Explosions as a Synthetic Tool? Cycloalkynes as Precursors to Fullerenes, Buckytubes, and Buckyonions

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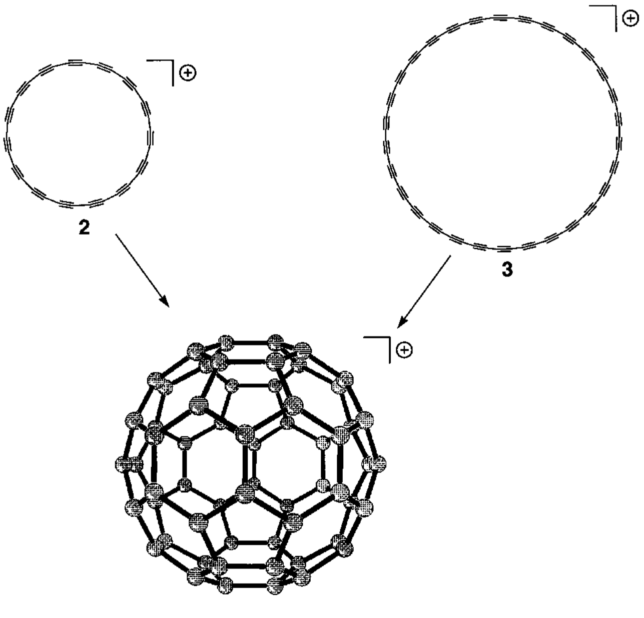
Why would anyone attempt to synthesize fullerenes from elaborate precursors if all it takes is graphite and a suitable energy source such as a strong electric field or laser power? One of the answers to this somewhat unfair question bears a certain philosophical charm reminiscent of the motto that the way is the goal. Of course, the benefit of the synthetic methodology developed to obtain carbon-rich materials in a rational fashion is multitudinous and undisputed.[1] But there is more. Firstly, research on endohedral fullerene complexes, in many ways the most exciting and the most unprecedented aspect of fullerene chemistry and physics, is severely limited because of the very low yields encountered in their preparation. A promising approach to improve the current situation lies in the development of synthetic strategies towards these molecules, and first steps in this direction have been made.[2] Secondly, knowledge about crucial stages of the fullerene formation process and about the rules that govern the observed product distribution remains rather sketchy. The design of more sophisticated fullerene precursors may allow the investigation of this process under conditions that are more controllable than the chaotic plasma of carbon atoms at around 3000 K.

Strained cycloalkynes are attractive starting materials for the energy-induced transformation of carbon-rich materials to fullerenes or related structured forms of carbon. In ideal cases, the high-energy content of a given cycloalkyne can lead to the coalescence of the cyclic structure to a thermodynamically more stable carbon sphere. Furthermore, incorporation of benzenoid or cyclopentadienyl substructures into cycloalkynes offers the opportunity to coordinate metal fragments, thereby providing a synthetic entry to endohedral fullerene complexes. Significant progress towards these goals has recently been made, and a selection of the (thermo)chemistry of new dehydrobenzoannulenes and alkyne-based cyclophanes is highlighted here.

The first evidence for the feasibility of a cycloalkyne →fullerene conversion was produced by Diederich et al.[3] shortly before macroscopic quantities of buckminsterfullerene C_{60} (**1**) were available.[4] In Fourier transform laser desorption (FT-LD) mass spectrometric experiments they observed that cations of cyclo-C_{30} (**2**) undergo an efficient ion–molecule coalescence to give fullerene ions such as $\mathbf{1}^+$ (Scheme 1). In a related series of experiments, cyclic cationic carbon structures such as **3** (depicted in D_{30h} symmetry) were also shown to rearrange to spherical C_{60} ions.[5] However, the preparation of bulk quantities of the neutral cyclocarbons and hence of the fullerenes from these precursors remains elusive.[6]



Scheme 1. Transformation of cationic carbon rings to C_{60}^+.

