

Direct Observation of Simple Fluorinated Carbanions

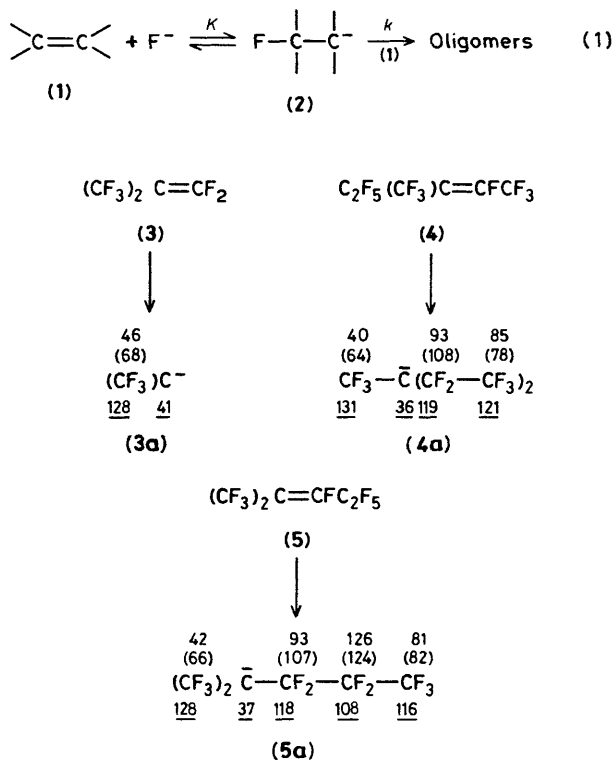
Andrew E. Bayliff, Martin R. Bryce, Richard D. Chambers,* and Raymond S. Matthews

Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, U.K.

Simple perfluorinated carbanions are generated and observed by ^{19}F and ^{13}C n.m.r. spectroscopy; curious low-field shifts are observed for sites adjacent to the charged centres.

In the light of a recent report¹ on the generation of observable, long-lived perfluoroalkyl anions, using $(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$ as the source of fluoride ion, we report some of our findings in which we have generated corresponding observable anions by the reaction of caesium fluoride with fluorinated alkenes in tetraglyme solvent, at room temperature.

The generation of perfluoroalkyl anions (2), using fluoride ion sources in reactions of fluorinated alkenes (1), is, of course well known² but these are rarely long-lived, since they promote oligomerisation reactions of the corresponding alkene [reaction (1)]. Obviously, only in cases where K is large or k is small will there be a long-lived carbanion intermediate



Scheme 1. Generation of perfluorinated carbanions (CsF, tetraglyme, room temp.) from fluoro-alkene precursors. ^{13}C shifts (underlined) in p.p.m. from SiMe_4 as external reference; ^{19}F shifts in p.p.m. from CFCl_3 as external reference. Upfield shifts quoted as positive. Values in parentheses refer to ^{19}F shifts of the corresponding bromo compounds (3b)—(5b).

(2). We have previously described some observable carbanions derived from perfluorobicyclobutylidene and related cyclic systems³ but we now find that perfluorinated alkyl anions may also be observed. Perfluoroisobutene† (3) and other fluorinated alkenes (4) and (5) shown in Scheme 1 react readily with caesium fluoride, forming simple carbanions (3a)—(5a). Other workers⁴ have described dimerisation of (3) using caesium fluoride in glyme solvents, and in other solvent

†Perfluoroisobutene is toxic and should be handled only with great care. Breathing apparatus is used by workers using this compound in our laboratory.

systems we have previously observed rapid exchange between fluoride ion and (3).⁵ However, using tetraglyme at room temperature (see Scheme 1) only *one* ^{19}F and two ^{13}C resonances were observed for (3a), showing that fluoride ion exchange is slow on the n.m.r. time-scale. The carbanions (3a)—(5a) were each quantitatively converted into the corresponding bromo derivatives (3b)—(5b) by quenching with bromine. Also, in the case of (3a), cooling caused the carbanion to crystallise. This was isolated and re-dissolved, giving the original spectrum and so demonstrating isolation of a solid perfluoroalkyl caesium compound. The ^{13}C chemical shifts of (3a) are remarkable for the fact that the carbon bearing negative charge is associated with an *upfield* shift from appropriate model compounds, but the adjacent carbon is associated with a *downfield* shift. The same downfield shift is reflected in the ^{19}F spectra, for sites adjacent to the charge. There is a suggestion of alternation of the effect but this is clearly rapidly attenuated by distance from the charge. An analogous *downfield* shift is observed in the ^{19}F spectra of the anions (4a), (5a) for sites adjacent to charge but the effect is more pronounced for adjacent CF_3 than CF_2 , while sites more remote are largely unaffected.

The concept of negative hyperconjugation has been used to account for the carbanion-stabilizing influence of fluorine substituents, adjacent to a carbanion centre $\text{F}-\text{C}-\text{C}^- \longleftrightarrow \text{F}=\text{C}=\text{C}$ and there is much support for the theoretical basis of such an effect.⁶ However, if such an effect is directly applicable, we would expect the resonance of fluorine substituents adjacent to the charge centres in (3a)—(5a) to be moved *upfield*, relative to appropriate neutral model compounds, e.g. (3b)—(5b). Consequently, at this time we have no adequate explanation to advance for the now clearly defined *downfield* shifts observed in ^{13}C and ^{19}F spectra for sites *adjacent* to charge in fluorinated carbanions.

Received, 25th April 1985; Com. 545

References

- 1 W. B. Farnham and B. E. Smart, Abstracts of papers, 7th Winter Fluorine Conference, Orlando, Florida, February 1985, paper 8.
- 2 R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973, p. 163 and references contained.
- 3 R. D. Chambers, R. S. Matthews, G. Taylor, and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 435.
- 4 D. P. Graham, *J. Org. Chem.*, 1966, **31**, 955; 958.
- 5 R. D. Chambers and M. Y. Gribble, unpublished observations.
- 6 D. S. Friedman, M. M. Francl, and L. C. Allen, *Tetrahedron*, 1985, **41**, 499 and references contained.