Nucleophilic Substitution of Fluorinated C$_{60}$

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Highly fluorinated C$_{60}$ is extremely reactive towards nucleophilic substitution, which may proceed by a novel mechanism; attachment of a wide range of functional groups to the fullerene cage can thus be accomplished.

We recently showed that highly fluorinated C$_{60}$ cannot be used as a lubricant because it undergoes nucleophilic substitution by water, with generation of HF.[1] The reaction is relatively slow due to the hydrophobic nature of the fluorinated material. However, the addition of a cosolvent such as acetone or tetrahydrofuran (THF) results in an instantaneous and exothermic reaction. Fluorinated C$_{70}$ appears to behave similarly.

This reaction is unusual, not only because alkyl fluorides are generally very resistant to nucleophilic substitution, but because the cage structure of C$_{60}$ renders the S$_N$2 mechanism impossible, whilst the S$_N$1 mechanism would be extremely improbable on electronic grounds.

The ease of this substitution suggests that reaction of the fluoro derivatives with nucleophiles will be a useful route to preparation of a wide range of C$_{60}$ derivatives. The very limited availability of both C$_{60}$ and its fluorinated derivatives renders impracticable the isolation and characterisation of the many individual components of the reaction products at this time. However, it is appropriate to describe results which we have thus far obtained, especially since methoxydechlorination of chlorinated C$_{60}$ has just been reported.[2]

Pure C$_{60}$, prepared as described previously,[3] was fluorinated with fluorine gas during six weeks, after which time fluorine uptake effectively ceased. The product contained an average of approximately fifty fluorine atoms per C$_{60}$ molecule, as determined by combustion analysis. The ^{19}F NMR spectrum exhibited broad humps centred at δ -144.4 and -158.0, together with a sharp peak at δ -150.4 showing that the product was a mixture of C$_{60}$ derivatives with differing fluorine content (cf. ref. 4). No attempt was made to separate this mixture into components; reactions were carried out at the milligram or sub-milligram level. The loss of fluorine was primarily monitored by ^{19}F NMR spectroscopy and the formation of derivatives was confirmed where possible by IR and ^{1}H NMR spectroscopy of the worked-up products. The latter spectra are not entirely unambiguous because some of the products appeared to be water soluble and are therefore partially lost in the work-up procedure. Also, at the reagent levels used, traces of impurities in the solvents (HPLC grade or equivalent) become significant, and interfere with the spectra.

The reaction between fluorinated C$_{60}$ and traces of water in THF solutions containing increasing amounts of water at room temperature was monitored by ^{19}F NMR spectroscopy [Figs. 1(a–c)]. The ratio of the peak integral for fluorinated C$_{60}$ relative to that for HF decreases from 12.1 to 5.0 with increasing water content. (Owing to hydrogen bonding, the position of the HF peak varies from -196.7 to -170.7 with increasing water content.)

On allowing the sample shown in Fig. 1(c) to stand, a peak at δ -130 appeared gradually due to reaction of HF with the NMR tube to give SiF$_4$. Addition of sodium carbonate (after 48 h) lead to replacement of the HF peak (and most of the SiF$_4$ peak) by a peak at δ -122.6 due to sodium fluoride. This spectrum was unchanged during a further 92 h, at which point a few drops of sodium hydroxide were added producing the spectrum in Fig. 2. The ratio of fluorinated C$_{60}$ to fluoride is 2.0, showing that approximately one-third of the original fluorine content of the fluorinated C$_{60}$ has been lost. In a further experiment when a higher concentration of sodium carbonate was added to the fluorinated material in THF, the ratio of unreacted fluorinated C$_{60}$ to fluoride was 3.14, 2.12 and 1.86 after 0, 18 and 41 h, respectively, the final spectrum being almost identical to that in Fig. 2. The product of reaction with sodium carbonate is yellow and water soluble, the colour intensity being deeper in basic solutions than in acid.

