PERKIN 2

Formation of [18]trannulenes derived *via* Bingel reactions between $C_{60}F_{18}O$ isomers and $CHBr(CO_2Et)_2$ and between $C_{60}F_{18}$ and $CHX(CO_2R)_2$ (X = Br, Cl; R = Me, Et)

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Through extended S_N2' nucleophilic substitution of three fluorine atoms in two isomers of $C_{60}F_{18}O$ by alkyl halogenomalonate anions $^-CBr(CO_2Et)_2$, (obtained from diethyl bromomalonate in the presence of DBU) we have prepared and characterised the [18]trannulenes, $C_{60}F_{15}O[CBr(CO_2Et)_2]_3$. Likewise we have prepared [18]trannulenes by the reactions between $C_{60}F_{18}$ and either $^-CBr(CO_2Me)_2$ or $^-CCl(CO_2Et)_2$ (obtained from the corresponding esters **1**, **2** and DBU). The formation of the trannulenes from either **1** or **2** shows that the $CBr(CO_2Me)_2$ and $CCl(CO_2Et)_2$ substituents, though smaller than $CBr(CO_2Et)_2$ are still large enough to bring about the extended S_N2' substitution, rather than direct nucleophilic substitution. The products from the oxides show that oxygen does not inhibit trannulene formation either sterically or electronically. Each derivative has the brilliant emerald-green colour of the corresponding [18]trannulene prepared from $C_{60}F_{18}$ and diethyl bromomalonate, arising from the presence of bands at *ca.* 615 and 660 nm; minor variations in wavenumber and relative intensities occur according to the derivative. Under less forcing conditions, mono- and bis-substitution products were obtained from the more available symmetrical oxide and from the reaction of the chloro- and bromo-esters with $C_{60}F_{18}$.

Introduction

Recently we described the isolation and full characterisation of the first [18]trannulene (all-*trans* annulene), in which the overall variation in bond length in the annulene chain is only 0.013 Å. This compound was obtained by nucleophilic substitution of three fluorine atoms in the fluorofullerene $C_{60}F_{18}$ by bromomalonate moieties (produced from reaction with diethyl bromomalonate-DBU) giving $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (Fig. 1, X = Br, R = CO_2Et). The key to the *trans*-annulene formation is the bulk of the substituent, which is forced to occupy a site δ to the departing fluorine, the overall process being the first proven example of an extended S_N2' substitution in a fullerene.[1,2]

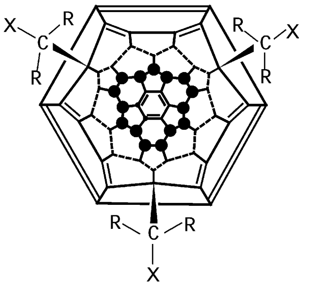

Fig. 1 Schlegel diagram of the structure of the [18]trannulene derived from $C_{60}F_{18}$ and diethyl malonate (R = CO_2Et, X = Br, ●; = F); the 18 π annulene chain is shown dotted.

The present work was undertaken with two aspects in mind. First we wished to see what the effect of oxygen in the cage structure (giving an oxahomofullerene, $C_{60}F_{18}O$) would be upon both the reaction and the UV spectrum. We had available small amounts of two such oxides from previous work, one symmetrical of 58 min retention time under our standard HPLC conditions (see the Experimental section) and one unsymmetrical of 44 min retention time.[3] Secondly we wished to see if employing a smaller substituent would enable the S_N2' mechanism to be retained. Accordingly two different esters were used in which: (i) the ethyl groups of diethyl malonate were replaced by methyls, (ii) bromine was replaced by chlorine.

The underlying interest in these compounds is in the preparation of suitable donor-acceptor assemblies, which is the most active area of current fullerene chemistry, as indicated by a plethora of recently published papers on this topic.[4] At present our work is focussed on exploring the extent of the reaction given the small quantities of $C_{60}F_{18}$ (<5 mg) currently available per experiment. Work is in hand to increase the amount of this fluorofullerene, so that a full range of spectroscopic properties can be explored on the most promising derivatives.

