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REACTIONS INVOLVING FLUORIDE ION. PART 26 [1] NITRANIONS FROM PERFLUOROAZACYCLOHEX-ENE AND -DIENE DERIVATIVES*

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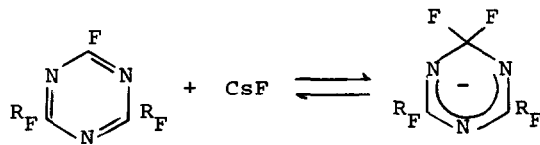
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SUMMARY

The anion generated by addition of CsF to perfluoroazacyclohexene is very stable in sulpholane. Reaction of CsF with perfluoro-4-isopropylazacyclohexa-1,4-diene gives a less-stable anion and its behaviour with temperature is described.

INTRODUCTION

In pursuing an analogy that can be drawn between proton-induced reactions of hydrocarbons and fluoride-ion induced reactions of fluorocarbons, as described earlier in this series, we observed some relatively long-lived fluorinated carbanions [2] and we now report studies on observable nitranions generated from azacyclohexene derivatives. Earlier workers have described nitranion salts of the form $(CF_3)_2N^-M^+$ ($M = K$ or Cs) [3,4]; we have observed [5] σ -complexes (1) obtained from tri-

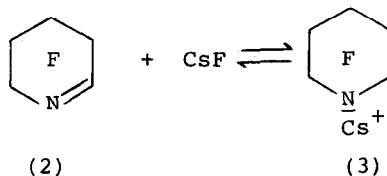
(R_F = F or perfluoroalkyl)

(1)

fluoro-1,3,5-triazine and perfluoroalkyl derivatives; and,

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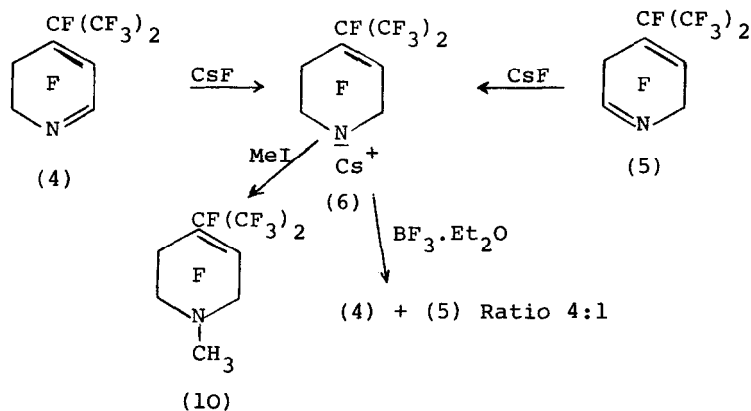
more recently, Banks and co-workers [6] described a nitranion (3), generated by reaction of perfluoroazacyclohexene (2) with caesium fluoride in acetonitrile.



RESULTS AND DISCUSSION

We have also generated the nitranion (3) but using sulpholan as solvent. It was reported [6] that, using acetonitrile as solvent, a heterogeneous system was obtained, giving relatively broad F-19 n.m.r. signals. In contrast, using sulpholan as solvent, we find that a homogeneous solution of (3) is obtained, giving sharp signals that did not significantly broaden with increase in temperature, up to 50°C. Our findings, therefore, confirm the earlier observations but highlight the fact that solvent can affect anion stabilities.

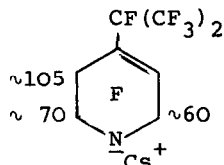
We have recently described [7] syntheses of the azacyclohexadiene derivatives (4) and (5) and the corresponding nitranion (6) may be generated from these systems using caesium



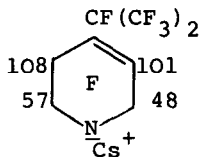
fluoride in sulpholan or acetonitrile. The anion (6) is formed readily and may be trapped with iodomethane. Also, the dienes, (4) and (5), are regenerated by reaction of (6) with boron

trifluoride etherate. This mixture of (4) and (5) is formed in the ratio of ca. 4:1 respectively and it is probable that (5) is produced because the benefits of conjugation in (4) are offset by greater eclipsing interactions in (4) than (5). The spectrum of the anion (6) in sulpholan was, surprisingly, not significantly different from the corresponding spectrum in acetonitrile, in spite of the effect of solvent noted for (3). However, the anion (6) is noticeably less stable than the anion (3), since exchange broadening in the F-19 n.m.r. spectrum of (6) is significant, even at room temperature. This lower stability of anion (6) may be attributable to the fact that introduction of a double-bond into the ring means that a degree of 'partial-eclipsing' occurs in (6), that is absent in (3). We have demonstrated earlier [2] that eclipsing effects are especially important in affecting the stability of carbanions derived from fluorinated cycloalkenes.

