# Reactions Involving Fluoride Ion. Part 34.[1] Stable Perfluorinated Carbanions

Andrew E. Bayliff and Richard D. Chambers *
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE

A remarkable series of perfluoroalkyl anions, generated by reaction of caesium fluoride with various perfluorinated alkenes have been observed by ^{19}F and [13]C n.m.r. spectroscopy. Trapping experiments are described and threshold temperatures are established for the onset of fluoride ion exchange. The effects of counter ions are compared and $(Me_2N)_3S^+$ (TAS) salts are more readily produced than Cs^+ salts, but exchange of fluoride ion with fluorinated alkenes occurs more readily with TAS salts. Ph_4P^+ and Bu_4N^+ salts could not be obtained. Competition experiments for CsF between various perfluoroalkenes has established orders of carbanion stability.

Carbanions take up a central role in the chemistry of unsaturated fluorocarbons[2] in a way that is analogous to the role of carbocations in the chemistry of unsaturated hydrocarbons. Indeed, many of the papers in this series are concerned with pursuing a formal analogy between the chemistry of fluorinated carbanions, generated by reaction of fluoride-ion with unsaturated fluorocarbons, and the known chemistry involving proton-induced formation of carbocations. The spectacular work of Olah and co-workers,[3] involving observable carbocations has, understandably, stimulated our search for observable fluorinated carbanions and we have previously described various perfluorinated *cyclic* anions[4] and σ-complexes.[5] The
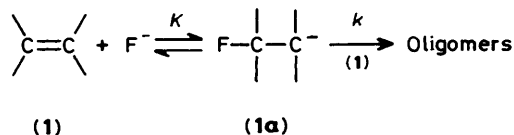
Scheme 1.

generation of perfluoroalkyl anions (1a), using fluoride ion sources in reactions of fluorinated alkenes (1), is well known[3] but these are rarely long-lived since they promote oligomerisation reactions of the corresponding alkene (Scheme 1). Obviously, only in cases where K is large, or the rate constant for oligomerisation k is small, will there be a long-lived carbanion intermediate (1a). Early attempts[6] to observe perfluorinated tert-alkyl anions by n.m.r. were complicated by exchange phenomena involving proton transfers arising from hydrogen difluoride ions, used as the fluoride ion source.

We now find that solutions of stable caesium salts of various simple perfluoroalkyl anions may be obtained and observed by n.m.r.; furthermore, some of these salts may even be obtained as solids. The most simple anion that we have observed, perfluoro-t-butylcaesium (2a), is obtained very simply by stirring a mixture containing perfluoroisobutene (2), caesium fluoride, and tetraglyme in a sealed system at room temperature. A clear homogeneous solution was obtained after removing excess of caesium fluoride and the n.m.r. spectra confirm, conclusively, formation of the salt (2a) (Figure 1). Quite clearly, the equilibrium lies completely on the side of the anion in solution and, from the sharpness of the spectra, exchange is slow on the n.m.r. timescale. On slight cooling (10—15 °C) solid separated from

$$CF_2=C(CF_3)_2 \longrightarrow (CF_3)_3C^- Cs^+$$

(2)   (2a)
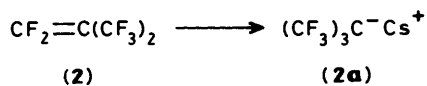
solution, which was filtered and, on redissolving the solid, the solution spectrum of the anion (2a) was identical with that obtained previously (Figure 1). Thus, the demonstration of a solid carbanion indicates the exciting possibility of growing crystals of crystallographic quality.

Using analogous procedures, various other fluorinated carbanions were generated and observed by n.m.r. spectroscopy and the results are contained in Table 1. In each case, sharp spectra were obtained and this excludes, therefore, fluoride ion exchange at a rate that is comparable with the n.m.r. time-scale.

In our previous studies,[4] using lowfield n.m.r. instruments, we were unable to identify resonances arising from 'tertiary' fluorine adjacent to carbanion centres, e.g. in anion (3a). We considered this to be suggestive of exchange-broadening but

(3)   (3a)   (3')
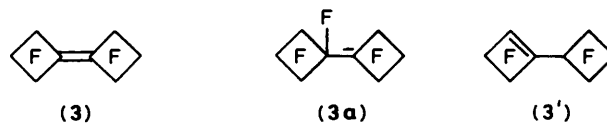
with highfield n.m.r. instrumentation we have now successfully identified the resonance arising from the 'tertiary' fluorine in structure (3a) and this was confirmed by the obvious doublet coupling of the attached carbon in the ^{13}C spectrum of (3a). The ^{13}C spectra of other systems where we have been unable to identify a 'tertiary' fluorine all shared the corresponding doublet. Therefore, this is further evidence that fluoride ion exchange does not occur in these systems at a rate which is fast on the n.m.r. timescale.

