

Organic chemists conquer the synthesis of C₆₀

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Fullerenes and particularly C₆₀, the new allotropic form of carbon, is arguably the most important discovery of a new class of compounds in the recent past¹. Named as the molecule of the year in 1991 it received tremendous prominence resulting in the award of Nobel prize to its discoverers². It continues to be a topic of interest across the fields, from chemistry, physics, biology to medicine. The successes in high temperature superconductivity, applications in medicine and potential applications in material science of its congener class of molecules, namely carbon nanotubes, have heightened the interest of this class of compounds. Although the truncated icosahedral structure for C₆₀ was conceived in the seventies, it remained of esoteric interest until its discovery in 1985.

However, the generation of fullerenes by arcing graphite or soot extraction is far from being any rational or controlled attempt and borders on black-box operations. Synthetic organic chemists like to boast that, given enough resources, any molecule that is capable of existence can be synthesized. Justifiably, the synthetic accomplishments include taxol, palytoxin, vancomycin, vitamin B₁₂, and many other complex natural compounds as well as molecules with aesthetically appealing shapes such as prismane, cubane, dodecahedrane adopting beautiful and elegant strategies, add credibility to such claims. However, even the first production of C₆₀ by physicists adopting not-so-rational methods was so embarrassing to the synthetic chemists that many synthetic chemistry groups were set out to achieve the synthesis of C₆₀ by rational means. One particular synthetic organic chemistry group of Chapman and UCLA has devised several carefully crafted synthetic attempts towards the synthesis of C₆₀, even in the post-fullerene era (prior to 85) albeit unsuccessfully³. However, the discovery of fullerenes has triggered off the quest to conquer the synthesis of C₆₀ in several synthetic organic chemistry groups across the globe. The renewed synthetic attempts towards this beautiful molecule began in early nineties but failed to achieve success until November 2001.

Scott *et al.*⁴ have reported the first rational synthesis of C₆₀. The synthesis involved carefully crafted synthetic strategies, years of work involving several computational and experimental studies on several smaller buckybowls followed by elegant execution using the state-of-art experimental techniques. The ground work for the successful synthesis was also revealed a few months ago in the same journal⁵. One vital aspect of the rational synthesis is choosing the right precursor, and in this successful case multi-gram quantities of precursor was prepared in 11 steps all of which are well known. The precursor molecules are arrived at in the following way, described in the author's own words: 'If you put a molecular model of C₆₀ on the table with a benzene ring at the south pole, then cut every other bond of the benzene ring at the north pole and peel it like a banana, you end up with this propeller-shaped molecule that has three arms radiating out of a central ben-

zene ring.' However, the unfunctionalized propeller type hydrocarbon C₆₀H₃₀ still required proper functionalization of at least three key positions to ensure the zipping of the molecule into C₆₀. Thus, the C₆₀H₂₇Cl₃ molecule, where the three Cl atoms are properly placed to initiate the stitching processing resulted in the formation of C₆₀, involving a cascade of cyclodehydrogenation reactions. In the published paper in *Science*, Scott points out that a decade of work in his laboratory is to be categorized as a rational synthesis, with careful planning, and adequately demonstrated the rationality of using FVP to convert a C₃₀ precursor into a bowl-like polyarene. It is important to note that they got what they set out to make and not random products. Figure 1 depicts the successful synthetic route employed by Scott *et al.* to obtain C₆₀.