Experimental

The general procedures followed those which we have reported previously,[1,2] and were carried out using 1.5–4 mg of the fluorofullerenes. The products were isolated by HPLC (High Pressure Liquid Chromatography) using a Cosmosil Buckyprep (10 mm × 250 mm) column with elution by toluene at 4.7 ml min^{-1} or a Cosmosil 5 Pye column as stated. The latter column gives faster elution so that the retention times of the two oxides (see the Introduction) become 47 and 39 min, respectively. The trannulenes were isolated in sub-milligram quantities at the following retention times: 8.0 min (2 ml min^{-1}, 5 Pye), symmetrical $C_{60}F_{18}O$-diethyl bromomalonate; 7.6 min (2 ml min^{-1}, 5 Pye), unsymmetrical $C_{60}F_{18}O$-diethyl bromomalonate; 3.9 min ($C_{60}F_{18}$-diethyl chloromalonate); 3.4 min ($C_{60}F_{18}$-dimethyl bromomalonate). All of these eluents were recycled because of contamination from *bis*-substitution products and all had the brilliant emerald green colour characteristic of the trannulene

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structure. Mono- and bis-substitution products were isolated from the chloro ester with respective retention times of 7.8 min {fragment ions at 1043 amu [$C_{60}F_{17}$]; 1235 amu [$C_{60}F_{17}CCl(CO_2Et)_2$]} and 5.5 min {fragment ions at 1024 amu [$C_{60}F_{16}$]; 1217 amu [$C_{60}F_{16}CCl(CO_2Et)_2$]}. A mono-substitution product of 8.2 min retention time was obtained from the methyl bromo ester {fragment ions at 1043 amu [$C_{60}F_{17}$]; 1174 amu [$C_{60}F_{17}C(CO_2Me)_2$]} and one from the symmetrical oxide eluted at 7.8 min (5 Pye) {fragment ions at 1059 amu [$C_{60}F_{17}O$]; 1217 amu [$C_{60}F_{17}OC(CO_2Et)_2$]}. These derivatives were not processed further.

Mass spectra were run under EI conditions (70 eV) and ^{19}F NMR at 376.5 MHz.

Results and discussion

Trannulene derivatives of the oxahomofullerenes, $C_{60}F_{18}O$

The EI mass spectra. The mass spectra of both the symmetrical and unsymmetrical oxides gave fragmentation ions at 1497 and 1021 amu resulting from loss of $CBr(CO_2Et)_2$ and $[CBr(CO_2Et)_2]_3$, respectively, from $C_{60}F_{15}O[CBr(CO_2Et)_2]_3$ (Fig. 2); the peak at 1021 amu is thus due to $C_{60}F_{15}O$. This fragmentation behaviour parallels that found for the product obtained from reaction with $C_{60}F_{18}$.

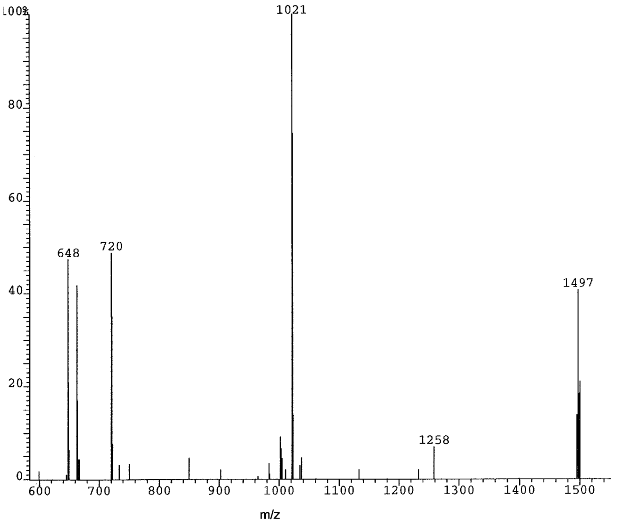

Fig. 2 EI mass spectrum (70 eV) for $C_{60}F_{15}O[CBr(CO_2Et)_2]_3$.

