



Rapid acquisition of a sixty-carbon fullerene precursor. A new synthetic approach to C₆₀

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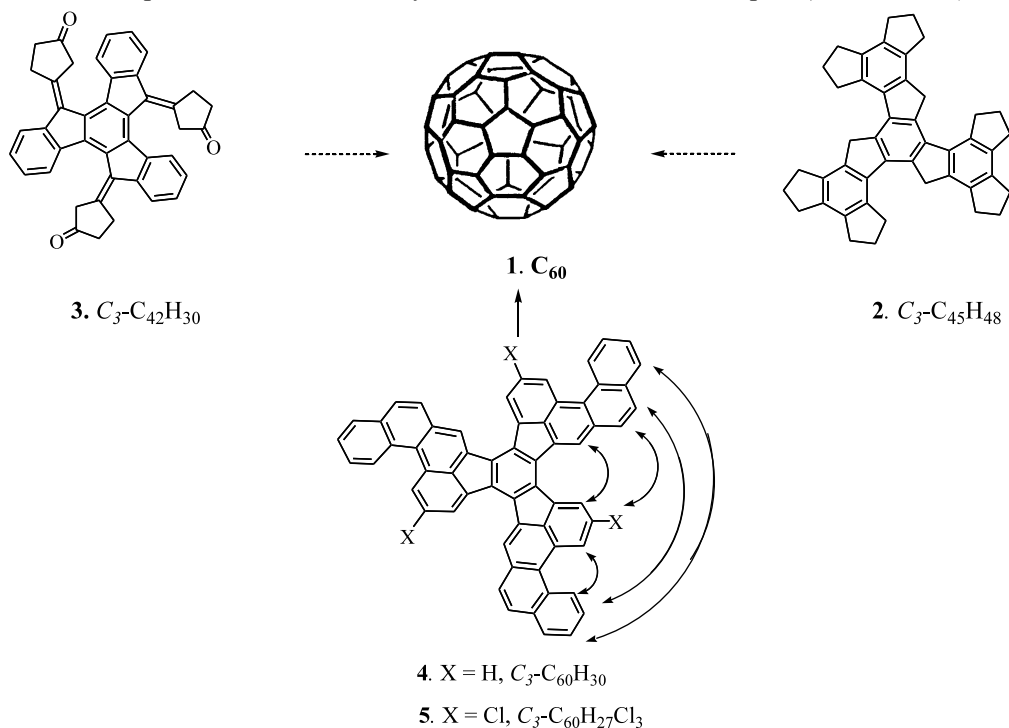
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Abstract—In a new approach towards C₆₀, two C₃-symmetric precursors having all the carbon content and thirteen rings have been assembled in just one step from readily crafted building-blocks through threefold Wittig–Horner coupling. © 2002 Published by Elsevier Science Ltd.

Ever since its conception,^{1a} detection^{1b} and preparative access,^{1c} C₆₀ **1** has enticed the synthetic community as a formidable synthetic objective.² Devising a rational synthesis of buckyball C₆₀, involving the generation of 32 rings and establishing 90 C–C bond connectivities, is by any reckoning a major intellectual and experimental challenge. Not surprisingly, during the past decade, many groups around the world have mobilised their ideas and resources in pursuit of a rational synthetic

route to C₆₀ and only a few months ago a synthesis, culminating in isolable amounts of **1**, has been reported.³ Early synthetic efforts towards C₆₀, emanating from triindanone derived **2**, C₄₅H₄₈,⁴ and truxenone derived **3**, C₄₂H₃₀,⁵ were bold and imaginative, but did not make further headway. In another approach, several groups assembled macrocyclic polyalkyne precursors that eject multiple fragments and collapse to C₆₀ on laser desorption/ionisation (LDI) mass spectro-

