

FLUORINE EXCHANGE IN SOME PHOSPHORUS AND ARSENIC COMPOUNDS

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The rate of intermolecular fluorine exchange in the system



was studied by ^{19}F and ^{31}P dynamic NMR techniques. The anion PhPF_5^- was generated by adding potassium fluoride in crown ether to PhPF_4 .

Attempts to initiate exchange in $\text{Ph}_2\text{AsF}_2\text{Me}$ by adding fluoride ion donors were unsuccessful, instead, fluoride acceptors such as HF produced rapid intermolecular fluorine exchange in $\text{Ph}_2\text{AsF}_2\text{Me}$, presumably via an intermediate cation $\text{Ph}_2\text{AsFMe}^+$. Experimental results and proposed mechanisms of fluorine exchange will be discussed.

NOVEL REACTIONS INVOLVING O-NITROSOBIS(TRIFLUOROMETHYL)-HYDROXYLAMINE WITH $\text{M}(\text{CF}_3)_3$ (M = P, As and Sb) AND SOME OLEFINS

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O-Nitrosobis(trifluoromethyl)hydroxylamine gives novel reactions with tris(trifluoromethyl)phosphine, -arsine and -stibine to afford mainly the corresponding bis(trifluoromethyl)nitroxy derivatives. Tris(trifluoromethyl)phosphine affords $(\text{CF}_3)_2\text{NOP}(\text{O})(\text{CF}_3)_2$ and $(\text{CF}_3)_2\text{NNO}$. Tris(trifluoromethyl)arsine also gives $(\text{CF}_3)_2\text{NNO}$ in high yield, together with smaller amounts of $(\text{CF}_3)_2\text{NOAs}(\text{CF}_3)_2$, $\text{CF}_3\text{N} = \text{CF}_2$, COF_2 and a polymeric white solid. With tris(trifluoromethyl)stibine, no oxidation nor addition reactions occurred. Instead, $(\text{CF}_3)_2\text{NO}_3\text{Sb}$ and $(\text{CF}_3)_2\text{NO}_3\text{SbCF}_3$ were obtained in high yields. The stoichiometry of the reactions suggests that the additional amounts of bis(trifluoromethyl)nitroxy groups bonded to antimony are derived from the trifluoromethyl groups bonded to antimony. O-Nitrosobis(trifluoromethyl)hydroxylamine gives addition products at room temperature with 1,1-difluoro-2,2-dichloroethylene and 1,1-difluoro-2-fluoro-2-bromoethylene. No reactions occurred with a few other chlorinated and fluorinated olefins even at elevated temperatures.

The above reactions are compared with those given by perfluoro(2,4-dimethyl-3-oxa-2,4-diazepentane).

Mechanisms to rational the above reactions are proposed.