Chemical shift and coupling constant data for various perfluoroalkyl anions are shown in Table 1. The chemical shift data for perfluoro-t-butylcaesium (2a) are remarkable for the fact that the carbon bearing the 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 spectrum, for the site adjacent to the charge. In all of the other ions contained in Table 1, the same dramatic sequence is shown in ^{13}C spectra of upfield and downfield shifts for carbanionic and adjacent carbon atoms respectively, as well as the downfield shift of the fluorine resonance, associated with CF centres adjacent to the carbanionic sites. The anions (4a) and (5a) both have CF_3 and CF_2 groups adjacent to the charged sites and it is most interesting that the downfield shift of the CF_3 groups significantly exceeds those of the CF_2. Even more interesting are the chemical shift data for the anion (9a), only obtained as the TAS salt (see later), where we have CF_3, CF_2, and CF sites adjacent to the carbanionic centre. It is clear, from a comparison with
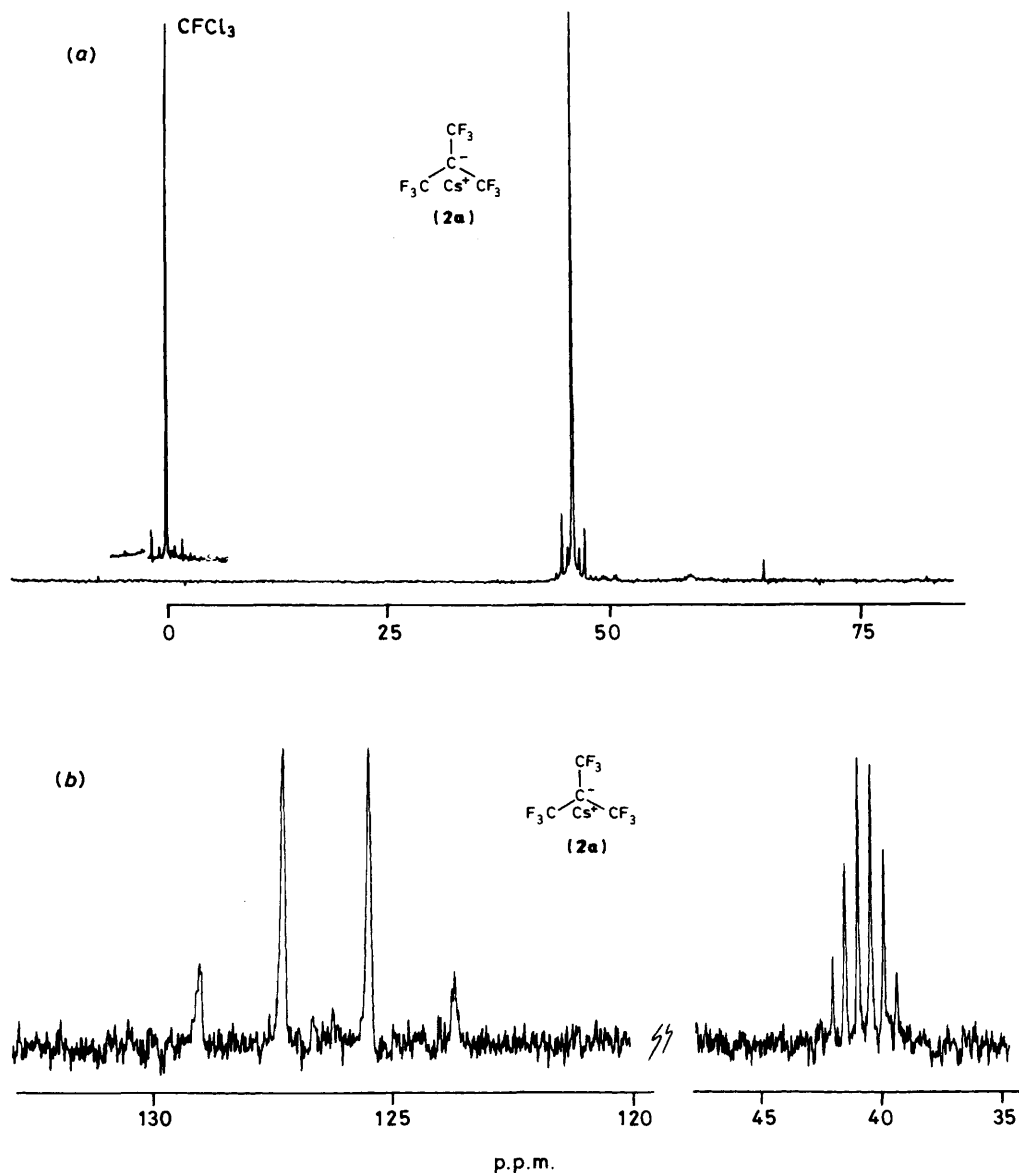
Figure 1. (a) ^{19}F n.m.r. spectrum; (b) ^{13}C n.m.r. spectrum

data for the model compound (9c) that a massive downfield shift is observed for the resonance associated with CF_3 and a modest shift is associated with the CF site. There is a suggestion of alternation of the effect along a chain but this is clearly rapidly attenuated by distance from the charge.

We are then faced with the interpretation of these dramatic substituent chemical shift data. Fundamental to the discussion, therefore, is the state of the theory of substituent chemical shifts itself. Conventionally, it has been common to relate higher shielding (i.e. increased electron density) with higher field resonance[7] and indeed the charged sites, i.e. the carbanionic carbon atoms, lead to high field resonances (see Table 1). However, it is clear from recent work that the basic theory is in some disarray because key studies[8] have demonstrated that, at saturated sites, fluorine shifts to lowfield may be induced by electron donating substituents removed from the site of substitution. That increased electron density is associated with lowfield shifts in these systems has been very convincingly demonstrated,[8] e.g. with benzyl fluorides (10),[9] and it has been pointed out that this is counter to accepted substituent chemical

shift theory. A carbanionic centre would lead to increased electron density in an adjacent carbon–fluorine bond and, in comparison with neutral models, we would have previously assumed that this would be associated with a highfield shift, i.e. the opposite of our observations (Table 1). However, on a purely empirical basis, it is now reasonable to conclude that lowfield shifts may also be associated with increased electron density at a saturated carbon–fluorine site.

The concept of negative hyperconjugation has been used to account for the carbanion-stabilising influence of fluorine substituents, adjacent to a carbanion centre $F-C-\bar{C} \longleftrightarrow \bar{F}\ C=C$. There is much support for the theoretical basis of such an effect,[10] but its manifestation through effects on reaction rates etc. have been far from convincing.[11] The very substantial lowfield shifts for positions adjacent to the carbanionic centre that we have observed (Table 1) provide, we would argue, some of the best evidence so far for the effect. Also, recent structural evidence on the trifluoromethoxide ion is very compelling.[12]

It is pertinent to point out that Seebach and co-workers have examined ^{13}C spectra of a wide range of organolithium

