

PREPARATION AND PROPERTIES OF PERFLUOROCHLOROMETHYL-
MERCAPTOPHOSPHORYLDICHLORIDES AND -CHLOROPHOSPHANES

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In Arbuzov-type reactions $\text{CF}_n\text{Cl}_{3-n}\text{SCl}$ reacts with ROPCl_2 ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) to give $\text{CF}_n\text{Cl}_{3-n}\text{SP(O)Cl}_2$ ($n = 3, 2, 1, 0$). The corresponding reaction with CF_3SeX ($\text{X} = \text{Cl}, \text{Br}$) produces $\text{CF}_3\text{SeP(O)Cl}_2$ in good yields only in the presence of catalysts such as SbCl_5 or BCl_3 . Reactions between P_4 and the sulfenylchlorides produce $(\text{CF}_n\text{Cl}_{3-n}\text{S})_x\text{PCl}_{3-n}$ ($n = 3, 2, 1$ and $x = 1, 2$). On heating $\text{CF}_{n'}\text{Cl}_{3-n'}\text{SP(O)Cl}_2$ ($n' = 2, 1, 0$) decompose to P(O)Cl_3 and $\text{SCF}_{n'}\text{Cl}_{2-n'}$. During this process fluorination of P(O)Cl_3 to P(O)F_3 by SCF_2 is observed. A Cl/Br exchange between $\text{CF}_n\text{Cl}_{3-n}\text{SP(O)Cl}_2$ ($n = 3, 2$) and PBr_3 was proved ^{19}F - and ^{31}P -NMR-spectroscopically.

Chemical and physical properties of the newly synthesized compounds will be discussed.