^{19}F NMR spectra. *(a) The symmetrical oxide.* The spectrum obtained from the symmetrical isomer (Fig. 3) comprises fifteen lines at δ_F −91.94 (1 F), −91.99 (1 F), −140.5 (1 F), −145.81 (2 F coincident), −146.08 (2 F, coincident), −148.03 (2 F, t, *J* 24 Hz), −148.12 (2 F, t, *J* 24 Hz), −148.92 (2 F, coincident), −159.16 (2 F, br s). The peaks appear mainly in almost coincident pairs showing that there is slight asymmetry in the structure (Fig. 4), attributable to restricted rotation of one of the substituents (most probably that nearest to the ether oxygen), evident also in the complexity of the ^1H NMR spectrum (not shown). The two most downfield lines are due to the fluorines adjacent to this oxygen and the single line at −140.5 ppm can be assigned to the fluorine on the pseudo C_s symmetry plane. In the absence of a 2 D spectrum (for which there was insufficient material) the other peaks cannot be assigned reliably, but in general for derivatives of $C_{60}F_{18}$, the six fluorines that are adjacent to the central aromatic ring appear more downfield than those that are one more bond further away.

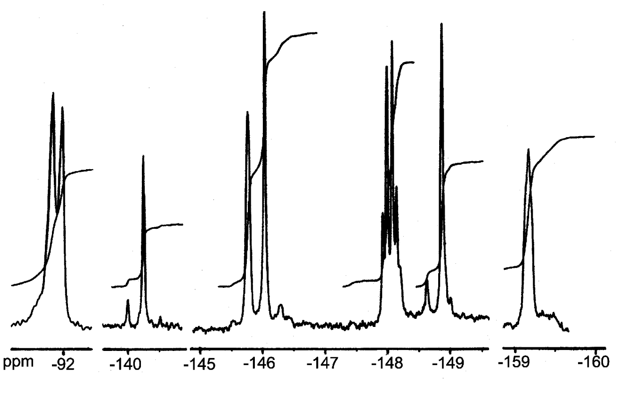

Fig. 3 ^{19}F NMR spectrum of the derivative of the C_s isomer of $C_{60}F_{18}O$.

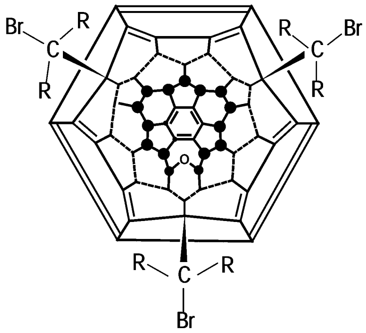

Fig. 4 Schlegel diagram of the trannulene derivative of the C_s isomer of $C_{60}F_{18}O$; (R = CO_2Et, ● = F); dotted lines indicate the 18 π band of electron delocalisation.

(b) The unsymmetrical oxide. The spectrum obtained from this isomer (Figs. 5 and 6) comprises fifteen lines at δ_F −92.9 (1 F, d, *J* 20 Hz), −99.2 (1 F, t, *J* 20 Hz), −138.88 (1 F, s), −141.24 (1 F, s), −142.21 (1 F, br s), −145.28 (1 F, br s), −146.05 (1 F, br s), −146.62 (2 F, s), −147.75 (1 F, br s), −148.14 (1 F, dd, *J* 19 and 8 Hz), −150.24 (1 F, d, *J* 24 Hz), −150.59 (1 F, dd, *J* 26 and *ca.* 7 Hz), −152.11 (1 F, dd, *J* 20 and *ca.* 7 Hz), −155.88 (1 F, t, 22 Hz). The two downfield peaks are due to the fluorines adjacent to oxygen and the similarity of their locations is consistent with the positions in the precursor oxide where the peaks also appear close together (at −74.6 and −77.9 ppm).