Table 1. N.m.r. spectral data on observable carbanions

|			^{19}F		^{13}C		Bromo derivatives (2c)—(5c) ^{19}F		^{13}C	
Alkene	Counterion	Carbanion	δ	J	δ	J	δ	J	δ	J
(2)	Cs$^+$	(2a)	45.8	(s)	127.8	264 (q)	68.3	(s)		
					40.7	39 (dec)				
(3′) (3)	Cs$^+$, TAS$^+$	(3a)	128.7, 134.0	218 (AB) }(6F)			131.1	(s)		
			124.4, 128.2	218 (AB)			126.3	(m)		
			133.6 (1F)	(m)	96.6	233 (d)	168.3	(m)		
					52.2	(s)				
			87.2 (4F)	47 (d)	121.1	284 (t)	130.7, 125.5	230 (AB)		
			124.8 (2F)	(s)			122.1, 108.4	220 (AB)		
(4)	Cs$^+$, TAS$^+$	(4a)	42.4 (6F)	19 (t) 6 (t)	128.4	263 (q)	66.4	(s)	119.5	288 (q)
					37.0	(m)			57.5	27 (t)
			92.8 (2F)	(m)	118.0	255 (t) 32 (t)	106.8	(m)	112.1	273 (t) 33 (t)
			126.3 (2F)	(m)	107.5	296 (t)	123.7	(m)	108.3	273 (t) 33 (q)
			81.1 (3F)	10 (t)	116.6	286 (q)	82.3	(m)	116.7	288 (q) 34 (t)
(5)	Cs$^+$, TAS$^+$	(5a)	84.6 (6F)	(s)	121.1	250 (q) 37 (t)	77.9	7 (q)	117.5	281 (q) 38 (t)
			93.3 (4F)	19 (q)	119.0	250 (t) 37 (q)	107.5	(m)	111.5	270 (t) 40 (q)
					36.2	36 (oct)			72	(m)
(6)	Cs$^+$, TAS$^+$	(6a)	39.9 (3F)	(m)	131.0	260 (q)	63.9	7 (sep)	120.3	287 (q)
			77.8 (6F)	11 (q)						
			106.0 (4F)	(m)						
			54.3 (3F)	(m)						
			43.0 (3F)	(m)						
			79.0 (2F)	(broad)						
			70.3 (3F)	12 (q)						
							Chloro derivative (7c)			
(7)	Cs$^+$, TAS$^+$	(7a)			94.9	196 (d) 29 (pen)	166.0	(s)		
					33.9	(m)				
			79.9	(m)	118.7	244 (t)				
(8)	TAS$^+$	(8a)	80.5	29 (d)						
(9)	TAS$^+$	(9a)	36.72 (3F)	(s)						
			74.85 (3F)	(s)^a						
			78.8 (3F)	(s)						
			82.75 (3F)							
			88.8, 90.2 (2F)	245 (AB)						
			114.6, 118.9 (2F)	289 (AB)						
			170.3 (1F)	(s)						
		(9c)	81.3 (6F)	(m)	120	288 (q)				
			113.6 (4F)	(m)	117	(m)				
			70.3 (6F)	(m)	121	289 (q)				
			180.9 (2F)	(m)	99	225 (d)				

^{a} Ref. 17.

compounds[13] and one of the striking features of these systems is the fact that replacing H or halogen by lithium leads to *upfield* shifts, *i.e.* in complete contrast to the perfluoroalkylcaesium salts reported here. However, one of the important aspects of the work by Seebach and co-workers is that they were able to demonstrate the levels of *association* of various organolithium compounds, *i.e.* dimers, tetramers etc. Consequently, it would appear from the contrasting directions of ^{13}C chemical shifts for the α-carbon atoms of alkyl-lithiums and perfluoroalkyl-caesiums that the latter are *not* associated. Indeed, the fact that

chemical shifts are virtually identical for different counter-ions, *i.e.* Cs$^+$ and (Me$_2$N)$_3$S$^+$, for some of the systems shown in Table 1 is strong evidence against association.

Adcock and co-workers have also demonstrated that $^1J_{C-F}$ values vary significantly with electron density at the CF bond,[8] the values decreasing with increasing electron density. This effect is also very noticeable in the carbanions shown in Table 1, in comparison with neutral models.

The stereochemistry of carbanions is of considerable interest and, *a priori* we would expect planar systems which would

All unmarked bonds to F

(4) (4a) (5) (5a)

(6) (6a) (7) (7a)

(8) (8a)

$$CF_3(C_2F_5)C=C(CF_3)C_2F_5$$

(9)

(9a) (9c)
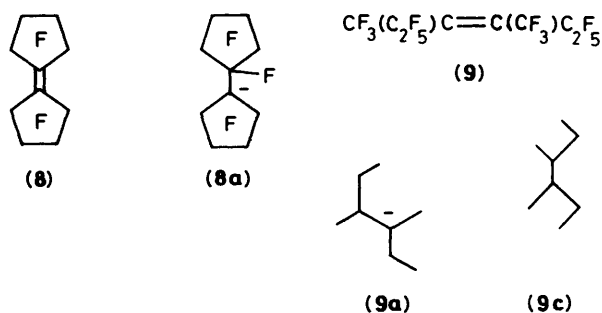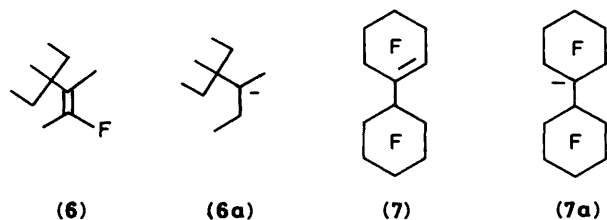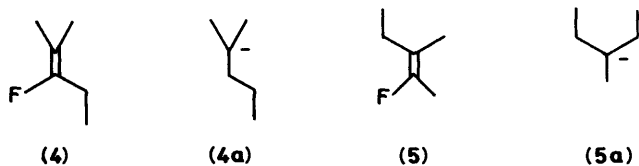
minimise the quite considerable steric requirements of perfluoroalkyl groups. In this context, it is worth emphasising that, with such groups, covalent radii are themselves an insufficient indication of steric requirements because the systems are
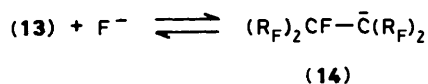

(10)
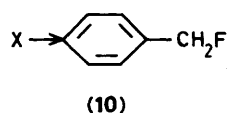
abundant in non-bonding electron pairs and their associated repulsions. In principle, we could distinguish tetrahedral from planar if non-equivalent, *i.e.* diastereotopic geminal fluorine atoms were observed in a system $-CF_2C^-R_FR'_F$, and we have such a structure in ion (5a). However, in this system the geminal fluorine atoms gave a sharp quartet that showed no signs of inequivalence (where such geminal coupling would be considerable) at temperatures down to the freezing point of the solvent. It seems more reasonable therefore to regard ion (5a) as planar, rather than a rapidly inverting tetrahedral system.

