A hexaallyl[60]fullerene, $C_{60}(CH_2CH=CH_2)_6$

Ala'a K. Abdul-Sada, Anthony G. Avent, Paul R. Birkett,* Harold W. Kroto, Roger Taylor and David R. M. Walton

The Fullerene Science Centre, School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, Sussex, UK BN1 9QJ

$C_{60}Cl_6$ Reacts with allyltrimethylsilane in the presence of $TiCl_4$ to form a C_s symmetrical, hexaallyl addended [60]fullerene derivative, $C_{60}(CH_2CH=CH_2)_6$, in 58% yield; $C_{60}(CH_2CH=CH_2)_5Cl$ is separated as a minor reaction product in 14% yield.

During our research into the chemistry of the fullerenes we have successfully employed electrophilic aromatic substitutions by $C_{60}Cl_6$ to produce pentaaryl addended [60]fullerene derivatives, $C_{60}Ar_5Cl$, as the major reaction products.[1,2] Synthesis of hexaaryl[60]fullerenes which retain the addition pattern found in $C_{60}Cl_6$ has proved to be extremely difficult due to both steric and electronic considerations; however small quantities of C_1 symmetrical hexaaryl[60]fullerenes can be isolated from the foregoing reaction mixtures.[3] We therefore decided to investigate the electrophilic substitution of allyltrimethylsilane by $C_{60}Cl_6$ in the expectation that the steric problems encountered during the aromatic substitutions would be circumvented. In this communication we report the synthesis of a C_s symmetrical hexaallyl addended [60]fullerene, $C_{60}(CH_2CH=CH_2)_6$ (1) (Fig. 1) as the major reaction product.

An excess of allyltrimethylsilane reacted with $C_{60}Cl_6$ in dichloromethane in the presence of $TiCl_4$ at room temperature over three days producing $C_{60}(CH_2CH=CH_2)_6$ 1 in 58% yield (Fig. 2) as the major reaction product; a minor product was subsequently isolated in 14% yield and identified as C_{60}-$(CH_2CH=CH_2)_5Cl$ 2. Use of $FeCl_3$ as Lewis acid catalyst in the above reaction also produces 1, however the yield is substantially reduced under these reaction conditions. There is no evidence from the ^{1}H NMR spectrum of the crude reaction mixture for the occurrence of either the ene reaction which results from [60]fullerene reacting with substituted allyl derivatives[5] or the $TiCl_4$ catalysed [3 + 2] dipolar cycloaddition of allylsilanes which occurs with electron deficient alkenes;[6] however we have found that the cycloaddition does occur with some fullerene derivatives.[3]

The ^{1}H NMR spectrum $[CS_2–(CD_3)_2CO]$ of 1 shows three groups of overlapping resonances in the ratio of 1:2:2. The signals between δ 6.33–6.20 (6 H) are assigned to the =CH protons of the allyl groups, those between δ 5.45–5.25 (12 H) are assigned to the =CH_2 protons and those between δ 3.6–3.2 (12 H) are assigned to the methylene protons of the allyl groups. It is possible to distinguish between the methylene protons of the two allyl groups which lie on the plane of symmetry of the molecule ('on-axis') and those which lie off it. Thus the chemical shifts of the two protons of each methylene group of the on-axis allyl groups must be the same and so each multiplet appears as a simple ddd signal (double double doublet, three couplings) due to splitting by the =CH and =CH_2 protons. For the remainder of the methylene protons the chemical shifts must be different which results in AB quartet patterns with further splitting from the other protons within the group. Furthermore, the on-axis methylene protons are found to be distinctly downfield (δ 3.53 and 3.48) of the off-axis methylenes (δ 3.23–3.40); this may be a result of steric factors which force the on-axis methylene protons into an orientation which places
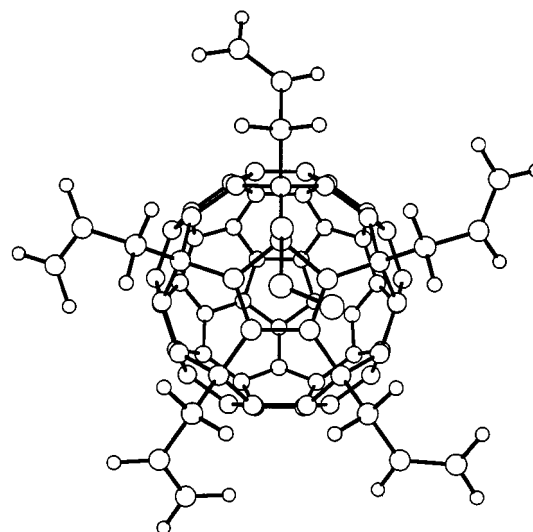