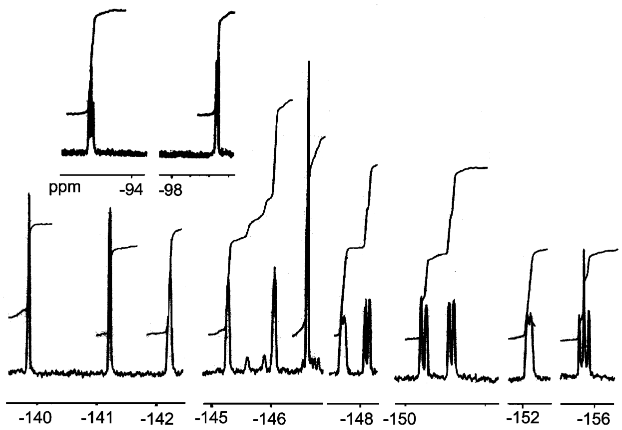

Fig. 5 ^{19}F NMR spectrum of the derivative of the unsymmetrical isomer of $C_{60}F_{18}O$.

Trannulene derivatives of $C_{60}F_{18}$

(a) $C_{60}F_{15}[CBr(CO_2Me)_2]_3$. The mass spectrum of the emerald green fraction that eluted at 3.4 min from the HPLC separation showed only the fragmentation ion at 1005 amu due to

Table 1 Values of λ_{max} for trannulenes derived from $C_{60}F_{18}$ and isomers of $C_{60}F_{18}O$

Precursor	Ester	λ_{max}/nm			
$C_{60}F_{18}$	$CHBr(CO_2Et)_2$	395	437	612	662
Absorbance		0.595	0.222	0.134	0.191
Rel. abs.		1	0.372	0.227	0.321
$C_{60}F_{18}O$ (sym.)	$CHBr(CO_2Et)_2$	395	441	620	666
Absorbance		0.49	0.16	0.10	0.12
Rel. abs.		1	0.337	0.204	0.245
$C_{60}F_{18}O$ (unsym.)	$CHBr(CO_2Et)_2$	396	440	613	663
Absorbance		0.61	0.215	0.13	0.18
Rel. abs.		1	0.352	0.213	0.295
$C_{60}F_{18}$	$CHBr(CO_2Me)_2$	393	438	610	660
Absorbance		0.24	0.076	0.048	0.071
Rel. abs.		1	0.315	0.20	0.295
$C_{60}F_{18}$	$CHCl(CO_2Et)_2$	392	436	612	660
Absorbance		0.174	0.059	0.34	0.051
Rel. abs.		1	0.340	0.195	0.293

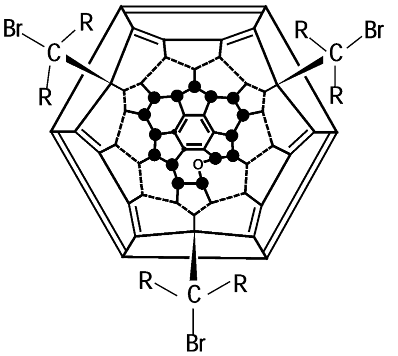

Fig. 6 Schlegel diagram of the trannulene derivative of the unsymmetrical isomer of $C_{60}F_{18}O$; (R = CO_2Et, ● = F); dotted lines indicate the 18 π band of electron delocalisation.

$C_{60}F_{15}$. Loss of either one or three of the malonate moieties is characteristic of the behaviour of the trannulenes. The ^{19}F NMR spectrum showed three lines at δ_F −136.73 (1 F), −143.80 (2 F) and −143.93 (2 F) *cf.* −136.72, −143.87, −143.96 for the corresponding ethyl derivative,[1,2] thereby confirming the trannulene structure and showing that this minimum size of the alkyl group is insufficient to cause a mechanistic change from the S_N2' substitution pattern. The small change in the size of the alkyl group has only a trivial effect on the chemical shifts of the fluoro addends, consistent with the distance between the alkyl groups and the cage surface. In due course we hope to produce derivatives with much larger alkyl and other groups in the malonate moiety for which significant interactions may occur.