At -30°C , the F-19 n.m.r. spectrum of (6) in acetonitrile showed four sharp signals, (a) - (d), in addition to those arising from $(\text{CF}_3)_2\text{CF}$. Integrations demonstrated that (a) - (d) are related and that these correspond to seven fluorine atoms in the intensity ratios 2:2:1:2 i.e. δ_{F} (CFCl_3) 48.5(a), 57.7(b), 101.2(c), and 108.3(d) p.p.m. respectively. From the chemical shifts observed for (3), in comparison with (2), we may estimate the chemical shifts of some of the signals in (6), based on the values for (4) and using the observed shifts for (3). These are shown in (7) and, on this basis, the assignments shown in (8) seem reasonable. As the temperature was raised, exchange broadening occurred which was most significant with



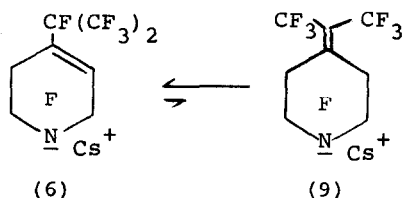
(7) (Estimated shifts)



(8) (Observed shifts)

signal (a). However, the increase in temperature was accompanied by the gradual appearance of minor signals at δ_{F} (CFCl_3) 54.4 and 104.0 p.p.m. (rel. ratio 1:1). Total

integrations indicated that this species did not retain 'tertiary' fluorine of the $(CF_3)_2CF$ group but did contain the trifluoromethyl groups. Therefore, the only explanation consistent with these data is the gradual formation of anion (9). At higher temperatures, exchange broadening of other



signals occurred but, under these conditions, the process was not reversible i.e. on cooling, anion (6) was not observed.

EXPERIMENTAL

Spectroscopic data were obtained using the following spectrometers: i.r., Perkin-Elmer 577; mass, V.G. Micromass 12B linked with g.l.c.; n.m.r., Brüker HX90E. Trichlorofluoromethane was used as external standard and upfield shifts (p.p.m.) are recorded as positive. G.l.c. was carried out using a Varian Aerograph instrument fitted with a gas density balance detector and a column containing 20% di-isodecylphthalate on Chromosorb P.

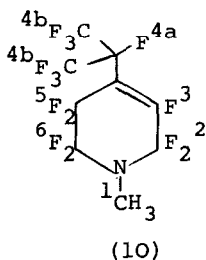
Perfluoro-1-azacyclohex-1-ene (2)

Compound (2) [8] (1.45 g, 5.9 m.mol) was added to a 10 ml round bottomed flask containing dry caesium fluoride (1.0 g, 6.6 m.mol) and sulpholane (5 ml). This mixture was stirred in a stoppered flask at room temperature for 38 h. Excess caesium fluoride was allowed to settle and an n.m.r. spectrum of the resultant homogeneous solution showed three fairly sharp signals at 62.3, 127.1 and 131.1 p.p.m., which are in agreement with those reported by Banks and co-workers [6], for the anion (3), taking into account the change of solvent and external reference. No significant amount of exchange broadening could be observed on increasing the temperature to 50°C.

Perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene (4)

Compound (4) [7] (2.3 g, 6.4 m.mol) was added to a 10 ml round bottomed flask containing dry caesium fluoride (1.1 g, 7.2 m.mol) and acetonitrile (5 ml). This was stirred at room temperature for 25 h. Excess caesium fluoride was allowed to settle and n.m.r. spectra of the resultant homogeneous solution were recorded at a range of temperatures between -30°C and 60°C . At -30°C fairly sharp ^{19}F signals were observed at 48.5 (Int. 2), 57.7 (Int. 2), 74.0 (Int. 6), 101.2 (Int. 1), 108.3 (Int. 2), and 183.9 (Int. 1) p.p.m. which were assigned to the anion (6). (A description of the behaviour of n.m.r. spectra at subsequent temperatures is given in the discussion section.) A sample of the solution after addition of BF_3 -etherate was shown to contain a 4:1 mixture of the dienes (4) and (5) by comparison of the n.m.r. spectrum with those of authentic samples [7]. Iodomethane (0.91 g, 6.5 m.mol) was added to the remainder of the solution and stirring continued for a further 24 h., followed by addition of water (5 ml). The lower fluorocarbon layer was then separated and transferred under vacuum from P_2O_5 , giving a colourless liquid (1.7 g). This was shown (g.l.c. 70°C) to contain one major component and a small amount of unreacted methyl iodide. Preparative g.l.c. gave N-methyl-1-aza-4-perfluoroisopropyl-2,2,3,5,5,6,6-heptafluorocyclohex-3-ene (10) (65%) (Found: C, 27.4; H, 0.6; F, 67.7; N, 4.0%; M^+ 391. $\text{C}_9\text{H}_3\text{F}_{14}\text{N}$ requires: C, 27.6; H, 0.8; F, 68.0; N, 3.6%; M, 391). ν_{max} 1723, 2970 cm^{-1} . δ_{F} 76.9 (3F, 4b or 4c-F), 77.3 (3F, 4b or 4c-F), 89.5 (2F, 2-F), 103.7 (2F, 6-F), 105.7 (1F, 3-F), 111.5 (2F, 5-F), and 186.1 (1F, 4a-F) p.p.m., and δ_{H} (ext Me_4Si) 1.90 p.p.m.

A similar experiment was carried out using sulpholane as solvent. N.m.r. spectra of this solution were shown not to be significantly different from those obtained using acetonitrile at corresponding temperatures.



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