All of the anions that we have observed so far using *caesium fluoride* are derived from perfluorinated alkenes of the form (11) or (12) but, in contrast, with the exception of perfluorobicyclo-

$$(R_F)_2C=CF_2 \qquad (R_F)_2C=CFR_F \qquad (R_F)_2C=C(R_F)_2$$

(11) (12) (13)
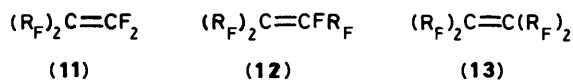
R_F = perfluoroalkyl

$$(13) + F^- \rightleftharpoons (R_F)_2CF-\bar{C}(R_F)_2$$

(14)

butylidene (3), we have been unable to generate carbanions from alkenes of the type (13). This is puzzling, at first sight, because the corresponding anions (14) would be tertiary systems and correspondingly stable. However, there are several factors which probably contribute to making the conversions of compound (13) into the ion (14) difficult: (a) the 'tertiary' fluorine in ion (14) involves a weaker C–F bond as, it is well known that bond strength decreases in the order $CF_3 > CF_2 > CF$; (b) addition of fluoride to systems of the type (13) produces a branched chain, attached to the carbanion centre and, therefore, adds to the steric requirements of the system; and (c) perfluorinated alkenes of the type (13) are more stable than corresponding alkenes with fluorine atoms directly attached to the double bond. All of these factors will work towards limiting the formation of the ion (14). Correspondingly, we have been unable to form anions from systems (9), (8), and (15) using caesium fluoride. (However, see Table 1 for the generation of TAS salts.)

(15)

(unmarked bonds to F)

Trapping of the anions shown in Table 1 was carried out effectively with bromine, chlorine, iodomethane, benzyl bromide, and tetrafluoropyridazine (16). Surprisingly, further conversion of compound (17) into a disubstituted derivative did not occur


(16) (17)
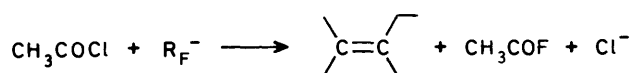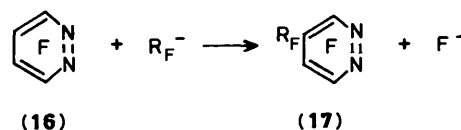
R_F^- = (4a)

(unmarked bonds to F)

using a range of conditions. In contrast, acetyl chloride acts as a fluoride-ion acceptor in a reaction with compound (4a) to give acetyl fluoride.

Exchange Phenomena.—We have already pointed out that there is no evidence for exchange broadening at room temperature for the caesium salts shown in Table 1, but we have also raised the temperature to explore the onset of exchange. Surprisingly, for the caesium salts the onset of observable exchange occurs over a comparatively small temperature range (see Figure 2) and it is important to note that these temperatures were not dependent on concentration of the caesium salts. Generally, tetraglyme is the best solvent for caesium salts and to obtain solutions in acetonitrile some of these salts required addition of a cryptand (18). Although salt (6a) is the most difficult to produce, *i.e.* dilute solutions were obtained only after

$$N(CH_2CH_2OCH_2CH_2OCH_3)_3 \qquad (18)$$
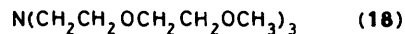
stirring for long periods of time, it showed the highest threshold temperature for the onset of fluoride ion exchange. Clearly, steric crowding raises the activation energy for elimination of fluoride ion from (6a), as is observed in other elimination
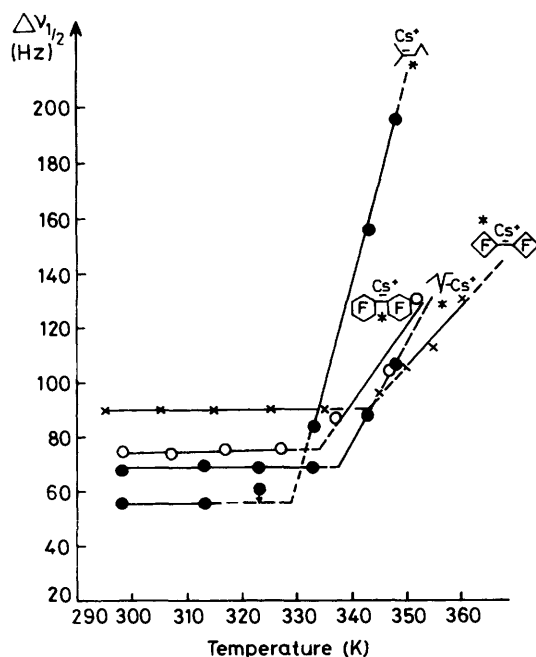
Figure 2. Variable temperature linewidths Cs⁺ carbanion solutions

* Starred positions were used for the data (all unmarked positions bonded to F)

processes.[14] In a different sense, ion (3a) is stabilised by the angle strain that would be reintroduced in forming compound (3).

The fact that fluoride ion exchange does occur rapidly in the caesium salts at various temperatures means that they can also act as fluoride ion sources. Indeed, we have already referred to the fact that the salt (4a) acts as a fluoride ion donor to acetyl chloride. However, these solutions are then effective sources of *soluble* fluoride and we demonstrated the potential utility of these systems in reaction with perfluorocyclopentene (19) (Scheme 2). A dimer (8) was formed readily at 70 °C (a
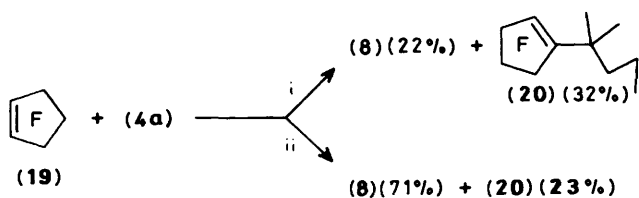
Scheme 2. *Reagents:* i, tetraglyme, room temp.; ii, tetraglyme, 70 °C. All unmarked bonds to F

temperature at which fluoride ion exchange occurs rapidly) as the main product, whereas a control experiment using finely divided caesium fluoride afforded no detectable conversion into compound (8) under the same conditions. At 20 °C, reaction as a carbanion predominated giving compound (20) as the main product. Also, use of these solutions as effective bases is possible[15] and further work in this area is proceeding.