(b) $C_{60}F_{15}[CCl(CO_2Et)_2]_3$. The mass spectrum of the emerald green fraction that eluted at 3.9 min from the HPLC separation showed fragmentation ions at 1391–1395 amu {$C_{60}F_{15}[CCl(CO_2Et)_2]_2$} and 1005 amu ($C_{60}F_{15}$). The ^{19}F NMR spectrum showed two lines at δ_F −136.68 (1 F) and −143.90 (4 F, two coincident lines). This confirmed the trannulene structure and showed that reduction of the size of the halogen is insufficient to divert the substitution mechanism from S_N2'. Calculations indicate that if the substituent becomes the size of CCl_3 then direct substitution should prevail.[2]

UV-VIS spectra

The spectrum for $C_{60}F_{18}$ (Fig. 7 and inset) shows main bands at 207, 218, 249 and 339 nm, a small shoulder at 269 nm and a weak band at 449 nm in the visible region. Fig. 8 is the spectrum for $C_{60}F_{15}[CBr(CO_2Me)_2]_3$, which by contrast shows pronounced bands at 393, 438, 610 and 660 nm. Table 1 collates the spectra for the four compounds reported here and for $C_{60}F_{15}[CBr(CO_2Et)_2]_3$, reported previously.

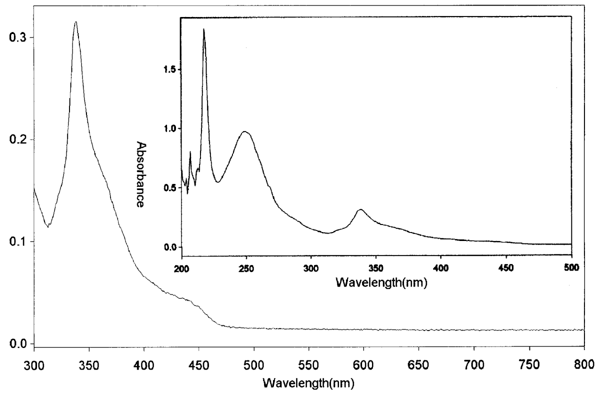

Fig. 7 UV-VIS spectrum for $C_{60}F_{18}$.

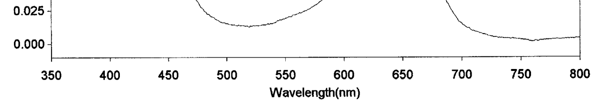

Fig. 8 UV-VIS spectrum for $C_{60}F_{15}[CBr(CO_2Me)_2]_3$.

The marked emerald-green colour of the corresponding [18]trannulenes prepared from $C_{60}F_{18}$ arises from the bands at *ca.* 615 and 660 nm. Between each derivative, there are minor variations in wavenumber and relative intensities. The most evident variation is the slight red-shift of the λ_{max} values for the oxide derivatives (especially the symmetrical oxide) compared to the others, which may represent some through-space interaction between the oxygen orbitals and the annulene belt.

The substitution mechanism

We have described the substitution mechanism in this and earlier papers[1,2] as S_N2'. Strictly speaking this symbolism refers to substitution at the allylic position and there appears to be no defining term for substitution at two carbons further removed from the leaving group (Fig. 9). Provisionally, we propose S_N2'' and refer also to the process as *extended* S_N2'.

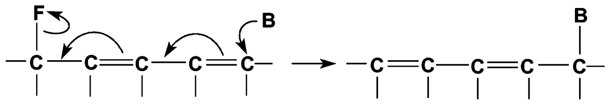

Fig. 9 Extended S_N2' (mechanism S_N2'') for substitution by a base **B** at a position δ to a fluorine in a fullerene.

We hope to explore further the spectroscopic and other properties of trannulenes derived from fluorofullerenes.

Acknowledgements

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