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Synthetic Studies Directed Towards Bucky-Balls and Bucky-Bowls

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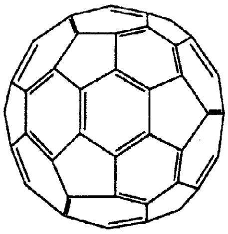
1. INTRODUCTION

Discovery of spheroidal carbon clusters [1-7] in 1985 heralded a new era in the understanding of forms and characterstics of ubiquitous carbon[6,7]. These carbon clusters, aptly called fullerenes (named after American architect, R. Buckminster Fuller) and popularly known as 'buckyballs' possess spherical cage structures built-up of hexagonal and pentagonal rings. The pentagons, absent in planar polycylic aromatic hydrocarbons (PAHs), provide the necessary curvature to form spherical structures. Although, fullerenes with almost unlimited range, from C_{28} (bucky baby) to C_{540} (giant bucky), and diverse symmetry properties are possible, only a few of them have been isolated and even fewer have been characterized so far. Among these, C_{60}-fullerene **1** and C_{70}-fullerene **2** are the best known. In recent years, possibly no other class of molecules has made more impact in the field of chemistry than fullerenes and their discoverers H. W. Kroto (University of Sussex, UK), R. F. Curl and R. E. Smalley (both from Rice University, USA) have been awarded the Nobel Prize in Chemistry for the year 1996 [1-3].

Buckminsterfullerene, C_{60} **1**, is the smallest stable fullerene known to-date. It is also the most abundant member of this exotic family and is endowed with a truncated icosahedral (I_h) symmetry. It is made up of 12 pentagonal and 20 hexagonal rings with 60 vertices and 32 faces. The C_{70}-fullerene-D_{5h}, **2**, is a sibling of **1** with which it co-occurs in the soot formed by laser vaporization of graphite. It is also a stable molecule which can be isolated and purified along with **1**. C_{70} **2** is made up of 12 pentagonal and 25 hexagonal rings with 70 vertices and 37 faces. Both C_{60} and C_{70} can be readily made [8], are also available commercially and have been widely targeted for a variety of physico-chemical studies.

While C_{60} was discovered in 1985 during the studies on the nucleation of carbon plasmas, preparative access to carbon clusters, particularly of C_{60}-fullerene-I_h (**1**, buckminsterfullerene) and C_{70}-fullerene-D_{5h} **2** in 1990, through the efforts of Kratschmer and co-workers [8] has generated intense research activity in this area. The prospect of employing fullerene derivatives in areas ranging from material science to medicine has motivated chemists to explore their unusual reactivity and profile their functionalization behavior. C_{60} **1** and C_{70} **2** exhibit a range of chemical reactivity and undergo facile electrophilic, nucleophilic and radical additions as well as [n+2]-cycloaddition reactions characteristic of electron deficient polyolefins with a variety of reacting partners [7]. Both C_{60} and C_{70} can be reduced readily with hydrogen, dissolving metals and by electrochemical methods amongst others. However, separation of regioisomers and full characterization of products in many cases is a daunting task. C_{60} also undergoes oxidative ring opening reactions and metal complexation. Other fullerenes, like C_{70}, also exhibit similar reactivity but their detailed chemistry is only emerging now. Fullerenes are also attracting attention as biologically active agents and some promising leads have been obtained [9] but their toxicity still remains a grey area.



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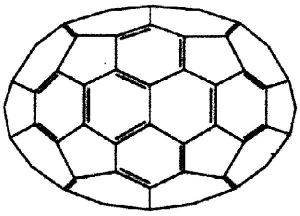

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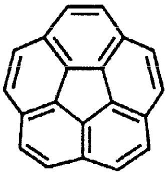
2. FULLERENE FRAGMENTS AND BUCKYBOWLS

While several familiar aromatic entities such as benzene, naphthalene, phenanthrene and pyracylene can be recognized in fullerenes, the non-planar PAHs with imbibed pentagon rings, which form structural motifs on the fullerene surface, begin to emerge only after assembling twenty carbons. When the complex cage structures of **1** and **2** are progressively dismantled to smaller fragments and hydrogens are attached to the end-carbons to satisfy the valence requirements, a range of non-planar PAHs can be generated. In their stable form, these non-planar PAHs acquire characteristic bowl-shape (buckybowls [10]), with a defined curvature [11]. The curvature as well as the bowl-depth, and consequently the strain, increases as additional pentagonal rings are annulated to the carbon-framework. In the fullerene fragments that are "deep-bowls", there is an additional source of strain derived from the van der Waals contact between peri-hydrogens present on rim-carbons.

The bowl-shaped PAHs have evoked considerable interest as they are expected to exhibit properties, much different from their planar analogs, on account of the characteristic curvature they possess [10-13]. The curvature not only enhances the strain in the molecule and makes them more reactive, but also creates two distinct surfaces on them *viz.* endohedral (concave) and exohedral (convex). Thus, they may act as selective complexing agents for metal ions either through endohedral or exohedral complexation [10]. Also, it should be interesting to assess the requirement of bowl-depth in PAHs for displaying fullerene like reactivity. Since the fullerene fragments possess aromatic end-carbons in addition to pyramidalized core-carbons (*cf.* corannulene **3**), the two are expected to exhibit different reactivity. Some of the bowl-shaped PAHs like corannulene **3** exhibit bowl-to-bowl inversion phenomena (*vide infra*). It would be rewarding to study this process in other fullerene fragments in order to define the limits of structural requirements for arresting the inversion process. Some bowl-shaped PAHs can be chiral and therefore have the potential to be employed as chiral catalysts in organic synthesis. The bowl-shaped PAHs can be used as drug-markers, as they show UV/VIS characteristics similar to fullerenes.



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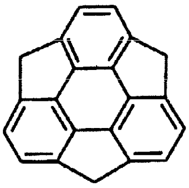

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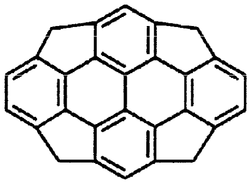

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Before dwelling on the synthetic aspects related to fullerenes, it will be appropriate to identify and examine the various important fragments embedded within them. Several non-planar PAHs can be readily identified as sub-structures in **1** and **2** and are attractive and challenging synthetic targets in their own right. Many of these non-planar PAH fragments are common to **1** and **2**, *e.g.* corannulene **3** and sumanene **4**, but a few are unique to either of the two, such as pinakene **5** for **2**. From the synthetic point of view, the methodologies evolved towards buckybowls e.g.. **3-5,** can be adopted for the construction of fullerenes themselves. It is also possible that some of these PAHs could serve as direct precursors to fullerenes. For example, fullerene **1** is produced by pyrolysis of corannulene **3** between 650°C and 1200°C either with or without catalyst (Pd/C, Co) [14].

Although, carbon clusters **1** and **2** can be readily accessed *via* arc vaporization of graphite, the methodology is a kind of "black box" operation [4,8]. Besides graphite, several hydrocarbons (*e.g.* benzene, naphthalene, cyclopentadiene, biphenylene and pyrene), organometallics (*e.g.* ferrocene, nickelocene, lithium cyclopentadienide) and even highly oxygenated aromatics (*e.g.* mellitic acid trianhydride) on pyrolysis are known to furnish fullerenes, particularly, **1** [15]. However such operations, besides being preparatively inefficient, are not always predictable or understandable and not amenable to yield desired intermediates along the way. Thus, synthesis of fullerenes based on classical organic reactions and employing the elements of rational synthetic design is an interesting and formidable proposition. Efforts along these lines are expected to provide access to fullerene fragments enroute, with curved surfaces, which themselves could exhibit rich chemistry [10,11]. In spite of the strain that is expected to be present in these fullerene-fragments, theoretical calculations show that they can be accessed synthetically as their strain energies are comparable to or less than that of known strained hydrocarbons such as cubane, [5]-prismane, etc. [16,17] Indeed, some of these fragments are likely to be the stepping-stones on the way to C_{60} and C_{70}.

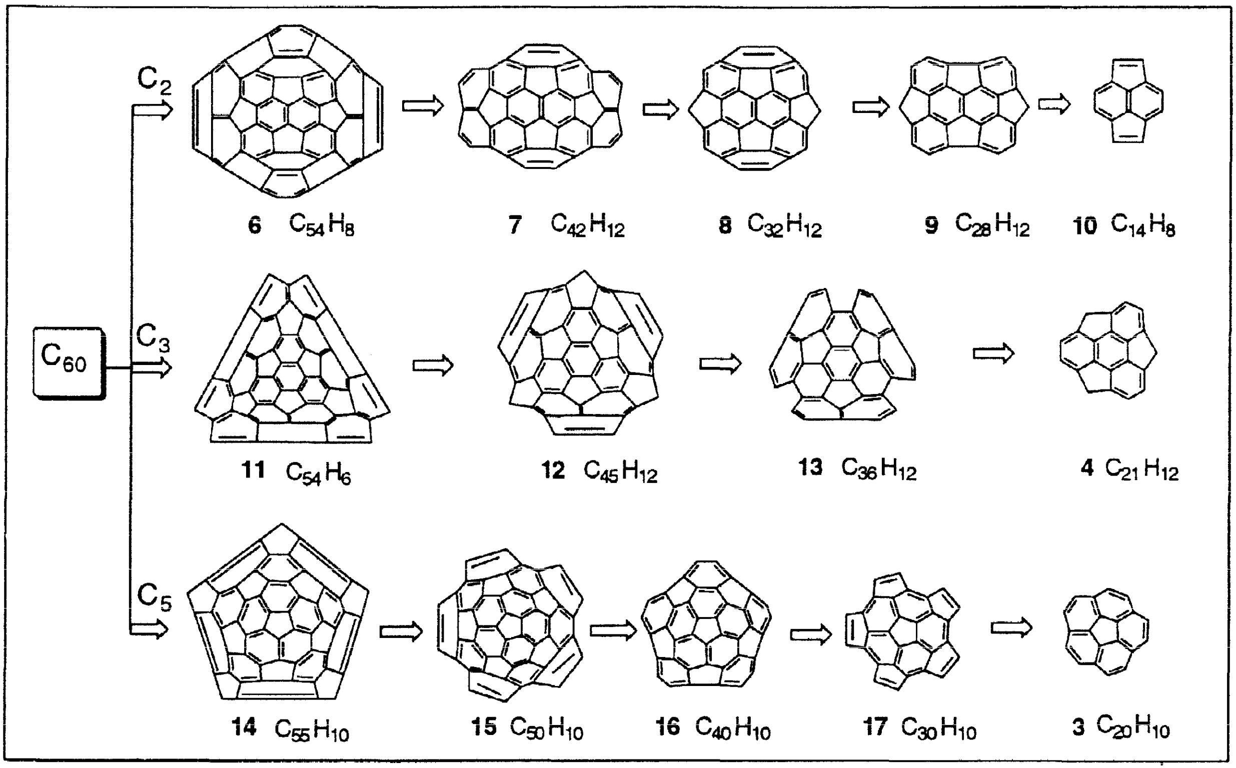
In this account, we summarize the progress (till the end of 1997) achieved towards the synthesis of various fullerene fragments. Many bowl-shaped target structures that are retrosynthetically derivable from C_{60} and C_{70}, and are important in the context of the classical synthesis of fullerenes, have been identified. Important physico-chemical properties and phenomenon associated with the bowl-shaped fragments of fullerenes have also been highlighted. Synthetic approaches that have been aimed at C_{60} and C_{70} but have made limited headway thus far are also discussed.

3. DOMINANT STRUCTURAL MOTIFS ON C_{60}- AND C_{70}-FULLERENES

While smaller buckybowls such as corannulene **3** and sumanene **4** can be readily recognized as structural motifs on C_{60} **1** and C_{70} **2**, many more such bowls can be generated and visualized through systematic dismantling of the spheroidal structures, keeping in mind symmetry considerations (Schemes 1 and 2) [16,17]. As a part of this exercise C_{60} **1** can be taken apart in a retrosynthetic sense to generate smaller fragments *via* three conceptually different routes that retain C_2, C_3 and C_5 symmetry (Scheme 1). On the other hand C_{70} **2** can be reduced to smaller fragments along C_2, and C_5 symmetry path-ways. The valence requirements of the dangling carbons are satisfied by attaching hydrogens and for better appreciation of the symmetry, the buckybowls are shown in the form of two-dimensional (Schlegel) diagrams.

Retrosynthetic analysis of C_{60} along the C_2-symmetry route by removing the hexagonal ring cap leads to the hydrocarbon $C_{54}H_8$ **6**. Continuing the dismantling process along the route generates hydrocarbons $C_{42}H_{12}$ **7**, $C_{32}H_{12}$ **8**, $C_{28}H_{12}$ **9** and pyracylene $C_{14}H_8$ **10**. Similar analysis along the C_3-symmetry path eventuates in hydrocarbons $C_{54}H_6$ **11**, $C_{45}H_{12}$ **12**, $C_{36}H_{12}$ **13** and finally sumanene $C_{21}H_{12}$ **4**. The exercise along the C_5-route produces hydrocarbons $C_{55}H_{10}$ **14**, $C_{50}H_{10}$ **15**, $C_{40}H_{10}$ **16**, $C_{30}H_{10}$ **17** and ultimately corannulene, $C_{20}H_{10}$ **3** [16].

Two pathways **a** and **b** are available (Scheme 2) for dismantling C_{70} by taking C_2-symmetry into consideration. Divesting **2** of the hexagonal ring "cap" along C_2 pathway-**a** generates a "pot-shaped" fragment $C_{64}H_6$ **18**. Progressive removal of carbon atoms from the periphery results in the fragments $C_{58}H_{12}$ **19**, $C_{48}H_{12}$ **20**, $C_{46}H_{12}$ **21**, and pinakene, $C_{28}H_{14}$ **5**. Sequential removal of carbon atoms from the periphery of **2** along C_2 pathway-**b** results in fragments $C_{64}H_8$ **22**, $C_{60}H_8$ **23**, $C_{54}H_8$ **24**, $C_{42}H_{12}$ **25**, and $C_{22}H_{12}$ **26**. Removal of the five-membered ring "cap" in **2** along the C_5-route leads to the "pot-shaped" fragment $C_{65}H_{10}$ **27**. Disengagement of peripheral carbons from **27** leads to $C_{60}H_{10}$ **28**, $C_{50}H_{10}$ **15**, $C_{40}H_{10}$ **16**, $C_{30}H_{10}$ **17**, and to corannulene **3** [17]. The buckybowls **15**, **16**, **17** and **3** are common to both C_{60} and C_{70} along the C_5-symmetry route which reflect the sibling relationship between C_{60} and C_{70}.

