Isolation and characterisation of $C_{70}O$

PERKIN 2

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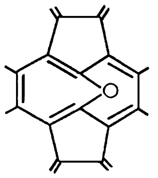
$C_{70}O$ has been isolated in *ca.* 0.5% yield by HPLC separation of the soot extract obtained from a novel arc-discharge reactor for fullerene production. The reactor (DC conditions) can be operated continuously for 24 h, employs a rotating cathode and an anode consisting of continuously-fed strips cut from a carbon sheet. The ^{13}C NMR spectrum of $C_{70}O$ shows that two isomers (1,2-epoxy[70]fullerene and 5,6-epoxy[70]fullerene) are present in a ratio of *ca.* 43 : 57 and all 37 peaks corresponding to each isomer have been identified. These are the first [70]fullerene derivatives in which 5,6-addition is preferred over 1,2-addition, this preference probably deriving from the considerable strain that accompanies bridging with a single atom; the greater curvature across the 1,2-positions compared with the 5,6-positions therefore disfavours the former. Differential polarisabilities of the electrons of the 1,2- and 5,6-bonds, a factor producing a variation in reactivity order according to the attacking reagent (but not considered hitherto in the context of fullerene chemistry) may also be significant. The epoxides are unstable towards EI mass spectrometry, in contrast to epoxides possessing additional addends, and this may reflect the reduced cage strain present in the latter.

$C_{70}O$ was first reported to be present in fullerene-containing soot by Diederich *et al.*, who identified it by its UV–VIS spectrum and electrospray mass spectrometry (which also showed a main peak at *m*/*z* 840 indicating extensive fragmentation).[1] An oxidoannulene structure (**1**) was conjectured, but was later argued to be unlikely since it placed double bonds in two pentagons, the alternative epoxide structure (**2**) being more probable.[2]



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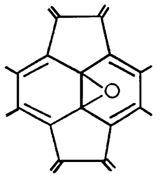

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Other workers have also reported the existence of $C_{70}O$,[3,4] and milligram quantities have been obtained very recently by oxidation of [70]fullerene (either by irradiation of a toluene solution containing rubrene or by the use of *m*-chloroperbenzoic acid as oxidant).[5] In this latter work, $C_{70}O$ was detected by laser-desorption time of flight mass spectrometry ([70]fullerene was again present through fragmentation); the 1,2- and 5,6-isomers [Figs. 1(*a*) and (*b*), respectively] were isolated in approximately equal amounts but the peaks in the ^{13}C NMR spectrum could not be resolved sufficiently to enable assignment to one or other isomer to be made. Nevertheless the data ruled out the oxidoannulene structure, as did the corresponding data for $C_{60}O$;[6] an oxidoannulene structure involving 1,4-bridging across the equator, which had been indicated by calculations to be a stable species,[7] was likewise ruled out.

In general, macroscopic amounts of $C_{70}O$ have been obtained only by oxidation of [70]fullerene, and not directly from fullerene-containing soot. A contributing factor may be the reported rapid degradation by alumina of $C_{60}O$[6] (and presumably also of $C_{70}O$), resulting in low yields using column chromatography with alumina. Given that $C_{70}O$ is readily formed from [70]fullerene by reaction with ozone,[4] then the combination of oxygen traces in the reactors, and the arc-discharge, should produce appreciable quantities of ozone and hence $C_{70}O$. Preliminary examination of soot produced by our arc-discharge reactor indeed indicated the presence of significant amounts of $C_{70}O$ (and also of $C_{60}O$). We decided therefore to process some soot extract entirely by high pressure liquid chromatography (HPLC).

A further reason for isolating $C_{70}O$ was the anomalous reported relative yields of the two isomers,[5] which is at variance with preferential addition across the 1,2-bond shown by all other reactions of [70]fullerene (Table 1). Comparison of our result

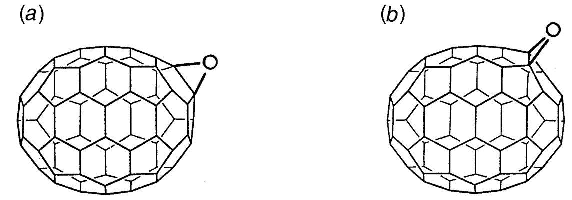

Fig. 1 Structures of (*a*) 1,2- and (*b*) 5,6-epoxy[70]fullerenes

Table 1 Isomer yields (%) in additions to [70]fullerene[a]