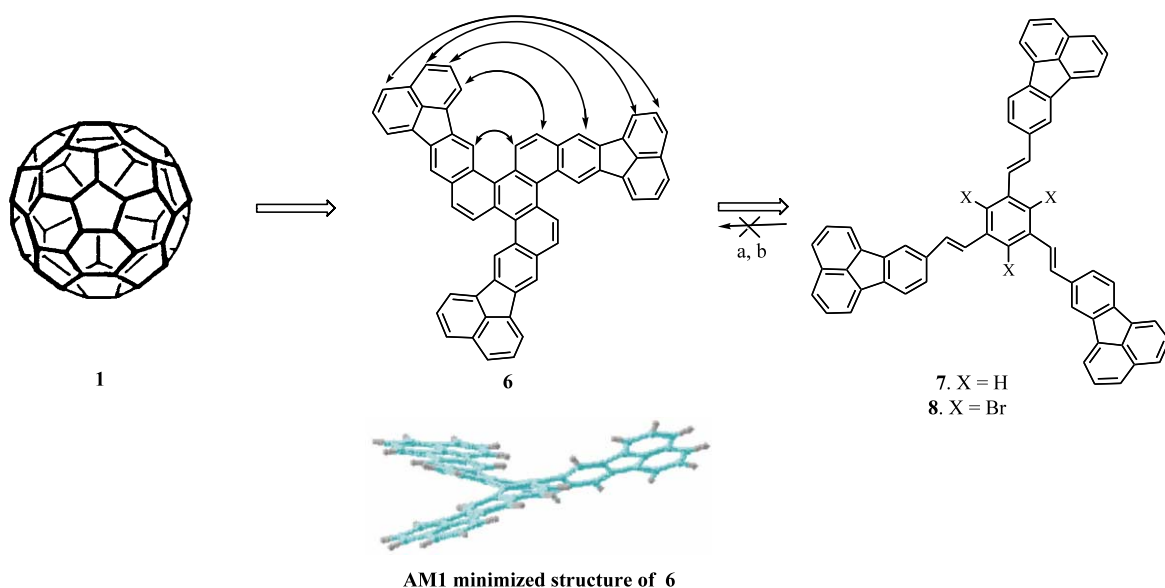


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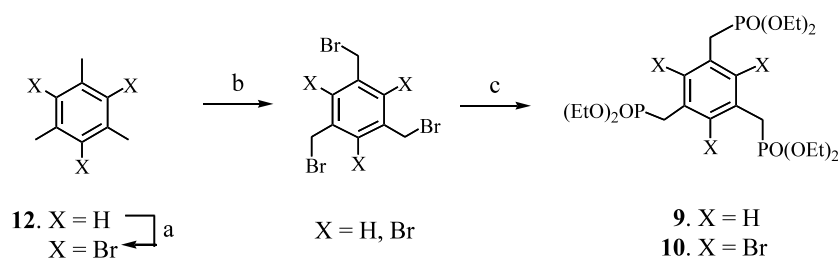
metry.⁶ However, from a preparative and classical synthesis perspective, much attention has been bestowed on C_3 -symmetric precursor **4**, $C_{60}H_{30}$, which can undergo unimolecular, 15-fold tandem cyclisation (see arrows) to C_{60} .^{3,7} Indeed, laser irradiation of **4** has led to the observation of $C_{60}^{+\bullet}$ by mass spectrometry^{7d,e} and a tris-halo derivative **5** of **4** on FVP produced isolable³ quantities of **1**. The key precursors **4** and **5** of C_{60} in turn, have been assembled through multi-step synthetic sequences.^{3,7}

As part of our⁸ ongoing interest in the synthesis of buckyball **1** and its curved fragments (buckybowls), we have conceived of an approach different from oth-

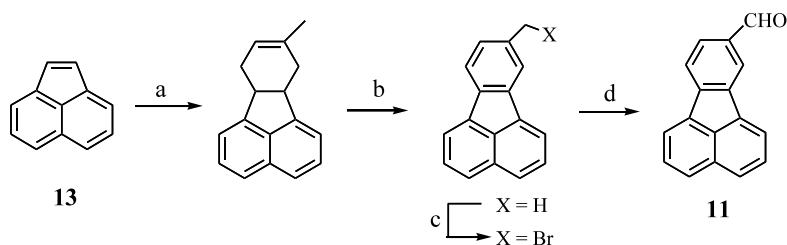
ers in which the novel hydrocarbon **6**, $C_{60}H_{30}$, occupies a pivotal role and can deliver C_{60} through 15-fold unimolecular cyclisation (see arrows), forming alternating five- and six-membered rings on FVP. The hexadecacyclic hydrocarbon **6** has an interesting propeller shaped topology as indicated by its energy-minimised structure (Scheme 1). Retrosynthetic considerations indicated that **6** can be accessed from **7** or its tribromo derivative **8** through threefold photocyclisation or intramolecular Heck coupling,⁹ respectively, Scheme 1. It was proposed to assemble the key C_{60} precursors **7** and **8** in one-step through a threefold Wittig–Horner type reaction of C_3 -symmetric building-blocks.