The addition of sodium methoxide–methanol to fluorinated C$_{60}$ at room temperature was also monitored during 140 h, whence approximately 65% of the fluorine was replaced, with 20% being replaced almost immediately; Figs. 3(a) and (b) show the inital and final spectra. The ^{1}H NMR spectrum of the product showed a broad multiplet centred at δ 3.7, similar to that reported very recently[2] in methoxydechlorination of chlorinated C$_{60}$.

These reactions indicate that the rate of replacement of fluorine diminishes as the fluorine content of C$_{60}$ diminishes. The replacement rate also depends upon the reactivity of the nucleophile. Diethylamine, being a strong nucleophile, reacts very vigorously with the fluorinated material. Fig. 4 shows the ^{19}F NMR spectra of the fluorinated material in THF initially, and after 1 h following addition of diethylamine; the peak at δ -121.3 is due to Et$_2$NH$_2$$^+F^-$. The replacement of approximately 55% of the fluorine appeared to take place instantly, but the accumulation time of the spectrum was 1 h; after 12 h 65% of the fluorine had been replaced. By contrast, the reaction with acetic acid–sodium acetate was very slow, with only ca. 15% of the fluorine being replaced after 550 h. The IR
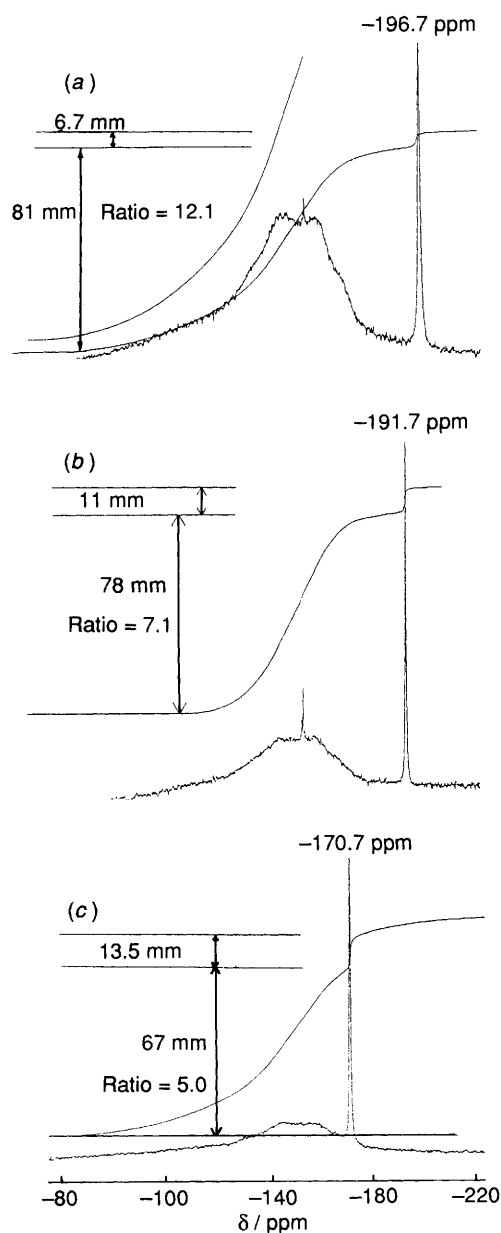
Fig. 1 ^{19}F NMR spectra of fluorinated C[60] in THF solutions of different water contents: (a) 'dry' THF; (b) normal THF; (c) 1-2 drops of water added

Fig. 2 ^{19}F NMR spectrum of fluorinated C[60] showing the effect of the addition of aq. Na₂CO₃ followed by NaOD at room temperature (see text)

Fig. 3 ^{19}F NMR spectra of fluorinated C[60] showing the effect of added MeOH–NaOMe at room temperature: (a) t = 0 h; (b) t = 140 h, integration sensitivity is twice that in (a)

spectrum of this product (Fig. 5) shows the C=O and C–O stretch bands, the latter as a shoulder on the side of the C–F stretching band. This, the first ester derived from C[60], had a discernible pleasant odour.

