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Steps toward the synthesis of a geodesic $C_{60}H_{12}$ end cap for a C_{3v} carbon [6,6]nanotube

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Dedicated to Professor Reginald H. Mitchell
on the occasion of his 65th birthday

ABSTRACT

Several shape-persistent carbon-rich nanomolecules with diameters exceeding 1.7 nm have been prepared by the aldol trimerization of 20-carbon aromatic ketones bearing chlorine atoms at various sites. These $C_{60}H_{27}Cl_3$ and $C_{60}H_{24}Cl_6$ polycyclic aromatic compounds represent attractive intermediates for the synthesis of a geodesic $C_{60}H_{12}$ end cap of a C_{3v} carbon [6,6]nanotube.

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1. Introduction

Carbon nanotubes have been widely touted for their potential to fulfill dreams in materials science and in the emerging realm of nanotechnology.[1–4] They also hold considerable intrinsic scientific interest owing to their unusual curved networks of trigonal carbon atoms. Despite intense scrutiny by scientists and engineers worldwide for nearly two decades, however, these fascinating carbon-rich materials are still being made today by poorly understood empirical methods.[5–8] We contend that such targets should be accessible by rational chemical synthesis and that the successful realization of the requisite synthetic methods will revolutionize the science of carbon-rich materials. Our 12-step laboratory synthesis of fullerene-C_{60} by chemical methods in 2002[9–11] represents one milestone in the journey toward that goal.

In recent years, we have begun to focus our research on the development of chemical methods for the rational, structure-specific synthesis of single-chirality, all-carbon, single walled nanotubes (SWNTs). The structural variety possible for carbon nanotubes is virtually limitless.[3,12,13] They come in all different diameters. The orientation of the benzene rings along the shaft can be chiral (helical) or achiral, and the chiral tubes vary according to the pitch of the helix. Achiral tubes are classified according to the appearance of their rims as either ‘zig-zag’ or ‘armchair’. Both ends can be open, or both can be closed, or a single tube may have one end of each type. Superimposed on all of that, carbon nanotubes can be single walled, double walled, or multiwalled, with more than 10 coaxial tubes nested together.[3,12,13] Carbon nanotubes from all of these classes are already known, and their properties vary as a function of structure.[3,12,13] Unfortunately, empirical methods[5–8] do not produce homogeneous samples in which all the carbon nanotubes have the same predefined diameter and chirality (ring orientation). The problem is compounded by the fact that, unlike the fullerenes, carbon nanotubes made in this way cannot be separated and purified to homogeneity by chromatographic methods, because they are totally insoluble.[14,15] This problem represents a clear challenge to synthetic organic chemists!

Where should one begin? We have chosen the achiral, armchair, all-carbon, single walled nanotubes (e.g., [6,6]SWNTs) as our highest priority targets. Such nanotubes are expected to exhibit metal-like behavior, regardless of diameter.[1,3,12,13] Consequently, they all hold the potential to find use as ultra-thin, super-strong, electrically conducting nanowires in myriad nanoelectronic devices. Most zig-zag tubes and chiral tubes, by contrast, are expected not to exhibit metal-like behavior.[1,3,12,13] The choice of initial targets thus seems obvious to us. This paper describes one approach to the chemical synthesis of [6,6]SWNTs.

1.1. General strategy

The course we are pursuing builds on our previous experience with syntheses of open geodesic polyarenes.[11,16,17,18] Figure 1 illustrates the general strategy, as applied to a proposed synthesis of [6,6]SWNTs that are closed at one end and open at the other. As we see it, two major hurdles must be surmounted to produce SWNTs by this general strategy: (1) synthesis of a geodesic polyarene that has the initial armchair rim and six fully unsaturated five-membered rings, as required for a hemisphere by Euler's theorem[19] and

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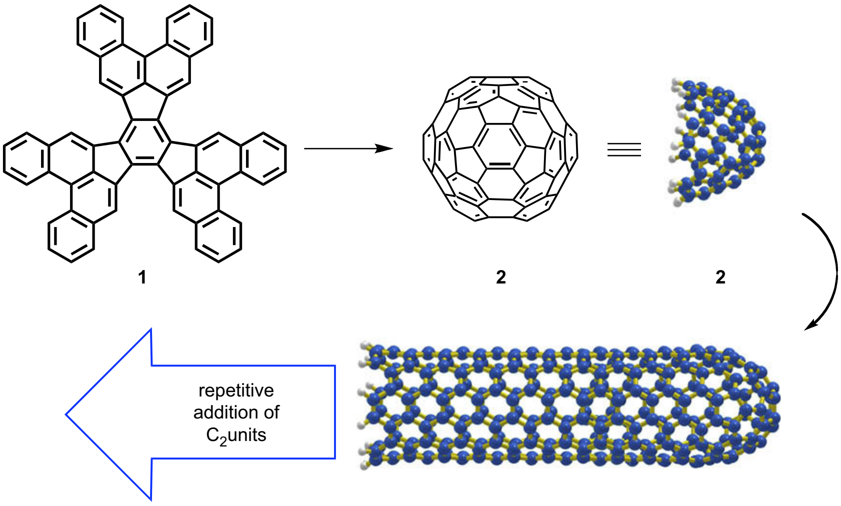

Figure 1. General plan for building a hemispherical end cap and extending it to produce an armchair SWNT.

