Formation and characterisation of alkoxy derivatives of [60]fullerene

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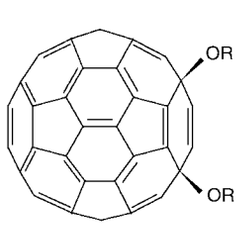
Heating $C_{60}Cl_6$ with either methanol or propan-2-ol under reflux during 140 h yields 1,4-$(MeO)_2C_{60}$ and 1,4-$(iPrO)_2C_{60}$, respectively, the latter reaction being faster due to the greater nucleophilicity of propan-2-ol. The reaction between $C_{60}Cl_6$ and ROH–NaOR yields $C_{60}(OR)_5Cl$ (R = Me, Et) both of which are isostructural with $C_{60}Ar_5Cl$. A by-product of the reaction with ethanol–sodium ethoxide is 1,4-$(EtO)_2C_{60}$ showing that chlorine elimination accompanies substitution; this parallels the formation of 1,4-Ph_2C_{60} from the reaction between $C_{60}Cl_6$ and benzene–$FeCl_3$.

Introduction

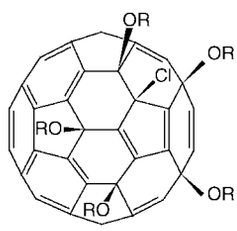
Although the functionalisation of fullerenes is now well developed,[1] the chemistry of alkoxyfullerenes has largely been neglected, due in particular to the difficulty in analysing reaction products, especially by mass spectrometry. Thus, although radicals $C_{60}RO^{\bullet}$, generated by the photolysis of either peroxides (ROOR)[2] or dialkoxy disulfides (ROSSOR)[3] have been detected by EPR, no derivatives were isolated; the formation of 1-hydroperoxy-2-benzyloxy[60]fullerene, an unstable intermediate, was implied in the formation of a 1,3-dioxolane.[4] Reaction of alkoxides with [60]fullerene typically results in a complex mixture of multiple addition products,[5,6] mass spectrometric analysis of which was defeated by the ease with which elimination occurred to form $C_{60}O$,[6] though negative ion electrospray mass spectrometry could detect the presence of methoxylated anions $C_{60}(OMe)_n^-$.[5]

The most promising method of producing alkoxylated derivatives should involve nucleophilic substitution on a halogenated precursor, though the site locations are then limited to those present in the precursor. Replacement of chlorine by methoxy was demonstrated in the reaction of $C_{60}Cl_{24}$ with KOH–MeOH under reflux during 3 h, which gave a mixture of products, containing up to twenty-six OMe groups, that showed a broad envelope of peaks at δ 3.7 in the ^{1}H NMR spectrum.[7] A similar NMR spectrum was obtained from the reaction of fluorinated [60]fullerene with NaOMe–MeOH at room temperature.[8] Very recently we have isolated some benzyloxyfullerenes from reaction of chlorofullerenes with phenols in the presence of aq. KOH, the products being partly stabilised here by oxidative ring closure to give the corresponding benzofurofullerenes.[9]

This encouraged us to re-examine the alkoxydehalogenation reaction, and we now report the successful isolation and characterisation of 1,4-dimethoxy-1,4-dihydro[60]fullerene (**1**), 1,4-diethoxy-1,4-dihydro[60]fullerene (**2**), 1,4-diisopropoxy-1,4-dihydro[60]fullerene (**3**), 2-chloro-1,4,11,15,30-pentamethoxy-1,2,4,11,15,30-hexahydro[60]fullerene (**4**), and 2-chloro-1,4,11,15,30-pentaethoxy-1,2,4,11,15,30-hexahydro-[60]fullerene (**5**). Whilst this work was in progress a Chinese group also reported the successful formation of (**1**) using a photochemical technique.[10]



1 R = Me
2 R = Et
3 R = iPr



4 R = Me
5 R = Et

Experimental

1,4-Dimethoxy-1,4-dihydro[60]fullerene 1

$C_{60}Cl_6$ was prepared as described previously,[11] and a solution of 25 mg in dry benzene (50 ml) was heated under reflux with HPLC grade methanol (5 ml) for 140 h. TLC (CCl_4) of the reaction mixture gave a spot with an R_f value of 0.34. indicating that a derivative had been formed. The solvent was therefore removed, and the residue was washed with pentane. A solution in CCl_4 was passed through a short silica-gel column to give four fractions, the last of which was the desired product, obtained in low yield (2.3 mg, 11%).

