Bicyclopentene Addend on [60]Fullerene: Epoxidation and *cis*-Bromine Addition

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Bromine adds *cis* to the double bond in the addend of the [60]fullerene–cyclopentadiene adduct, so that both bromines are directed away from the cage. The epoxide, formed by peracetic acid oxidation of the double bond of the addend, also points away from the cage. These results are attributed to a combination of steric hindrance and polar repulsion by the fullerene cage, the first time such effects have been reported to control addition. The epoxide appears to extrude CO during mass spectrometry to give a cyclobutane derivative of [60]fullerene.

Previously, we and others reported the formation of an adduct between cyclopentadiene and [60]fullerene.[1,2] We showed that this adduct could be stabilised towards mass spectroscopic examination by reduction or bromination of the double bond in the addend, thereby preventing the retro Diels–Alder reaction.[1] We now report that the addition of bromine takes place *cis*, giving the dibromo derivative in which the bromines lie *exo* with respect to the cage. Moreover, reaction of the adduct with peracetic acid results in formation of the epoxide derivative of the addend; here too the oxygen points away from the cage.

Bromination.—Selective addition to the addend is possible because bromination of the cage[3] only takes place with very concentrated solutions of bromine. Thus the cyclopentadiene–[60]fullerene adduct, 1,2-{[1,3]epi(2,3-dihydro-1*H*)cyclopenta}[60]fullerene, prepared from [60]fullerene (10 mg, 0.0138 mmol) and 1.25 equiv. of freshly distilled cyclopentadiene monomer was stirred with 1 equiv. of bromine in carbon tetrachloride at room temp. for 24 h. After removal of volatiles, the residue was dissolved in benzene and the solution chromatographed through a short column (Al_2O_3–0.5% H_2O, benzene) to give a red–brown solution which, after removal of benzene, gave a dark-brown solid (11.2 mg, 85%). The mass spectrum (Fig. 1) shows the parent ions of the dibromo addition product at 944, 946 and 948 amu (see inset) in the required 1:2:1 intensity ratio. There is no loss of HBr by fragmentation indicating that H and Br are not *cis* to each other (thermal eliminations require a *cis* β-relationship). By contrast, the relative intensities of the parent ion and [60]fullerene show that considerable elimination of bromine takes place under the (positive EI) conditions, commensurate with a *cis* β-disposition of the bromine atoms.

The ^1H NMR (500 MHz, CS_2, $CDCl_3$) spectrum of the cyclopentadiene–[60]fullerene adduct [δ 7.11 (2 H, t), 4.54 (2 H, t), 3.49 (1 H, d) and 2.57 (1 H, d)], confirms our previous report (the resonances are 0.20 ppm downfield, due to solvent effects). The main features of the ^1H NMR spectrum of the dibromo derivative (500 MHz, CS_2, $CDCl_3$, Fig. 2) are δ 5.74 (2 H, d, J 2.1 Hz, H_d), 4.15 (2 H, t, J 1.6 Hz, H_a), 3.60 (1 H, dm, J 11.7, 2.0 and 1.6 Hz, H_b) and 3.37 (1 H, dt, J 11.7 and 1.6 Hz, H_e); there is no coupling between H_a and H_d because the C–H bonds are orthogonal. [A minor byproduct gave multiplets at δ 2.55 (2 H), 3.19 (2 H), 4.45 (*ca.* 1 H) and 5.61 (1 H) (*cf.* ref. 1), indicating it to possess a reduced double bond, and a single bromine in the methylene bridge. This conclusion is supported by the ^1H NMR resonances at δ 6.82 (alkene protons), 5.62 ($\equiv H_a$) and 4.44 ($\equiv H_b$) for the bicyclopentene–[60]fullerene adduct, substituted with bromine in the methylene bridge.[4]]

The peak assignments (inset to Fig. 2), use the same notation for corresponding hydrogen atoms as that given in ref. 1.

