

## Brèves communications - Kurze Mitteilungen Brevi comunicazioni - Brief Reports

Les auteurs sont seuls responsables des opinions exprimées dans ces communications. - Für die kurzen Mitteilungen ist ausschliesslich der Autor verantwortlich. - Per le brevi comunicazioni è responsabile solo l'autore. - The editors do not hold themselves responsible for the opinions expressed by their correspondents.

### A Novel Fluorination Reaction: The Interaction of Perchloryl Fluoride with Active Methylene Compounds

When perchloryl fluoride (PF) gas is bubbled through a solution of an active methylene compound in the presence of a base, fluorination occurs. The overall reaction may be represented as follows:



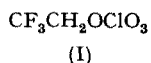
The solvents employed have been either ethanol or ether, and the usual bases used were either sodium ethoxide or sodium metal. In the presence of sufficient base all the available active hydrogens are replaced. For example, reaction of PF with diethyl malonate in the presence of 1 mole of sodium ethoxide in ethanol affords 50% unreacted malonate and 50% diethyldifluoromalonate.

Three types of anions have been employed in this nucleophilic displacement on halogen:

(1)  $\text{C}^-$ : With carbanions reaction is as described above, when A and B are both of the type  $\text{C}=\text{X}$  or  $-\text{C}\equiv\text{X}$ . When only one such group is present other reactions, e. g. oxidation or coupling, supercede fluorination.

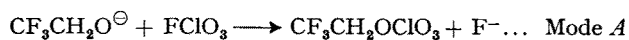
(2)  $-\text{S}^-$  (or  $>\text{S}$ ): With either thiophenoxide ion, or thiophenol itself, in either ethereal or ethanol solution, PF affords diphenyl disulfide.

(3)  $-\text{O}^-$ : With sodium ethoxide in ethanol, PF affords diethyl ether and sodium perchlorate. With sodium trifluoroethoxide in trifluoroethanol, PF yields sodium fluoride and trifluoroethyl perchlorate (I). When (I) is treated with base, sodium chlorate is formed and the

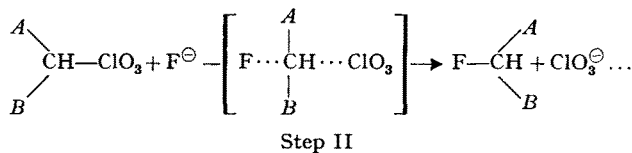
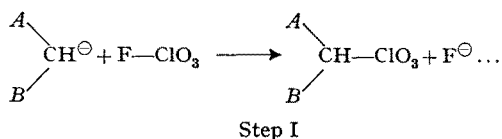


organic residue is oxidized. The oxidation product has not yet been identified.

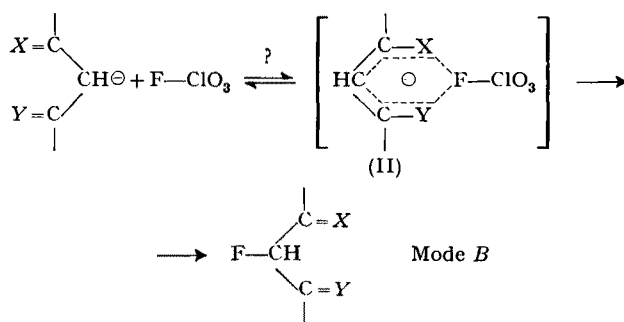
It seems possible that as the anionic functional atom is varied its nucleophilicity towards halogen would change and hence several mechanisms may be operative within the above gamut of reactions. One such mechanism appears to be the direct heterolysis of PF for (example with oxyanion bases).



With carbanions a similar sequence is possible, for example:



This appears unlikely however, as in the presence of bases more nucleophilic towards carbon<sup>1</sup> than fluoride, for example ethoxide, or chloride, ions, none of the anticipated competition with Step II is realized. The heterolysis of PF may then take place in a different manner, for instance:



The essential postulate in Mode B is a one-step fluorination process. The possibility exists, based on the type of compounds, which PF fluorinates, that reaction may proceed through some form of complex such as II. Decision between Mode A and Mode B from the physical structure of PF is not possible, *a priori*, as dipole moment and other physical studies<sup>2</sup>, shows PF is neither III nor IV but is essentially electrostatically balanced.



This work will be published in fuller detail elsewhere.

C. E. INMAN, E. A. TYCZKOWSKI,  
R. E. OESTERLING, and F. L. SCOTT

*Research and Development Department, Pennsalt Chemicals Corporation Wyndmoor, Pennsylvania U.S.A., July 11, 1958.*

#### Zusammenfassung

Die Reaktion von Perchloryl Fluorid (PF) mit Anionen wurde untersucht. Eine leichte Difluorierung fand statt mit Carbanionen vom Typus  $^-\text{CH}$  ( $\text{C}=\text{X}$ ). Mechanismen für die verschiedenen Heterolysen von PF werden vorgeschlagen.

<sup>1</sup> A. STREITWIESER, Chem. Review 56, 602 (1956).

<sup>2</sup> A. A. MARVOTT and S. J. DRYDER, J. chem. Physics 27, 1221 (1957) and further references therein.