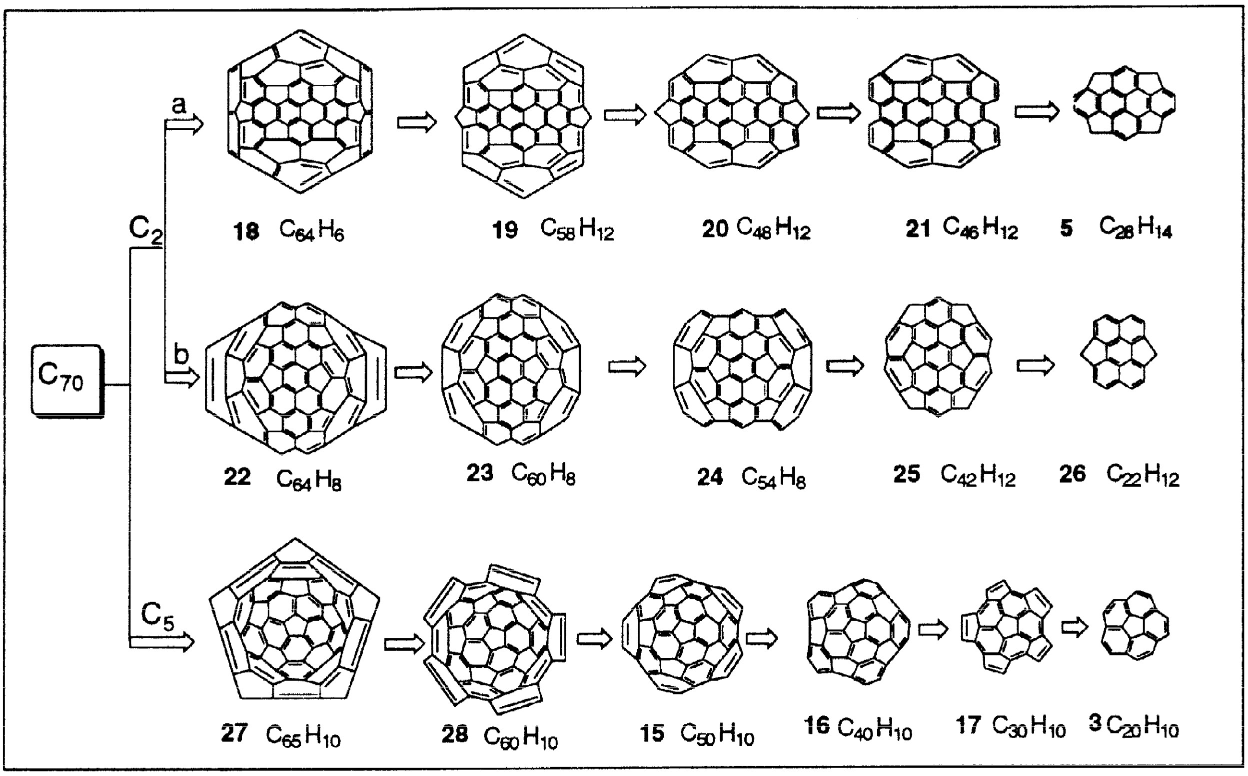


Scheme 1. *Retrosynthetic analysis of C_{60} along C_2, C_3 and C_5-symmetry routes*

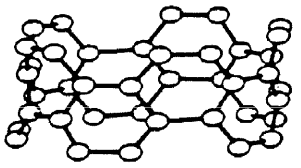
Among the various fragments depicted in Schemes 1 and 2, $C_{50}H_{10}$ **15** is particularly significant and interesting, since placing [5]-radialene "cap" on it leads to C_{60} **1** while placing corannulene **3** "cap" leads to C_{70}-fullerene **2**. In addition to the above buckybowls various other fragments of **1** and **2** are conceivable through either cyclopenta- or benzoannulation of the fragments already identified or by dismantling of the parent molecules through non-symmetric modes.

Besides the bowl-shaped fragments identified above, it is possible to generate belt-like fragments from C_{60} **1** and C_{70} **2** by removing "caps" from opposite ends of the molecule [16]. Structures $C_{40}H_{20}$ **29** and $C_{50}H_{20}$ **30** are examples of such belt-like molecules and in their own right constitute interesting synthetic objectives.

Before describing the synthetic efforts towards buckybowls and C_{60}, it will be appropriate to examine the key experimental strategies generally employed for the formation of crucial carbon-carbon bonds that result in the generation of curved surfaces.



Scheme 2. *Retrosynthetic analysis of C_{70} along C_2a, C_2b and C_5-symmetry routes*



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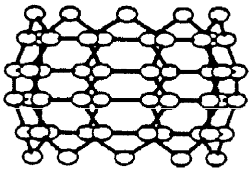

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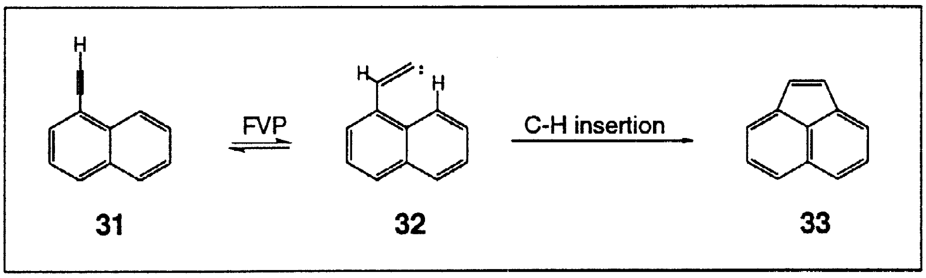
4. SYNTHETIC STRATEGIES

4.1 Flash Vacuum Pyrolysis (FVP) Mediated Dehydrogenative and Dehydrohalogenative Ring Closures and Stone-Wales Rearrangement Processes

Several methodologies such as oxidative photocyclizations, inter- and intramolecular electrophilic aromatic substitutions, conventional dehydrogenations (S, Se, Pd etc.), aryl-aryl coupling reactions (Heck, Suzuki, Stille etc.) amongst others, are available for the assembly of PAHs. Such approaches are routinely employed for generating a variety of PAHs exhibiting helicity as well as deviations from planarity. However, to access curved bowl-like analogs requires recourse to reactions where formation of key carbon-carbon bonds will impart the requisite curvature to the molecule. Such process should also take into account build up of enormous strain while folding of the planar PAH takes place. Moreover, such reactions are highly endo-energic in nature. Flash vacuum pyrolysis (FVP) technique, in which the molecule is made to pass through a hot quartz tube (800-1300°C), under vacuum (10^{-4} - 1 Torr) is particularly well suited for this purpose [18]. In this process suitable substituents are strategically positioned on the aromatic surface of the PAH such that they preferentially secede during the short contact times ($\sim 10^{-6}$ sec.) to initiate the cyclization process. Under the FVP conditions, aromatic rings in PAHs not only seem to bend and stretch with facility, but also generate reactive intermediate species like carbenes, benzynes, aryl radicals etc., well suited for the critical C-C bond formation through the insertion into the nearest peri-C-H bonds. The unfavorable high energy conformations required for generating curved structures are generally not available under standard reaction conditions. Under FVP conditions, another reaction path is available, in which one or more benzenoid rings of the polycyclic aromatic system undergo ring contraction-rearrangement (Stone-Wales rearrangement)[19-22]. Thus, FVP reactions leading to buckybowls are critically dependent on the applied vacuum and temperature [23]. A few examples will be cited here to highlight the efficacy of FVP technique in generating reactive species and in the formation of new rings through key C-C bond connectivity as well as through benzene ring contraction and rearrangement. Later in the sequel, specific examples leading to several fullerene fragments will be cited.

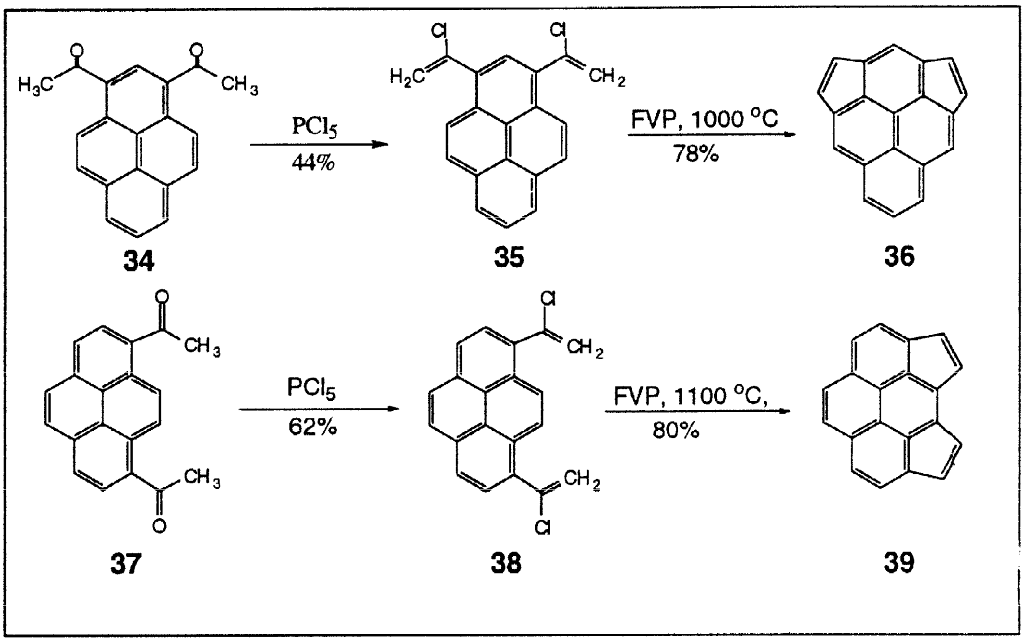
Brown *et al.* have shown that, under FVP conditions, terminal alkynes *e.g.*, **31** are in equilibrium with isomeric vinyl carbene intermediates *e.g.*, **32**, which then insert into sterically proximate peri-C-H bond to furnish cyclopentene annulated products such as **33** (Scheme 3) [24]. This reaction has been effectively employed by several research groups to generate buckybowls.



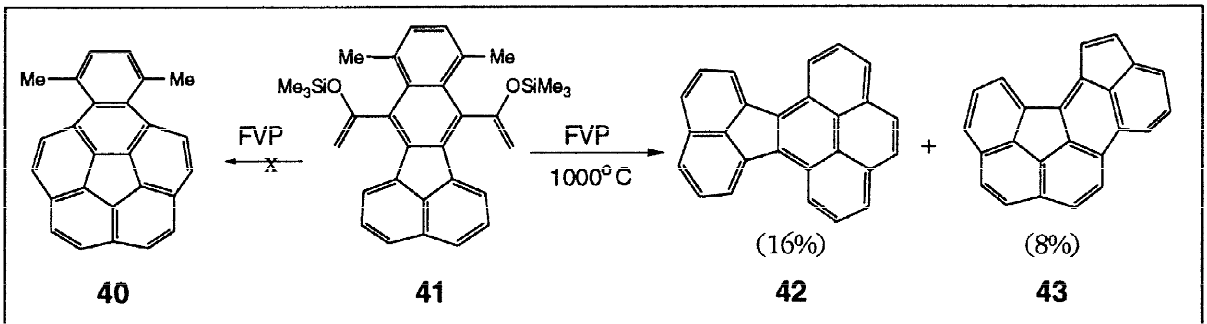
Scheme 3

Scott *et al.* have shown that in addition to terminal alkynes, vinyl halides can also be employed for this purpose to furnish cyclopentannulated products. For example, FVP of the bis-vinyl halides **35** and **38** readily obtainable from the *bis*-acetylpyrenes **34** and **37**, resulted in **36** and **39** respectively (Scheme 4) [25]. Since vinyl halides, particularly vinyl chlorides and vinyl bromides, can be generated from the corresponding methyl ketones, this reaction has wider applicability. The cyclizations in these cases proceed through acetylenic intermediates.

In some cases, when, vinyl halides are either unstable or are difficult to prepare, silyl enol ethers can also be employed for the cyclization reaction under FVP conditions. In an approach towards the benzo-annulated corannulene derivative **40**, *bis*-silyl enol-ether **41** was subjected to FVP. However, only cyclized products **42** and **43** were realized instead of the desired **40**, Scheme 5 [26].