Features of the spectrum that confirm that the product is 1,2-[1,3-epi(1*S*,3*R*,4*R*,5*S*)-4,5-dibromocyclopentano][60]fullerene are: (*i*) its simplicity shows that the molecule must possess high symmetry; (*ii*) the downfield shifts of the hydrogens compared with those in the corresponding all-hydrogen compound,[1] 1,2-(1,3-epicyclopentano)[60]fullerene, are as follows—H_d, 2.82 ppm due to the α-bromine, H_a, 0.30 ppm, due to the β-bromine, H_b, −0.02 ppm, due to the γ-bromine (*i.e.* insignificant effect), H_e, 0.87 ppm; inductive effects alone would predict that H_e would experience the same negligible shift as for H_b, the large downfield shift observed is attributable to a direct field effect between H_e but only if the bromines are *exo* to the cage; (*iii*) the *exo* position of the bromines is confirmed by the W-coupling between H_b and H_d of 2.1 Hz; by contrast there is no coupling between H_e and H_d.

The ^{13}C NMR spectrum requires four peaks in the sp^3 region, with approximate intensity ratio of 2:2:2:1; these peaks are found at δ 72.82 (C1 and C2 of the cage), 60.53 [C(Br)], 55.77 [C(H_a)] and 32.04 [C($H_{b,e}$)]. The sp^2 region should show 27 peaks of intensity 2 and four of intensity 1; in fact we find 28 and two respectively, thus two of the single intensity peaks must be coincident. The peaks occur at δ 153.32, 151.45, 146.98, 146.03, 145.98, 145.88, 145.85, 145.83, 145.32, 145.20, *145.16*, 145.07, 145.03, *144.69*, 144.54, 144.23, 144.03, 142.78, 142.37, 142.33, 141.78, 141.77, 141.58, 141.48, 141.46(5), 141.45(5), 140.08, 139.81, 137.29 and 136.15 (half-intensity peaks italicised). The ^{13}C NMR spectrum (125.76 MHz, CS_2, $CDCl_3$) was run with added $Cr(acac)_3$ using gated decoupling and a total delay between pulses of 3.4 s.

Bromine usually adds *trans* to a double bond, with formation of a bridged bromonium ion intermediate.[5] However, examples of non-stereospecificity are known, *e.g.* addition of bromine–CCl_4 to 1-phenylpropenes,[6] and is usually favoured either by solvents of high dielectric constant (enhanced formation of a free bromonium ion), or when free radicals are involved. Electrophilic addition is unlikely due to the strong-electron withdrawal by the fullerene cage. Although reaction occurs in the dark, radical involvment is not ruled out, a view supported by the formation of the by-product containing a bromomethylene group.

Calculations (Molecular Simulations CERIUS 3.2 package, using the minimizer module employing UNIVERSAL-BETA force field and UNIVERSAL parameters[7]) predict total energies for the possible isomers as (kcal mol^{-1}):* *exo*, 926.1; *endo*, 937.3; *exo,endo*, 933.5. Though these differences are

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* 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