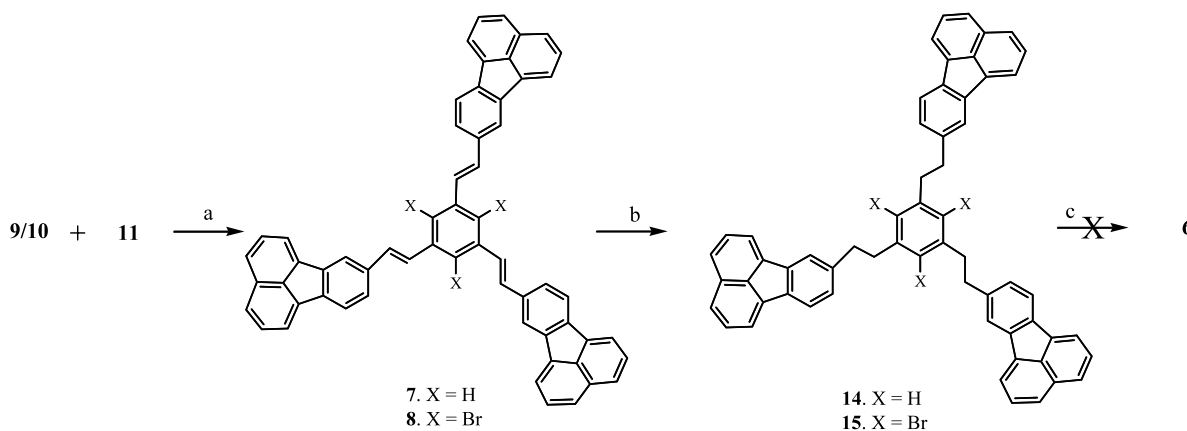
Scheme 1. Reagents and conditions: (a) For **7**, $h\nu$, benzene, propylene oxide, I_2 ; (b) for **8** $Pd(OAc)_2$, $BnMe_3NBr$, K_2CO_3 , DMF, $140^\circ C$.



Scheme 2. Reagents and conditions: (a) Br_2 , Fe, 59%; (b) NBS, AIBN, CCl_4 , 30%; (c) $P(OEt)_3$, $160^\circ C$, ~100%.



Scheme 3. Reagents and conditions: (a) isoprene, sealed tube, $175^\circ C$, 40%; (b) DDQ, benzene, Δ , 70%; (c) NBS, $(PhCOO)_2$, CCl_4 , 80%; (d) $(Bu_4N)_2Cr_2O_7$, $CHCl_3$, Δ , 86%.



Scheme 4. Reagents and conditions: For **7** X=H, (a) NaH, DMF, 4 days, 70%; (b) 10% Pd/C, H₂, EtOAc, 60%; (c) 10% Pd/C, sealed tube, 400°C. For **8** X=Br, (a) NaH, DMF, 70°C, 4 days, 66%.

For the assembly of **7** and **8**, C₃-symmetric Wittig–Horner reagents **9/10** and fluoranthene based tetracyclic aldehyde **11**¹⁰ were identified as reaction partners and were prepared from mesitylene **12** and acenaphthene **13**, respectively, as shown in Schemes 2 and 3. Gratifyingly, threefold coupling between tris-phosphonate reagent **9**¹⁰ and aldehyde **11** in the presence of NaH was smooth and led to C₃-symmetric all *trans*-**7** as a bright yellow solid, Scheme 4.¹⁰ Formation of **7** was indicated by its mass spectrum (MALDI-TOF) which showed a molecular ion at *m/z* 757.3 amu (M⁺), calcd for C₆₀H₃₆=756.93 amu. While **7** was insoluble in most organic solvents, its ¹H NMR spectrum could be recorded in 1,1,2,2-tetrachloroethane-*d*₂ at 333 K and the characteristic ABq pattern centred at δ 7.38 with *J*=16.2 Hz secured the *trans* disposition of the olefinic bonds. However, the next critical step, the threefold oxidative photocyclisation of **7** to the desired C₆₀ precursor **6**, under a variety of conditions, met with repeated failure, Scheme 1. Attributing this failure to the inhibition of *cis*–*trans* isomerisation in **7**, a necessary requirement for its photocyclisation to **6**, due to steric overcrowding by the bulky benzo-fluoranthene moiety, we considered an alternative possibility. On catalytic hydrogenation **7** furnished the hexahydro product **14**, with improved solubility in organic solvents and its 20 line ¹³C NMR spectrum with signals at δ 38.5 (CH₂) and 38.2 (CH₂) fully secured its structure.¹⁰ As planned, **14** was subjected to cyclodehydrogenation under a variety of conditions (e.g. Pd/C at 400°C), but only fragmented products like 8-methyl-fluoranthene were isolated and the desired compound **6** was not detected.