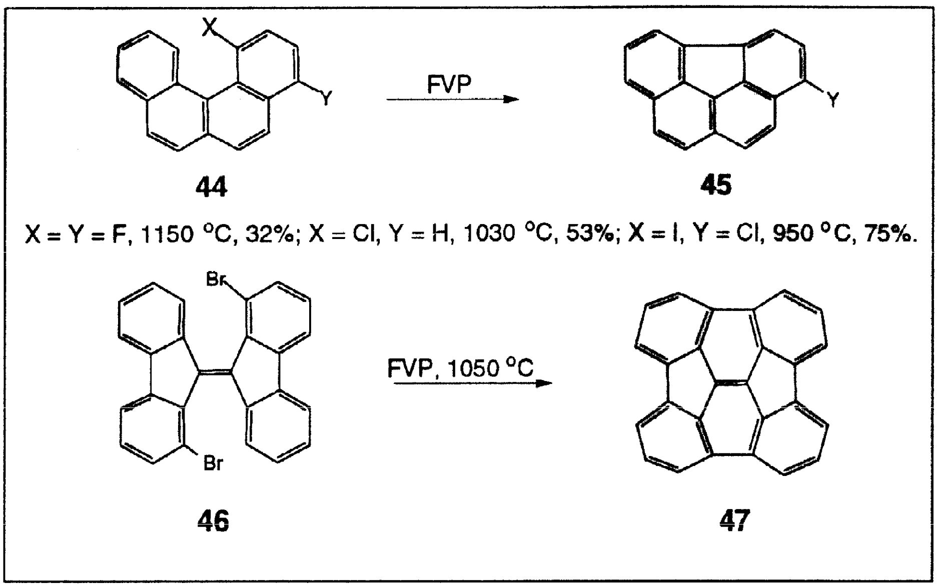


Scheme 4



Scheme 5

FVP mediated dehydrohalogenative cyclization reactions of suitably substituted aromatic halo-compounds are particularly efficacious in creating strategic Ar-Ar bonds in a regiospecific manner to furnish cyclized products e.g., **44**→**45**, and **46**→**47** (Scheme 6) [27,22]. As expected, dehydroiodination is more efficacious in terms of yield and thermal activation required for effecting the cyclization [28]. Under FVP conditions, homolytic fission of the aryl halogen bond takes place with ease to generate aryl radicals which insert into sterically closer carbon-hydrogen bonds leading to cyclized products. The facilitating role of the halogen substituent in such cyclizations is quite apparent from the fact that the unsubstituted benzo[c]phenanthrene **48** does not undergo similar cyclization under identical conditions. However, at elevated temperatures **48** does cyclize through transannular dehydrogenation to furnish **45** (Y = H) along with other Stone-Wales rearrangement and fragmentation products **49** and **50**, respectively, Scheme 7 [23]. The steric compression among the peri-hydrogens in benzo[c]phenanthrene **48** is perhaps the driving force for the cyclization to **45**, which probably proceeds through a radical pathway with the initial cleavage of the C-H bond.

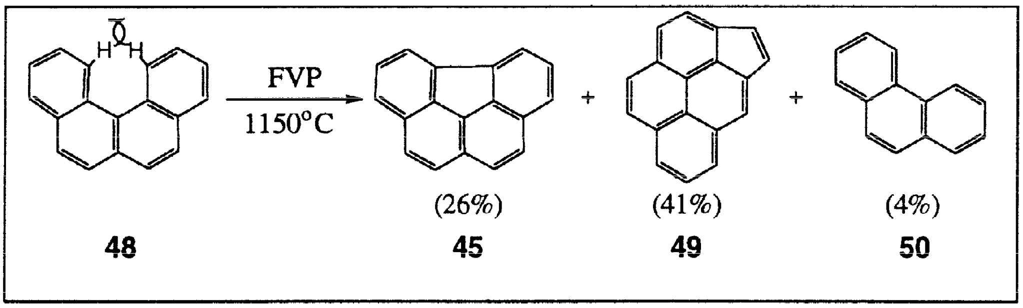


44 **45**

X = Y = F, 1150 °C, 32%; X = Cl, Y = H, 1030 °C, 53%; X = I, Y = Cl, 950 °C, 75%.

46 **47**

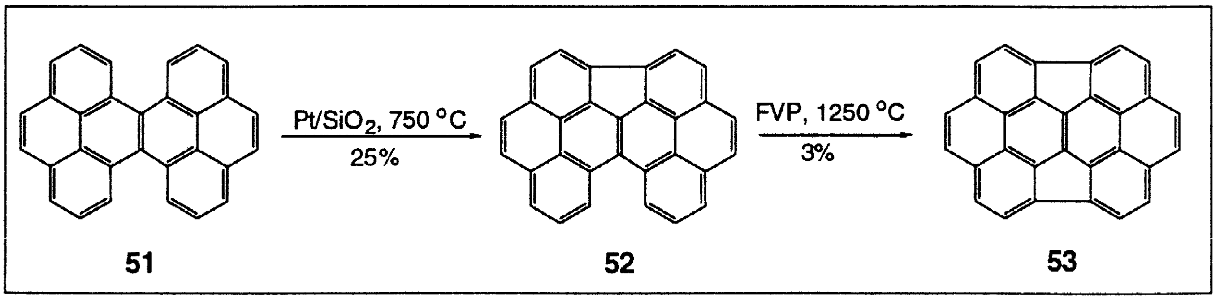
Scheme 6



48 (26%) **45** (41%) **49** (4%) **50**

Scheme 7

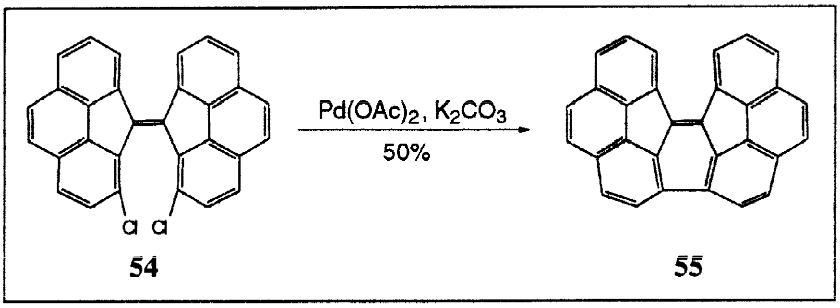
Dehydrogenative-cyclizations of the type **48**→**45** can also be performed through metal catalysis under thermal activation as shown by **51**→**52** transformation (Scheme 8) [29]. However, if high temperature FVP conditions are employed, further cyclization to the bowl shaped **53** can be accomplished [30].



51 **52** **53**

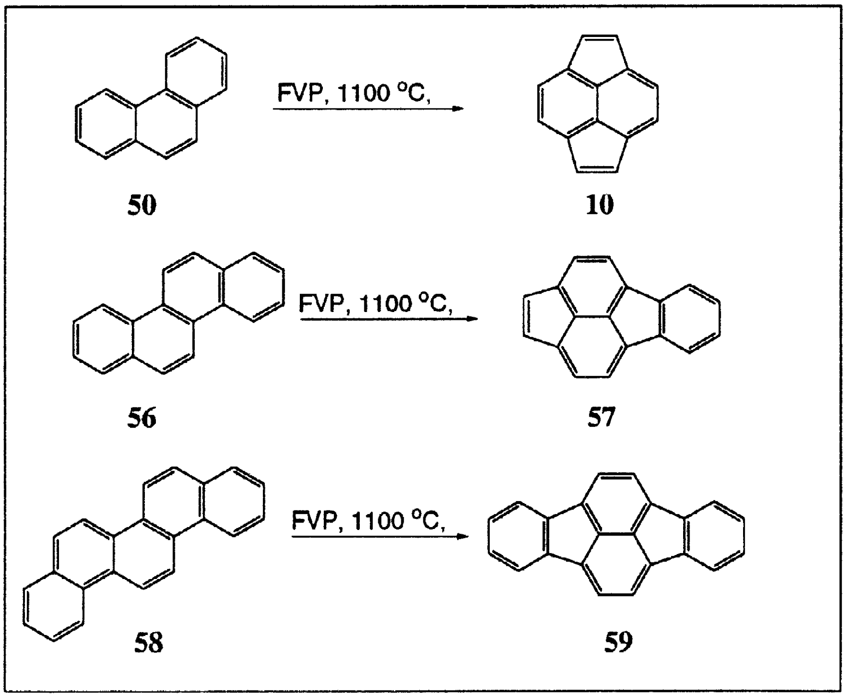
Scheme 8

As an alternative to FVP, a palladium mediated reductive coupling reaction has been explored as a key carbon-carbon bond forming reaction for generating buckybowl precursors (Scheme 9) [31]. Reductive dechlorination of **54** furnished the monobridged planar buckybowl precursor **55** in almost 50% yield. It should be noted that, this method employs much milder conditions compared to the extremely high temperatures required for the FVP technique and such reactions are worthy of further investigation and applications.



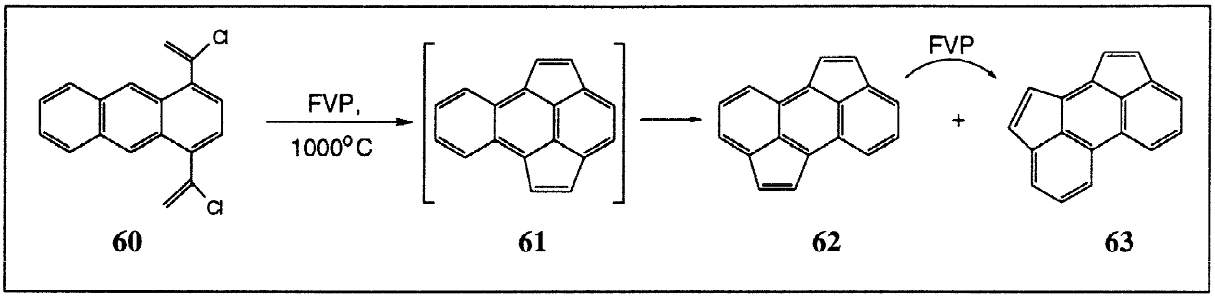
Scheme 9

Several simple PAHs, particularly those which have bay region, exhibit propensity towards Stone-Wales rearrangement, under FVP activation, to furnish fullerene fragments. Scott *et al.* demonstrated the generality of this process and shown that phenanthrene **50** rearranges to pyracylene **10**, where as its higher homologue chrysene **56** with an additional benzene ring rearranges to benzopyracylene **57**. Similarly, picene **58** rearranges to 4,5-*o*-phenylenefluoranthene **59** (Scheme 10) [20]. While the conversions during the FVP process are modest, the cyclization products are the only monomeric species isolated in these reactions. Besides being synthetically useful, these observations on the FVP of bay region polycyclic benzenoid hydrocarbons into fullerene fragments, are important in the understanding of the mechanism of fullerene formation.



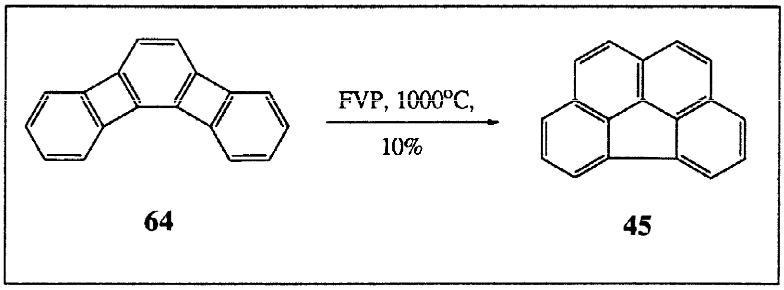
Scheme 10

Since extremely high temperatures are employed in the FVP, there is scope for deep-seated and unprecedented rearrangements to occur and a few such observations have been reported recently. Scott *et al.* have reported that ethynyl groups located on the periphery of PAHs could "walk around". For example, FVP of 1,4-*bis*(1-chlorovinyl)anthracene **60** leads to the cyclopentenoid intermediate **61** in which the cyclopentene ring opens up to transfer the ethynyl group on to the middle ring of the anthracene moiety. Further insertion of the ethynyl group on the unsubstituted aromatic ring leads to **62**. On the other hand, Stone-Wales rearrangement of **62** leads to **63** (Scheme 11) [32].



Scheme 11

Another interesting example of unusual thermal rearrangement that has surfaced recently is the FVP of angular [3]phenylene **64** to furnish benzo[*ghi*]fluoranthene **45** in 10% yield along with a small amount of chrysene (Scheme 12) [33]. The proposed mechanism involves cascade rearrangement processes leading to the relatively more stable benzofluoranthene **45**. This result indicates that uncommon and strained precursors could also serve as starting materials for fullerene fragments.

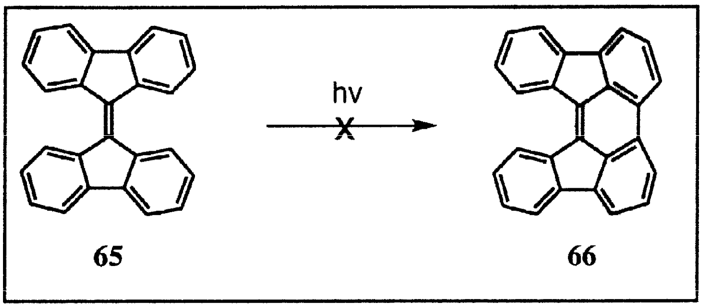


Scheme 12

The examples mentioned above as well as those to follow demonstrate that FVP is an effective technique for accessing strained bowl-shaped hydrocarbons. However, under FVP conditions, rearrangements are competing reactions. Nonetheless, to date, it remains the most promising strategy to access the non-planar, bowl-shaped topologies.

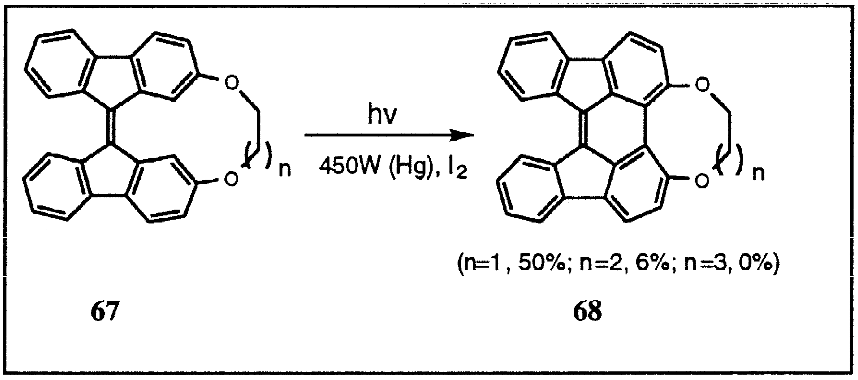
4.2 Oxidative Photocyclization

The oxidative photo-cyclization reaction is commonly employed in the synthesis of planar PAHs, the transformation of stilbene to phenanthrene being a prototypical example of such a process [34]. Such cyclizations proceed through conrotatory photochemical ring closure involving 6-π electrons followed by dehydrogenation. However, the photocyclization route has seldom been applied to generate bowl-shaped PAHs, as the 6-π electrons in cyclopentylidene bearing aromatic precursors are not able to position themselves in a proper configuration as the reacting terminal carbons are too far apart. An often cited example in this context, which has relevance to fullerene fragments, is the failure of photocyclization of bifluoroenylidene **65** to **66**, Scheme 13 [35].



