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## OXIDATIVE DIRECT-FILIORINATION OF UNPROTECTED ELEMENTORGANICS

## Ingo Ruppert

Anorganisch-Chemisches Institut der Universität, Gerhard-Domagk-Strasse 1, D-5300 Bonn (F.R.G.)

Fluorinations of non-perfluorinated elementorganics by free fluorine are still little familiar to preparative chemists. Besides the problematic handling of gaseous fluorine this may be due to the prejudice of a low selectivity.

By the F<sub>2</sub>-addition to low- and medium-valent organic derivatives of the p-elements |(R-) E | I want to show systematically that the interaction of elemental fluorine does not lead necessarily to the cleavage of the element-carbon bond or to the destruction of the organic periphery by non-specific CH-substitution.

$$(R-)_nEI + F_2 \xrightarrow{(CFCI_3)} (R-)_nE \xrightarrow{F}$$

E  $\triangleq$  element of 4. – 7.th main group – e.g.: C, P, As, Sb, Bi, S, Se, Te, I R  $\triangleq$  organyl

The importance and range of this 'oxidative liquid-phase fluorination' shall be demonstrated by the alternative preparations of element - fluorides

and

the synthesis of hitherto unknown classes of compounds.

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## QUANTITATIVE CADY-CODISTILLATION — A VERSATILE TECHNIQUE FOR THE INVESTIGATION OF VOLATILE FLUORINE COMPOUNDS

F. Steel\*, J. Roth, R. Stein

The University of the Saarland, Saarbruecken (F.R.G.)

In 1959 G.H.Cady and D.P.Siegwarth (Anal.Chem. 31, 618) described a method for the separation and identification of small amounts of volatile substances by a carrier-gas volatilization technique in which the separation is dependent upon liquid-vapor (or solid-vapor) equilibria in a packed U-tube with a temperature gradient. An improved apparatus has now been developed which enables to conduct the volatilization process with high reproducibility and at constant temperatures. The composition of the evaporating gas mixtures is recorded by a gas density balance first introduced in 1956 by A.J.P.Martin and A.T.James (Biochem.J. 63, 138). The new technique allows the evaluation of vapor pressures, thermodynamic data of vaporization, molar masses, the separation of subliming and distilling mixtures, and gives informations on the ideal or non ideal behaviour of low boiling mixtures (formation of azeotropes). Finally molecular complexes can be recognized and characterized thermodynamically.

The utility of the new codistillation technique will be demonstrated in the field of the chemistry of lower sulfur fluorides.