Fig. 1 Computer generated molecular structure of 1 using Cerius[2] and minimised with UNIVERSAL 1.01 force field[4] in which the hydrogen atoms of the central allyl group have been removed for clarity
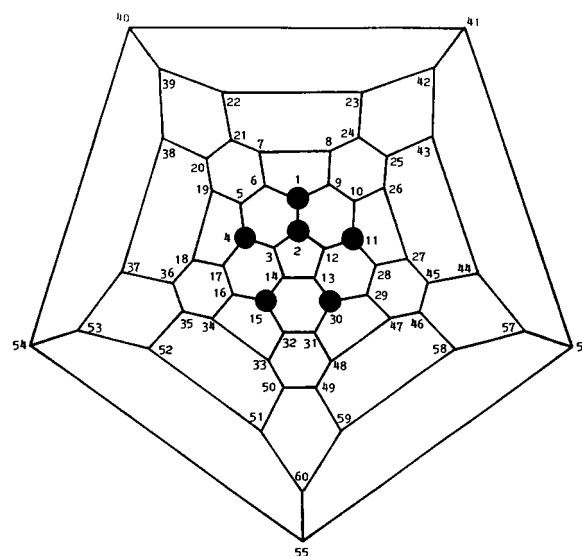

Fig. 2 Schlegel diagram showing the IUPAC numbering system[8] and the sites of allyl addition in 1 (in 2 a chlorine atom from $C_{60}Cl_6$ is retained at C2)

them nearer to the fullerene cage.[7] The ^{13}C NMR spectrum $[CS_2–(CD_3)_2CO]$ of 1 confirms the C_s symmetry of the product having 28 (26 × 2 C and 2 × 1 C) resonances due to the fullerene cage sp^2 carbon atoms between δ 155.63 and 142.60. There are also four fullerene cage sp^3 carbon atom signals (2 × 2 C and 2 × 1 C) and three sets of four allyl resonances in the required ratios (2 × 2 C and 2 × 1 C; there are co-incident signals in the =CH_2 resonances which produces a ratio of 1 × 3 C, 1 × 2 C and 1 × 1 C). Comparison of the ^{13}C NMR data obtained for

**Table 1** Selected ^{13}C NMR data [125.76 MHz; CS$_2$–(CD$_3$)$_2$CO] of **1** and **2** (figures in brackets give the integration of each resonance). Assignments are given as fullerene carbon atom attachment site followed by carbon atom type

C$_{60}$(CH$_2$CH=CH$_2$)$_6$ **1**		C$_{60}$(CH$_2$CH=CH$_2$)$_5$Cl **2**	
Chemical shift (δ/ppm)	Assignment	Chemical shift (δ/ppm)	Assignment
147.91 (1 C)	C55/C60	148.03 (1 C)	C55/C60
146.69 (1 C)	C55/C60	146.86 (1 C)	C55/C60
136.35 (1 C)	1-CH$_2$*C*H=CH$_2$	135.33 (1 C)	1-CH$_2$*C*H=CH$_2$
134.61 (2 C)	4/11-CH$_2$*C*H=CH$_2$	134.43 (2 C)	4/11-CH$_2$*C*H=CH$_2$
134.27 (2 C)	15/30-CH$_2$*C*H=CH$_2$	133.80 (2 C)	15/30-CH$_2$*C*H=CH$_2$
132.96 (1 C)	2-CH$_2$*C*H=CH$_2$	no equivalent signal	
119.25 (2 C)	4/11-CH$_2$CH=*C*H$_2$	120.28 (1 C)	1 CH$_2$CH=*C*H$_2$
119.20 (3 C)	1- and 15/30-CH$_2$CH=*C*H$_2$	119.75 (2 C)	4/11-CH$_2$CH=*C*H$_2$
		119.73 (2 C)	15/30-CH$_2$CH=*C*H$_2$
119.01 (1 C)	2-CH$_2$CH=*C*H$_2$	no equivalent signal	
63.58 (1 C)	C2	76.91 (1 C)	C2
57.47 (1 C)	C1	57.84 (1 C)	C1
57.37 (2 C)	C4/C11	57.03 (2 C)	C4/C11
54.96 (2 C)	C15/C30	54.88 (2 C)	C15/C30
45.50 (2 C)	4/11-*C*H$_2$CH=CH$_2$	48.59 (1 C)	1-*C*H$_2$CH=CH$_2$
44.92 (1 C)	1-*C*H$_2$CH=CH$_2$	44.58 (2 C)	4/11-*C*H$_2$CH=CH$_2$
42.54 (2 C)	15/30-*C*H$_2$CH=CH$_2$	42.46 (2 C)	15/30-*C*H$_2$CH=CH$_2$
38.52 (1 C)	2-*C*H$_2$CH=CH$_2$	no equivalent signal	

1 and **2** allows tentative assignments for some resonances to be made (Table 1). In particular the high field resonances of each of the three sets of the allyl carbon signals of **1** may be assigned to carbon atoms of the allyl group attached to C2. EI–MS of **1** was inconclusive, however a weak molecular ion signal (M$^+$ + 1) at m/z = 967 was detected using FAB–MS.