Scheme 13

One way to get around such a problem is to employ tethered precursors. The tether forces the reacting terminal carbons to move closer so that the crucial carbon-carbon bond formation can take place. Luh and coworkers have demonstrated this possibility through the oxidative photocyclization of tethered bifluorenylidene derivative **67** to furnish the mono-cyclized product **68**, Scheme 14 [36]. They have elegantly demonstrated that the photocyclization is a function of tether length and strain in the product formed. This photochemical strategy, with tactical modifications, holds promise as a useful protocol for the synthesis of curved aromatic surfaces.



Scheme 14

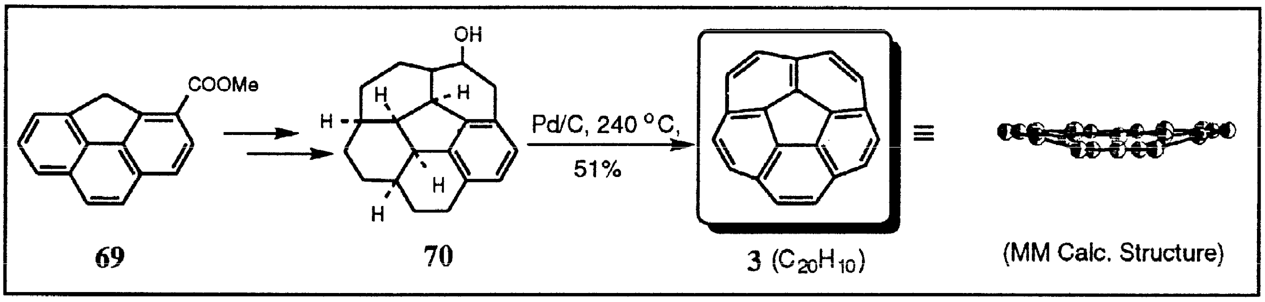
5. CORANNULENE AND DERIVATIVES

5.1 Corannulene

Corannulene **3**, the $C_{20}H_{10}$ hydrocarbon, is the smallest, bowl-like subunit composed of a central pentagonal ring or core with a periphery of five hexagonal aromatic rings, that readily fits into the surface of fullerenes. It forms both the "cap" and the "bottom" of C_{60} and C_{70}.

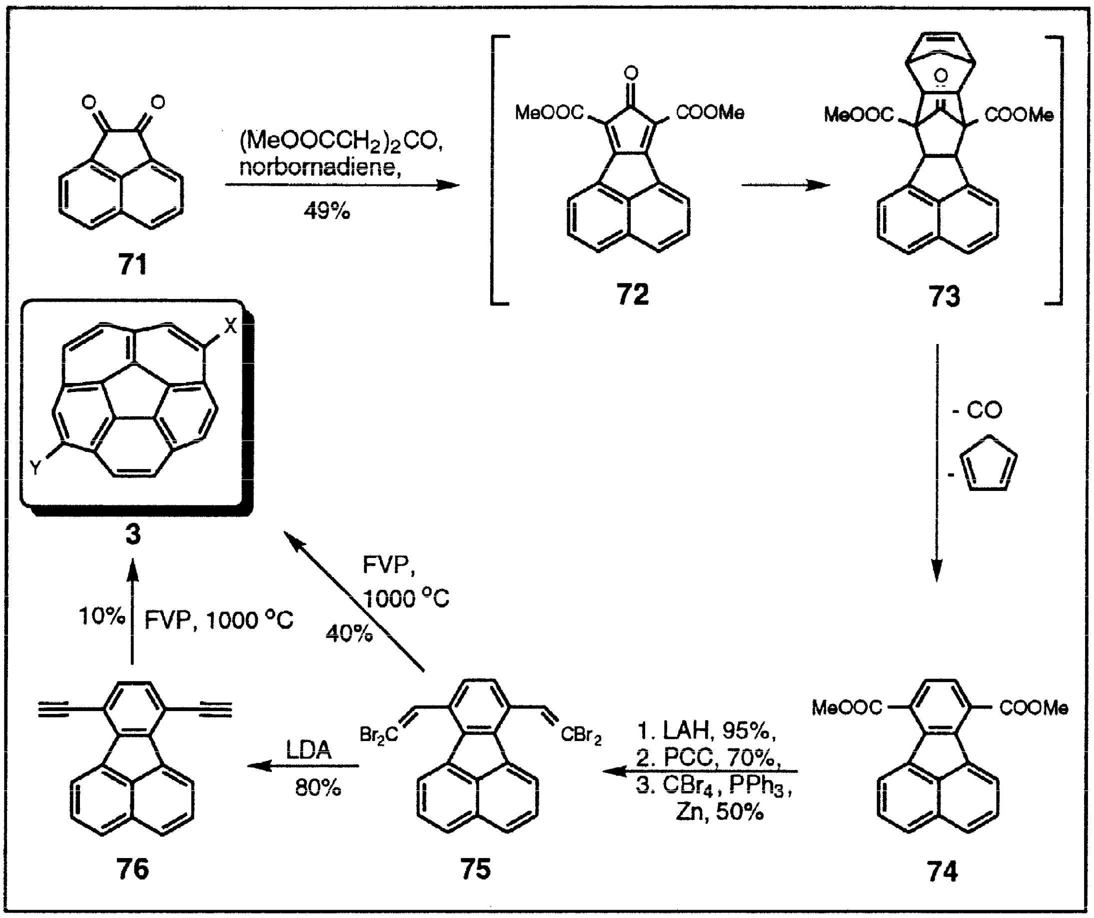
Barth and Lawton were the first to report a synthesis of corannulene **3** (cora = heart or within; annula = ring; Latin) in 1967, almost 20 years before the discovery of fullerenes. It was a landmark effort at that time and has been well reviewed [37, 38, 39] The synthesis of **3** was achieved in 17 steps, starting from 3-carbomethoxy-4*H*-

cyclopenta[*def*]phenanthrene **69** following a classical route involving multiple functional group alterations and ring annulations in a sequential manner. The key to success in the approach by Barth and Lawton was the initial build-up of the entire carbon framework with minimal unsaturation and as a final step, aromatization was affected through exhaustive dehydrogenation on **70** to deliver **3** (Scheme 15). The structure of 3 followed from its ^{1}H NMR spectrum (δ 7.81, s). The ^{13}C NMR spectrum of **3** was later shown to exhibit resonances at δ 135.8, 130.8 & 127.1 [40]. The structure was further confirmed by X-ray crystal structure analysis [41], which clearly exhibited the bowl-shaped conformation of the molecule, with a bowl depth of 0.87Å from terminal carbon to the core-carbon (Scheme 15). The X-ray analysis of **3** also showed that there is little bowl-to-bowl stacking in the crystals and the molecules are arranged in several different relative orientations.



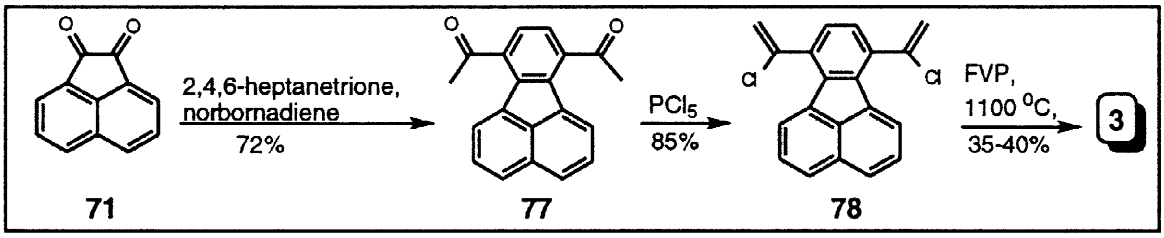
Scheme 15, *Barth and Lawton's synthesis of corannulene*

Discovery of fullerenes in 1985 has rekindled world-wide interest in corannulene **3** and its derivatives. Several successful syntheses of **3** have appeared in recent literature, and in most of them, FVP has played a crucial role in establishing the final carbon-carbon connectivities to generate the curved framework. In this context Scott *et al.* in 1991 published a seminal approach towards the synthesis of corannulene **3** based on the premise that a curved network of trigonal carbon atoms can be formed under high energy conditions in the gas phase from flat aromatic precursors [40]. In this approach, methyl 7,10-fluoranthenedicarboxylate **74**, a key intermediate in the sequence, was prepared from acenaphthenequinone **71** in a one-pot operation involving a double Knoevenagel condensation (**71**→**72**), a Diels-Alder reaction with norbornadiene (**72**→**73**), decarbonylation and a retro-Diels-Alder reaction (**73**→**74**). In this reaction cascade, norbornadiene acts both as a solvent and as an acetylene equivalent. The diester **74** was transformed to *bis*-acetylenic compound **76** through straightforward functional group transformations *via* **75**, and further subjected to FVP to furnish corannulene **3** (X, Y = H) in 10% yield, Scheme 16. In fact, the tetrabromide intermediate **75**, served as a better precursor for **3** (X, Y = H) under FVP conditions and yields up to 40% could be realized in this key step. Conversion of tetrabromide **75** to **3** may proceed either through electrocyclic ring closure, followed by aromatization and pyrolytic loss of bromine atoms or through the homolysis of carbon-bromine bonds to generate vinyl radicals followed by cyclization. When the pyrolysis of tetrabromide **75** was conducted at a lower temperature *i.e.* at 900°C, bromocorannulene **3** (X= Br, Y= H) and 1,6-dibromocorannulene **3** (X, Y = Br) could be obtained along with corannulene [42]. The bromocorannulene **3** (X= Br, Y= H) served as a precursor for the preparation of 2-corannulenyl-2-propanol **3** (X= Me_2COH, Y = H), a substrate used for the study of bowl-to-bowl inversion of the corannulene nucleus [42]. Employing dynamic NMR methods, the ring inversion barrier in **3** has been measured to be 10.2 kmol^{-1}. A similar value of 10.5 kmol^{-1} was obtained for *bis*-bromomethylcorannulene [43]. These experimental values are in good agreement with the values calculated at semiemperical (8.3 kmol^{-1}, MNDO) and *ab initio* levels (8.8 kmol^{-1}, STO-3G) [44, 45, 46]. These values indicate that the corannulene bowl inverts more than 2 x 10^5 times a second at room temperature.



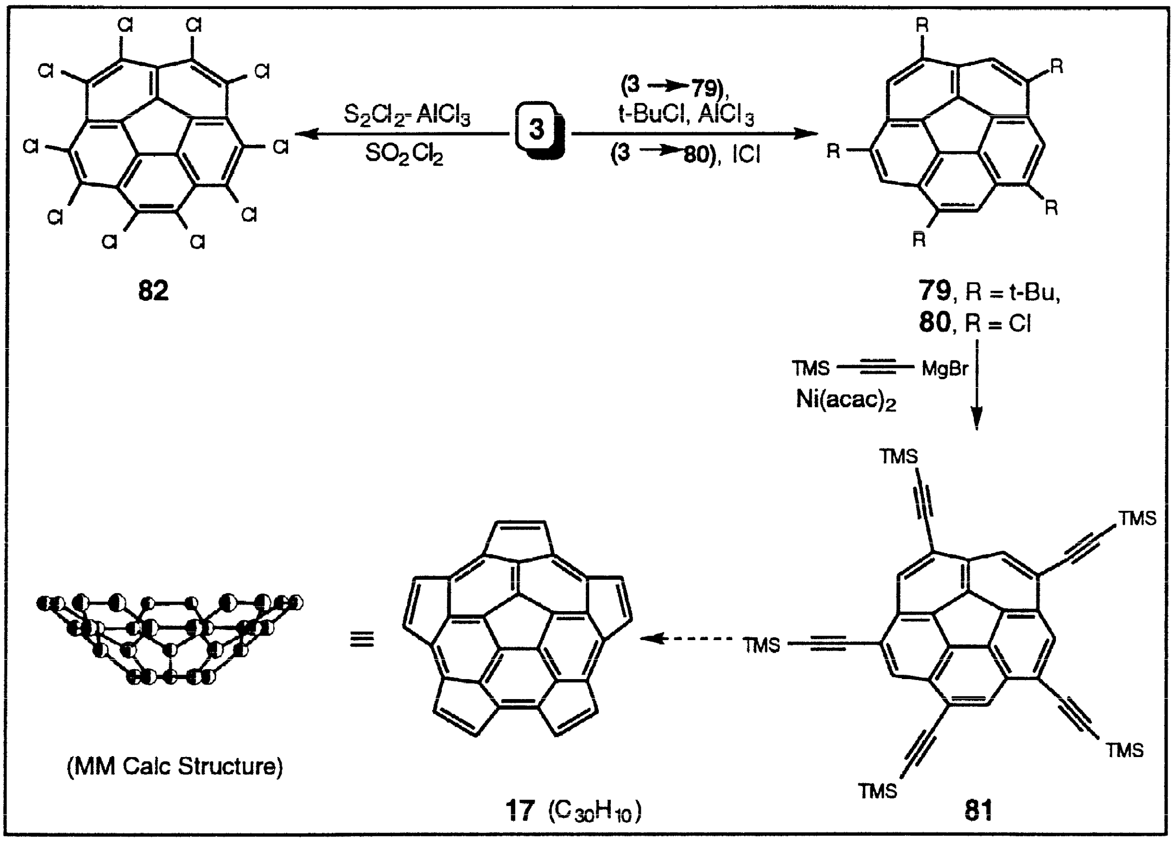
Scheme 16, *Scott's synthesis of corannulene and bromocorannulenes*

In an innovation of the earlier syntheses of corannulene, Scott *et al.* have disclosed a facile, high yielding, three step synthesis of **3** from commercially available starting materials (Scheme 17) [47]. Benzoannulation on acenaphthenequninone **71** using 2,4,6-heptanetrione and norbornadiene furnished the diketone **77**, which was converted to the divinyl chloride **78**. On FVP at 1100°C, **78** could be transformed to corannulene in about 35-40% yield.