The carbanions shown in Table 1 now provide an excellent probe for comparing the effectiveness of counter ions. Indeed, recent work carried out at the Du Pont Company, while these studies were in progress, described the use of (Me₂N)₃S⁺-(Me₃SiF₂) (*i.e.* TAS-F) (21)[16] as a soluble fluoride source, and the isolation of several interesting TAS salts.[12,17] Indeed,

carbanions derived from compounds (8), (9), and (15) were described,[16] which we have been unable to observe using CsF. The conclusion has been drawn that carbanions derived from TAS are more stable than those of caesium, but this is an over-simplification.
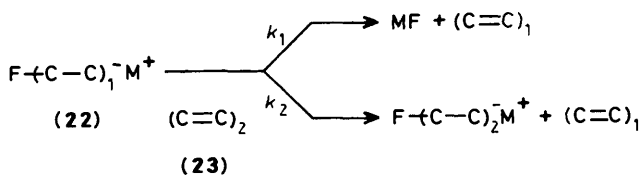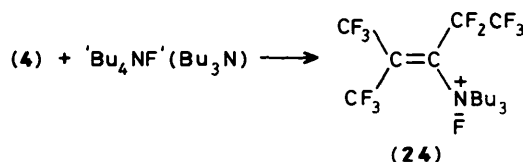

Figure 3.

There are two ways in which a carbanion (22) can lose fluoride ion; either to the counter ion (k_1) or to a third molecule, *e.g.* an alkene (23)(k_2). In the absence of an excess of alkene, then it is reasonable to assume that the TAS salts are much more reluctant to undergo elimination (k_1 to form S–F bonds) than the caesium salts are to form caesium fluoride. However, exactly the *converse* is true for exchange of F⁻ with alkene (k_2). This is clear from the fact that TAS–Me₃SiF₃ (21) has the unusual property of taking into solution more than one molar equivalent of the F–alkene. For example, with compound (4), if excess of the F–alkene is present in solution, then the n.m.r. spectrum of *e.g.* (4a) shows rapid fluoride ion exchange (k_2) between carbon and excess of alkene, with consequent considerable line-broadening of signals associated with fluorine atoms at positions β to the charge. This is not the case with the caesium salts under the same conditions.

We have attempted to compare the effect of other counter ions, *e.g.* K⁺, Ph₄P⁺,[18] and Bu₄N⁺,[19] as the use of the corresponding fluorides of the last two systems has received significant attention in recent years, for preparative processes. We have found that potassium salts are significantly less stable than the corresponding caesium salts but we were unable to even generate stable carbanions using Ph₄PF and compound (4), whereas the latter forms anions very readily indeed with Cs and TAS as counter ions. With Bu₄N, the situation is more complex: it is claimed that Bu₄NF·3H₂O can be dehydrated simply by prolonged exposure to high vacuum at 40—45 °C,[20] but, in our hands, using these and other conditions, continuous weight loss occurs from the system as long as exposure to high vacuum is maintained. That the 'dehydrated' salt contains Bu₃N is demonstrated by the fact that reaction with compound (4) gave a product of nucleophilic displacement (24).

Only the caesium salts are sufficiently stable so that k_2 (Figure 3) is slow on the n.m.r. timescale. Therefore, it is considered reasonable that competition experiments with this system do determine the relative stabilities of the carbanions involved. Clearly, there are potential limitations to this procedure in that, in principle, the position of equilibrium (see below) between perfluorinated alkenes could be determined principally by solubility in the medium. We have conducted various competition experiments and examined changes in the systems over very long periods of time, and the results suggest that solubility is an important factor. This is clear because

Table 2.

Alkene A (g, mmol)	Alkene B (g, mmol)	CsF (g, mmol)	Tetra-glyme (ml)	Time (days)	Carbanions (%A)	(%B)
(4)	(5)					
0.102, 0.34	0.102, 0.34	0.0507, 0.33	0.6	0.3	45	55
				7	48	52
				30	47	53
(4)	(3)					
0.069, 0.23	0.097, 0.30	0.0337, 0.22	0.35	0.3	5	95
				7	35	65
				30	33	67
(5)	(3)					
0.087, 0.29	0.123, 0.38	0.0432, 0.28	0.50	0.3	14	86
(4)	(7)					
0.078, 0.26	0.136, 0.26	0.0348, 0.23	0.35	0.3	98	2
				7	98	2
				30	98	2
(4)	(6)					
0.086, 0.28	0.145, 0.29	0.0429, 0.28	0.50	0.3	100	0
				7	100	0
				30	100	0

Table 3.

Carbanion	Alkene (g, mmol)		CsF (g, mmol)	Tetraglyme (ml)	Time (days)
(3a)	(3)	0.5, 1.5	0.3, 1.9	0.5	3
(3a)	(3')	1.7, 5.2	0.7, 4.6	4	3
(7a)	(7)	2.3, 4.4	0.9, 5.9	3	14
(2a)	(2)	5.3, 26.5	4.2, 27.7	7	3
(4a)	(4)	2.5, 8.3	1.9, 12.5	5	4
(5a)	(5)	2.7, 8.9	1.5, 10.0	4	4
(6a)	(6)	4.5, 9.0	1.7, 11.2	5	11

some of the systems were slow to reach equilibrium but the results shown in Table 2 are those after periods when no detectable further change in equilibrium was apparent. From this we obtain the following stability order of carbanions:

$$F(C-C)_1^- + (C=C)_2 \rightleftharpoons (C=C)_1 + F(C-C)_2^-$$
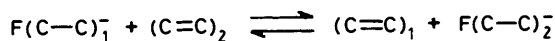
(3a) ≥ (5a) ≈ (4a) ≥ (7a) and (6a). It is worth emphasising the fact that the high threshold temperatures for fluoride ion exchange from ion (6a) (Figure 2) are a consequence of a kinetic barrier to elimination from (6a), rather than its thermodynamic stability. The remarkable stability of (3a) is, as we indicated earlier, one further manifestation of the high level of angle strain in the perfluorinated alkene (3).