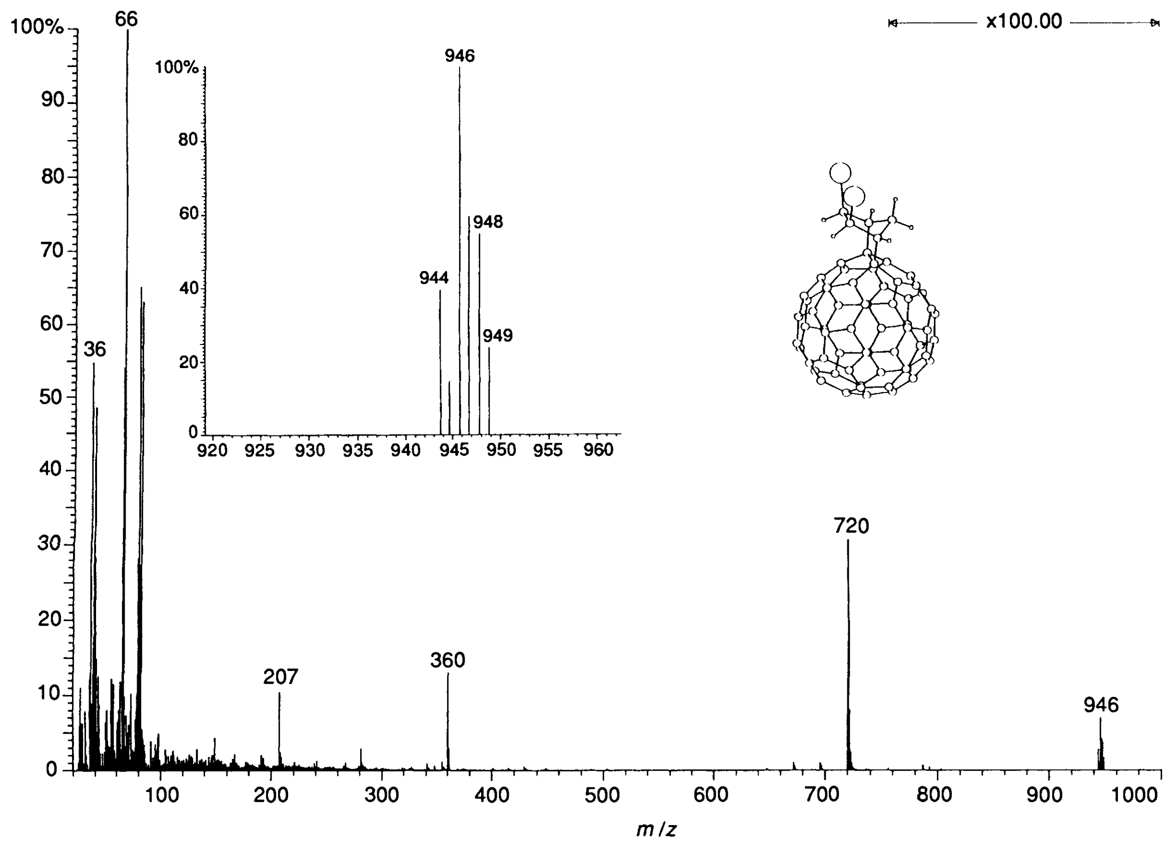


Fig. 1 Mass spectrum (EI conditions) of the product of bromination of the adduct of cyclopentadiene and [60]fullerene (inset shows expanded spectrum)

