

REACTION OF ALKENYLDICHLOROPHOSPHINES WITH ETHYLENE OXIDE AND ETHYLENE SULFIDE

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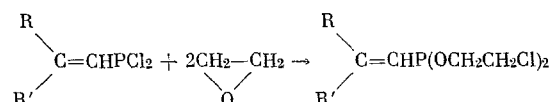
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The condensation of alkene α -oxides with trivalent phosphorus acid chlorides [1] has been studied extensively and is used in practice. The opening of the α -oxide ring by these reagents proceeds with the insertion of the oxyalkene group at all of the P-Cl bonds of the acid chloride molecule.

The reactions of thiranes with P(III) chlorides have received little study. Besides the patent data [2, 3], which are not reproduced in the case of the phosphorus chlorides, it was shown [4, 5] that PCl_3 forms with ethylene sulfide a mixture of the mono-, di-, and triaddition products. Propylene sulfide reacts with PCl_3 only in the presence of ZnCl_2 . The alkyl- and aryl-dichlorophosphines react with the ethylene and propylene sulfides without a catalyst. However, only the condensation products of one P-Cl bond were isolated in this case [6-8].

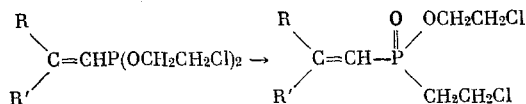
The initial act in the discussed reactions can be considered to be donor-acceptor interactions of the π type, where the orbitals of the π -electrons of the heteroatom and the d-orbitals of the phosphorus atom are the boundary orbitals. In such case a comparison of the reactivity of oxirane and thirane compounds will make it possible to indirectly judge the efficiency of the interaction of the d-orbitals of P(III) and the π -electrons of the valence L- and M-layer. For this purpose we made a comparative study of the reactions of ethylene oxide (EO) and ethylene sulfide (ES) with the styryl- and isobutenyldichlorophosphines [9, 10].

Anhydrous toluene and dioxane were used as the solvents. As was to be expected, EO adds smoothly to the styryl- and isobutenyldichlorophosphines at 20-25°. An induction period (15-20 min) is observed in toluene solutions, after which the reaction is exothermic. This phenomenon is absent in dioxane and exothermic reaction is observed when the first portions of EO are added, which is completed at 20° after the addition of two moles of the reactant per mole of dichlorophosphine. Differences in the reactivity of the styryl- and isobutenyldichlorophosphines are practically absent here. As a result, the reaction of EO proceeds in harmony with the following equation.



The condensation products of EO with alkenyldichlorophosphines are easily isomerized during fractional distillation. Consequently, before distillation the reaction mass is first refluxed until the test for P(III) is negative.

The solvent also exerts an effect on both the rate and direction of the isomerization, especially of the bis-(2-chloroethyl) alkenylphosphinites. The isomerization proceeds more rapidly in dioxane than in toluene, and leads to monomolecular transformation products in high yield.



*The reactions were checked via the Cl^- in the hydrolyzate of a sample of the reaction mass.

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TABLE 1

Com- pound	Formula	Yield, %	Bp, °C (p, mm of Hg)	d ₄ ²⁰	n _D ²⁰	Formula	Found, %		Calculated, %	
							Cl	P	Cl	P
(I)	(C ₆ H ₅) ₂ C=CHP(O)ORR *	45 (toluene)	110-112 (0.61)	1.2062	1.4680	(C ₆ H ₅) ₂ C=CHP(O)ORR *	23.44	13.01	23.38	12.05
(II)	C ₆ H ₅ CH=CHP(O)ORR	82 (dioxane)	120-122 (0.25)	1.3439	1.5398	C ₆ H ₅ CH=CHP(O)ORR	24.75	10.93	24.20	10.58
(III)	(CH ₃) ₂ C=CHPR ₂ †	40 (toluene)	100-102 (0.04)	1.2668	1.5835	(CH ₃) ₂ C=CHPR ₂ †	25.21	11.47	25.63	11.12
(IV)	(CH ₃) ₂ C=CHP(R')Cl	86 (dioxane)	100-102 (0.04)	1.2668	1.5835	(CH ₃) ₂ C=CHP(R')Cl	32.41	14.09	32.71	14.28
(V)	C ₆ H ₅ CH=CHPR ₂ ‡	58	106 (1)	1.2656	1.5575	C ₆ H ₅ CH=CHPR ₂ ‡	22.01	10.00	21.88	9.53

*R = CH₂CH₂Cl.†R' = SCH₂CH₂Cl.

‡Found: S 23.32%. Calculated: S 23.14%.

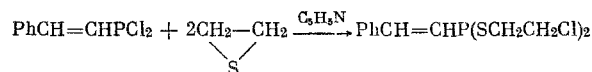
**Found: S 14.45%. Calculated: S 14.74%.

††Found: S 19.37%. Calculated: S 19.69%.

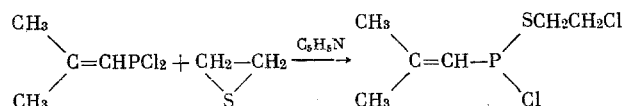
A large amount of tarry products is formed during isomerization in toluene.

The course of the reaction of ES with alkenyldichlorophosphines was checked by the refractometric method. As it proved, ES does not react with dichlorophosphines at 50-60°. The reaction proceeds slowly in the presence of HCl, and quite rapidly when catalyzed with either pyridine hydrochloride or pyridine.