Addend	1,2	5,6	7,21	7,23	Ref.
$Ir(CO)Cl(PPh_3)_2$	100				8
HMe, HPh	100				9
$C(CO_2Et)_2$	100				10
H_2 (diimide)	96	4			11
H_2 (diborane)	67	33			12
Pyrazoline ($\rightarrow CH_2$)	87	13			13
4-Methoxyphenylisoxazoline	75	25[b]			14
Methylisoxazoline	67	33[b]			14
2,4,6-Trimethoxyisoxazoline	65	35			15
OsO_4	68	32			16
Me_5-cyclopentadiene	Mainly	(Detected)			17
N-Methylazomethine ylide	46	41[c]	13		18
Benzyne	43	12	12	34	19
$(MeO)_2$-*ortho*-quinodimethane	24	10	1.5		20

[a] An entry of 100% in a column indicates that only this isomer was detected. Yields in other reactions are scaled to a total yield of 100%.
[b] The ^{13}C NMR data are also consistent with this being the 7,23-isomer.
[c] The ^{1}H NMR data are also consistent with this being the 7.23-isomer.

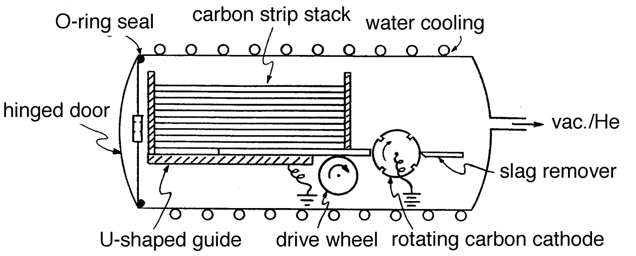

Fig. 2 Schematic (not to scale) of the fullerene soot-producing reactor

with that reported would also show if the isomer yields exhibited any appreciable dependence upon the oxidation method.

Experimental

The reactor employed is shown schematically in Fig. 2 (which is not drawn to scale). It consists of a water-cooled chamber, 450 mm long and 280 mm in diameter, one end of which is fitted with a hinge door equipped with an O-ring seal. The cathode consists of a slowly rotating notched carbon wheel (70 mm diameter) which passes a scraper to remove accumulated slag, thereby presenting a continually cleaned surface to the anode; the notches facilitate removal of the slag. The anode strips 7 mm wide × 3.5 mm thick × 400 mm long, made from compressed carbon sheet, are loaded into a hopper, 24 at a time. They are then gravity fed onto the U-shaped guide at the bottom of the hopper, the lowest strip being then slowly driven forward by the rotating drive, so as to maintain the preset electrode gap. Each strip takes 1 h to consume, and the whole charge lasts 24 h, yielding 100–200 g of soot; the atmosphere in the reactor was the customary 100 mmHg helium for fullerene-producing arc-discharge reactors. At the end of the run, the end door is opened, the soot removed and a new batch of strips inserted. Interestingly, and despite the moving cathode, the soot produced contained a small yield of nanotubes.

The soot was soxhlet-extracted with chloroform, and the resultant extract purified by HPLC without any preliminary removal of either [60]- or [70]-fullerene. The column employed was a 10 mm × 25 cm Cosmosil column with toluene eluent, operated at a 4.5 ml min^{-1} flow rate, followed by further purification using a 4.6 mm × 25 cm Cosmosil column operated at 1 ml min^{-1} flow rate. Under these latter conditions the retention times (min) of the fullerenes are: C_{60}, 7.8; $C_{60}O$, 8.85; C_{70}, 13.0; $C_{70}O$, 15.7; C_{76}, 18.2; C_{78}, 19.75 and 20.6; C_{84}, 24.95.

Results and discussion

The yield of recovered $C_{70}O$ indicated it to be *ca.* 0.5% of the fullerene extract, enabling us to obtain *ca.* 10 mg quantities. The high yield may be derived not only from the lack of column prepurification referred to above, but also to the fact that the carbon strips used to produce the fullerenes are made from compressed carbon sheet, which may contain substantial quantities of trapped oxygen. It may be anticipated, that with increased use of carbon column chromatography,[21] or HPLC, other workers will report the separation of significant quantities of $C_{70}O$. The elution of $C_{60}O$ between the much greater quantities of C_{60} and C_{70} means that only manual collection is possible and so was not atttempted at this stage.