Though the EI mass spectrum showed only the presence of C_{60} due to fragmentation, a small peak at 782 amu (3%) in the MALDI spectrum indicated formation of a dimethoxy compound. However, a negative ion electrospray mass spectrum, run *without attachment of further addends to the molecule* [*i.e.* unlike previous use of this technique (see *e.g.* ref. 5)], gave an excellent parent ion at 782 amu *with no fragmentation* (Fig. 1). Details of the IR and NMR spectra (Figs. 2 and 3) are given in Table 1.

1,4-Diisopropoxy-1,4-dihydro[60]fullerene (3)

A solution of $C_{60}Cl_6$ (30 mg) was dissolved in dry benzene (50 ml) and heated under reflux with dry propan-2-ol (5 ml) for 140 h. TLC (CCl_4) of the reaction mixture gave a spot with an R_f value of 0.27. The solvent was removed, the residue washed with pentane, and a solution in CCl_4 passed through a short

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Table 1 IR and NMR data for 1,4-$(RO)_2C_{60}$ (R = Me, iPr)

	1,4-$(MeO)_2C_{60}$	1,4-$(iPrO)_2C_{60}$
IR/cm^{-1} (KBr)	2919, 2817, 1453, 1428, 1091 (main) and 1078 (C–O stretch), 979, 927, 762, 727, 540, 528, 522, 464	2967, 2925, 1572, 1520, 1460, 1380, 1366, 1090, 1057, 1044 (main, C–O stretch), 762, 730, 706, 528
^{1}H NMR δ	4.26	5.322, 5.310 (2 H, q, *J* 6.1 Hz), 1.697, 1.685 (12 H, d, *J* 6.1 Hz)
^{13}C NMR δ_C[a]	149.60, 148.81, 148.36, 147.21, 146.95, 146.90, 146.81, 146.61, 146.42, 145.72, 145.65, 144.37, 144.29, 144.20, 144.11, 143.80 (1 C), 143.73, 143.57, 143.24, 143.21 (4 C), 143.192, 143.187, 143.05 (1 C), 142.80, 142.23 (1 C), 142.15, 141.20, 140.59 (1 C), 139.78, 138.36, 80.14 (cage-O), 55.09 (MeO)	150.45, 149.49, 148.71, 147.18, 147.16, 146.82, 146.67, 146.41, 146.36, 145.66, 145.50, 144.36, 144.21, 144.18, 144.07, 143.79, 143.71 (1 C), 143.57, 143.167, 143.160, 143.154, 143.141, 143.04, 142.985 (1 C), 142.86, 142.154, 142.14, 141.18, 140.49 (1 C), 139.25, 138.39, 78.90 [2 C, *C*(cage)-O], 69.86 (2 C, *C*H), 24.863 (2 C, CH_3), 24.829 (2 C, CH_3)

[a] All 2 C except where indicated.

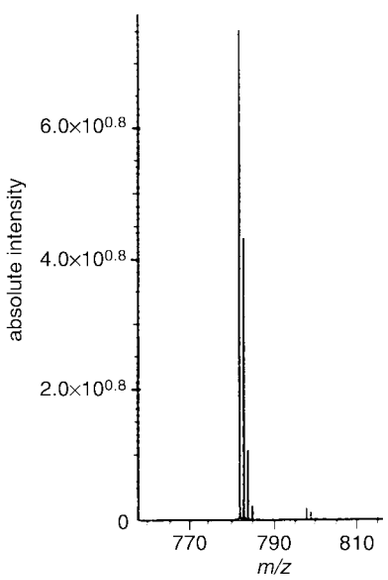


Fig. 1 Electrospray mass spectrum of showing the parent ion at 782 amu.

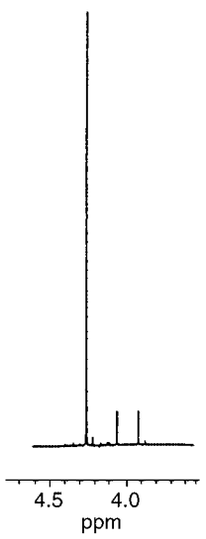


Fig. 2 ^{1}H NMR spectrum of 1,4-$(MeO)_2C_{60}$.