The ^{1}H NMR spectrum [CS$_2$–(CD$_3$)$_2$CO] of **2** has three groups of resonances at δ 6.38–6.22 (=CH, 5 H), 5.44–5.24 (=CH$_2$, 10 H) and 3.51–3.36 (CH$_2$, 10 H). One multiplet in the methylene region, which appears as a ddd (three couplings), is shifted significantly downfield to δ 3.61 and can be assigned to the on-axis allyl group. The other methylene signals comprise AB quartets with further splittings in the range δ 3.36–3.47. Substitution of an allyl group for chlorine at C1 rather than C2 is confirmed by NOE enhancements between the downfield shifted methylene protons and only the =CH protons of the allyl groups attached to C1 and C4/C11; enhancements would be expected with all of the signals in the multiplet if the allyl group were attached to C2. The ^{13}C NMR spectrum [CS$_2$–(CD$_3$)$_2$CO] of **2**, which has the same symmetry as **1**, has the required number of fullerene cage carbon resonances. The allyl carbon signals appear at chemical shifts similar to those of **1** but in groups of three resonances (2 × 2 C and 1 × 1 C) as required. FAB–MS of **2** produced a m/z signal at 925 for (M$^−$ − Cl).

C$_{60}$Cl$_6$ behaves as a typical electrophile when reacting with allyltrimethylsilane in the presence of TiCl$_4$ producing allyl[60]fullerene derivatives **1** and **2**. The electrophile attacks at =CH$_2$ of the allyl system, reducing the steric requirement of the reaction in comparison to aromatic electrophile substitution, and generates a carbocation stabilised by the neighbouring silicon–carbon bond, the trimethylsilyl group being displaced subsequently (Scheme 1).[9] The characterisation of **1** rather than
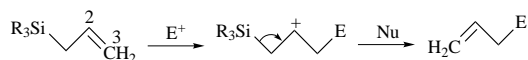
Scheme 1

2 as the major reaction product verifies the fact that steric considerations play a primary role in the isolation of C$_{60}$Ar$_5$Cl from aromatic electrophile substitutions, though the role of electronic considerations (the formation of the anti-aromatic cyclopentadienyl carbocation from **2** is required for substitution to occur at C2 of C$_{60}$Ar$_5$Cl) is still open to question. The attempted conversion of **2** to **1**, which is currently under

investigation, will answer this query. Furthermore the scope of the reaction and the chemistry of the allyl[60]fullerene derivatives are being investigated further.

Experimental

Preparation of C$_{60}$(CH$_2$CH=CH$_2$)$_6$ 1 and C$_{60}$(CH$_2$CH=CH$_2$)$_5$Cl 2
An excess of allyltrimethylsilane (0.72 g, 6.3 mmol) and titanium tetrachloride (1.0 M solution in dichloromethane) (2.0 cm^3, 2 mmol) were added to a solution of C$_{60}$Cl$_6$ (61.7 mg, 0.066 mmol) in dichloromethane (100 cm^3) and the reaction mixture stirred under argon for 3 days at room temperature. The orange reaction mixture was washed with saturated aqueous sodium hydrogen carbonate (2 × 25 cm^3) and water (1 × 25 cm^3). The organic layer was collected, filtered through Celite and dried over MgSO$_4$. Evaporation of the solvent under reduced pressure gave a red solid residue which was dissolved in pentane and the reaction products separated using chromatography on silica gel with cyclohexane as eluent. A small amount of [60]fullerene was eluted first, followed by C$_{60}$(CH$_2$CH=CH$_2$)$_6$ **1** which after evaporation of solvent under reduced pressure gave an orangey red solid (38.1 mg, 58%); ν_{max}(KBr)/cm^{-1} 3074, 2961, 2922, 2852, 1639, 1460, 1433, 1413, 1384, 1285, 1262, 1234, 1200, 993, 919, 863, 803, 720, 706, 609, 570, 563, 548, 543, 525; δ_H[500 MHz; CS$_2$–(CD$_3$)$_2$CO (lock); J/Hz] 3.24–3.40 [8 H, m (AB q), CH$_2$], 3.48 (2 H, ddd, J 7.1, 1.2 and 1.2, CH$_2$), 3.53 (2 H, ddd, J 7.0, 1.0 and 1.0, CH$_2$), 5.27–5.37 (10 H, m, =CH$_2$), 5.39–5.43 (2 H, m, =CH$_2$), 6.20–6.33 (6 H, m, =CH); δ_C[125.76 MHz; CS$_2$–(CD$_3$)$_2$CO (lock)]; δ_C(number of carbon atoms) 38.52 (1 C), 42.54 (2 C), 44.92 (1 C), 45.50 (2 C), 54.96 (2 C), 57.37 (2 C), 57.47 (1 C), 63.58 (1 C), 119.01 (1 C), 119.20 (3 C), 119.25 (2 C), 132.96 (1 C), 134.47 (2 C). 134.61 (2 C), 136.35 (1 C), 142.60 (2 C), 143.66 (2 C), 143.74 (2 C), 143.76 (2 C), 143.78 (2 C), 143.88 (2 C), 144.27 (2 C), 144.95 (2 C), 144.97 (2 C), 144.99 (2 C), 145.18 (2 C), 145.81 (2 C), 146.69 (1 C), 146.89 (2 C), 146.97 (2 C), 147.77 (2 C), 147.86 (2 C), 147.88 (2 C), 147.91 (1 C), 148.01 (2 C), 148.17 (2 C), 148.35 (2 C), 148.46 (2 C), 148.58 (2 C), 152.53 (2 C), 153.47 (2 C), 155.37 (2 C), 155.62 (2 C); m/z (FAB–MS) 967 (M$^+$ + 1 for C$_{78}$H$_{30}$, 12%), 720 (C$_{60}$, 100%).