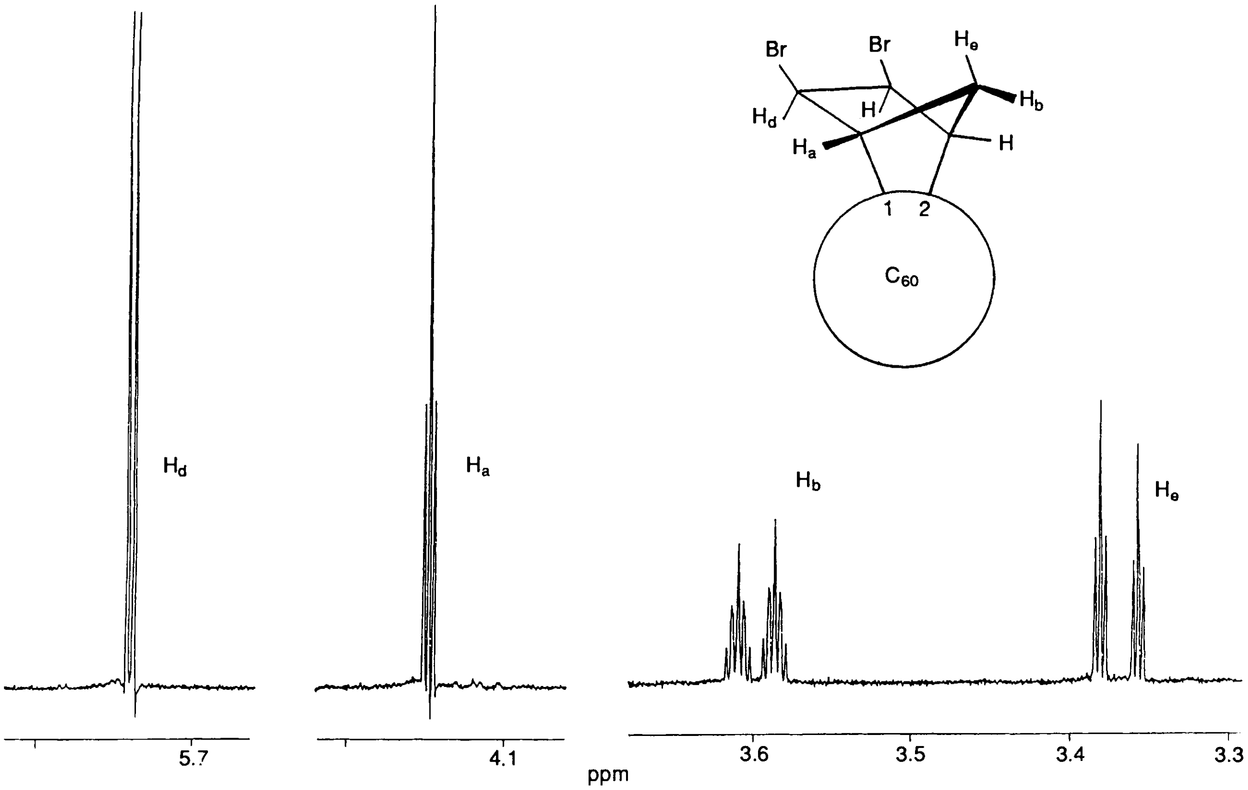


Fig. 2 ^{1}H NMR spectrum of the product of bromination of the adduct of cyclopentadiene and [60]fullerene

surprisingly small, they do predict the observed isomer to be the more stable one. A combination of steric and electronic effects is considered to be responsible.

Epoxidation.—A solution of the cyclopentadiene–[60]fullerene adduct (10 mg, 0.0138 mol) in benzene (10 cm^3) was treated with a solution of peracetic acid (5 cm^3 of a 32% solution in acetic acid), and stirred at room temp. for 72 h. Water (20 cm^3) was added and the mixture stirred for 24 h. The benzene layer was repeatedly washed with water (5 × 20 cm^3)

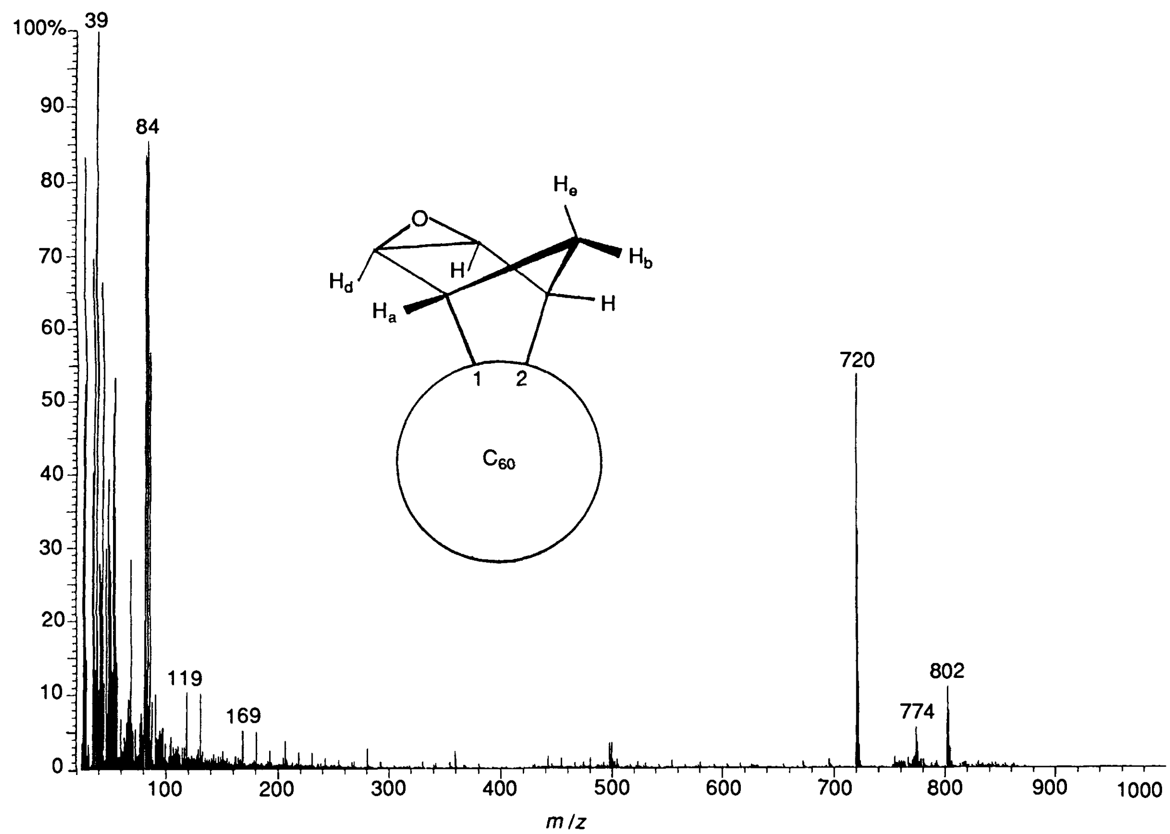
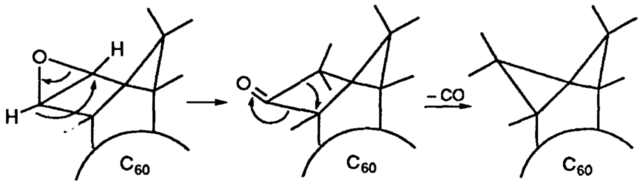