We have observed also very vigorous reactions between fluorinated C[60] and a variety of other nucleophilic reagents, such as methylmagnesium bromide, vinylmagnesium bromide, ethynylmagnesium bromide, phenyllithium, tris-(trimethylsilyl)methyllithium and lithium aluminium hydride. The latter reaction is especially vigorous (more so than with brominated C[60]) and results in total and instantaneous loss of fluorine. Moreover, only aqueous-soluble products are formed, and these (after addition of HCl) gave unidentified major and minor singlets at δ −154.7 and −153.8, respectively, together with a small broad peak at δ −161.7, due probably to HF. The reaction between fluorinated C[70] and methylmagnesium bromide resulted in an approximately 50% instantaneous loss of fluorine, and the ^{19}F NMR spectrum of the aqueous layer (after HCl work-up) gave singlets at δ −130 and −166.5, typical of a fluoride ion in the presence of HCl.
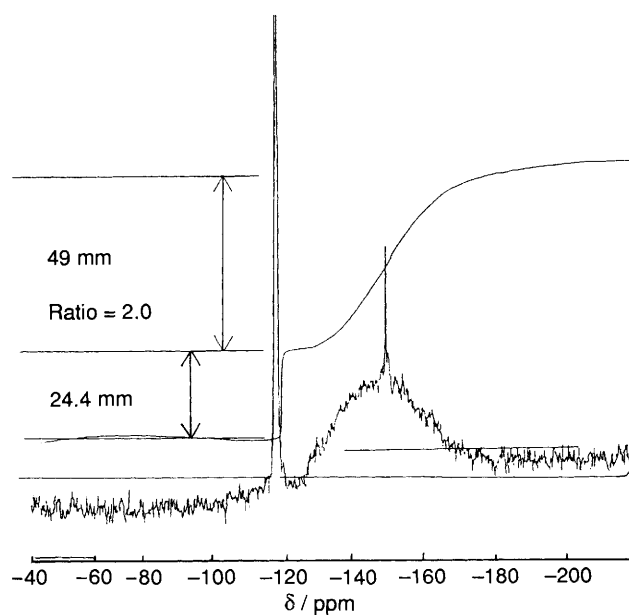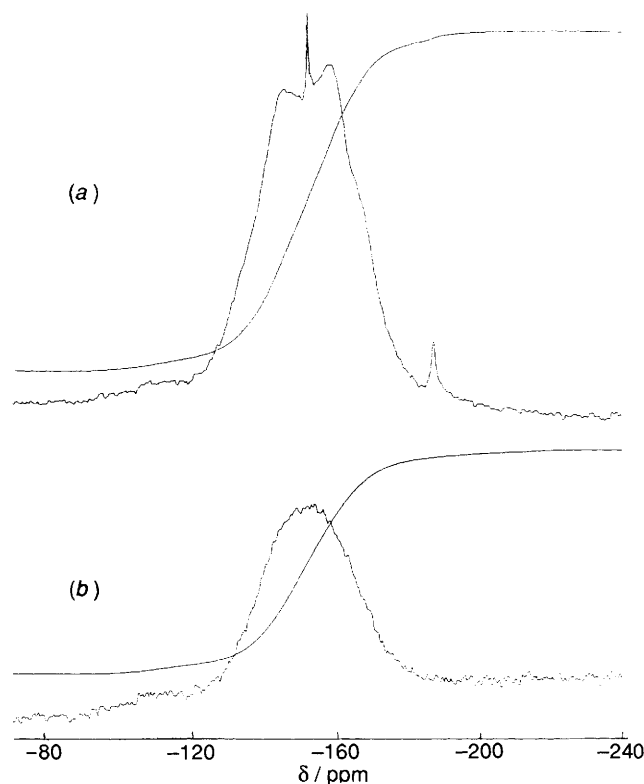
Direct replacement of fluorine by hydrogen through reaction with triethylsilane appeared not to occur, although hydrogen fluoride present in the solution was converted to triethylsilyl fluoride.

