Fluoride-ion-initiated Reactions of Acetylenes†

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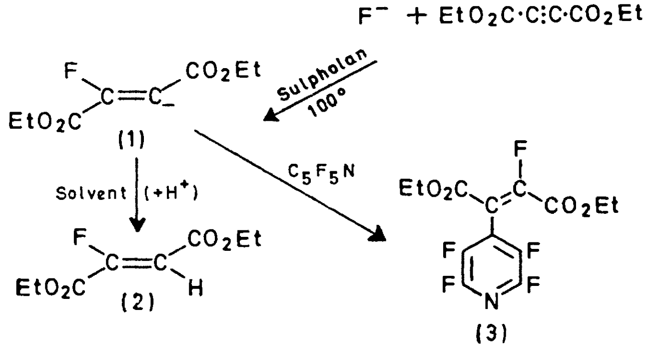
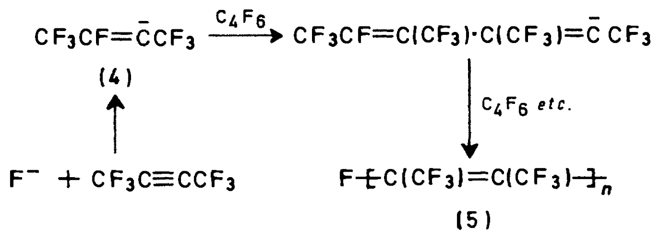
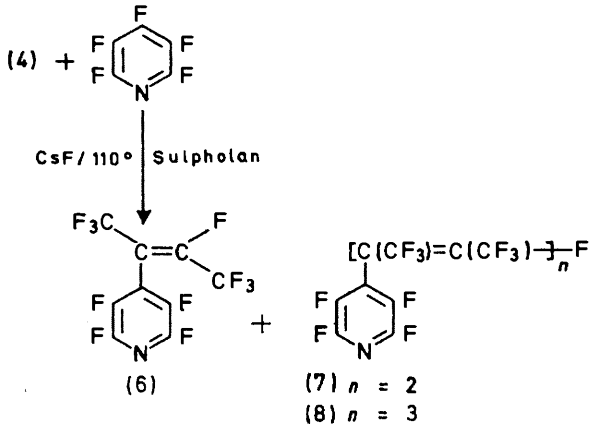
Summary Substituted vinyl anions generated from acetylenes by addition of fluoride ion are trapped by reactive polyfluoroaromatic compounds.

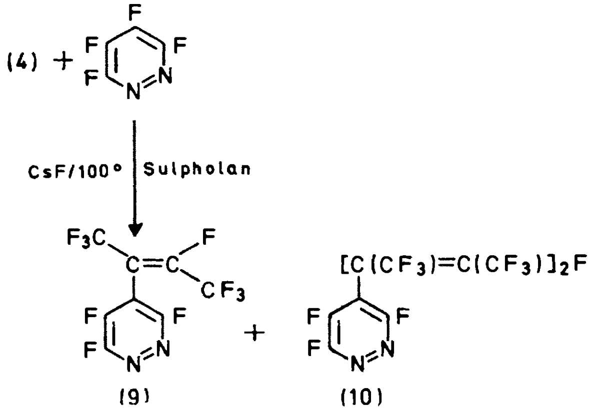
IT has previously been reported that polyfluoroalkyl anions, generated by reaction of fluoride ion with fluoro-olefins, react with activated polyfluoroaromatic compounds.[1] We have now shown that vinyl anions may be generated from acetylenes by fluoride ion and some reactions of these anions are described.

Acetylenedicarboxylic ester gives the anion (1) which may be trapped by *e.g.* pentafluoropyridine to give the diester (3) or by extraction of a proton from the solvent giving (2). In each case a single isomer, (2) and (3), was formed; the value of J_{HF} (31 Hz)[2] in the n.m.r. spectrum of (2) establishes the *trans*-structure shown and a *trans*-structure is therefore also attributed to (3). A corresponding anion (4) is generated from hexafluorobut-2-yne but in reactions under autogeneous pressure, using caesium fluoride in an autoclave and in the presence of pentafluoropyridine, only a homopolymer (5) of the acetylene was obtained *i.e.* under these conditions the acetylene itself competes much more effectively than pentafluoropyridine for reaction with (4). The unusual structure (5) is indicated by a regular cracking pattern in the mass-spectrum and the polymer is also being investigated by *X*-ray-induced photoelectron spectroscopy.[3] In reactions carried out at atmospheric pressure, however, the concentration of acetylene in solution is reduced and nucleophilic aromatic substitution then competes with self-condensation; with pentafluoropyridine at 110° compounds (6)—(8) were isolated in *ca.* 10, 18, and 10% yields, respectively. Using tetrafluoropyridazine, even more effective competition for (4) occurred, giving substitution products (9) and (10) with less accompanying polymer (5). Single isomers of (6) and (9) were obtained under these conditions and the structures shown were established by the values of $J(\mathrm{CF_3{-}F})$ vicinal of 21 Hz and $J(\mathrm{CF_3{-}CF_3})$ 1 Hz in both (6) and (9), diagnostic of *cis*-$\mathrm{CF_3{-}F}$ and *trans*-$\mathrm{CF_3{-}CF_3}$ coupling.[2] We have not yet established the structures of the other products; although the relative *trans*-arrangement of $\mathrm{CF_3}$ groups is clearly most favourable the presence of at least two isomers of (8) was indicated by g.l.c. The orientation of substitution in pentafluoropyridine[4] (6)—(8) and in tetrafluoropyridazine[5] (9, 10) was established from the fluorine chemical shifts of the ring fluorine atoms in the products.









Initial attack exclusively at the 4-position in both pentafluoropyridine and tetrafluoropyridazine had been observed with a variety of other nucleophiles except in acidic media.[4,5] Conjugation in these products is very severely restricted since there is little variation in the u.v. spectra of (6)—(8) and between (9) and (10), which accounts for the rather surprising fact that the highly unsaturated polymer (5) is a greyish solid.

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Haszeldine and his co-workers[6] recently reported products analogous to (6) and (7) but not (8) in fluoride-ion-initiated reactions using pentafluorobenzonitrile, although no conditions were given. In deductions similar to theirs, we suggest that (7) and (8) are formed by reactions of anions $FC(CF_3)=C(CF_3)\cdot C(CF_3)=\bar{C}(CF_3)$ and $F[C(CF_3)=C(CF_3)]_2C(CF_3)=\bar{C}(CF_3)$ with pentafluoropyridine rather than *e.g.* by successive reaction of (4) with (6) *etc.*

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[2] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, 1965, Vol. II, p. 910.

[3] D. T. Clark, personal communication.

[4] Ref. 1 and references contained.

[5] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1968, 2989, and references contained.

[6] W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Comm.*, 1970, 371.