^{13}C NMR spectroscopy

The ^{13}C NMR spectrum [125 MHz, CS_2–CD_3COCD_3, Cr(acac)$_3$] is shown in Fig. 3; the shoulder peak at 137.5 ppm is due to a trace of occluded toluene. The spectrum consists of three lines in the sp^3 region and 71 in the sp^2 region (two lines coincide at 144.51 ppm and the integrated intensity shows that one line comes from each isomer). Each of the 1,2- and 5,6-epoxy[70]fullerenes requires 37 lines in the spectrum, making a total of 74, as observed. The 1,2-isomer requires two lines in the sp^3 region, whereas the 5,6-isomer requires only one. These peaks appear at 92.42, 90.99 and 85.78 ppm, respectively [*cf.* 91.84, 90.41 and 85.20 ppm recorded by Smith *et al.*[5] who used deuteriochloroform as lock signal (which generally results in a more upfield set of resonances)]; the discrepancy is a constant 0.58 ppm.

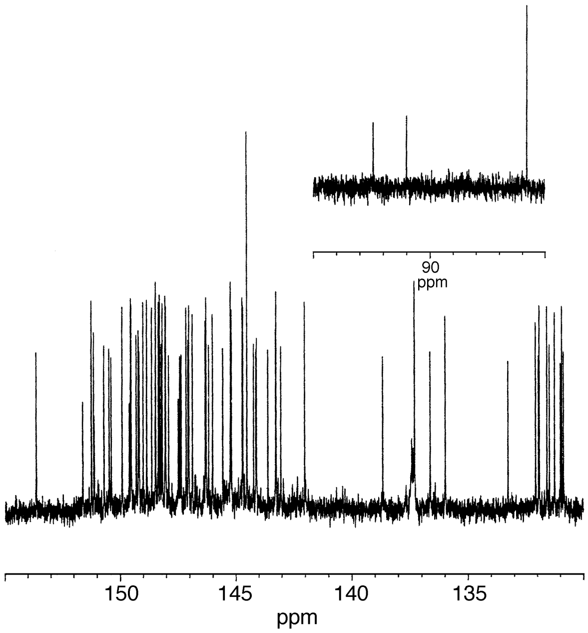

Fig. 3 ^{13}C NMR spectrum of $C_{70}O$; inset shows the sp^3 region

The integrated peak intensities are unequal and show that the ratios of the 1,2- and 5,6-isomers are approximately 43:57, and this is confirmed by the peak intensities in the sp^2 region.[22] Moreover, the unequal concentrations of the isomers allows us to assign all of the peaks in the sp^2 region. The overall spectrum for each compound is as follows with all peaks being 2 C intensity except where indicated.

1,2-Epoxy[70]fullerene. δ_C 153.61, 151.135, 151.115 (1 C), 150.69, 150.47, 150.38, 149.31, 149.22, 149.20, 149.17, 148.47, 148.21, 147.89, 147.41, 147.35, 147.06, 146.312 (1 C), 146.308, 146.17, 145.56, 145.23, 144.51, 144.22, 144.12, 144.09, 143.60, 143.26, 143.04, 138.66, 136.62, 133.26, 131.94, 131.47, 130.98, 130.85, 92.42 (1 C) and 90.99 (1 C).

5,6-Epoxy[70]fullerene. δ_C 151.61 (1 C), 151.24, 149.92, 149.60 (1 C), 149.55, 149.52, 149.00, 148.85, 148.63, 148.46, 148.34, 148.287 (1 C), 148.284, 148.17, 148.04, 148.02, 147.48 (1 C), 147.14, 147.02, 146.87, 146.27, 146.00, 145.22, 145.18, 144.71, 144.68, 144.51, 143.24, 142.01, 137.30, 135.97, 132.07, 131.90, 131.57, 131.24, 130.92 and 85.78.

Given the downfield location (150.07 ppm) of the resonances for *a*-type carbons in [70]fullerene,[23] the resonance for the carbon on the symmetry axis at 151.115 ppm for the 1,2-isomer can be confidently assigned to C-58 (*a*-type), and hence that at 146.312 ppm can be assigned to C-41 (*b*-type); in [70]fullerene, the resonances for *b*-type carbons appears at 146.82 ppm. (For numbering in [70]fullerene,[24] see Fig. 4.) Likewise the resonances for on-axis carbons in the 5,6-isomer at 151.61 and 149.60 ppm are assigned to either of the *a*-type carbons C-2 and C-58, and those at 147.48 and 148.287 ppm are assigned to either of the *b*-type carbons C-1 and C-41.