Scheme 17, *Scott's second generation synthesis of corannulene*

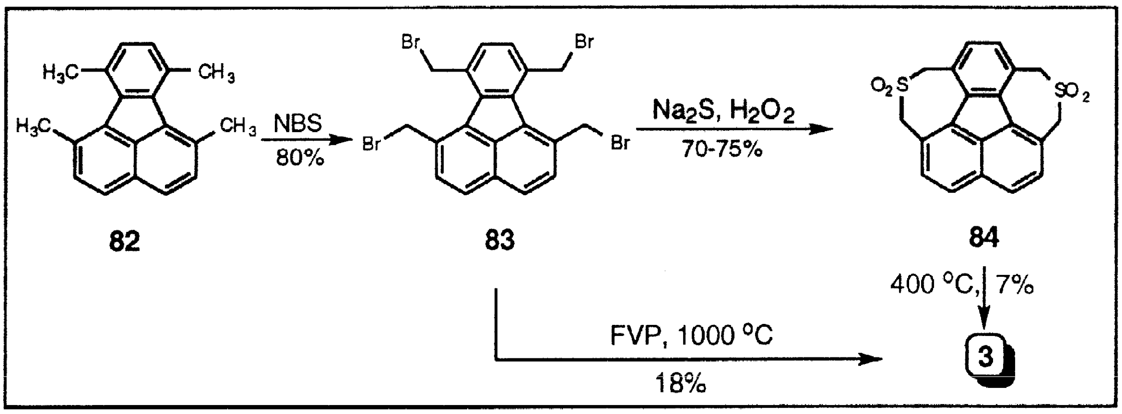
Besides being interesting in its own right, corannulene **3** has the potential to serve as the launching pad for gaining access to advanced fullerene fragments and fullerenes themselves. With substantial quantities of **3** in hand, Scott *et al.* were able to initiate synthetic manipulations towards elaborating it into deeper bowls *via* successive annulation protocols (Scheme 18) [20]. For this purpose, selective as well as extensive functionalization of **3** was a prerequisite. Through classical electrophilic substitutions **3** could be elaborated to symmetrical penta-*t*-butylcorannulene (R=*t*-Bu) **79** and pentachlorocorannulene (R=Cl) **80** using electrophilic aromatic substitution reactions. Coupling of **80** with trimethylsilylethynyl magnesium bromide in the presence of a nickel catalyst furnished pentaethynylcorannulene **81** which was anticipated to serve as a precursor for C_5-semibuckminsterfullerene **17**. Similarly, perchlorination of corannulene furnished decachlorocorannulene **82** which has the potential to be transformed into decaethynylcorannulene for further elaboration to a $C_{40}H_{10}$-buckybowl **16** [20].



Scheme 18, *Scott's synthesis of Functionalization of corannulene*

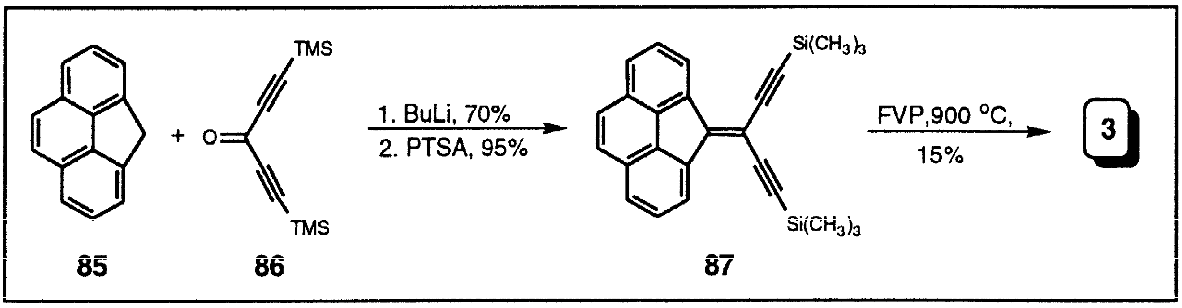
Almost concurrently with Scott's work, Siegel *et al.* reported the synthesis of **3** through the intermediacy of 1,6,7,10-tetramethylfluoranthene **82**, which in turn was prepared from 2,7-dimethylnaphthalene, Scheme 19 [44]. FVP of the tetrabromoderivative **83** obtained from **82** furnished **3** in about 18% yield. Alternatively, the tetrabromo compound **83** was converted to *bis*-sulphone **84**, which on pyrolytic extrusion of sulfur dioxide led to **3** in about 7% yield.

Zimmermann *et al.* have reported a short synthesis of corannulene **3** from 4*H*-cyclopenta[*def*]phenanthrylidene derivative **87** which involved the formation of two adjacent hexagonal rings during the FVP steps, Scheme 20 [48]. Hydropyrolysis of *bis*-trimethylsilyl substituted 3-(4*H*)-cyclopenta[*def*]phenanthrylidene-1,4-pentadiyne



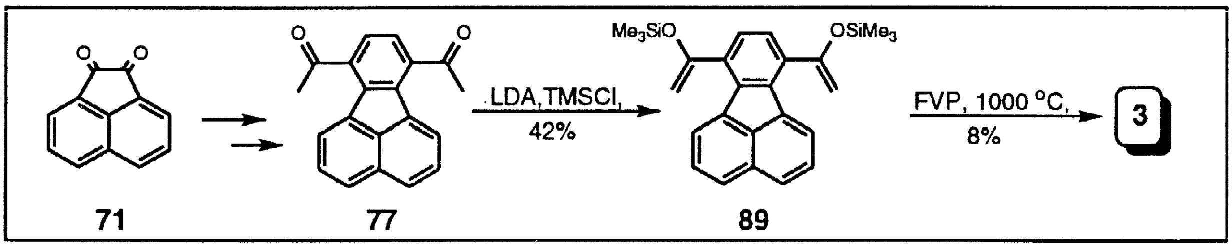
Scheme 19 *Siegel's synthesis of corannulene*

derivative **87**, prepared from 4*H*-cyclopenta[*def*]phenanthrene **85** and 1,5-*bis*-trimethylsilyl-1,4-pentyne-3-one **86**, at 900°C resulted in the formation of corannulene **3** in about 15% yield. In addition, the pyrolysate consisted of minor amounts of PAHs such as pyrene, cyclopenta[*cd*]pyrene, benzo[*e*]pyrene and benzo[*ghi*]fluoranthene as revealed by various sophisticated analytical techniques. These products in all probability originate through a homoallyl-cyclopropyl rearrangement. Formation of **3** from **87** has been rationalized by the authors in terms of vinyl radical intermediates (formed by the addition of H-atoms to the triple bonds of **87**) [48].



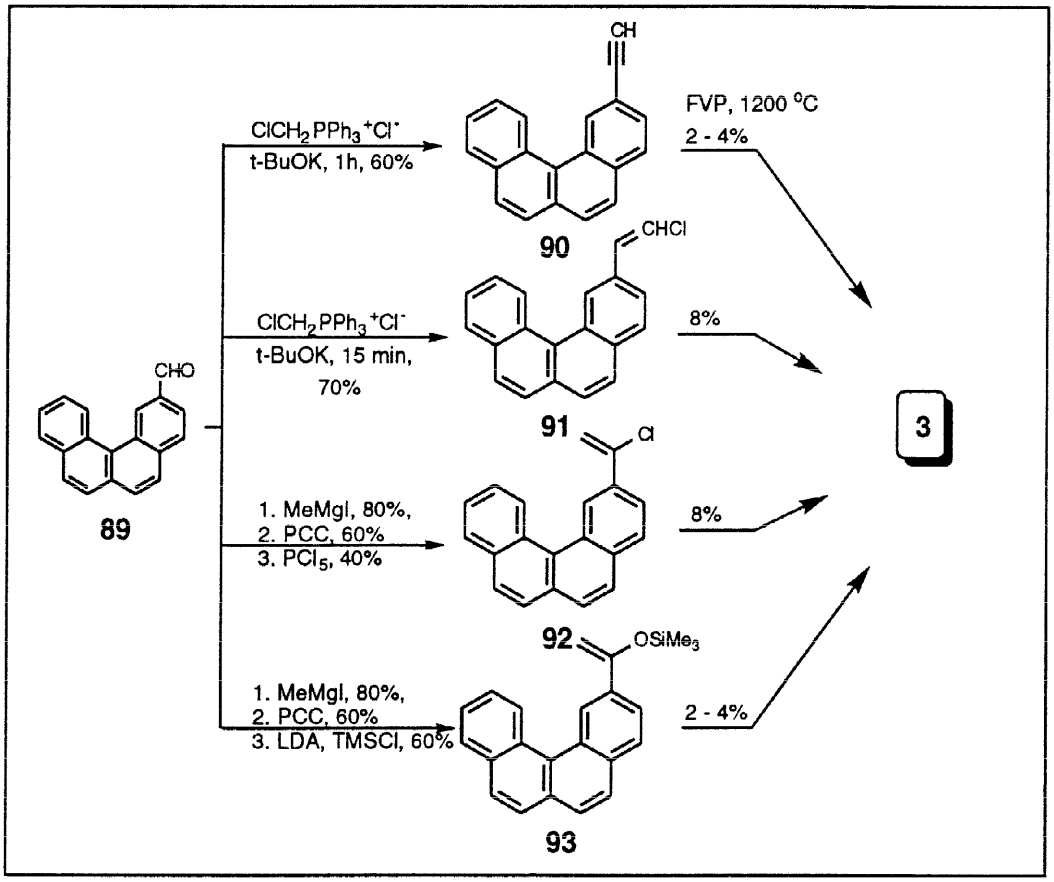
Scheme 20, *Zimmermann's synthesis of corannulene*

Rabideau and Liu have reported a synthesis of corannulene, patterned after Scott's methodology, in which pyrolysis of a *bis*-silyl vinyl ether was the pivotal step (Scheme 21) [26]. The *bis*-trimethylsilyl vinyl ether **89** derived from 7,10-diacetylfluoranthene **77** (prepared from acenaphthenequinone **71**), on pyrolysis under FVP conditions furnished **3** in about 8% yield. Application of a similar strategy to the synthesis of the benzocorannulene derivative failed (*vide supra*, Scheme 5), which indicates that steric hindrance has a critical role in directing the cyclization step.



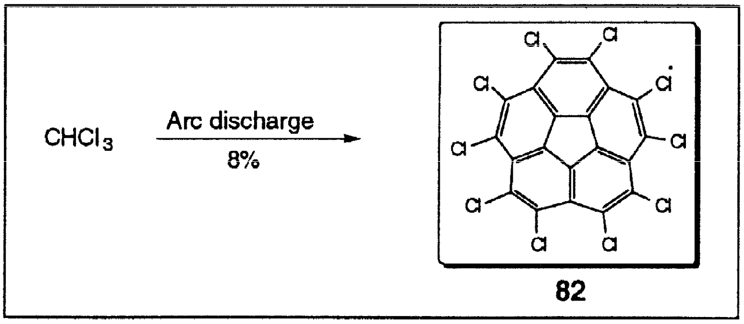
Scheme 21, *Rabideau's synthesis of corannulene*

Mehta and Panda have outlined a simple and conceptually different route to corannulene wherein both pentagonal and hexagonal rings are formed during the FVP step [49]. According to this strategy, commercially available 2-methylnaphthalene and *p*-tolualdehyde were elaborated to 2-formylbenzo[c]phenanthrene **89** following routine steps. Aldehyde functionality in **89** was transformed into several corannulene precursors **90**, **91**, **92** and **93**, each of which on FVP furnished **3** (Scheme 22). Best yield of **3** (8%) could be obtained from the vinyl chloride derivatives **91** and **92**.