(2) extension of the rim by adding C_2 units across the 'bay regions' to produce new six-membered rings.

For such a synthesis to be practical, the last step must be fully self-replicating, i.e., it must transform hydrocarbon bay regions into new, fully unsaturated, six-membered rings under a single set of conditions, without intervention by the chemist. Such a process would extend an armchair rim indefinitely, until the C_2 feedstock was consumed or the source shut off (not unlike a polymerization with 'living polymers'). In fact, catalytic methods for growing carbon nanotubes to lengths in excess of 1 mm, using acetylene as the C_2 feedstock, have already been reported,[20,21] so this aspect of the problem may already be solved, at least in principle. Conceivably, methods may even be found to extend such a nanotube template by uncatalyzed processes.

Herein lies the big payoff to the synthetic organic chemist. Only a few *micrograms* of the appropriate geodesic polyarene 'seed' need to be extended to a length of 1 mm or more in order to produce *gram quantities* of homogeneous SWNTs! The SWNTs derived in this manner will all necessarily have the same diameter and armchair rim structure, by virtue of the growth mechanism. The tremendous amplification in dimension (ca. $1\,\text{nm} \rightarrow 1\,\text{mm} = 10^6$ increase) will compensate for any low yields endured earlier in the synthesis.

What follows is a summary of our progress toward a synthesis of the C_{3v} nanotube end cap **2**, the geodesic $C_{60}H_{12}$ hydrocarbon that would result from 'stitching together' the arms of the $C_{60}H_{30}$ hydrocarbon **1**, a carbon-rich $C_{2n}H_n$ molecule of nanometer dimensions.

1.2. Retrosynthetic analysis

Figure 2 shows the loci of the nine new bonds that must be formed in stitching up **1** to give **2**.

Flash vacuum pyrolysis (FVP) has proven effective as a general method for transforming planar polycyclic aromatic hydrocarbons (PAHs) and halogenated derivatives thereof into their bowl-shaped counterparts by joining together carbon atoms that lie far apart in the planar conformations.[16–18] It has been our experience, however, that respectable yields of the desired geodesic polyarenes require the orchestrated generation of aryl radicals (or carbenes) at the sites where the new bonds must be formed.[22,23] Once curvature has been introduced, a 'cascade effect' seems to operate to close additional rings by thermal cyclodehydrogenations, without the need for additional radical generating groups.[18] Our FVP synthesis of C_{60} represents an extreme example of the cascade effect; in our $C_{60}H_{27}Cl_3$ synthetic intermediate, three chlorine atoms were incorporated at strategic sites, and FVP effected the closure of 15 new C–C bonds to produce isolable quantities of C_{60}, with an average yield of >60% per bond.[10,11]

We recognized at the outset of this project that the most difficult part of stitching together the arms of **1** by FVP would be formation of the first three bonds, those closest to the core, marked *a* in Figure 2. Closing these three new six-membered rings would introduce curvature comparable to that in C_{60}, and the cascade effect might then take over to form the remaining six bonds. Unfortunately, the incorporation of halogen atoms as radical precursors in the crowded fjord regions of molecules related to **1** has proven problematical, presumably for steric reasons.[24,25] In such

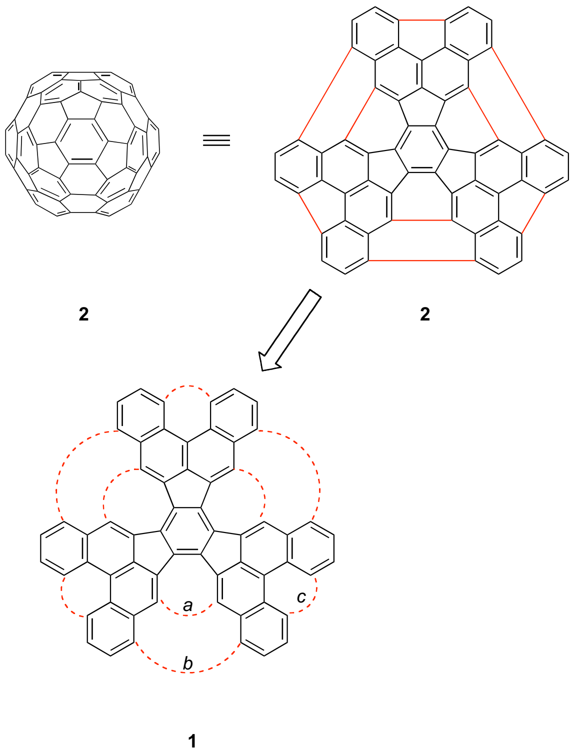

Figure 2. Nine new bonds must be formed in stitching up **1** to give **2**.

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