REACTIONS OF ALKENES WITH PHOSPHORUS PENTACHLORIDE AND TRICHLOROSILANE

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In [1] it was shown that the adducts of alkenyltetrachlorophosphors with PCl_5 are smoothly reduced by hydrosilanes. Starting with visual observations, the rules that were discovered between the structure of the reactants and the reduction conditions, and also the effect of solvents, a theory was expressed regarding the mechanism of these reactions, according to which the alkenyltetrachlorophosphors initially form complexes with the hydrosilanes.

$$RPCl_4 \cdot PCl_5 + HSiR_3' \rightarrow RPCl_4 \cdot HSiR_3' \rightarrow RPCl_2$$

The validity of this theory can be verified by studying the reactions of alkenes with PCl_5 and hydrosilanes using equimolar ratios of the reactants. The yield of the alkenyldichlorophosphines in these reactions, which exceeds 50%, serves as proof that the hydrosilanes can compete for the PCl_5 in forming the adducts with the alkenyltetrachlorophosphors. The results of studying the reactions of alkenes with PCl_5 in the presence of trichlorosilane are given in this paper.

For reaction we took alkenes that differed in the conditions of condensation with PCl_5 and in the character of the transformations of the transition complexes (isobutylene, styrene, vinyl acetate, methyl vinyl sulfide, isoprene, and piperylene). Benzene and toluene were used as the solvents. Depending on the conditions of mixing the reactants and the conditions of destroying the transition complexes, the reactions in the indicated systems proceed along two directions: phosphorylation and chlorination of the alkenes. In all cases the transition complexes are formed at 0°C and even at negative temperatures. Of the alkenes taken by us the easiest to react are the dienic hydrocarbons. Methyl vinyl sulfide and isobutylene react with somewhat greater difficulty. The phosphorylation of styrene proceeds more slowly, while that of vinyl acetate proceeds at minimum speed. However, in all cases the alkene is almost quantitatively bound in the complex after vigorous stirring for 6-8 h at 0-5°.

As a result, the conditions for the formation of the adducts in the discussed systems are nearly the same as in the previously studied reactions without the hydrosilanes. The complete inclusion of the alkene in the complex testifies to the fact that in the presence of trichlorosilane the process does not stop at the stage of forming the complexes of the alkenyltetrachlorophosphors with PCl_5.

The destruction of the formed complexes proceeds with noticeable speed only at ~20° and is usually completed in 20-30 h. The destruction rate increases noticeably with increase in the temperature. The amount of chlorination products of the alkene increases simultaneously with this. The latter process proceeds to substantially less degree when excess trichlorosilane is present in the reactive mass.

The dichlorophosphines are obtained in 60-80% yield under the optimum conditions (25-50% excess trichlorosilane, formation of the complex at 0-5°, and its destruction at 20-25°). Mixing the reactants at 20-25° leads to exothermic reaction, with the resultant formation of a substantial amount of chloroalkenes, and the yield of the dichlorophosphines drops to 30-60%.

The elemental analysis data (Table 1) and the IR spectra of the obtained dichlorophosphines testify to the fact that the character of the phosphorylation processes in the discussed systems is the same as in the

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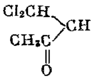
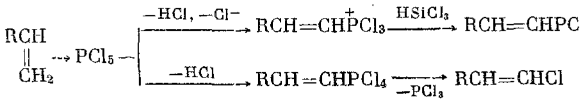
TABLE 1. Properties of Alkenyldichlorophosphines $RPCl_2$