The notable feature of the results is that the 5,6-isomer is the most abundant and this is the first addition reaction of [70]-fullerene in which 5,6-addition is predominant (*cf.* Table 1). Though calculations mostly predict that 5,6-addition should predominate over 1,2-addition,[25] the observed preference for the latter has been interpreted in terms of the greater curvature

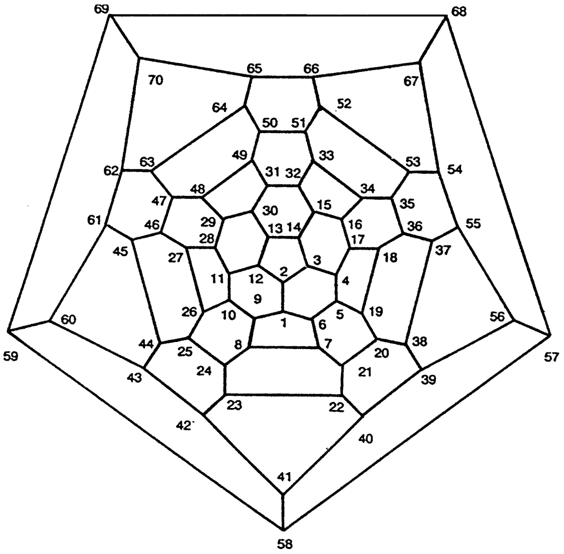

Fig. 4 Numbering for [70]fullerene[23]

across the 1,2-position.[26] Thus the preference for 1,2-addition arises from relief of this strain. Previously, one of us has suggested that strain in the product (or transition state leading to it) may also be important.[19] In circumstances where this applies, then 5,6-addition should predominate, and the present result would seem to constitute just such an example. Nevertheless, the seemingly almost exclusive 1,2-addition observed in the Bingel reaction[10] appears to argue against this notion, since the strain in the cyclopropyl ring should be comparable to that in the epoxide ring. There is however, a significant difference between the two additions, arising from the nature and bulk of the substituents on the bridging carbon, which is likely to cause repulsive interactions between them and the cage. Given the differential curvature on the [70]fullerene surface, such interactions will favour 1,2- over 5,6-addition; a similar explanation was first used to account for the exclusive 1,2-addition of iridium to [70]fullerene.[8]

Another factor which may be involved is a difference in polarisability of the electrons of the 1,2- and 5,6-bonds. For example, in reactions of aromatic derivatives, the variable electron release of substituents according to reagent demand is a well-known phenomenon, and is the reason for the need to use the Yukawa–Tsuno version[27] of the Hammett equation for accurate correlation of reactivity data. A definitive example is the reactivity of the *para*-position in fluorobenzene, which can be either greater than that of a position in benzene (as in hydrogen exchange)[28] or less (as in nitration);[29] the electrophile in hydrogen exchange is weaker than in nitration, so greater electron supply from the substituent is required to assure reaction. If the electrons of the 1,2- and 5,6-bonds are not equally polarisable, then reaction across either one or the other bond may be dominant according to the reagent involved.

Mass spectrometry

Although $C_{70}O$ was entirely free of C_{70} (as shown by HPLC), the EI mass spectrum indicated the presence of very little of the oxide, the main peak occurring at m/z 840. This instability of the epoxide is consistent with the observations of other workers (see Introduction), but contrasts with observations of the stabilities towards EI mass spectrometry of oxygenated derivatives (presumed to be epoxides) derived from phenylated fullerenes.[30] A reasonable explanation is that the additional addends in the latter reduces the cage strain and so renders the accommodation of the three-centred epoxide ring less energetically unfavourable.

Note added in proof: Addition of tetraalkoxyethenes also takes place mainly across the 1,2-position (X. Zhang, A. Fan and C. S. Foote, *J. Org. Chem.*, 1996, **61**, 5456) as does the addition of various methano derivatives CHR, where R = COR′, CONR′R″, CO_2R' (46–84%) (Y. Wang, D. I. Schuster and S. R. Wilson, *J. Org. Chem.*, 1996, **61**, 5198).

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