More recent developments exploit the energy content of readily accessible cycloalkynes based on phenyl–alkynyl structural motives, albeit not always with fullerene formation in mind. For example, the strained dehydrobenzoannulene **4**[7] could be converted by light, heat (145 °C), or pressure

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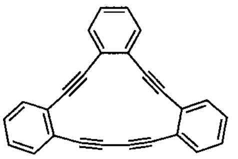

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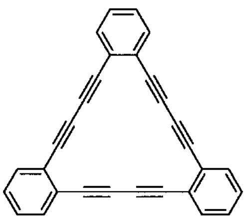

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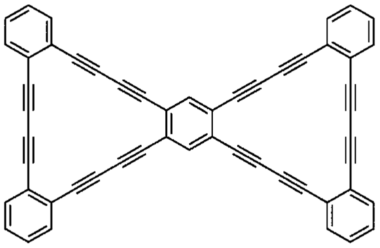

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(1380 bar) in a topochemical polymerization reaction that is typical for butadiynes into a deeply colored polymer. A similar thermochemical behavior (strongly exothermic transformation around 200 °C) was observed for compounds **5** and **6**.[8] However, none of the systems **4**–**6** shows any tendency to produce spherical forms of carbon under the conditions investigated.

The situation is drastically different when the thermochemistry of cycloalkyne **7**[9] is considered (Figure 1). The high energy content of **7** becomes apparent when the compound is heated to 245 °C. At this temperature **7** "explodes violently with a flash of orange light".[9] An investigation of the black, carbonaceous residue by transmission electron microscopy revealed the presence of not only amorphous carbon and graphite, but also of closed-shell carbon particles, namely, buckytubes and buckyonions.[10] It is not unlikely that the molecular structure of **7** observed in the crystal (Figure 1) supports its explosive transformation to these fullerenoid carbon allotropes. While **7** is commonly, and deceivingly, depicted as a planar rectangle, the X-ray structural analysis reveals that **7** adopts a nonplanar, twisted D_2-symmetric conformation in the crystal in which the two butadiynyl linkages are crossing on top of each other.

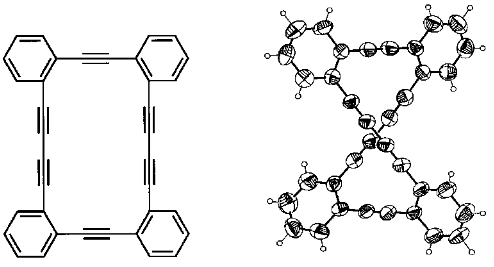

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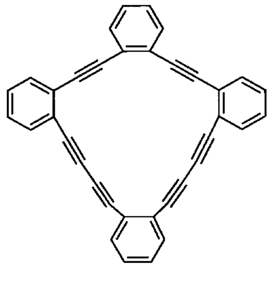
Figure 1. The structure of **7** in the crystal deviates considerably from that suggested by the structural formula.

The thermal decomposition of **7** into fullerenic substructures is a milestone in fullerene formation and represents the first example of a macroscopic preparation of closed-shell carbon particles from acetylenic precursors. However, molecular allotropes of carbon, such as C_{60} or higher fullerenes, were not found among the decomposition products. It is interesting to note in this context that **8**,[11] a structural isomer of **7** with a saddle-shaped solid-state conformation, also shows thermal transformations, but in this case they occur at temperatures of around 50 °C lower than those of **7** and are accompanied by a release of 50 kJ mol^{-1} more energy. Although an insoluble carbonaceous material is formed during this process, further details of its nature are currently not known.



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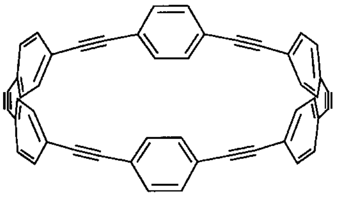
Cyclophanes have previously been envisioned as precursors to the fullerenes,[12] and alkynyl-based cyclophanes ("cyclophynes") are beginning to play an eminent role in this field. Two experimental results may serve to demonstrate the substantial energy content of these molecules. Firstly, belt-shaped [6]paraphenylacetylene **9**[13] explodes when heated to 80 °C in the presence of oxygen. Under inert gas, temperatures of about 240 °C are needed to induce decomposition. No attempts have been made to characterize the decomposition products that are described as a brown, polymeric mixture. Secondly, [8.8]paracyclophaneoctayne **10**[14] could only be prepared in a protected form in which four of the eight alkynyl units are complexed by μ-acetylene(hexacarbonyl)dicobalt moieties. Efforts to release the highly strained hydrocarbon from its octacobalt complex resulted in large amounts of insoluble material.