Fig. 3 Mass spectrum (EI conditions) of the product of epoxidation of the adduct of cyclopentadiene and [60]fullerene

and separated, and the volatiles were removed *in vacuo* to yield a dark red–brown solid. The mass spectrum (Fig. 3) shows a peak at m/z = 802 u, due to the epoxide, and a smaller one at m/z = 774 which corresponds to a cyclobutane derivative. This could be produced by CO extrusion, requiring two consecutive bond rearrangements as shown in Scheme 1. We hope eventually to be able to isolate this derivative. The mass spectrum also shows the presence of [60]fullerene arising from fragmentation.



Scheme 1 Probable mechanism for formation of the cyclobutyl derivative of [60]fullerene from the epoxide

The ^1H NMR spectrum (360 MHz) shows main peaks (each with undetermined secondary splittings) at δ 4.26 (2 H, s), 4.09 (2 H, m), 3.02 (1 H, dm, J 15.7 Hz) and 2.48 (1 H, dt, J 15.7 and 2.5 Hz). This is consistent with the proposed structure (inset to Fig. 3), the comparison of the spectrum with that for the bromo derivative (above) shows the following features: (*i*) the resonances for both H_b and H_e are both more upfield, owing to the lower-electron withdrawal by the single oxygen compared with the two bromines, moreover, the upfield shift of H_e (δ 0.89) is greater than that for H_b (δ 0.58) because it is the hydrogen nearer to the electronegative substituents; (*ii*) the resonances for H_a (which is almost orthogonal to the substituents) is only δ 0.06 upfield in the epoxide, as expected; (*iii*) the resonances for H_d are much more upfield in the epoxide (δ 1.48) because not only is there a reduction in the number and electronegativity of the adjacent substituents, but there must be reduced steric compression between the oxygen and H_e compared with that between the bromines and H_e, and so H_d will not be forced so close to the electron-withdrawing cage. Nevertheless, the marked downfield resonance for H_d confirms that it is pointing towards the cage and not away from it. Were this latter the case, then there would be little interaction between the oxygen and H_e which would therefore experience a much greater upfield shift than that observed.

Corrigendum.—Labels (*c*) and (*d*) in Fig. 2 of ref. 1 should be interchanged; they are correctly assigned in the text.

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