Scheme 22, *Mehta-Panda synthesis of corannulene*

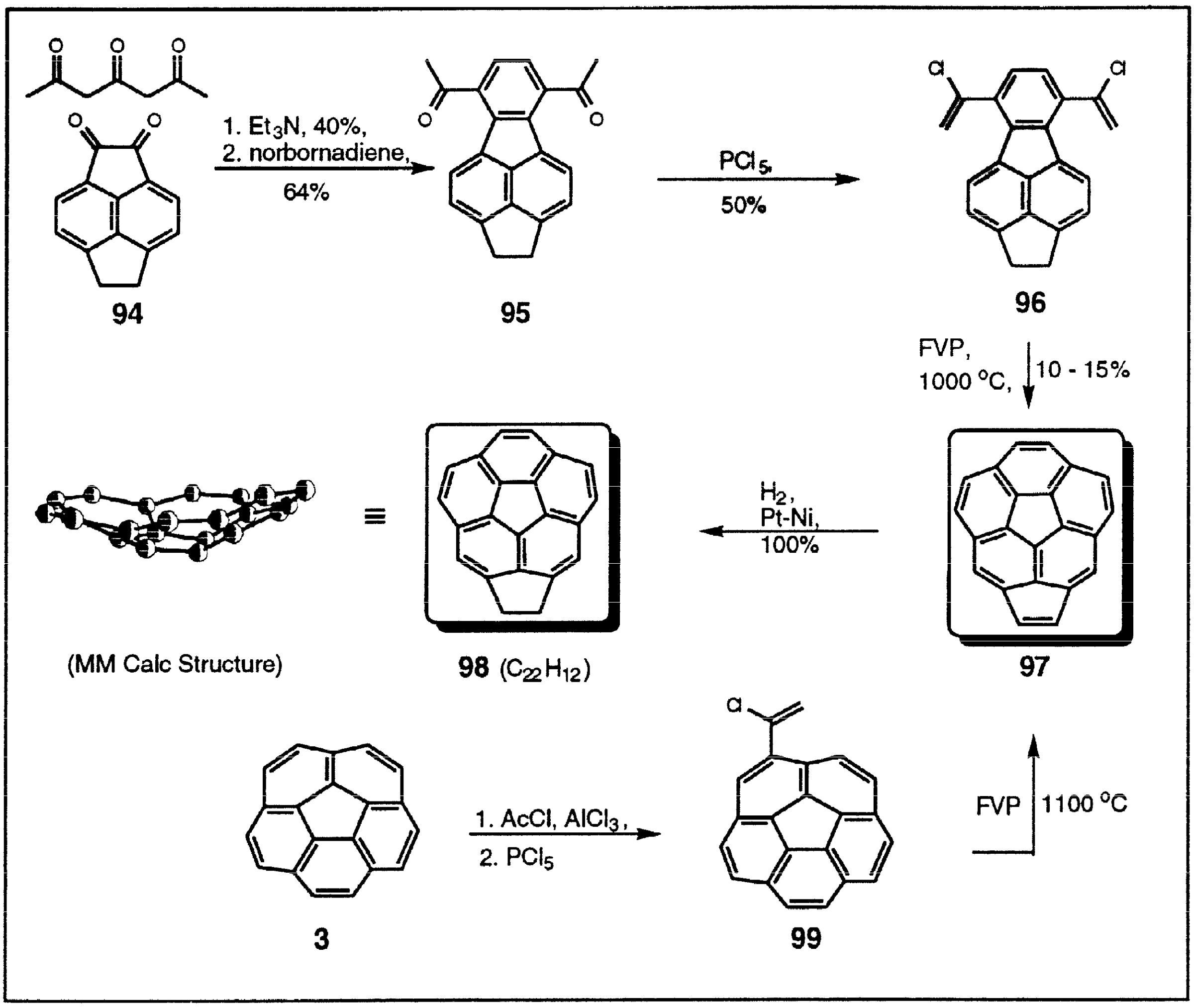
Zheng *et al.* have reported an interesting preparation of decachlorocorannulene **82**, $C_{20}Cl_{10}$, and formation of other perchlorinated fullerene fragments like hexachlorobenzene, C_6Cl_6, octachloronaphthalene, $C_{10}Cl_8$, octachloroacenaphthylene, $C_{12}Cl_8$ and decachlorofluoranthene, $C_{16}Cl_{10}$, through electrical discharge in liquid chloroform (Scheme 23) [50]. Ready access to perchlorinated fullerene fragments from a C_1 - building block is not only synthetically very useful but has important consequences for the understanding of the mechanism of fullerene formation.



Scheme 23, *Zheng's preparation of decachlorocorannulene*

5.2 Cyclopentacorannulenes

Looking beyond corannulene 3, its cyclopenta- and benzo-annulated derivatives can be readily recognized as structural motifs on the C_{60} and C_{70}-fullerene surface. They have drawn attention as the synthetic strategies successfully applied to corannulene can be logically extended to them through tactical modifications. Studies with annulated corannulenes are expected to provide an assessment of the factors that control the degree of pyramidalization and bowl-to-bowl inversion barriers.



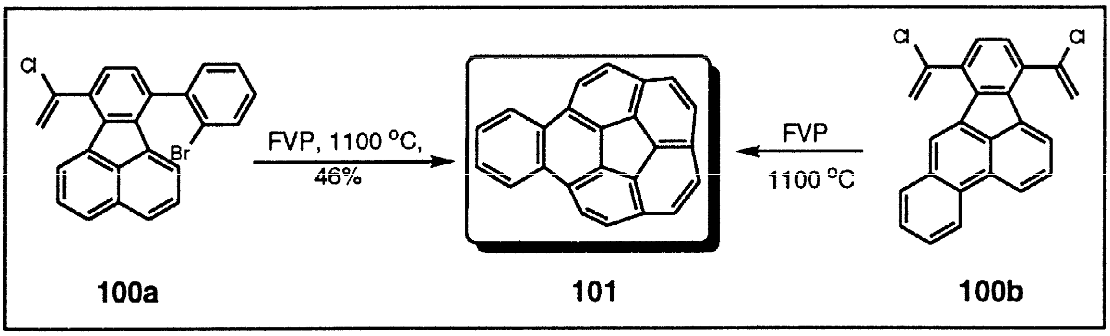
Scheme 24, *Rabideau's and Scott's synthesis of cyclopentacorannulene*

Rabideau *et al.* reported the first synthesis of an annulated corannulene, through an extension of Scott's protocol for corannulene synthesis [51]. Readily available 1,2-diketopyracene **94** was benzo-annulated to the key precursor **96** *via* **95** through sequential Knoevenagel condensation with 2,4,6-heptanetrione, cycloaddition with norbornadiene, decarbonylation, cyclo-reversion, and chlorovinylation of the carbonyl groups. (Scheme 24). FVP of *bis*-vinyl chloride **96** led to corannulene-type ring closure as well as dehydrogenation to furnish cyclopenta[*bc*]corannulene **97**. The pyrolysate from **96** also contained corannulene **3**, formed by the fragmentation of the ethano bridge. The cyclopentene double bond in **97** on catalytic reduction furnished **98**. The structure of **97** was confirmed by X-ray crystal structure analysis which revealed an expected increase in the curvature and bowl-depth due to the incorporation of an additional five-membered ring on the corannulene framework [52]. The X-ray crystal structure also showed interesting long-range packing in the solid state with the bowl-shaped molecules stacked in a concave-convex fashion. The semiemperical AM1 calculations revealed that the difference in energy between **98** and its planar conformations is 39 kcal mol^{-1}[51]. DNMR studies by Rabideau *et al.* on **98d$_2$** clearly showed that the molecule does not undergo bowl-to-bowl inversion at room temperature. Spin-polarization transfer experiments at 127°C allowed the estimation of the barrier to be 26 kcals mol^{-1} as the lower limit [53]. Theoretical calculations at *ab initio* level also indicated that **98** is effectively locked in a single conformation [46].

In a different approach, Scott *et al.* have reported the cyclopentene annulation of corannulene **3** to furnish cyclopenta[*bc*]corannulene **97** (Scheme 24) [20]. Friedel-Crafts acylation of **3** resulted in acetylcorannulene which was converted to the vinyl chloride precursor **99**. FVP of **99** at 1100°C resulted in the formation of cyclopenta[*bc*]corannulene **97**.

5.3 Benzocorannulene

Scott *et al.* have achieved the synthesis of monobenzocorannulene following the extension of their corannulene synthesis while incorporating necessary tactical modifications [54, 55]. Thus, the pyrolysis of 7-(2-bromophenyl)-10-(1-chlorovinyl)fluoranthene **100a** and 9,12-di(1-chlorovinyl)benzo[*e*]acephenanthrylene **100b** under FVP conditions furnished **101** (Scheme 25). Reflecting the C_2-symmetry of the compound, the ^{13}C NMR spectrum of **101** showed 13 lines and the ^{1}H NMR spectrum revealed the deshielded bay region hydrogens as a double doublet and a doublet (~ 9 ppm). X-ray crystal structure of **101** has been determined and like corannulene it does not show organized bowl-to-bowl packing in the crystal lattice [54].



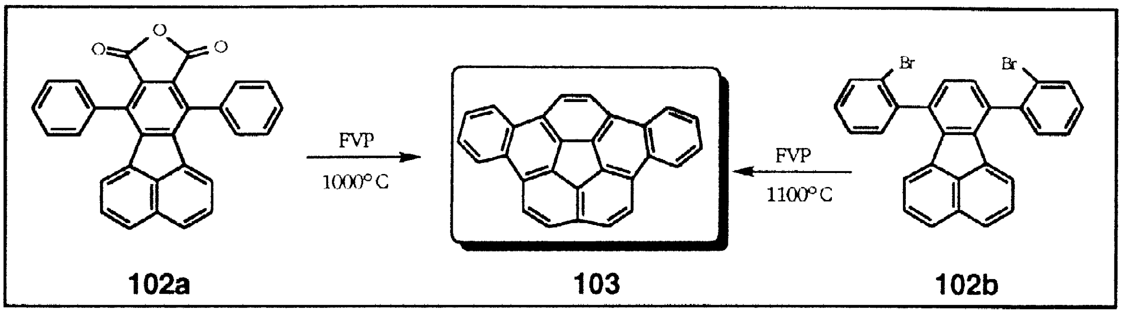
Scheme 25, *Scott's synthesis of benzocorannulene*

5.4 Dibenzocorannulene

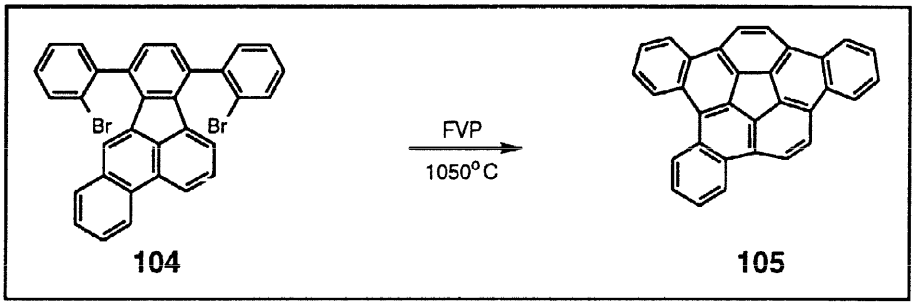
Scott *et al.* have, in a preliminary form, disclosed the synthesis of dibenzocorannulene **103** starting from diphenylfluoranthene derivatives **102a** and **102b** (Scheme 26) [56]. While FVP of the anhydride **102a** probably proceeds through a benzyne intermediate, pyrolysis of **102b** leads to cyclization involving radical intermediates.

5.5 Tribenzocorannulene

Scott *et al.* have also been successful in the synthesis of tribenzo[*adj*]corannulene **105** *via* the FVP of 9,12-di(2-bromophenyl)benzo[*e*]acephenanthrylene **104** in yet another variation of their corannulene strategy (Scheme 27) [54].



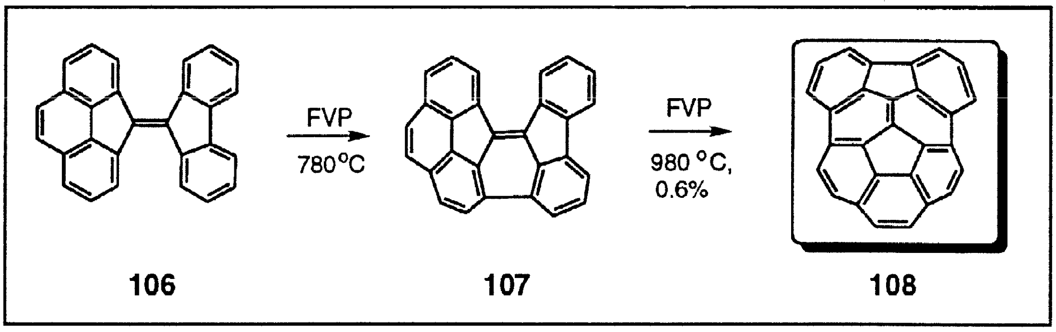
Scheme 26, *Scott's synthesis of dibenzocorannulene*



Scheme 27, *Scott's synthesis of tribenzocorannulene*

5.6 Fluorenocorannulene

Zimmermann *et al.* have investigated FVP of 4[9*H*-fluorenylidene(9)]-4*H*-cyclopenta[*def*]phenanthrene **106** and observed the formation of a monocyclized product diindeno[4,3,2,1-*cdef*;1',2',3'-*hi*]chrysene **107** and a rearrangement product benzo[*p*]naphtho[1,8,7-*ghi*]chrysene (Scheme 28) [57]. Further FVP of **107** at the elevated temperature of 980°C, enabled the establishment of the more strained C-C bond and fluoreno[1,9,8-*abcd*]corannulene **108** was obtained in 0.6% yield. The low yield of the bowl-shaped product **108** has been attributed to the enormous build-up of strain energy to the extent of 58.3 kcals mol^{-1} in the cyclization step.



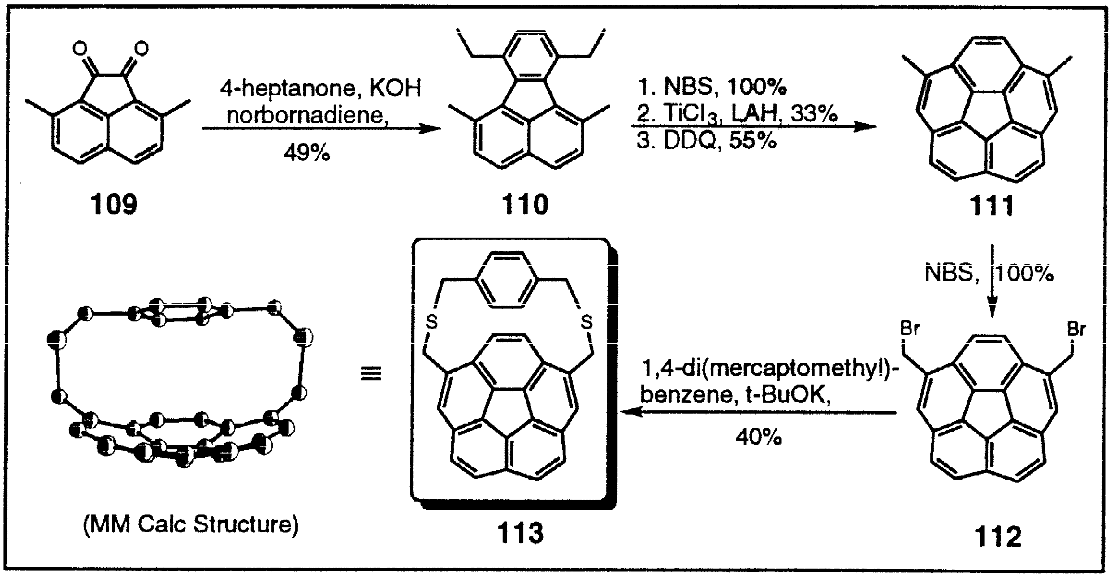
Scheme 28, *Zimmermann's synthesis of fluorenocorannulene*

5.7 Cyclophane-corannulene

Encouraged by the success achieved in the synthesis of corannulene **3** and its annulated derivatives, synthetic chemists have sought new molecular entities and hybrids composed in part of buckybowls.