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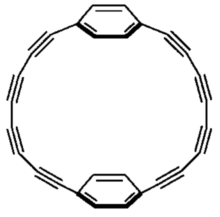

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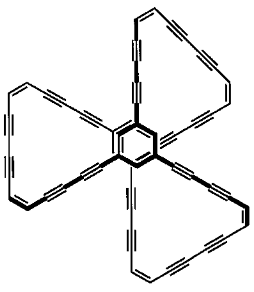
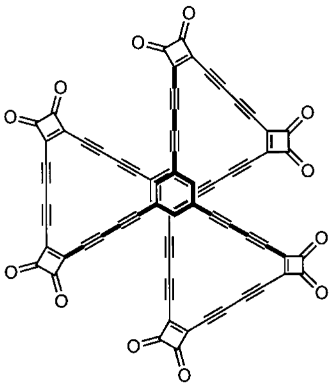
Major steps towards the transformation of acetylenic cyclophanes into fullerenes have recently been made by Rubin et al. At the center of their promising approach[15] lies a preformed sixty-carbon cyclophyne cage, which is meant to be brought by appropriate activation techniques to coalesce to buckminsterfullerene C_{60}. The prototypical cyclophyne **11**[16] ($C_{60}H_{18}$), skillfully assembled in only four steps from 1,3,5-triethynylbenzene, is stable for weeks in dilute solutions in the dark. The cyclophyne **11** adopts a chiral, helical D_3 conformation in the solid state, and according to calculations racemizes rapidly even at low temperatures. Disappointingly, **11** was very reluctant to loose hydrogen in matrix-assisted



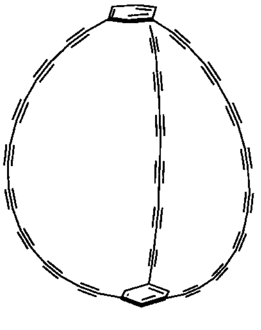
11
($C_{60}H_{18}$)



12
[$C_{60}H_6(CO)_{12}$]

LD-MS experiments and does not collapse under dehydrogenation to fullerene C_{60}. The most abundant ion (negative-ion mode) corresponds to the parent ion of **11** and only partial dehydrogenation to $C_{60}H_{14}^-$ is observed. The authors speculate that the reasons for the failure of **11** to produce fullerenes are the pronounced flexibility of the system and, more importantly, the remaining hydrogens of the $C_{60}H_{18}$ hydrocarbon are poor leaving groups.

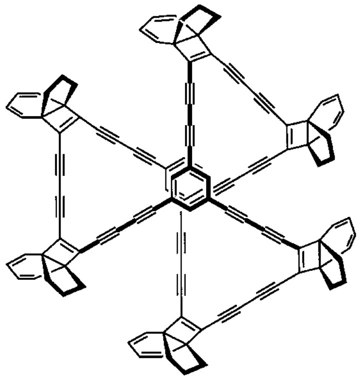
In a straightforward refinement of their concept Rubin et al. have turned to cyclophyne **12**,[17] in which the vinylic hydrogen atoms of **11** are replaced by 1,2-dioxocyclobuteno groups. This cyclic diketone moiety has been used previously[6, 18] as a synthetic equivalent for alkynyl groups, which can be generated from the dione by thermally or photochemically induced CO expulsion. Successive decarbonylation of **12** should ultimately lead to cyclophyne **13** with the composition $C_{60}H_6$. In contrast to the synthesis of cyclophyne **11**, the preparation of **12** is a more tedious, multistep (eight synthetic steps) procedure that furnished a sensitive material that is stable in CH_2Cl_2 solution for only two hours. The instability of **12** notwithstanding, the mass spectrometric behavior of the compound proved to be intriguing. The parent ion of **12**, $C_{60}H_6(CO)_{12}$, can neither be observed in the positive- nor in the negative-ion mode, but fragments thereof resulting from the loss of eight to eleven CO groups are detectable. The most abundant ions observed in the negative ion mode are $C_{60}^{\bullet -}$ and $C_{60}H_6^{\bullet -}$. The anion of the carbon cluster C_{60} was unambiguously identified as a fullerene, since its fragmentation pattern shows the successive loss of C_2 units that is typical for spherical carbon particles. $C_{60}H_6^{\bullet -}$ on the other hand does not lose C_2 fragments, which suggests that it does not have a fullerene structure.