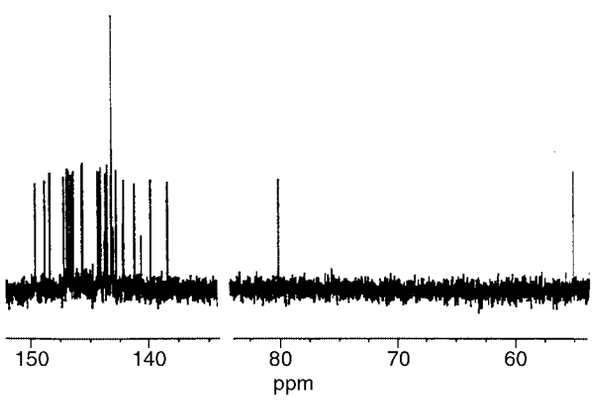


Fig. 3 ^{13}C NMR spectrum of 1,4-$(MeO)_2C_{60}$.

silica-gel column to give four fractions, the last of which was the desired product (8 mg, 30%).

The EI mass spectrum of this product just showed C_{60}, but it was not possible to obtain an electrospray mass spectrum due to long-term equipment failure. However, the structure was proved by NMR spectroscopy, as described below. Details of the IR and NMR (Fig. 4) are given in Table 1.

2-Chloro-1,4,11,15,30-pentamethoxy-1,2,4,11,15,30-hexahydro-[60]fullerene (4)

Two solutions were prepared, each containing $C_{60}Cl_6$ (30 mg, 0.0032 mmol) dissolved in dry benzene (50 ml). Methanol (6 ml) was added to one flask, together with a few drops of a freshly prepared solution of NaOMe, whilst NaOMe only was added to the other. Each turned brown on addition of the methoxide, and was heated under reflux for 43 h. After this time, TLC (CCl_4) of the solution containing methanol showed that all of the $C_{60}Cl_6$ had been consumed, but attempted separation of the products on an alumina column with elution by CH_2Cl_2 progressing through to 1 : 1 CH_2Cl_2–MeOH failed.

TLC (SiO_2, 80 : 20 CH_2Cl_2–MeOH) of the second sample indicated that reaction had occurred, two spots being present with R_f values of 0.913 and 0.765. The sample was separated on an alumina column with elution first by $CHCl_3$ (which gave five fractions), then CH_2Cl_2 (one fraction) and finally 1 : 1 CH_2Cl_2–MeOH (two fractions). Preliminary analysis indicated that the required product was present in the chloroform fractions nos. 2 and 3. These were combined and further pre-purified by column chromatography, and then further purified by HPLC (high pressure liquid chromatography) using a 10 mm × 25 cm Cosmosil 5 μm PYE column with toluene elution at 4 ml min^{-1}. The required product eluted with a retention time of 9.6 min (4.4 mg, 15%); in a preliminary study using a Cosmosil Buckyprep column (same conditions) this component eluted with a retention time of 4.9 min. Details of the NMR (Fig. 5) are given in Table 1.

2-Chloro-1,4,11,15,30-pentaethoxy-1,2,4,11,15,30-hexahydro-[60]fullerene (5)

Sodium ethoxide, (65 mg, 1 mmol) and ethanol (4 ml) were added to a solution of $C_{60}Cl_6$ (15 mg 0.0016 mmol) in redistilled benzene (30 ml), and the mixture was stirred at room temperature for 2 weeks, during which time the colour changed from orange to deep red. Normal work-up followed by column chromatography (70–230 mesh silica gel, toluene elution) gave two fractions. The first was unreacted $C_{60}Cl_6$, the second yellow

Table 2 NMR data for $C_{60}(OR)_5Cl$ (R = Me, Et)

