

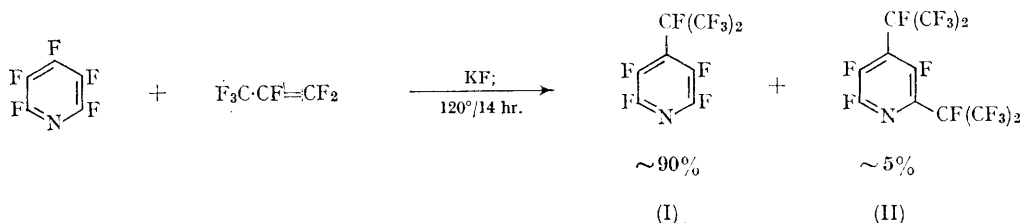
## Polyfluoroalkylation. The Nucleophilic Equivalent of Friedel-Crafts Reactions

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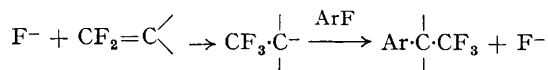
WHEREAS the chemistry of hydrocarbon olefins and aromatic compounds more frequently involves electrophilic reagents and carbonium ions, the chemistry of fluoro-olefins<sup>1</sup> and polyfluoroaromatic compounds<sup>2,3</sup> involves nucleophilic reagents and carbanions. Fluoro-olefins are known to react with fluoride ion in aprotic solvents<sup>1,4</sup> and there is, to some extent, an analogy between the role of fluoride ion in fluorocarbon chemistry and the

assignments are also consistent with the orientation of other nucleophilic displacements.<sup>3,5</sup>

Pentafluoronitrobenzene and pentafluoropyridine are of comparable reactivity towards nucleophiles<sup>3</sup> and, under the conditions described, the former with hexafluoropropene gave mainly the mono-(III) and di-(IV) substitution products each in about 30% yield together with a mixture of isomeric compounds not yet characterised but



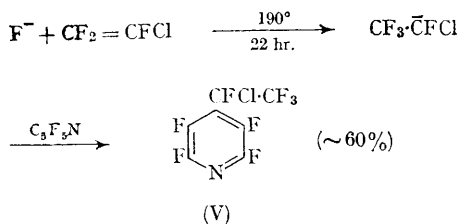
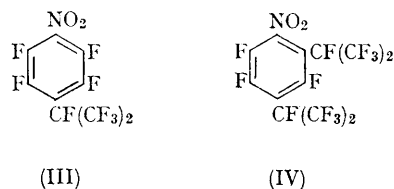
proton in hydrocarbon chemistry. This suggests the possibility of the nucleophilic equivalent of Friedel-Crafts reactions using a fluoro-olefin and a polyfluoroaromatic compound, in the presence of fluoride ion.



Pentafluoropyridine has been found to be particularly reactive to nucleophilic reagents<sup>3</sup> and we have now achieved reaction between the former and hexafluoropropene in the presence of potassium fluoride in sulpholane.

The mixtures were contained in Carius tubes and the mono-(I) and di-(II) substitution products were separated by v.p.c. Orientations of (I) and (II) were established from the <sup>19</sup>F n.m.r. spectra because the chemical shifts for 2,6-; 3,5-; and 4-fluorines in a polyfluoropyridine can easily be distinguished.<sup>3</sup> Also, coupling between the tertiary fluoride of the heptafluoroisopropyl group and adjacent ring-fluorine atoms is observed. Extensive broadening of peaks occurs in the spectra of the disubstituted compound (II) and the assignment is based mainly on the coupling of the two tertiary fluorine atoms (a triplet and a doublet) but both

arising from displacement of the nitro-group. The orientation of the disubstitution product (IV) was assigned mainly by analogy.



Extension of the reaction to other olefins appears feasible because, under forcing conditions, chlorotrifluoroethylene and pentafluoropyridine gave mainly (V).

Fluoride ion-initiated rearrangements of fluoro-olefins can be obtained in the absence of solvent<sup>1</sup> but the solvent was essential to the reactions described here. Also, using potassium fluoride, we have been unable to obtain reaction with hexa-fluorobenzene, this being less susceptible to

nucleophilic attack. However, caesium fluoride may prove a more effective initiator and the scope of the reaction is now being investigated.

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<sup>1</sup> R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50.

<sup>2</sup> J. C. Tatlow, *Endeavour*, 1963, **22**, 89, and references contained therein.

<sup>3</sup> R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1966, 220, and references contained therein.

<sup>4</sup> W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.

<sup>5</sup> R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 3737.