Siegel *et al.* have conceived of a corannulene-cyclophane **113**, in which 1,6-carbon atoms of corannulene moiety are linked to a benzene ring in the 1,4-positions through three atom bridges (Scheme 29) [43, 58]. A synthesis of **113** in which 1,6-Dimethyl-7,10-

diethylfloranthene **110** served as the key precursor has been accomplished. The fluoranthene derivative **110** in turn was accessed through benzoannulation of 2,7-dimethylacenaphthenequinone **109** following Scott's protocol. Benzylic bromination of **110**, followed by reductive coupling in the presence of a Ti(0) species and dehydrogenation with DDQ furnished 2,5-dimethylcorannulene **111** This synthesis of the corannulene system was accomplished without recourse to FVP as the critical step. It indicates that organometallic mediated coupling and dehydrogenation can be a viable substitute for the high temperature gas-phase reactions in the preparation of buckyballs. Further benzylic bromination of **111** gave the dibromo corannulene derivative **112** Treatment of **112** with 1,4-*bis*(mercaptomethyl)benzene in the presence of potassium *tert*-butoxide resulted in the cyclophane-corannulene **113**, which has been described as a covered basket [43].



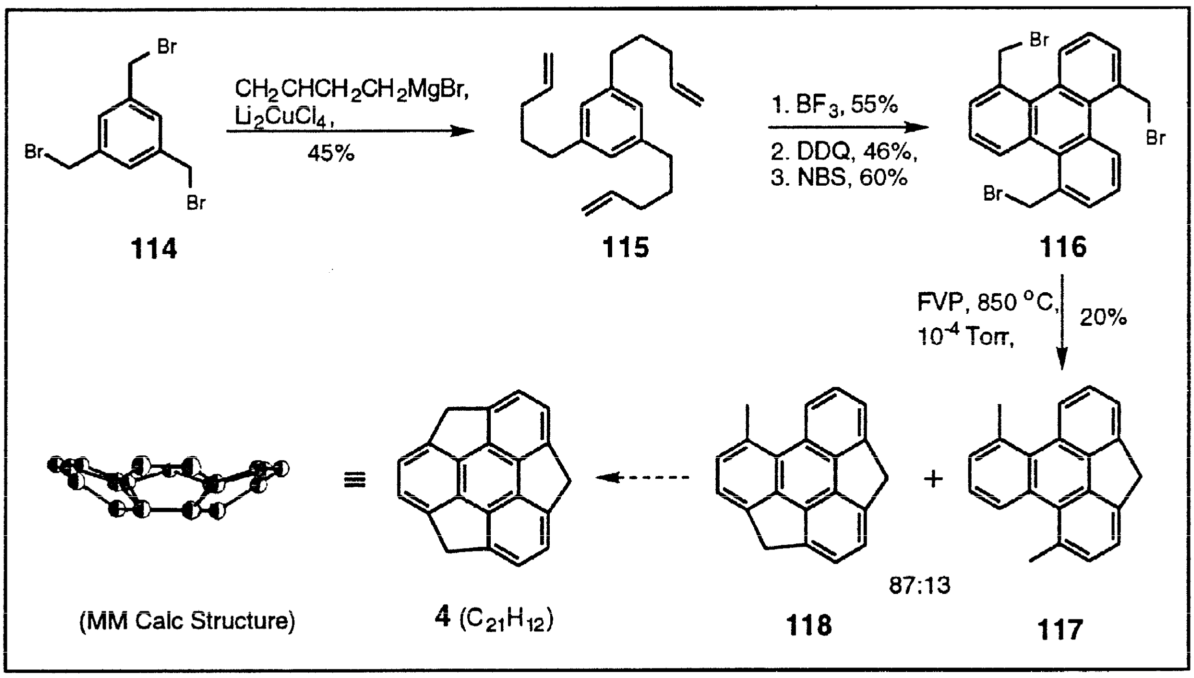
Scheme 29, *Siegel's synthesis of cyclophane-corannulene*

The cyclophane-corannulene **113** has been the subject of extensive NMR studies and theoretical calculations. The bowl-depth in **113** was calculated to be 0.87Å, which is similar to that found in corannulene, indicating that the dithia-bridges do not add to the curvature of the molecule. The minimum barrier for inversion was calculated to be 18 kcals mol^{-1}. Variable temperature NMR studies indicated that the structure of **113** is locked in a single conformation without bowl-to-bowl inversion [43]. Moreover, the rotation of the aromatic ring along 1,4-axis is also arrested by the two hydrogens in the 2', 3' positions directed into the cavity of the bowl. Consequently, these hydrogens resonate at δ 1.89 ppm, dramatically up-field from the usual position expected for aromatic protons. This shift can be attributed to the shielding effect of the 14-electron aromatic ring current prevalent on the rim.

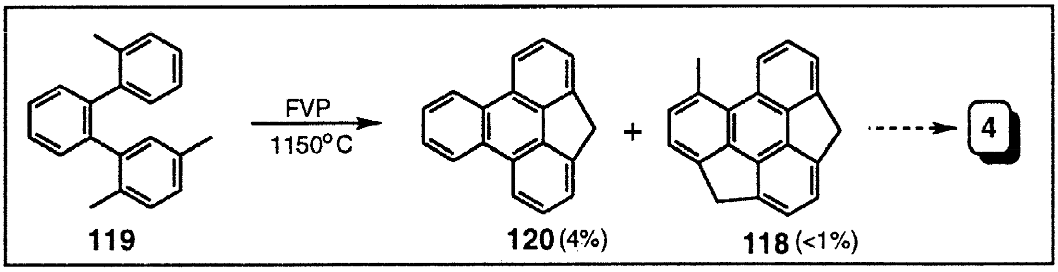
6. SUMANENE

Sumanene, $C_{21}H_{12}$ **4**, (Suman=flower, Sanskrit) forms a readily recognizable and dominant structural motif on C_{60}-fullerene **1**, when the retrosynthetic analysis is done along the C_3-route (Scheme 1). Although sumanene **4** has just one extra carbon compared to corannulene **3** ($C_{20}H_{10}$), it has two additional pentagonal rings that impart greater strain and curvature to the molecule. Theoretical calculations reveal that the bowl-depth in sumanene is about 1.15Å which is 0.26Å greater than that of corannulene [16].

Mehta *et al.* have reported an approach towards the synthesis of sumanene starting from C_3-symmetric 1,3,5-(tribromomethyl)benzene **114**, which was transformed into 1,5,9-tribromomethyltriphenylene **116** through a sequence during which C_3-symmetry was maintained (Scheme 30) [59]. Copper catalyzed cross coupling reactions between **114** and butenyl magnesium bromide furnished **115**, which on Lewis acid catalyzed cyclization, dehydrogenation, and benzylic bromination led to **116**. When **116** was subjected to FVP at 850°C monomethano-bridged **117** and dimethano-bridged **118** compounds were obtained in 20% yield, but no sumanene **4** was isolated from the pyrolysate. A similar approach to sumanene **4** emanating from the terphenyl derivative **119** has been explored. FVP of **119** also furnished the dimethano-bridged **118**, along with demethylated monobridged **120** (Scheme 31) [60]. The failure to obtain **4** could be due to a large strain build-up (49 kcal) during the formation of the third methano-bridge [16]. Theoretical calculations (MNDO) on sumanene **4** predict a bowl-to-bowl inversion barrier of 26 kcal mol^{-1}, which indicates that it may exist in a locked conformation [16].

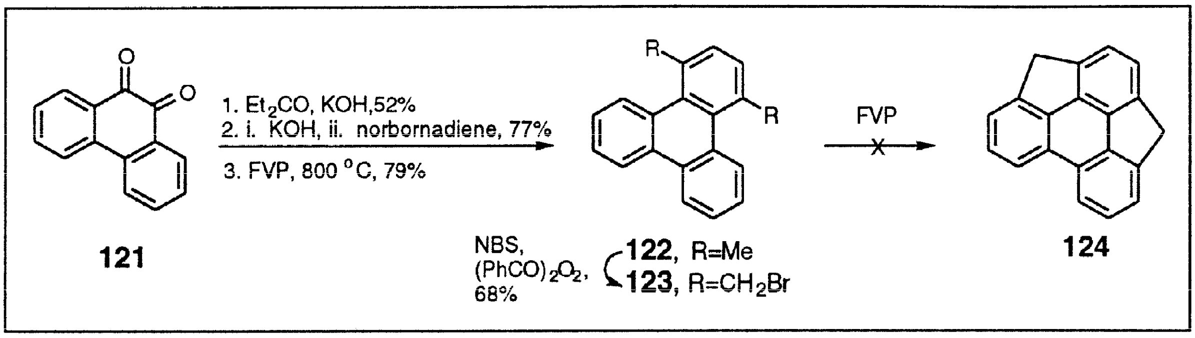


Scheme 30, *Mehta's approach to sumanene*



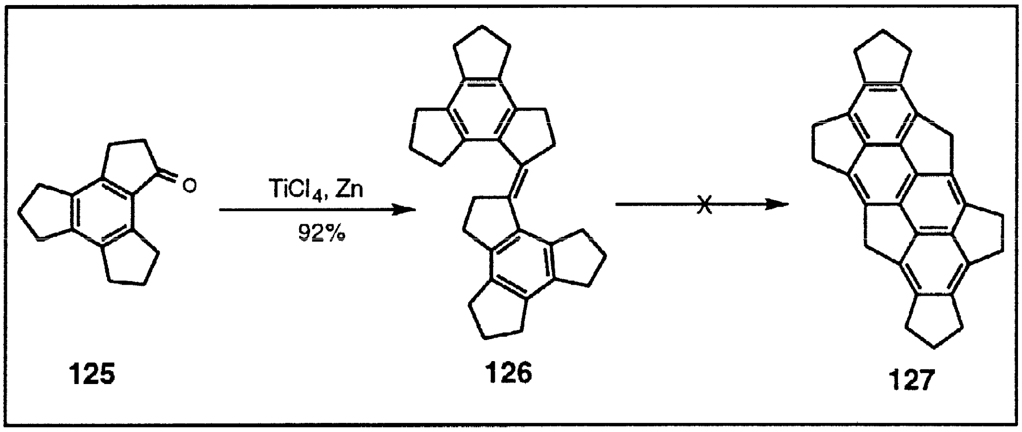
Scheme 31, *Mehta's alternate approach to sumanene*

Plater and coworkers reported the synthesis of 1,4-dimethyltriphenylene **122**, a possible precursor for cyclopenta-fused buckybowls such as sumanene **4** and pinakene **5** [61,62]. Phenanthroquinone **121** was converted into dimethyltriphenylene **122**following Scott's benzoannulation protocol. Neither **122** , nor *bis*-benzyl bromide **123** on FVP yielded any cyclopenta-fused products like **124**, Scheme 32.



Scheme 32

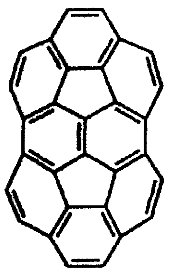
Dehmlow and Kelle have pursued a strategy to generate a sumanene-like structural motif from a trindane derivative (Scheme 33) [63]. The ketone **125** derived from trindane was readily dimerized through reductive coupling to **126**. However, further twofold oxidative ring closures to **127** could not be effected under a variety of conditions.



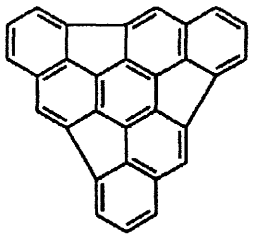
Scheme 33

7. SEMIBUCKMINSTERFULLERENES

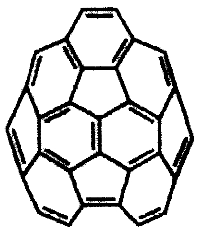
Several bowl-shaped $C_{30}H_n$ hydrocarbons, representing half the carbon content of C_{60} and embodying a significant motif on its curved surface, are conceivable. While **17** has been displayed in the retrosynthetic pathways in Schemes 1 & 2, some others (**128-132**) are shown below. However, to date, only two of them, C_{2v} semibuckminsterfullerene (5,5-fulvalenecirculene) **128** and C_3-hemibuckminsterfullerene **129** (triindenotriphenylene) possessing the molecular formula $C_{30}H_{12}$, have been synthesised.