Compound	R	Yield, %	bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found, %		Empirical formula	Calculated, %	
						Cl	P		Cl	P
(I)	$ClCH_2C(CH_3)CHCH_2$	61,5	79—81(1)	1,3660	1,5354	51,57	14,84	$C_5H_8Cl_3P$	51,82	15,09
(II)	$CH_3CHClCH{=}CHCH_2$	75,0	84—85(1)	1,3701	1,5245	51,56	15,25	$C_5H_8Cl_3P$	51,82	15,09
(III)	$(CH_3)_2C{=}CH$	80,0	82—84(35)	1,2723	1,5100	45,59	19,43	$C_4H_7Cl_2P$	45,22	19,74
(IV)	$C_6H_5CH{=}CH$	70,5	109—111(1)	1,3427	1,5944	34,82	14,95	$C_8H_7Cl_2P$	34,63	15,12
(V)	$CH_3SCH{=}CH$	63,5	104—106(10)	1,4150	1,6228	40,83	17,34	$C_3H_5Cl_2PS$ *	40,57	17.71
(VI)		81,0	45—46 $(2{,}3\cdot10^{-3})$	1,5671	1,5075	58,40	12,32	$C_4H_5Cl_4PO$	58,68	12,81

*Found: S 18.12%. Calculated: S 18.29%.

reactions of the alkenes with PCl_5 without the hydrosilanes. Thus, the structure of 4-chloroalkenyl-2,3-dichlorophosphines can be assigned to reaction products (I) and (II), which were obtained from dienic hydrocarbons. This structure is supported by the vibration frequencies of the C–H, C=C, and P–Cl bonds (ν_{C-H} 2960 and 2908; δ_{C-H} 1440, 1374, 1360, $\nu_{C=C}$ 1606, 1650, ν_{P-Cl} 480 cm^{-1}). The structure of compounds (III)-(V) is also confirmed by the frequencies of the stretching vibrations of the C = C and P–Cl bonds [for (III) $\nu_{C=C}$ 1596, 1568, ν_{P-Cl} 480 cm^{-1}; for (IV) $\nu_{C=C}$ 1606, ν_{P-Cl} 475 cm^{-1}]. The IR spectrum of compound (VI) ($\nu_{C=O}$ 1772, ν_{C-H} 2967 and 2915, δ_{C-H} 1350 cm^{-1}) is in agreement with the structure of 2,2-dichloro-1-acetylethyldichlorophosphine. However, the strong shift of the stretching vibrations of the P–Cl bond (ν_{P-Cl} 560 and 537 cm^{-1}) does not permit making unequivocal conclusions and additional studies are needed in order to ascertain its structure.

The obtained results are in agreement with the previously expressed [1] concepts regarding the mechanism of the processes for the formation of alkenyldichlorophosphines from the adducts of alkenyltetrachlorophosphors and PCl_5. In addition, they permit speaking about the character of the processes for the phosphorylation of alkenes with PCl_5, which proceed in the presence of chlorine anion acceptors (PCl_5, hydrosilanes). Both the literature data and the data obtained by us testify to the fact that the ability of the alkenes to enter into the discussed reactions correlates with their π-donor properties. From this the donor–acceptor interactions of the πv type can be regarded as being the primary interactions of the alkene and PCl_5 molecules. Their realization, with the formation of the C–P bond, is possible only via a stabilization of the transition states of the v acceptors. The chlorination of the alkene occurs in the opposite case.



EXPERIMENTAL METHOD

Preparation of Alkenyldichlorophosphines (Typical Experiment). With stirring and cooling to 0°, in a nitrogen atmosphere, 0.3 mole of trichlorosilane was added to a suspension of 0.25 mole of PCl_5 in either 100 ml of dry benzene or toluene, and then 0.25 mole of the alkene was slowly added in drops. After adding the alkene the reaction mass was kept at 0-5° for 6-8 h, and at 20-25° until all of the adduct had dissolved. The $SiCl_4$, PCl_3, excess $HSiCl_3$, and solvent were vacuum-distilled below 40°, while the residue was fractionally distilled. The yield and properties of the obtained compounds are given in Table 1.

CONCLUSIONS

Alkenyldichlorophosphines are formed in high yields when alkenes are phosphorylated by treatment with PCl_5 in the presence of hydrosilanes under conditions that promote the formation of trimolecular complexes of alkene, PCl_5, and hydrosilane.

LITERATURE CITED

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