These studies are a further illustration of the remarkable degree to which the analogy between the role of fluoride ion and that of the proton, may be taken.

Experimental

Details of instrumentation have been described previously.[21] High field [19]F n.m.r. spectra were recorded on a Bruker AC250 operating at 235.3 MHz. [19]F N.m.r. shifts are quoted relative to CFCl3 with upfield taken as positive. Caesium fluoride was dried by heating under high vacuum and periodic grinding in a glove bag. All manipulations with caesium fluoride and TAS-F were made using dried apparatus under a current of dry nitrogen.

Perfluoro-t-butylcaesium.—(CAUTION: **Perfluoroisobutene is highly toxic by inhalation. This material should only be manipulated in a well ventilated fumes hood. Workers using this compound in our laboratory wear positive pressure breathing apparatus.**) A flask was pre-charged with caesium fluoride (4.2 g, 27.7 mmol) and tetraglyme (7 ml) and cooled in liquid air. Perfluoroisobutene (5.3 g, 26.5 mmol) was transferred *in vacuo* to the flask and the resulting mixture stirred at room temperature for 36 h. Remaining caesium fluoride was removed by filtration and the resulting clear homogeneous liquid was shown to be a solution of *perfluoro-t-butylcaesium* (2a); δ_F 45.8 (sharp s, CF3); δ_C 40.7 (decuplet, *J* 39 Hz, C$^-$) and 127.8 p.p.m. (q, *J* 264 Hz, CF3). We acknowledge help from Mr. T. F. Holmes during this experiment.

Isolation of Solid Perfluoro-t-butylcaesium (2a).—Cooling the solution of compound (2a) to *ca.* 15 °C (tap water) caused rapid growth of large needles which, in 2 min, caused almost complete solidification of the mixture. Warming the resulting mixture caused rapid complete redissolution. This process could be repeated many times.

The tube was opened and the solid isolated by pipetting residual solvent under a nitrogen plume. After the mixture had stood at room temperature for about 0.5 h, tetraglyme was added which readily redissolved the solid to give a [19]F n.m.r. spectrum indistinguishable from the carbanion (2a).

Other caesium perfluorocarbanion solutions were generated in a similar manner by adding liquid perfluorinated alkenes (2)—(7) to a mixture of caesium fluoride and tetraglyme as detailed in Table 3.

Perfluoro-t-butylcaesium (2a) *with Bromine.*—Excess of bromine was added dropwise to a portion of a stirred solution of the carbanion (2a) and caused immediate precipitation of a white solid and formation of a colourless lower layer. The upper layer was shown ([19]F n.m.r.) to contain no detectable concentration of fluorocarbon and the lower layer was shown to be 2-bromononafluoro-2-methylpropane (pure by g.l.c.); δ_F 68.3 (s, CF3) by a comparison of [19]F n.m.r. data with literature values.[22]

Other trapping reactions were performed in the same way. [19]F N.m.r. data for the bromo derivatives are contained in Table 1.

Perfluoro-2-methylpentan-2-ylcaesium (4a) *with bromine.* Reaction yielded *perfluoro-2-bromo-2-methylpentane* (pure by g.l.c.) *m/z* (e.i.) 281 (*M* — F2Br); $v_{max.}$ 1 336, 1 240, 1 121, 959, 923, 822, 738, and 712 cm^{-1}.

Perfluoro-3-methylpentan-3-ylcaesium (5a) *with bromine.* Reaction yielded *perfluoro-3-bromo-3-methylpentane* (pure by g.l.c.) (Found: Br, 20.6; F, 61.0. C6F13Br requires Br, 20.0; F, 61.9%); *m/z* (n.i.) 319 (*M* — Br, 100%); $v_{max.}$ 1 210br, 1 082, 745, and 719 cm^{-1}.

Perfluoro-2-methylpentan-2-ylcaesium (4a) *with methyl iodide.* Reaction yielded 2-*methylperfluoro-2-methylpentane* (Found: C, 25.2; H, 1.0. C7H3F13 requires C, 25.2; H, 0.9%); *m/z* (e.i.) 315 (*M* — F); δ_H 2.0 (s, CH3); δ_F 69.2 (6 F, t, *J* 11 Hz, CF3CCH), 82.7 (3 F, t, *J* 11 Hz, CF3CF2), 111.8 (2 F, m, CF2CF3), and 124.7 (2 F, m, CF2CCH); $v_{max.}$ 1 340, 1 240, 1 088, 932, 732, and 705 cm^{-1}.

Perfluoro-3-methylpentan-3-ylcaesium (5a) *with methyl iodide.* Reaction yielded 3-*methylperfluoro-3-methylpentane* (Found: C, 25.3; H, 0.7; F, 74.3. C7H3F13 requires C, 25.2; H, 0.9; F, 73.9%); δ_F 68.0 (3 F, m, CF3CMe), 81.5 (6 F, m, CF3CF2), and 113.8 (4 F, m, CF2); δ_H 1.8 (br s, CH3); *m/z* (e.i.) 231 (*M* — C2F4H3); $v_{max.}$ 1 230, 1 096, 1 010, 733, and 712 cm^{-1}.
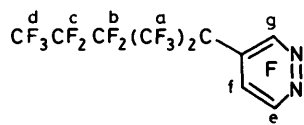
Perfluoro-2-methylpentan-2-ylcaesium (4a) *with allyl iodide.* Reaction yielded 2-*prop-2'-enylperfluoro-2-methylpentane* (Found: C, 29.7; H, 1.1; F, 69.0. C9H5F13 requires C, 30.0; H, 1.4; F, 68.6%); *m/z* 360 (*M*$^+$); δ_F 65.0 (6 F, t, *J* 11 Hz, CF3CCH2), 82.0 (3 F, t, *J* 14 Hz, CF3CF2), 108.6 (2 F, q, *J* 11 Hz,

CF_2CCH_2), and 124.7 (2 F, m, CF_2CF_3); δ_H signals between 1.2 and 4.0 p.p.m. unassigned; $v_{max.}$ 1 312, 1 240, 1 108, 872, 738, and 712 cm⁻¹.