	$C_{60}(OMe)_5Cl$	$C_{60}(OEt)_5Cl$
^1H NMR δ	4.024, 3.991, 3.969 (s, 2 : 2 : 1 ratio)	4.309 (2 H, q *J* 6.9 Hz) and overlapping quartets, all *J* 7.0 Hz, at 4.560, 4.542 (2 H), 4.376, 4.358 (2 H), 4.217, 4.213 (4 H), (CH_2); 1.456 (6 H, t, *J* 7.0 Hz), 1.363 (3 H, t, *J* 6.9 Hz), 1.349 (6 H, t, *J* 6.95 Hz), all CH_3
^{13}C NMR δ_C [a]	154.18, 151.40, 149.09, 148.96, 148.47, 148.44, 148.41 (1 C), 148.32, 148.22, 147.73, 147.66, 147.39 (1 C), 147.37, 147.21, 146.81, 145.41, 145.17, 145.03, 144.34, 144.30, 144.11, 144.02, 143.61, 143.41, 142.62, 142.43, 142.15, 138.10; 81.77 (1 C), 79.80 (2 C), 77.40 (2 C), 73.65 (1 C) (all cage carbons); 58.28 (1 C), 55.69 (2 C), 55.34 (2 C) (all OMe)	154.89, 152.35, 149.36, 149.26, 149.21, 148.79, 148.74 (1 C), 148.70, 148.68, 148.56, 148.00, 147.705 (1 C), 147.715, 147.56, 147.20, 145.79, 145.63, 145.38, 144.97, 144.93, 144.64, 144.36, 143.91, 143.74, 143.00, 142.94, 142.78, 138.74; 82.22 (1 C), 79.96 (2 C), 77.52 (2 C), 74.51 (1 C) (all cage carbons); 67.94 (1 C), 64.38 (2 C), 63.88 (2 C) (all OCH_2); 16.02 (2 C), 15.88 (2 C), 15.45 (1 C) (all CH_3)

[a] All 2 C except where indicated.

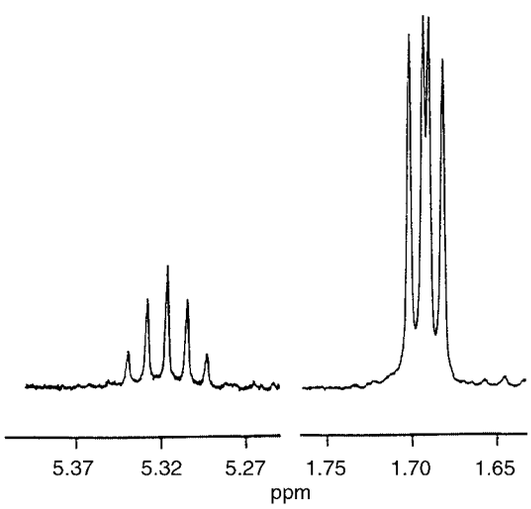


Fig. 4 ^1H NMR spectrum of 1,4-$(iPrO)_2C_{60}$.

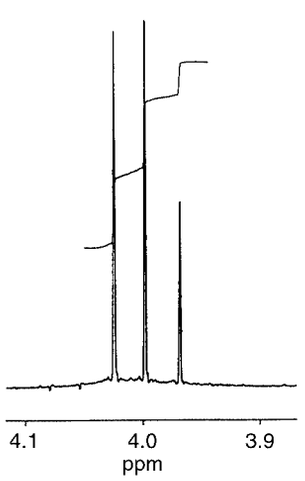


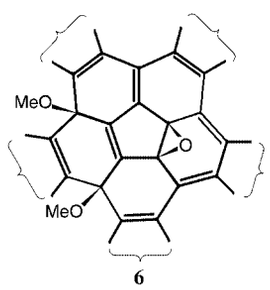
Fig. 5 ^1H NMR spectrum of $C_{60}(OMe)_5Cl$.

fraction (R_f 0.46) was mainly $C_{60}(OEt)_5Cl$, 3 mg, 19% (**5**). Further purification by HPLC (Cosmosil 5 μm PYE 25 cm × 10 mm column, toluene elution at 1.5 ml min^{-1}) yielded a main peak of 11.7 min retention time, together with a smaller one (see below) at 12.4 min. Data for the NMR spectrum are given in Table 2.

Discussion

1,4-Dimethoxy-1,4-dihydro[60]fullerene

The singlet at δ 4.26 in the ^1H NMR spectrum is due to the methoxy groups of 1,4-$(MeO)_2C_{60}$, the two smaller, equal-intensity singlets at δ 4.06 and 3.92 being assigned to unsymmetrical $(MeO)_2C_{60}O$ (*cf.* the peak at 798 amu in the electrospray mass spectrum). This could be an ether,[12] but is more probably an epoxide, given the known tendency for epoxides to form across one[9] (or even both)[13] of the double bonds in the central pentagon of $C_{60}Cl_6$-derived derivatives. Various structures can be conjectured (*e.g.* **6**), but the epoxide cannot be



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in the same ring as the 1,4-methoxy groups for the compound would then have C_s symmetry; moreover, the mutual repulsion between the three oxygens favours a remote location of the epoxide function. An alternative 1,2-dimethoxy epoxide (unsymmetrical) is ruled out as there is no NOE coupling between the two small singlets. No ^{13}C peaks arising from the epoxide were seen owing to the lack of symmetry.