13
($C_{60}H_6$)

It may be speculated that $C_{60}H_6^{\bullet -}$ is best represented by structure **13**. It is noteworthy that the formation of fullerene ions from acetylenic **12** is observed in the negative-ion mode, which is considered to be "milder" than the positive-ion mode, which was previously used to detect ionized carbon spheres. It thus appears that **12** is structurally predisposed for fullerene formation. However, attempts to perform the exhaustive decarbonylation on a macroscopic scale by irradiating dilute solutions of **12** in THF with pulsed laser light did not lead to the formation of buckminsterfullerene C_{60}.

An alternative strategy for fullerene production through the intermediacy of **13** was adopted (and pursued independently and simultaneously to the work described above) by Tobe et al.[19] Their attempt to overcome the difficulties encountered in the exhaustive dehydrogenation of **11** led to the design of a similar cyclophyne **14**, in which six alkynyl groups are masked by so-called [4.3.2]propellatrienes. Laser-induced [2+2] cycloreversion[20] cleave the bicyclic substructures to generate six equivalents of indane, thereby furnishing cyclophyne **13**. Consequently, the LD mass spectra (positive-ion mode) of **14** feature an intense signal for C_{60} cations with a C_2-fragmentation pattern. In the negative-ion mode, C_{60} anions are formed only to a minor extent, and the spectrum is dominated by $C_{60}H_6^{\bullet -}$ ions. Again, upon photolyzing solutions of **14** no indication for the macroscopic formation of fullerenes was observed, despite the promising fact that indane had been produced.



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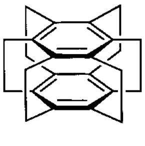
In light of the mass spectrometric results described above, a rational fullerene synthesis from cyclophyne precursors appears to be within reach. With superphane **15**[21] and superferrocenophane **16**[22] as established structural precedences, it may well be that reports about a successful synthesis of "superphyne" **17**, an acetylenic isomer of buckminsterfullerene, or even a corresponding "supermetallophyne" will appear in the near future.



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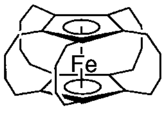

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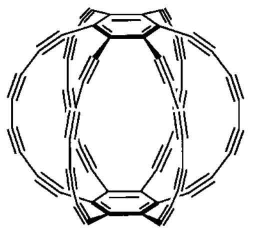

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Strategies for the Dynamic Integration of Combinatorial Synthesis and Screening[**]

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The generation and screening of large populations is a familiar concept in biology. It is central to recombinant DNA techniques and occurs in nature during evolution. Such approaches are only now being truly appreciated by chemists. Combinatorial organic synthesis, linked to high-throughput screening, has become an important part of the drug discovery process.[1] Areas such as materials science, catalysis, and engineered biosynthesis are also increasingly influenced by combinatorial ways of thinking.[2] Traditionally, library synthesis and screening are two separate activities which are performed sequentially. Here, recent examples are highlighted where the composition of a library undergoes fluid and dynamic change during selection for a desired property.[3]

This idea originated in the field of molecular recognition. When a metal cation is mixed with a set of ligands, a large number of complexes is possible. However, under equilibrating conditions, the actual composition is dictated by thermodynamic stability.[4] The best binder can be identified simply by determination of the predominant component without the need to test each ligand individually. Lehn et al.[5] have described this approach as a virtual combinatorial library.[6]

The Sanders group has used transesterification as a route to combinatorial libraries. For example, the steroidal hydroxy ester **1** (Scheme 1) was mainly converted into the macrocyclic trimer, tetramer, and pentamer (83:12:5 respectively, by mass percentage) upon heating.[7] When the experiment was repeated with an equimolar amount of NaI, the equilibrium

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