes. As examples of these, we chose bi-1-cyclohexen-1-yl, hexachlorocyclopentadiene, tetraphenylcyclopentadienone, cyclopentadiene, and anthracene.

All the reactions of phosphorochloridous esters with dienes were conducted with heating to 100-120° in presence of zinc chloride. Ethylene and (chloromethyl)ethylene phosphorochloridites react at approximately the same rate with bi-1-cyclohexen-1-yl. In both cases clear thick liquids are obtained which, after distillation in a high vacuum, gradually crystallize to white substances which are sparingly soluble in ether. This property was made use of for purification from the viscous product, possible bicyclohexenyl dimer. The course of the reaction can be represented as



The reactions of cyclic phosphorochloridites with tetraphenylcyclopentadienone are much faster. Here the phosphorochloridous ester is both a reactant and a solvent, and for this reason a four- or five-fold excess is taken. The reaction is complete in three hours at 100-120°. The end of the reaction is determined from the change in the color of the solution from dark red to pale yellow. After suitable treatment of the reaction products with water, purification by chromatography on alumina, and recrystallization from alcohol, we obtained the white crystalline product (III).



The structure of the product was proved by its infrared spectrum. This contains an intense absorption band at 1260 cm⁻¹ characteristic for the stretching vibrations of the P = O group. A very intense absorption band at 1712 cm⁻¹ undoubtedly indicates the presence of a carbonyl group.

All the products obtained by the reaction of ethylene and (chloromethyl)ethylene phosphorochloridites with cyclic dienes are white crystalline substances, readily soluble in hot alcohol, but insoluble in water. The melting points of the products, the results of analysis for phosphorus and other elements, and their yields are given in Table 2.

Reaction between ethylene phosphorochloridite and hexachlorocyclopentadiene occurs very readily when the reactants are heated together in presence of zinc chloride in a water bath; a black solid is formed. We have not yet succeeded in isolating the product in a pure state.

Such reactive dienes as cyclopentadiene and anthracene do not undergo diene condensation with cyclic phosphorochloridites. In all our experiments we recovered the phosphorochloridites and dienes unchanged. The reactivity of dienes in diene condensation with cyclic phosphites can be explained as follows: by virtue of the unshared electron pair on the phosphorus atom cyclic phosphorochloridites are evidently electron-donating dienophiles. The reactivity of a diene in its reactions with them should be proportional to the accepting power of the diene, i. e., inversely proportional to its donating power, which is proportional to the rate of its reaction with acceptor dienophiles. The latter varies as follows [3]: cyclopentadiene > anthracene > bi-1-cyclohexen-1-yl > 2,3-dimethyl-1,3-butadiene > cyclohexadiene > butadiene > tetraphenylcyclopentadienone > hexachlorocyclopentadiene.

TABLE 2												
			Four	1d, %		U	alcula	ed, %			6 E - 242	
Structure of product	M. p., °C	ç	H	Ē.	ö	Ö	Ъ	<u>е</u>	CI	time, h	viero,	Formula
CH ₂ Cl	186—188	58,31	7,60	10,75		58,23	7,62	10,74		26	65,5	C14H2002PCI
*												
CH ₂ Cl O CHCl O CH2-O	110-110,5	53,21	6,93	9,31		53,41	6,82	9,19		24	60	C ₁₅ H ₂₁ O2PCl2
7										- <u>-</u>		-
	209-210	75,51	5,01	6,31	7,29	75, 23	4,85	6,27	7,18	ç	56	C ₃₁ H ₂₄ O ₃ PCI
· ¢ ₆ H ₅ ¢ ₆ H ₅												
	128—129	57,01	5,32	14,58		57,14	5,24	14,76		24(20°)	70	C ₁₀ H ₁₁ O ₃ P
HOV >				-	-							

• The ester grouping may have the structure $(ClCH_2)_2CH-O-$.

It is readily understood, therefore, why cyclic phosphorochloridites react readily with dienes at the end of this series (hexachlorocyclopentadiene and tetraphenylcyclopentadienone), when reaction appears to go in the direction: dienophile-donor, diene-acceptor [4].