Synthesizing C₆₀ in a rational manner based on organochemical transformations is a very valuable accomplishment

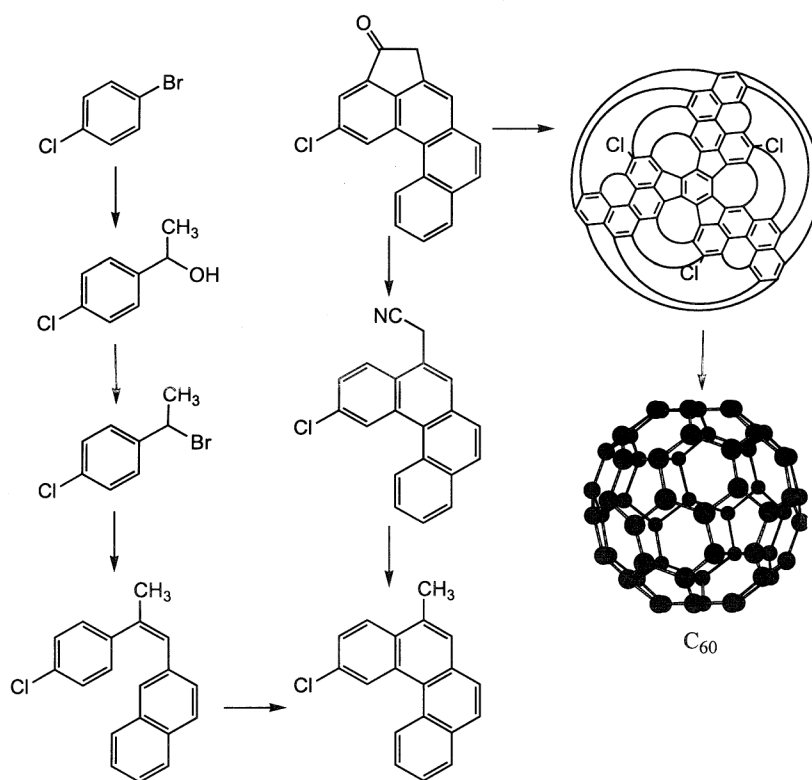


Figure 1. The schematic diagram of Scott's successful synthesis of C₆₀.

because it helps in devising strategies for producing the right derivatives. It may be argued that the first rational synthesis of C_{60} is the most significant total synthesis of a target molecule since the first synthesis of taxol or vancomycin. In addition to Scott's group, Rabideau and co-workers⁶ at Iowa State University, and Siegel's group at University of California-San Diego are notable⁷. Scott, Rabideau and Siegel's groups are responsible for development and extensive use of both pyrolytic and non-pyrolytic methods to achieve the syntheses of buckybowls. While the flash vacuum pyrolysis (a pyrolytic method) was used in the successful synthesis of fullerenes, the nonpyrolytic methods have shown substantial yield improvements and are amenable for scale up. Another earlier attempt towards C_{60} was also reported from the Rassat group⁸. In India, G. Mehta's group initially at Hyderabad University and later at Indian Institute of Science, Bangalore made elegant attempts towards these fascinating compounds and have obtained and conceived interesting buckybowl structures⁹.

Thus, although many synthetic attempts towards C_{60} had to face frustrating setbacks, the chemistry of the curved polycyclic aromatics has flourished and also lead to the development of useful techniques to achieve the synthesis of strained polycyclic systems. These compounds, popularly called as buckybowls, have become interesting in their own right. The considerable attention given to the C_{60} has led to renewed interest in the

curved polynuclear aromatic hydrocarbons known as buckybowls. Buckybowls appear to be the natural synthetic precursors in the rational attempts towards the synthesis of C_{60} and also these molecules are expected to potentially mimic some of the unique properties of C_{60} . Our group has reported interesting ways to modulate the curvature, dynamics and other physicochemical properties through site-specific substitution in buckybowls¹⁰. In this context, several beautiful molecules were synthesized which are interesting in their own right.

The synthetic success of C_{60} achieved by Scott and coworkers definitely adds one more illustrious feather in the cap of organic chemistry community. While the synthesis of C_{60} is certainly interesting from an academic point of view, the strategy employed to achieve it should pave the way to rationally design feasible synthetic methodologies to access the derivatives of fullerenes and related molecules of industrial importance. In recent years, the organic synthesis has had profound influence in a range of disciplines starting from biology to nanotechnology. Digging out more effective synthetic methods hidden in the mines of wisdom is a continuous challenge.

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