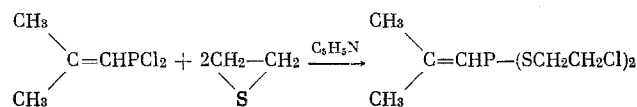
The pyridine-catalyzed reaction of ES with styryldichlorophosphine in toluene proceeds smoothly with the insertion of the thioethylene group at both P-Cl bonds.



Isobutenyldichlorophosphine reacts with more difficulty in the same reaction. The monoaddition product was obtained in toluene at 50-60°, even with a fourfold excess of ES.



In dioxane at 50-60° the condensation is completed in 1 h to give bis-(β-chloroethyl) isobutenyldithiophosphinite.

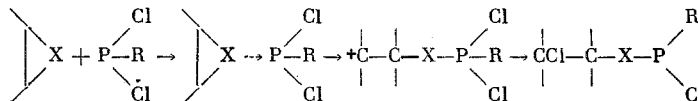


As a result, in contrast to EO, ES reacts with alkenyldichlorophosphines only in the presence of catalysts.

The obtained results correlate with the known data [4] that the thiirane ring is opened with much greater difficulty by trivalent phosphorus chlorides than the oxirane ring. Together with this, they testify to the fact that the ability of alkene sulfides to react with trivalent phosphorus chlorides is also determined by the structural traits of the latter, and can be associated with a certain "depletion" of the electron density on the phosphorus atom.

It is relevant to mention that the epithio compounds are more reactive in the reactions with the dialkyl(aryl)chloroarsines [11] than the oxiranes. Here a distinct tendency is observed for an increase in the exo-effect of the reaction as the I-effects of the substituents increase. The same rules were also observed in the reactions of oxiranes and thiiranes with dialkylisothiocyanoarsines [12].

The combination of the presented data is in agreement with the assumption that the primary acts in these reactions have a donor-acceptor nature, i.e., the phosphorus atom in dichlorophosphines (the same as the arsenic atom in arsines) is capable of functioning not only as a donor of unshared electrons (n-donor), but also as an acceptor of electrons via the unoccupied d-orbitals of the atom.



In this case, the same as in other exchange reactions that proceed via the interaction step involving the pd -orbitals [13, 14], the maximum effect of the reaction is observed under the condition of their $(n-1)p_{\pi}-nd_{\pi}$ bonding.

The catalytic effect of bases in the discussed reactions, and also the beneficial effect of solvents, can be explained by the specific solvation of the reagent (O- or S-heterocycle) or substrate (P(III) compound) molecules.

EXPERIMENTAL METHOD

Reaction of Isobutenyl- and Styryldichlorophosphines with Ethylene Oxide (typical experiment). With stirring, 0.3 mole of dry ethylene oxide was bubbled into a solution of 0.15 mole of the alkenyldichlorophosphine in 50 ml of abs. toluene (or dioxane) at 20–25°. Then the reaction mass was stirred at 20–25° for 1 h, under reflux for 1–4 h, and fractionally distilled. Compounds (I) and (II) (Table 1) were obtained by the same method.

2-Chloroethyl Ester of 2-Chloroethylisobutenylphosphonic Acid; yield either 46% (in toluene) or 82% (in dioxane), bp 110–112° (0.01 mm); d_4^{20} 1.2082; n_D^{20} 1.4860. Found: Cl 28.44; P 13.01%. $C_8H_{15}Cl_2PO_2$. Calculated: Cl 28.98; P 12.65%.

2-Chloroethyl Ester of 2-Chloroethylstyrylphosphinic Acid; yield either 40% (in toluene) or 86% (in dioxane); bp 120–122° (0.025 mm); d_4^{20} 1.3439; n_D^{20} 1.5398. Found: Cl 24.75; P 10.93%. $C_{12}H_{15}Cl_2PO_2$. Calculated: Cl 24.20; P 10.58%.

Reaction of Isobutenyl- and Styryldichlorophosphines with Ethylene Sulfide (typical experiment). With stirring, to a solution of 0.15 mole of the alkenyldichlorophosphine in 50 ml of abs. toluene or dioxane at 20° were added a catalytic amount of dry pyridine and 0.6 mole of ethylene sulfide. The reaction mass was stirred at 20° for 1 h, at 50–60° for 2–5 h, and then fractionally distilled. Compounds (III)–(V) (see Table 1) were obtained by the same method.

Bis-(β -chloroethyl) Isobutenyldithiophosphinite; yield 58%; bp 100–102° (0.01 mm); d_4^{20} 1.2668; n_D^{20} 1.5835. Found: Cl 25.21; P 11.47; S 23.32%. $C_8H_{15}Cl_2PS_2$. Calculated: Cl 25.63; P 11.12; S 23.14%.

(β -Chloroethyl) Isobutenylthiochlorophosphinite; yield 85.5%; bp 106° (1 mm); d_4^{20} 1.2656; n_D^{20} 1.5575. Found: Cl 32.41; P 14.09; S 14.45%. $C_6H_{11}Cl_2PS$. Calculated: Cl 32.71; P 14.28; S 14.74%.

Bis-(β -chloroethyl) Styryldithiophosphinite; yield 64.5%; bp 125–127° (0.0095 mm); viscous liquid. Found: Cl 22.01; P 10.00; S 19.37%. $C_{12}H_{15}Cl_2PS_2$. Calculated: Cl 21.88; P 9.53; S 19.69%.

CONCLUSIONS

In contrast to ethylene oxide, ethylene sulfide reacts with the styryl- and isobutenyldichlorophosphines only in the presence of catalysts. The course of the discussed reactions is facilitated by solvents with a high electron-donor capacity. The obtained results are discussed from the standpoint of primary donor-acceptor interactions of the reactants.

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