The reaction of cyclic phosphorochloridites with acyclic dienes goes with greater difficulty, and it does not go at all with strongly donating dienes (cyclopentadiene and anthracene). The most reactive cyclic phosphorohalidites in reactions with dienes were found to be o-phenylene phosphorochloridite and phosphorobromidite, which react with butadiene extremely readily at room temperature in absence of catalyst. The products are white solids which fume strongly in air. They are insoluble in diethyl ether, petroleum ether, and benzene, and are partially soluble in acetone. They are readily soluble in hot water, but the ester ring is then opened and halogen is lost. As a result of such treatment the same product, m. p. 128-129°, is obtained from the chlorine and bromine derivatives. A mixture of these melts without depression. An aqueous solution of this substance gives an intense violet color with ferric chloride, characteristic for a phenol. The course of the reaction can be represented as:



The structure of the product was confirmed by the infrared spectra. Its infrared spectrum contained an intense broad absorption band near 3225 cm^{-1} , characteristic for the stretching vibrations of a hydrogen-bonded hydroxyl, and absorption at 1265 cm^{-1} , characteristic for the P = O group. The spectra were run in mineral oil on the Hilger H-800 and the IKS-14 spectrophotometers. The characteristics of the products are given in Table 2.

EXPERIMENTAL

Procedure in the Addition of Cyclic Phosphorochloridous Esters to Dienes. All the cyclic phosphorochloridous esters were prepared by Gefter's method [5] by the reaction of phosphorus trichloride with diols in chloroform solution.

To an equimolecular mixture of the cyclic phosphorochloridite and the diene we added 0.8% of the weight of the mixture of freshly fused zinc chloride and 0.05 g of hydroquinone. This mixture was heated in a sealed tube at 100-120° until the volume no longer diminished. The products were purified by two or three vacuum distillations. The products of the reactions of ethylene and (chloromethyl)ethylene phosphorochloridites with bi-1-cyclohexen-1-yl, after vacuum distillation $(1.6 \cdot 10^{-2} \text{ mm})$, were left in porcelain dishes for crystallization. Crystallization started after a few days. The crystals were carefully washed from the viscous mass with dry ether. The characteristics of the substituted 2,5-dihydrophosphole-1-oxides synthesized are given in Tables 1 and 2. The hydrolysis of the products was conducted by the procedure described by us in [1].

Addition of Ethylene Phosphorochloridite to Tetraphenylcyclopentadienone. A mixture of 3 g of tetraphenylcyclopentadienone and 0.04 g of zinc chloride was heated in a five-fold excess of ethylene phosphorochloridite in a sealed tube at 100-110° until the color changed from dark red to light yellow (three hours). The thick yellow liquid was then poured into a beaker containing ice water. A fine yellowish precipitate was formed, was carefully washed with water to remove acidic reaction products, and was dried in air. We obtained 3 g (93.4%, based on the tetraphenylcyclopentadienone) of precipitate. This precipitate is readily soluble in many organic solvents (benzene, alcohol, chloroform, carbon tetrachloride, ethyl acetate, acetone). However, it is impossible to recover it in the crystalline state from these solvents—a resinous mass is obtained. The precipitate was purified chromatographically on alumina. Elution with benzene gave a little unchanged tetraphenylcyclopentadienone (0.1 g), and with absolute ethanol a white crystalline product was eluted slowly; after recrystallization from alcohol this had m, p. 209-210°. The yield was 56%, based on the tetraphenylcyclopentadienone.

Addition of o-Phenylene Phosphorochloridite (and Phosphorobromidite) to Butadiene. o-Phenylene phosphorochloridite and phosphorobromidite were prepared by Crofts's method [6] by heating a mixture of phosphorus trihalide and pyrocatechol in presence of a little water (0.858 g). 10 ml of butadiene was added to 20 g of o-phenylene phosphochloridite mixture was sealed in a tube. On the next day the white crystals formed, which fumed strongly in air, were washed with dry ether, and dried in dry air; m. p. 95-110° (determined in a sealed capillary). We obtained 23.6 g (90%, based on the o-phenylene phosphorochloridite). The product probably contained butadiene polymer impurity. Analysis gave a low chlorine content. Found: Cl 13.22%. $C_{10}H_{20}O_2PCl$. Calculated: Cl 15.53%. The product was then recrystallized twice from hot water. White, halogen-free crystals, m. p. 128-129°, were obtained. With ferric chloride a solution of these gave an intense violet color, characteristic for phenols. The same product was obtained from the reaction of o-phenylene phosphorobromidite with butadiene.

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SUMMARY

1. Linear and cyclic dienic hydrocarbons undergo diene condensation with cyclic phosphorochloridic esters with simultaneous intramolecular Arbuzov rearrangement.

2. By the addition of cyclic phosphorochloridous esters to various dienic hydrocarbons a number of substituted 2,5-dihydrophosphole-1-oxides were prepared.

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