Further elution with cyclohexane gave C$_{60}$(CH$_2$CH=CH$_2$)$_5$Cl **2** (8.5 mg, 14%) as a minor reaction product; ν_{max}(KBr)/cm^{-1} 3074, 2923, 2853, 1639, 1559, 1540, 1522, 1459, 1437, 1413, 1378, 1287, 1261, 1234, 1196, 1111, 991, 919, 726, 696, 600, 574, 569, 562, 547, 524; δ_H[500 MHz; CS$_2$–(CD$_3$)$_2$CO (lock); J/Hz]; 3.47–3.36 [8 H, m (AB q), CH$_2$], 3.61 (2 H, ddd, J 7.2, 1.2 and

1.2, CH$_2$), 5.24–5.44 (10 H, m, =CH$_2$) and 6.22–6.38 (5 H, m, =CH); δ_C[125.76 MHz; CS$_2$–(CD$_3$)$_2$CO (lock)]; δ_C(number of carbon atoms) 42.47 (2 C), 44.58 (2 C), 48.59 (1 C), 54.88 (2 C), 57.03 (2 C), 57.84 (1 C), 76.91 (1 C), 119.73 (2 C), 119.75 (2 C), 120.28 (1 C), 133.80 (2 C), 134.43 (2 C), 135.33 (1 C), 142.80 (2 C), 142.85 (2 C), 143.58 (2 C), 143.75 (2 C), 143.82 (2 C), 143.91 (2 C), 144.16 (2 C), 144.41 (2 C), 144.51 (2 C), 144.53 (2 C), 144.76 (2 C), 145.57 (2 C), 146.83 (2 C), 146.86 (1 C), 146.87 (2 C), 146.96 (2 C), 147.79 (2 C), 147.97 (2 C), 148.03 (1 C), 148.20 (2 C), 148.27 (2 C), 148.38 (2 C), 148.42 (2 C), 148.60 (2 C), 150.23 (2 C), 152.40 (2 C), 154.29 (2 C), 154.86 (2 C); m/z (FAB–MS) 925 (M$^+$ − Cl for C$_{75}$H$_{25}$, 8%), 720 (C$_{60}$, 100%).

References

1 A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1463.

2 P. R. Birkett, A. D. Darwish, A. G. Avent, I. Hahn, G. J. Langley, H. W. Kroto, J. O'Loughlin, R. Taylor and D. R. M. Walton, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 1121.

3 P. R. Birkett, unpublished results.

4 A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10 024.

5 K. Komatsu, Y. Murata, N. Sugita and T. S. M. Wan, *Chem. Lett.*, 1994, 635; S. Wu, L. Shu and K. Fan, *Tetrahedron Lett.*, 1994, **35**, 919; W. H. Miles and P. M. Smiley, *J. Org. Chem.*, 1996, **61**, 2559.

6 H.-J. Knölker, P. G. Jones and J.-B. Pannek, *Synlett*, 1990, 429; H.-J. Knölker, N. Foitzik, H. Goesmann, R. Graf, P. G. Jonesa and G. Wanzl, *Chem. Eur. J.*, 1997, **3**, 538.

7 M. F. Meidine, A. G. Avent, A. D. Darwish, H. W. Kroto, O. Ohashi, R. Taylor and D. R. M. Walton, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 1189.

8 E. W. Godly and R. Taylor, *Pure Appl. Chem.*, 1997, **69**, 1411.

9 T. H. Chan and I. Fleming, *Synthesis*, 1979, 761 and references cited therein.