I-19

FLUORINE EXCHANGE IN SOME PHOSPHORUS AND ARSENIC COMPOUNDS

A. F. Janzen*, C. R. Wang, K. Alam and R. K. Marat

Department of Chemistry, University of Manitoba, Winnipeg, R3T 2N2 (Canada)

The rate of intermolecular fluorine exchange in the system

$$PhPF_4 + PhPF_5^- \rightleftharpoons PhPF_4\text{-}F\text{-}PhPF_4^-$$

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 Ph_2AsF_2Me by adding fluoride ion donors were unsuccessful, instead, fluoride acceptors such as HF produced rapid intermolecular fluorine exchange in Ph_2AsF_2Me, presumably via an intermediate cation Ph_2AsFMe^+. Experimental results and proposed mechanisms of fluorine exchange will be discussed.

I-20

NOVEL REACTIONS INVOLVING O-NITROSOBIS(TRIFLUOROMETHYL)-HYDROXYLAMINE WITH $M(CF_3)_3$ (M = P, As and Sb) AND SOME OLEFINS

H. G. Ang* and K. K. So

Chemistry Department, National University of Singapore, Kent Ridge, Singapore 0511, (Republic of Singapore)

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 $(CF_3)_2NOP(O)(CF_3)_2$ and $(CF_3)_2NNO$. Tris(trifluoromethyl)arsine also gives $(CF_3)_2NNO$ in high yield, together with smaller amounts of $(CF_3)_2NOAs(CF_3)_2$, $CF_3N = CF_2$, COF_2 and a polymeric white solid. With tris(trifluoromethyl)stibine, no oxidation nor addition reactions occurred. Instead, $[(CF_3)_2NO]_3Sb$ and $[(CF_3)NO]_2SbCF_3$ 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-diazapentane).

Mechanisms to rationalize the above reactions are proposed.