At this stage, we turned towards **8** with the intent of effecting Heck coupling. A threefold Horner–Wittig reaction between the phosphonate ester **10**¹⁰ and tetracyclic aldehyde **11** in the presence of NaH was slow but the expected C₃-symmetric all *trans* tribromide **8**¹⁰ was realised in reasonable yield, Scheme 4. The mass spectrum (MALDI-TOF) exhibited the expected peak at *m/z*=993.4 (M⁺), calcd for C₆₀H₃₃Br₃=993.6 and the ¹H NMR spectrum of this very insoluble material in 1,1,2,2-tetrachloroethane-*d*₂ at 353 K not only secured

the structure but the ABq pattern at δ 7.12 confirmed the expected *trans* disposition of the olefinic bonds. Tribromo-**8** was now subjected to Pd(II) mediated Heck coupling under elevated temperature and the expectation was that under such a regime the *cis*–*trans* equilibrium might take place and cyclisation to **6** could occur.⁹ However, the outcome once again was disappointing. An obvious option at this stage was to reduce the olefinic double bonds in **8** to hexahydro-tribromide **15** and then attempt a Heck coupling as was demonstrated by us recently in similar systems.⁹

However, the seemingly straightforward reduction of the double bonds in **8** could not be achieved despite many efforts. It appears that the high insolubility of this substrate in most organic solvents is detrimental to its further evolution and efforts are underway to overcome this problem.

In short, we have rapidly assembled **7** (C₆₀H₃₆) and **8** (C₆₀H₃₃Br₃) having the full carbon content of C₆₀ and embedding thirteen rings in just one-step through Wittig–Horner reactions on appropriately crafted partners. Although, the proposed transformation of **7** and **8** to **6** has not been successful so far, the ready availability of precursors **7** and **8** is significant and provides stimulus for further efforts towards C₆₀.

Acknowledgements

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- All new compounds reported here exhibited satisfactory spectral characteristics. Selected spectral data: **7**: mp >350°C, UV (CHCl₃): λ_{\max} =242, 332 and 379 nm; IR (KBr): 3037, 2923, 1584, 1457, 954 cm⁻¹; ¹H NMR (300 MHz, C₂D₂Cl₄, 333 K): δ 8.17 (s, 3H), 8.05 (d, 3H, *J*=6.6 Hz), 7.98–7.86 (m, 12H), 7.72 (s, 3H), 7.72–7.61 (m, 9H), 7.42 and 7.34 (ABq, 6H, *J*=16.2 Hz); MS (MALDI-TOF): *m/z*=757.3 (*M*⁺), calcd for C₆₀H₃₆=756.93; **8**: mp >350°C, UV (1,1,2,2-tetrachloroethane): λ_{\max} 254, 296, 349 and 365 nm; IR (KBr): 3041, 1457, 963, 766 cm⁻¹; ¹H NMR (300 MHz, C₂D₂Cl₄, 353 K): δ 8.15 (s, 3H), 8.05 (d, 3H, *J*=6.6 Hz), 7.99–7.86 (m, 12H), 7.70–7.60 (m, 9H), 7.20 and 7.05 (ABq, 6H, *J*=16.5 Hz); MS (MALDI-TOF): *m/z*=993.4 (*M*⁺), calcd for C₆₀H₃₃Br₃=993.6; **14**: mp 180°C, IR (KBr): 3040, 2918, 1601, 1456, 769 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.88–7.74 (m, 15H), 7.63–7.57 (m, 9H), 7.09 (d, 3H, *J*=6.3 Hz), 6.92 (s, 3H), 2.97 (brs, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 141.8 (3C), 141.6 (3C), 139.7 (3C), 137.3 (3C), 137.1 (6C), 132.7 (3C), 130.0 (3C), 128.0 (3C), 127.9 (6C), 126.6 (3C), 126.5 (3C), 126.2 (3C), 121.8 (3C), 121.3 (3C), 119.9 (3C), 119.6 (3C), 38.5 (3C), 38.2 (3C); MS (*m/z*): 762 (*M*⁺). Anal. calcd for C₆₀H₄₂: C, 94.45; H, 5.55. Found: C, 94.65; H, 5.58.