Vinyl and Alkadienyl Carbanions. Formation and Reactions of such Carbanions from a Perfluoro-alkyne

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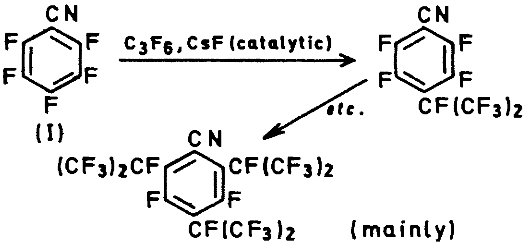
Summary Fluoride adds to hexafluorobut-2-yne to give a perfluorovinyl and a perfluoro-alkadienyl carbanion, which can displace fluoride ion from perfluoro-aromatic or -heterocyclic compounds to give alkenyl- and alkadienyl-aromatics or -heterocyclics $Ar[C(CF_3):C(CF_3)]_nF$ ($n = 1$ or 2); nucleophilic attack on a perfluoroalkenyl aromatic can displace vinylic or aryl fluorine.

IT is now well established that perfluoro-carbanions, generated by addition of fluoride ion to a perfluoro-alkene, often in a dipolar aprotic solvent, can displace fluoride ion from polyfluoro-aromatic compounds to give mono- or poly-perfluoro-alkylated derivatives,[1] *e.g.*,[2]

Satisfactory analytical and spectroscopic data have been obtained, and the individual isomers have been isolated.



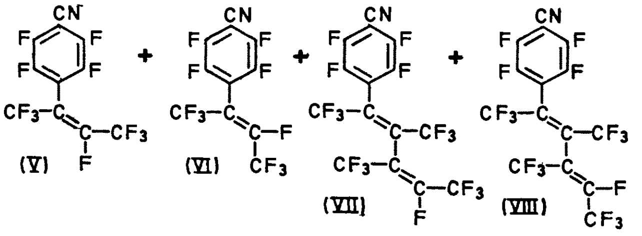
Loss of the cyano-group was not observed under controlled conditions (*cf.* R. D. Chambers *et al.*, ref. 1).

A related reaction involving fluoride ion attack on a perfluoro-acetylene to generate a perfluorovinyl carbanion is now reported which enables polyfluoro-alkenyl and -alkadienyl-aromatics and -heterocyclics to be prepared. Thus hexafluorobutyne (II) gives the *trans*-vinyl carbanion (III) and the alkadienyl carbanion (IV), and these can displace fluoride ion from (I) to give the perfluoro-alkenyl and -alkadienyl derivatives (V) (25% yield), (VI) (5%), (VII) (35%), and (VIII) (7%); further investigation has shown that under these reaction conditions (V) is in equilibrium with (VI) (5 : 1) and (VII) is in equilibrium with (VIII) (5 : 1). The compounds, separated by g.l.p.c., had satisfactory elemental analyses, mass, and n.m.r. spectra. Small amounts of other isomers and of compounds of higher molecular weight are also formed in the reaction.

$$\underset{\text{(II)}}{CF_3{\cdot}C{\vdots}C{\cdot}CF_3} \overset{F^-}{\rightleftharpoons} \underset{\text{(III)}}{CF_3{\cdot}CF{:}\bar{C}{\cdot}CF_3} \overset{\text{(II)}}{\rightleftharpoons}$$

$$\underset{\text{(IV)}}{CF_3{\cdot}CF{:}C(CF_3){\cdot}C(CF_3){:}\bar{C}{\cdot}CF_3}$$

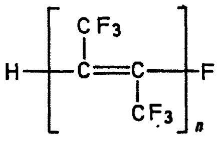
$$\text{(III)} + \text{(IV)} + \text{(I)} \xrightarrow[125^\circ]{\text{CsF, DMF}}$$



(V) (VI) (VII) (VIII)

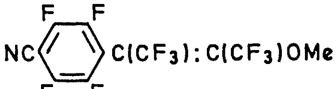
Separate experiments have shown that (VII) and (VIII) do not originate from the displacement of the vinyl fluorine of (V) by attack of carbanion (III). The u.v. and n.m.r. spectra of (V)—(VIII) indicate that the side-chains are not coplanar with the aromatic nuclei.

Careful control of the reaction conditions is necessary to avoid conversion of (II) into its homopolymer; mass spectrometric examination of the latter shows[3] it to have the structure (IX).

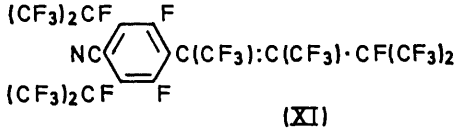


$$H\left[\begin{matrix} CF_3 \\ | \\ -C{=}C- \\ \quad | \\ \quad CF_3 \end{matrix}\right]_n F$$

(IX)



(X)



(XI)

Methoxide ion displaces the vinylic fluorine of (V) in preference to the aromatic fluorine to give (X), whereas an excess of the perfluoro-isopropyl carbanion leads to the displacement of both types of fluorine to give (XI); both (X) and (XI) are obtained as a mixture of *cis*- and *trans*-isomers.

As expected, pentafluoropyridine also reacts rapidly with (III) and (IV) to give polysubstituted products. The reactions described are only examples of a wide range shown by perfluoro-vinyl and -alkadienyl-carbanions.

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[1] J. A. Young, *Fluorine Chem. Rev.*, 1967, **1**, 359—97; R. N. Haszeldine, *Tilden Lecture*, November 1968 *Quart. Rev.*, (to be published); R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc.* (*C*), 1968, 2221.

[2] C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), to be published.

[3] W. T. Flowers, R. N. Haszeldine, A. Janik, and P. G. Marshall, unpublished results.