Two possible mechanisms for the substitution may be involved: the counterion for the nucleophile may first remove the fluorine, the resulting cation then reacting with the nucleophile in a step which may or not be rate determining. For molecules that are only partly fluorinated, nucleophilic
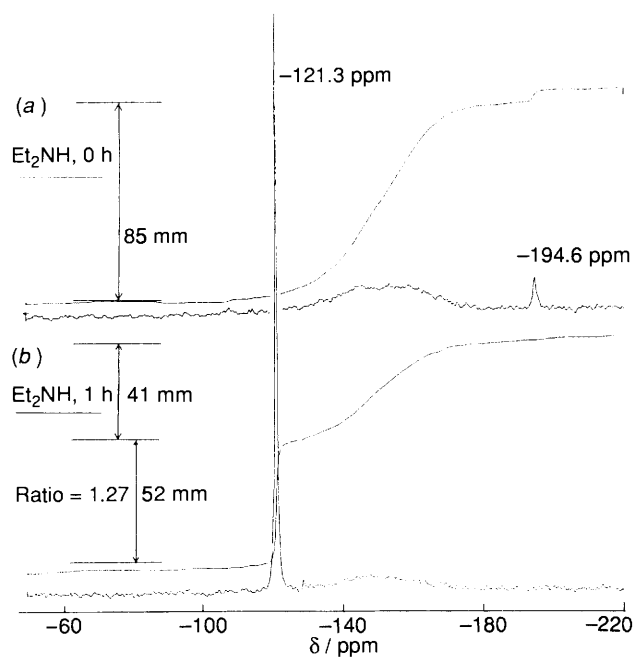
Fig. 4 ^{19}F NMR spectra of fluorinated C_{60} showing the effect of added diethylamine: (*a*) $t = 0$ h; (*b*) $t = 1$ h

Fig. 5 IR spectra of the product of reaction of fluorinated C_{60} with HOAc–NaOAc, $t = 550$ h

addition to a double bond may occur (C_{60} itself slowly reacts with methoxide ion[4] and other nucleophiles[5]) and could then be followed by loss of fluorine in the allylic position, with regeneration of the double bond in a new position; the double bond could gradually migrate around the whole cage as successive replacements of fluorine occur. If attack by the nucleophile is rate determining, then fluorinated C_{60} should be more reactive than brominated C_{60} which we find to be the case.

Lastly, our results account for the continuum (with masses greater than theoretical) obtained in mass spectra produced under fast atom bombardment (FAB) conditions.[6] Either alcohol or amine matrices will react rapidly with the fluorinated material, to give higher mass products.
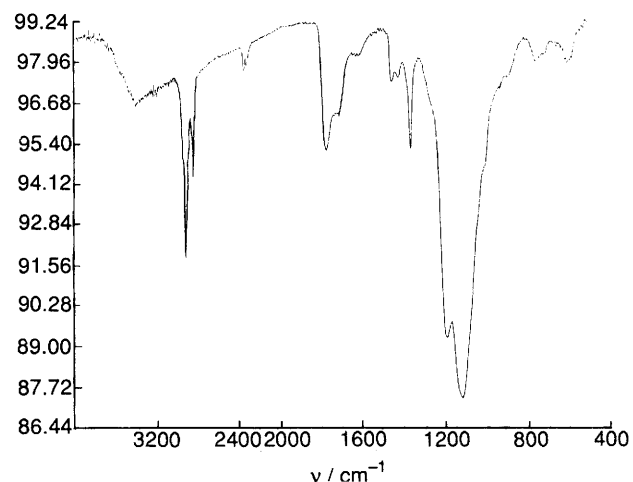
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