Overall the data show that the derivative is C_s symmetric 1,4-$(MeO)_2C_{60}$. Formation of the product requires concomitant loss of four of the chlorines, a feature of nucleophilic substitutions of $C_{60}Cl_6$, *e.g.* the production of $C_{60}Ph_2$ by reaction with benzene–$FeCl_3$.[14]

1,4-Diisopropoxy-1,4-dihydro[60]fullerene

The two overlapping quartets at δ 5.322 and 5.310 (2 H, *J* 6.1 Hz), and two overlapping doublets at δ 1.697 and 1.685 (12 H, *J* 6.1 Hz) in the ^1H NMR (Fig. 4) confirm both the C_s symmetry of the product and also the 1,4-addition. The latter requires each of the methyl groups of a given isopropoxy addend to lie over either a pentagon or a hexagon (see **7**), producing the small chemical shift differences. For 1,2-addition the spectrum would consist only of one doublet and one septet.

The two sets of methyl resonances in the ^{13}C NMR spectrum are due to their differences in location with respect to a cage pentagon and a hexagon, as depicted in **7**.

The higher yield in isoproproxylation compared to methoxylation is consistent with the greater nucleophilicity of OiPr compared to OMe.

2-Chloro-1,4,11,15,30-pentamethoxy-1,2,4,11,15,30-hexahydro-[60]fullerene (4)

The intensity ratio of the three singlets in the ^1H NMR (Fig. 5, Table 2) is consistent with the formation of C_s symmetry $C_{60}(OMe)_5Cl$ (**4**), confirmed by the presence of the required

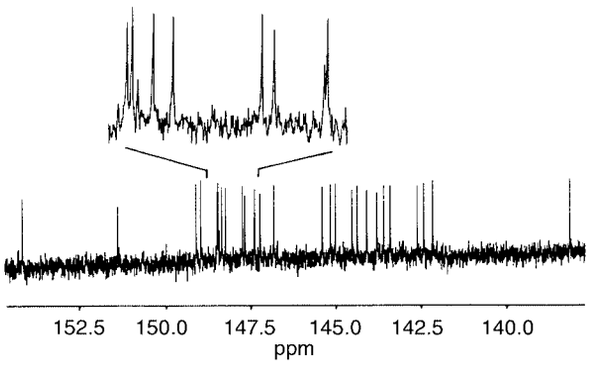


Fig. 6 ^{13}C NMR spectrum (sp^2 region) of $C_{60}(OMe)_5Cl$.

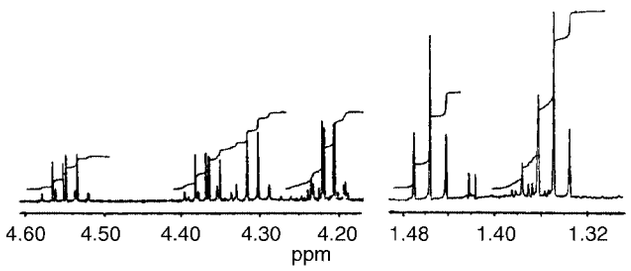
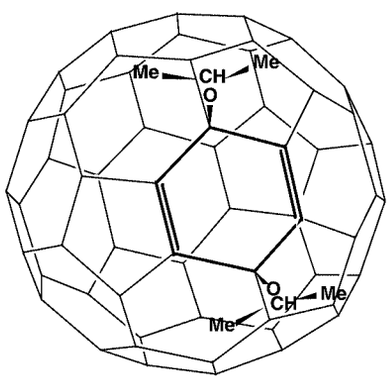


Fig. 7 ^1H NMR spectrum of $C_{60}(OEt)_5Cl$.



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twenty-eight peaks in the sp^2 region (Table 2) of the ^{13}C NMR spectrum (Fig. 6). Moreover, in the sp^3 region the cage carbons are in the required intensity ratio as are those for the methoxy group (Table 2). The single methoxy group is the most downfield as it is adjacent to chlorine, further supporting the structure.