Perfluoro-2-methylpentan-2-ylcaesium **(4a)** *with benzyl bromide.* Reaction yielded 2-benzylperfluoro-2-methylpentane (pure by g.l.c.) by a comparison of spectra with literature data.[23]

Perfluoro-4-ethyl-3,4-dimethylhexan-3-ylcaesium **(6a)** *with boron trifluoride–diethyl ether.* Reaction was conducted as above and the resulting lower layer was shown (g.l.c.) to be a single component and confirmed as perfluoro-4-ethyl-3,4-dimethylhex-3-ene **(6)** by a comparison of ¹⁹F n.m.r. data with authentic material.

Perfluoro-2-methylpentan-2-ylcaesium **(4a)** *with Tetrafluoro-pyridazine* **(16)**.—A solution of the perfluoro-2-methylpentan-2-yl anion **(4a)**, formed by stirring a mixture of caesium fluoride (6.2 g, 41 mmol), perfluoro-2-methylpent-2-ene **(4)** (8.0 g, 26.7 mmol), and tetraglyme (19 ml) at room temperature for 48 h (until no liquid lower layer was evident), was added to tetra-fluoropyridazine **(16)** (2.0 g, 13.1 mmol) and the resulting mixture stirred at room temperature for 72 h. Volatile material (6.3 g) was transferred *in vacuo* to a cold trap and shown (g.l.c., Col. 0) to consist of three components. These were shown (mass spectroscopy, g.l.c.) to be perfluoro-2-methylpent-2-ene **(4)** (29%), tetrafluoropyridazine **(16)** (35% recovered) (by a comparison of g.l.c. retention times) and a compound that was isolated by preparative scale g.l.c. and identified as *perfluoro-4-(2'-methylpentan-2-yl)pyridazine* **(17)** [83% based on consumed **(16)**] (Found: C, 26.3; F, 67.7; N, 6.6. $C_{10}F_{16}N_2$ requires C, 26.6; F, 67.2; N, 6.2%); *m/z* (c.i.) 453 (*M* + 1, 100%); δ_F 59.7 (6 F, m, a), 63.4 (1 F, m, g), 82.9 (3 F, t, *J* 17 Hz, d), 97.7 (1 F, dd, *J* 32 and 23 Hz, e), 105.0 (2F, m, b), 107.2 (1 F, m, f), and 124.3 (2 F, m, c); $v_{max.}$ 1 455, 1 400, 1 332, 1 230, 832, 820, and 720 cm⁻¹.

$$\overset{d}{CF_3}\overset{c}{CF_2}\overset{b}{CF_2}\overset{a}{(CF_3)_2}C$$

(17)

Similar reactions were conducted at temperatures between 20 and 50 °C but no further reaction could be detected by g.l.c./m.s.

Perfluoro-2-methylpentan-2-ylcaesium **(4a)** *with Acetyl Chloride.*—Excess of acetyl chloride was added to the perfluoro-2-methylpentan-2-yl anion **(4a)** in tetraglyme. The mixture became warm and, upon subsequent cooling, the lower layer was removed and shown to be perfluoro-2-methylpent-3-ene **(4)** by a comparison of ¹⁹F n.m.r. spectra with those of authentic material. The upper layer was shown (¹⁹F n.m.r.) to contain acetyl fluoride, δ_F −49, by a comparison of the ¹⁹F n.m.r. spectrum with literature data.[24]

Perfluoro-2-methylpentan-2-ylcaesium **(4a)** *with Perfluoro-cyclopentene* **(19)**.—Perfluorocyclopentene **(19)** (5.0 g, 23.5 mmol) was added to a solution of the perfluoro-2-methylpent-2-yl anion **(4a)**, formed by stirring a mixture of perfluoro-2-methylpent-2-ene **(4)** (6.0 g, 20.0 mmol) and caesium fluoride (3.1 g, 20.4 mmol) in tetraglyme (20 ml), and the resulting mixture was stirred at room temperature for 4 days. Volatile material (8.2 g) was transferred *in vacuo* to a cold trap with warming and shown to contain several components. These were identified as perfluoro-2-methylpent-2-ene **(4)** (30%) by a comparison of mass spectra with authentic material, perfluoro-cyclopentene **(19)** (5% recovered) by a comparison of mass spectra with authentic material, a compound, $C_{10}F_{16}$, and two isomeric compounds, $C_{11}F_{20}$. Preparative scale g.l.c. was used to isolate the compound, $C_{10}F_{16}$, and the major

component, $C_{11}F_{20}$, and these were identified as: (a) perfluoro-bicyclopentylidene **(8)** [22% based on **(19)** consumed] (Found: C, 28.4. Calc. for $C_{10}F_{16}$: C, 28.3%); by a comparison of spectra with authentic material; and (b) *perfluoro-(2'-methylpentan-2-yl)cyclopentene* **(20)** [32% based on **(19)** consumed] (Found: C, 25.5; F, 74.7. $C_{11}F_{20}$ requires C, 25.8; F, 74.2%); *m/z* (e.i.) 493 (*M* − F); δ_F 63.0 (6 F, dt, *J* 20 and 10 Hz, d), 72.7 (1 F, m, e), 83.3 (3 F, t, *J* 13 Hz, a), a broad resonance centred at 107.7 integrating to 4 F, assigned to f and h, 124.3 (2 F, m, c), 125.5 (2 F, d, *J* 18 Hz, b), and 136.0 (2 F, s, g); $v_{max.}$ 1 675, 1 394, 1 344, 1 240, 1 175, 1 125, 1 092, 1 021, 963, 741, and 732 cm⁻¹.
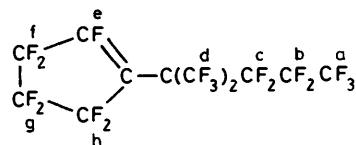
(20)

A similar reaction with perfluorocyclopentene **(19)** (7.0 g, 33.0 mmol), perfluoro-2-methylpentan-2-ylcaesium (2.4 mmol) in tetraglyme (6.5 ml) conducted at 70 °C for 72 h afforded perfluorocyclopentene **(19)** (54% recovered), perfluorobicyclo-butylidene **(8)** [71% based on **(19)** consumed] and perfluoro-(2'-methylpentan-2-yl)cyclopentene **(20)** [23% based on consumed **(4a)**] by a comparison of g.l.c. retention times and ¹⁹F n.m.r. spectra with authentic materials (see earlier).

