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# MECHANISM OF FLUORINATION BY PERCHLORYL FLUORIDE

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Perchloryl fluoride is a useful fluorinating agent, particularly for replacement of active hydrogens of methylene compounds by fluorine (1,2). Several mechanisms have been proposed (3,4,5,6), but none satisfactorily explains all the experimental facts or is compatible with accepted mechanistic ideas (for example, one mechanism requires that fluorine ion acts as a better nucleophile than alkoxide).

As a simple mechanism for reaction of anions with perchloryl fluoride, I propose that the most nucleophilic center in the anion (oxygen or other hetero atom related to carbon) always attacks the chlorine and never the more electronegative fluorine. For localized nucleophiles (like alkoxides), simple fluoride ion displacement occurs, but for the mesomeric ions (ambient electrophiles) an intramolecular (cyclic) transfer of fluoride ion can occur in the intermediate to give a carbon-fluorine bond. The high energy gained by forming the carbon-fluorine bond provides a strong driving force for this fluoride transfer and fluorine never has to achieve a highly unfavorable energy state with positive charge.

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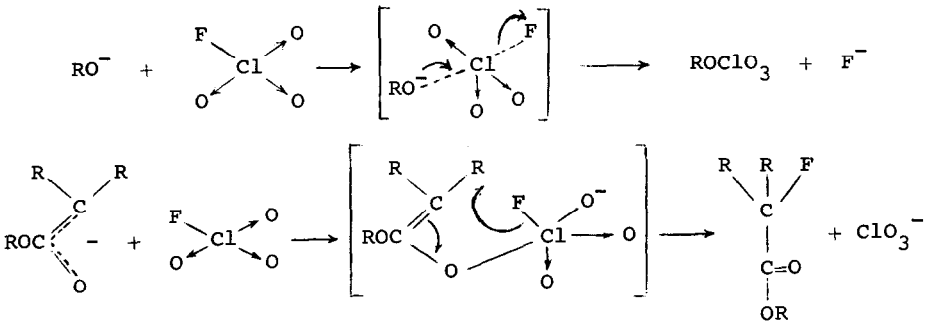

This new mechanism explains why, in reactions of perchloryl fluoride with organometallic reagents, phenyllithium gives perchlorylbenzene and not fluorobenzene whereas 2-lithiothiophene gives 2-fluorothiophene in high yield (6). Also, formation of by-products such as ethyl perchlorate in ethanol are expected and would lead to side-reactions of the type described recently (2).

This mechanism should be considered when any new perchloryl fluoride reactions are planned so that the conditions for optimum results can be defined in initial experiments.

## REFERENCES


(1) For a review of fluorination by perchloryl fluoride see W. A. Sheppard and C. M. Sharts, Organic Fluorine Chemistry, W. A. Benjamin, Inc., New York, N. Y., in press, Section 5-3B.

(2) For information on by-products and the best experimental procedure, see H. Gershon, J. A. A. Renwick, W. K. Wynn and R. D'Ascoli, J. Org. Chem., 31, 916 (1966).

(3) C. E. Inman, R. E. Oesterling and E. A. Tyczkowski, J. Am. Chem. Soc., 80, 6533 (1958).

(4) A. S. Kende and P. MacGregor, J. Am. Chem. Soc., 83, 4197 (1961).

(5) J. P. Freeman, J. Am. Chem. Soc., 82, 3869 (1960).

(6) R. D. Schuetz, D. D. Taft, J. P. O'Brien, J. L. Shea and H. M. Mork, J. Org. Chem., 28, 1420 (1963).