2-Chloro-1,4,11,15,30-pentaethoxy-1,2,4,11,15,30-hexahydro-[60]fullerene (5)

The ^1H NMR spectrum (Fig. 7) is significantly different from that for the methoxy derivative, and consists in the methylene region of seven quartets, most of which are overlapping, and three sets of triplets due to the methyl groups.

From the peak intensities, and given that the ethoxy group next to chlorine must lie along the C_s symmetry plane, the methyl and methylene groups at δ 1.363 and 4.309, respectively, can be assigned to this group. Conformational restrictions and the relationship of each hydrogen relative to the on-plane chlorine mean that the methylene groups on the other ethoxy groups are inequivalent, producing different chemical shifts. For the most upfield pair of methylenes, the shift between the hydrogens in the two environments is only 0.004 ppm, attributable to the ethoxy groups most remote from the chlorine, and associated with the methyl groups at 1.349 ppm. The shift difference of the hydrogens in the most downfield pair of methylenes is 0.184 ppm, and therefore associated with the downfield methyl at 1.456 ppm. The large shifts of one pair of ethoxy groups relative to the other provide confirmation (unachievable with mass spectrometry) that the chlorine is present on the cage, and in the position shown in **5**. The various couplings were confirmed by NOE.

The structure was confirmed further by the ^{13}C NMR spectrum, which shows the required 28 peaks in the sp^2 region, 4 peaks in the sp^3 region for the cage carbons, and there is a good linear correlation between all of the cage carbons for both the ethoxy and methoxy compounds. The carbons of the CH_2 and CH_3 groups of the ethoxy group were identified by H coupling–decoupling. Here the methylene carbon for the ethoxy group nearest to the chlorine appears most downfield.

Overall the data for the methoxy and ethoxy compounds are thus both fully self-consistent and consistent with the given structures.

The parallel with arylation of $C_{60}Cl_6$

An interesting feature of these results is that although the substitution mechanism is different, the pattern found in the reaction with benzene–$FeCl_3$ is seen here. For the arylation reaction, the chlorofullerene carries out electrophilic aromatic substitution into the aryl group, with ferric chloride acting as the Friedel–Crafts catalyst. However, the reaction may also be regarded as a nucleophilic substitution of the chlorine in the chlorofullerene by the arene, which provides a parallel between the two reactions, the alkoxy group being the nucleophile in the present reactions. However, the sixth chlorine is only replaced with difficulty in arylation,[15] attributable to steric hindrance, since for allylation, all six chlorines *are* readily replaced.[16]

One could anticipate therefore that in the present reactions, where steric hindrance appears to be less than in arylation, all six chlorines would have been replaced. The fact that this appears not to happen shows that much is yet to be learned about the parameters which influence product structure in fullerene chemistry. It may be that the mutual repulsion between adjacent oxygens of alkoxy groups is an important factor preventing 1,2-addition.

1,4-Diethoxy-1,4-dihydro[60]fullerene (2)

The minor component isolated in the HPLC purification of $C_{60}(OEt)_5Cl$ gave two main groups of peaks in the ^1H NMR spectrum at δ 4.232 (2 H, q, J 6.9 Hz, CH_2) and 4.222 (2 H, q, J 6.9 Hz, CH_2), 1.370 (3 H, t, J 6.9 Hz, CH_3) and 1.367 (3 H, t, J 6.9 Hz, CH_3) showing the compound to have C_s symmetry. A 1,4-position of the ethoxy groups is indicated by the similarity of the position of the resonances in the ^1H NMR spectrum to those for the 1,4-ethoxy groups in the chloropentaethoxy derivative, above. The dual sets of peaks arise because one of the methylene protons sits over a pentagon, the other over a hexagon.

The formation of this compound also has an exact parallel in the formation of 1,4-Ph_2C_{60} from the reaction between $C_{60}Cl_6$ and benzene–$FeCl_3$.[14] The nucleophilic substitution in each reaction is accompanied by elimination of four chlorine atoms, though the reason for this is presently unclear. A comparable elimination in the arylation reaction also gives rise to unsymmetrical Ph_4C_{60},[14] so one might anticipate the parallel formation of unsymmetrical $(MeO)_4C_{60}$ in the present reaction. This compound was not identified, but may account for the presence of unassigned minor methylene and methyl peaks in the spectrum of 1,4-$(OMe)_2C_{60}$.

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