Perfluorocyclopentene **(19)** was recovered unchanged after being stirred with an excess of finely ground caesium fluoride in tetraglyme at 70 °C for 72 h.

Perfluoro-2-methylpentan-2-ylcaesium **(4a)** *with Benzyl Bromide at 80 °C.*—A flask was charged with benzyl bromide (2.5 g, 14.7 mmol) and heated with stirring to 80 °C. A solution of the perfluoro-2-methylpentan-2-yl anion **(4a)**, formed by stirring a mixture of perfluoro-2-methylpent-2-ene **(4)** (3.8 g, 12.7 mmol) and caesium fluoride (1.95 g, 12.8 mmol) in tetraglyme (8 ml) at room temperature for 48 h, was added slowly and stirring continued for *ca.* 10 min. The lower layer (5.3 g) thus formed was removed and shown (¹⁹F n.m.r.) to contain 2-benzylperfluoro-2-methylpentane (see earlier) and perfluoro-2-methylpent-2-ene **(4)** in the ratio 8:2. The upper layer was shown to contain benzyl fluoride, δ_F 207.6, by comparison of ¹⁹F n.m.r. spectra with literature data.[22]

General Procedure for Generation of TAS Perfluorocarbanion Salts.—Unless otherwise stated, a calculated slight excess of a known concentration of TAS–F in MeCN was added in an air tight syringe to the required alkene in a pre-dried n.m.r. tube. After being shaken for 10 min at room temperature, the resulting solution was examined by ¹⁹F n.m.r. spectroscopy. The solutions could be stored for weeks at room temperature provided moisture was rigorously excluded but some decomposition was sometimes observed after this period. The details are given in Table 4.

Table 4.

Alkene (g, mmol)		TAS–F (g, mmol)	MeCN (ml)
(4)	0.15, 0.50	0.30, 1.1	0.5
(5)	0.19, 0.63	0.30, 1.1	0.5
(3) **(3')**	}0.16, 0.49	0.16, 0.58	0.5
(6)	0.51, 1.0	0.37, 1.3	0.8
(8)	0.38, 0.90	0.60, 2.1	0.6

Table 5.

Alkene (4) (g, mmol)	CsF (g, mmol)	(18) (g, mmol)	Solvent (ml)
1.8, 6.0	1.0, 6.6	1.9, 5.9	DMSO, 2.5
2.0, 6.7	0.9, 5.9	2.1, 6.5	Tetraglyme, 3
1.3, 4.3	0.7, 4.6	1.3, 4.0	MeCN, 3

Tetrabutylammonium Fluoride with Perfluoro-2-methylpent-2-ene (**4**).—Commerical tetrabutylammonium fluoride trihydrate (Aldrich) (3.7 g, 11.2 mmol) was placed in a dry flask and stirred and heated for 48 h at 40—45 °C under 0.01 mmHg. During this time the sample had liquefied into a straw-coloured syrup and had been reduced to 3.1 g in weight. Acetonitrile (10 ml) and compound (**4**) (2.1 g, 7 mmol) were added and the resulting mixture was stirred at room temperature for 1 h. The resulting homogeneous solution was removed and found to give a broadened ^{19}F n.m.r. spectrum. Dry nitrogen was blown across the solution surface for 3 h and the resulting mixture found (^{19}F n.m.r.) to contain a compound that was deduced to be the perfluoroalkenylammonium derivative (**24**) as the only detectable species, by comparison of the spectrum with literature values[25] for an analogous triethylammonium derivative; δ_F 48.0 (3 F, m, a), 54.0 (3 F, q, b), 80.3 (3 F, s, c), and 116.3 (2 F, q, d).

(24)
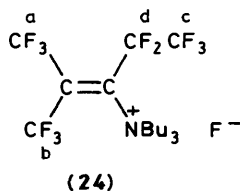
Tetraphenylphosphonium Fluoride with Perfluoro-2-methylpent-2-ene (**4**).—A solution of tetraphenylphosphonium fluoride (1.1 g, 3.1 mmol) in acetonitrile (2 ml) was added to perfluoro-2-methylpent-2-ene (**4**) (0.9 g, 3.0 mmol) with stirring. The resulting yellow solution gave a complicated ^{19}F n.m.r. spectrum not consistent with the anion (**4a**).

Generation of Fluorocarbanions using Cryptand (**18**): *General Procedure.*—A mixture of the alkene (**4**), caesium fluoride, the cryptand (**18**), and solvent were stirred at room temperature for *ca.* 24 h. After being allowed to stand for 0.5 h, the coloured upper layer was removed and examined by ^{19}F n.m.r. Quantities are contained in Table 5.

Variable Temperature N.M.R. Studies: General Procedure.— Unless otherwise stated, homogeneous fluorocarbanion solutions contained in pre-dried n.m.r. tubes were placed in the pre-shimmed Bruker AC250 (235 MHz) instrument and the spectra accumulated at 10 °C intervals above ambient temperature. Equilibration time (0.5 h) was allowed before the spectral aquisition. The peak widths (Hz) at half height ($\Delta v1/2$) were measured for resonances adjacent to the charge centre and a graph of temperature *vs* $\Delta v1/2$ plotted. The threshold temperatures for the onset of line broadening were then determined from line breaks on the graphs.

Competition Experiments: General Procedure.—A small quantity of dry caesium fluoride was carefully introduced into a dry n.m.r. tube and weighed. Equal molar quantities of each

alkene corresponding to the amounts of caesium fluoride were introduced into the tube by syringe. Tetraglyme (1 ml per 0.8 g CsF) was added to the tube and the resulting mixture agitated efficiently for the required time. Simple ^{19}F n.m.r. analysis of the solvent layer afforded the ratio of the carbanions in solution.

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