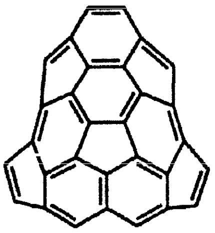
128 $C_{30}H_{12}$



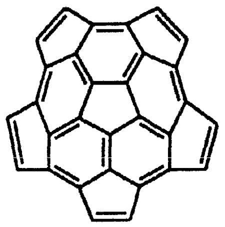
129 $C_{30}H_{12}$



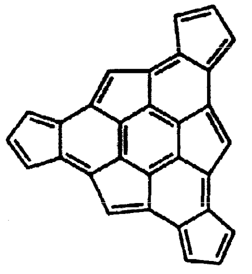
130 $C_{30}H_{10}$



131 $C_{30}H_{10}$



17 $C_{30}H_{10}$

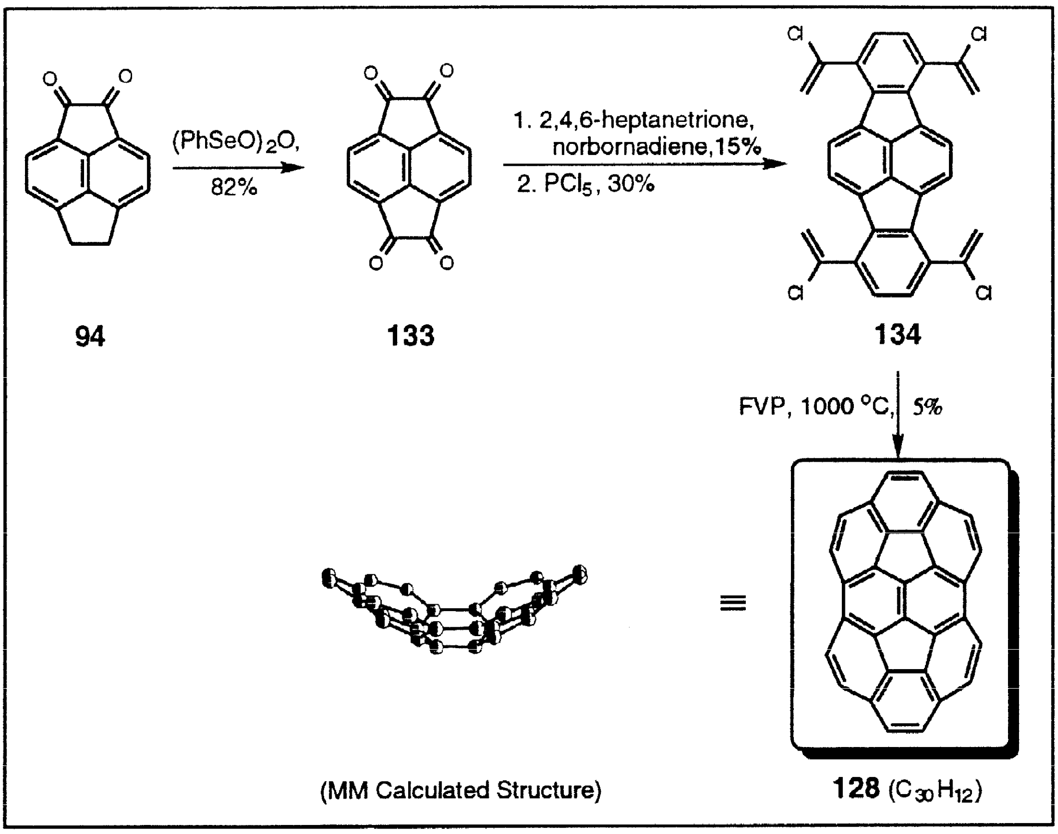


132 $C_{30}H_{12}$

The two semibuckminsterfullerenes **128** and **129** possess curvature similar to that of C_{60}-fullerene. In spite of the large strain associated with them, these C_{30}-buckybowls are stable and are amenable to further studies. Although, both **128** and **129** have half the number of carbon atoms of C_{60}, only triindenotriphenylene **129** can be regarded as the exact half, since its dehydrogenative dimerization could lead to the parent molecule. On the other hand, C_{2v}-semibuckminsterfullerene **128** does not possess the carbon framework, which is the exact half of **1**, and its dehydrogenative dimerization would result in C_{60}-fullerene of D_{2d} symmetry [64, 65].

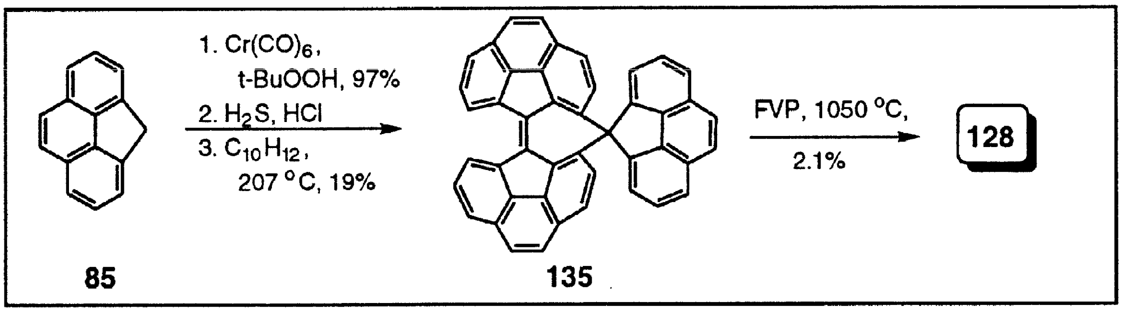
7.1 C_{2v}-Semibuckminsterfullerene

Rabideau *et al.* were the first to achieve the synthesis of C_{2v}-semibuckminsterfullerene **128** through a clever extension of Scott's highly successful benzoannulation-gas phase FVP based synthesis of corannulene, from acenaphthenequinone **71** [66]. The starting material, in this case, was 1,2,5,6-tetraoxopyracene **133** which was prepared *via* convenient benzylic oxidation of 1,2-dioxopyracene **94** with benzeneseleninic anhydride, Scheme 34 [67, 68]. The tetraketone **133** was elaborated through Knoevenagel condensation at two sites and *bis*-benzoannulation to a tetraacetyl compound, which was converted to the tetravinylic chloride **134**. Quite remarkably, on subjecting **134** to FVP, four-fold cyclization occurred to furnish semibuckminsterfullerene **128** in 5% yield. The ^{1}H NMR spectrum of **128** displayed the expected AB quartet and a singlet in the ratio of 2:1 and the ^{13}C NMR exhibited three methine and five quaternary carbon atoms. Theoretical calculations revealed a bowl-shape for **128** with a bowl-depth of 2.7Å. Estimation of curvature by POAV1 analysis showed the maximum pyramidalization angle to be 11.4° which is quite close to that in C_{60}-fullerene-I_h (11.6°). Calculations at *ab initio* (HF/6-31G*//3-21G) level predict about 57 kcal mol^{-1} for the inversion barrier in **128**, and thus, it exclusively exists in a bowl conformation under normal conditions [66].



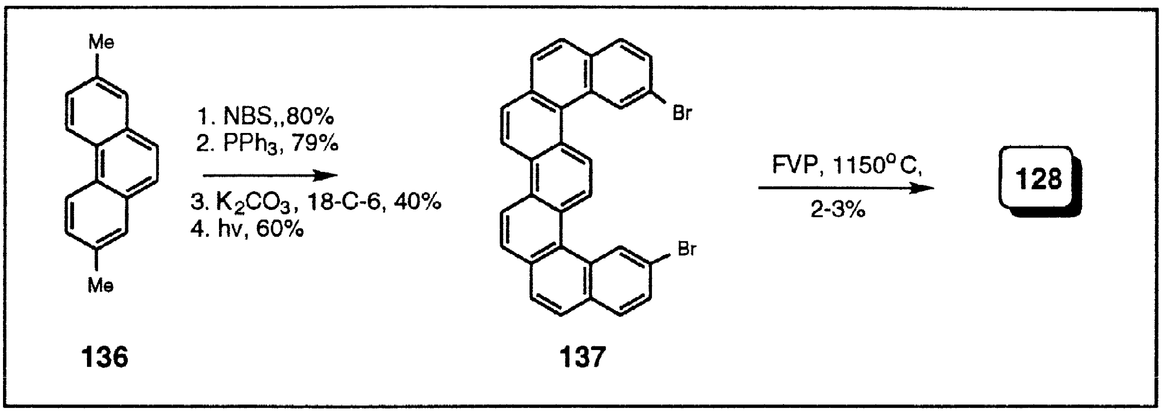
Scheme 34, *Rabideau's synthesis of C_{2v}-semibuckminsterfullerene*

Zimmermann and Scott have reported a synthesis of C_{2v}-semibuckminsterfullerene **128** from the bifluorenylidine derivative **135** through gas-phase pyrolysis (Scheme 35) [30]. In this remarkable conversion, extrusion of the 4*H*-cyclopenta[*def*]phenanthrene moiety takes place along with double cyclization. The spiro precursor **135** was generated from cyclopenta[*def*]phenanthrene **85** in a serendipitous reaction.



Scheme 35, *Zimmermann and Scott's synthesis of C_{2v}-semibuckminsterfullerene*

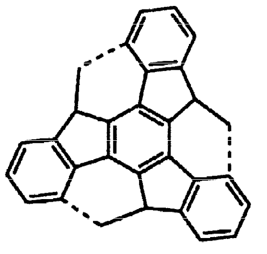
Mehta and Panda reported a novel synthesis of **128** through the FVP of dibromodibenzopicene **137** (Scheme 36) [69]. The starting PAH **137** was made from 2,7-dimethylphenanthrene **136** *via* , benzylic bromination, Wittig olefination with *p*-bromobenzaldehyde and oxidative photocyclization. FVP of **137** at 1150°C resulted in tandem three-fold cyclization leading to the buckybowl **128**. The bromine atoms present in the precursor **137** act as promoters of the cyclization by generating either aryl radicals or benzyne-like intermediates.



Scheme 36, *Mehta-Panda synthesis of C_{2v}-semibuckminsterfullerene*

7.2 C_3-Hemibuckminsterfullerene and Related Compounds

For the synthesis of **129** and its derivatives, two approaches have been widely pursued and have met with limited success. The first set of approaches is *via* the trialkylbenzo[*afk*]trindane (truxene) system **138** in which tribenzoannulation in the gas phase, of a suitably functionalized derivative, was envisaged as the key step (see dotted lines in **138**). The other approaches have emanated from the tribenzo[*cio*]triphenylene system **139** wherein three-fold transannular C-C bond formation leading to the generation of three five membered rings under FVP conditions was to be the pivotal manoeuvre (see dotted lines in **139**).



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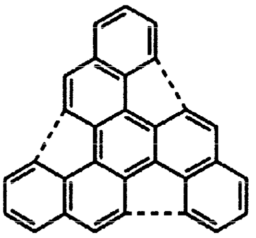
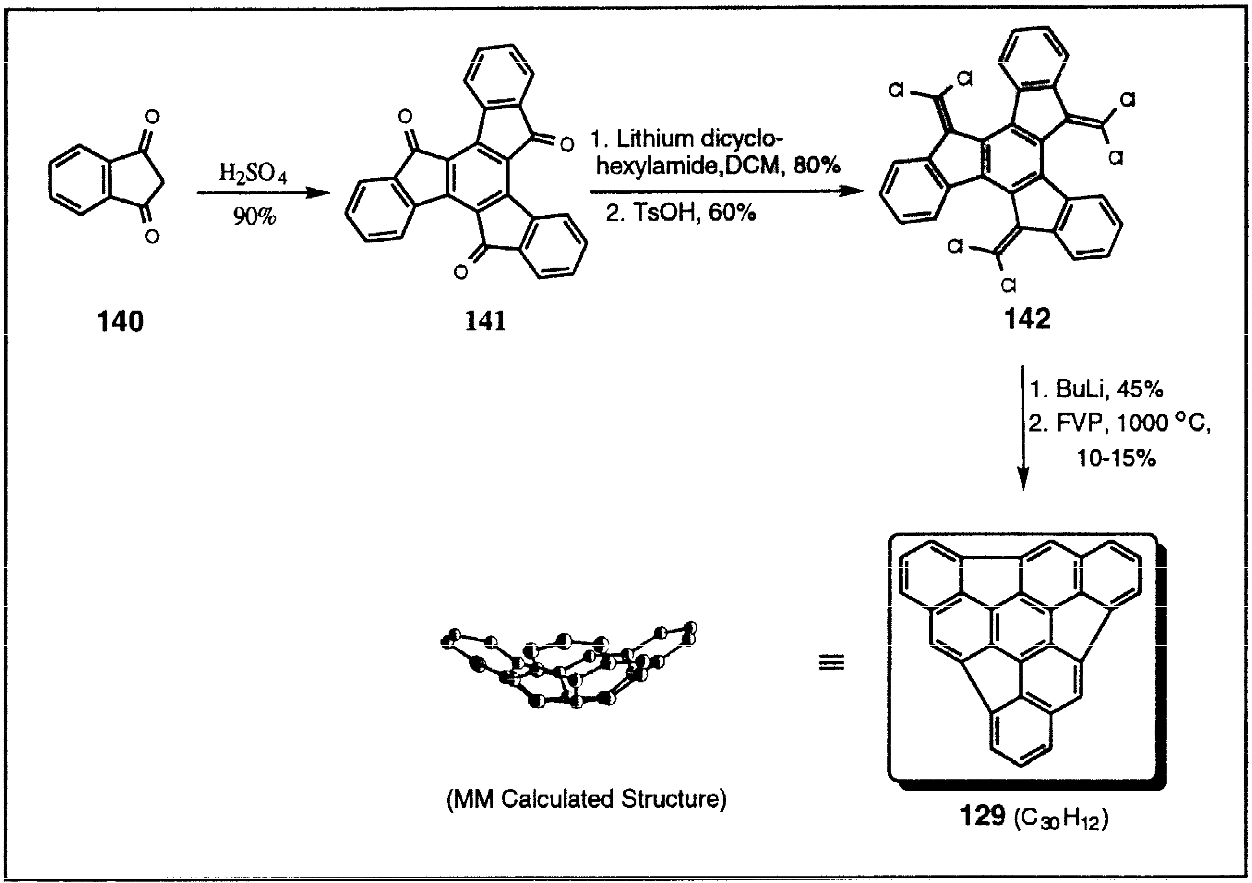


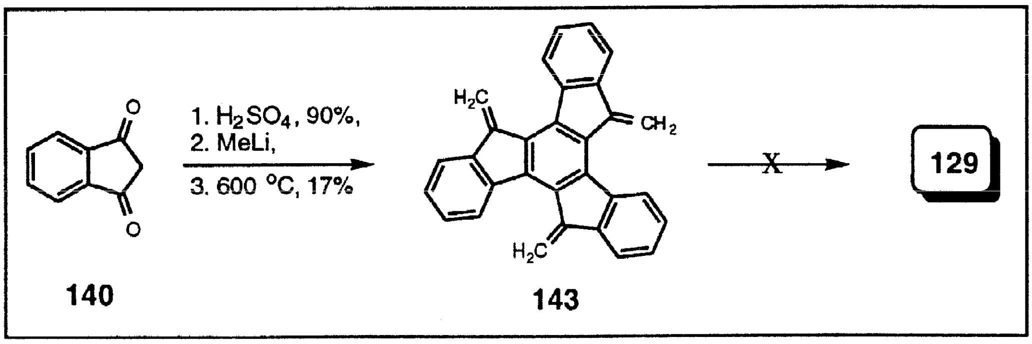
139

To Rabideau *et al.*. goes the credit for the first synthesis of C_3-hemibuckminsterfullerene **129**, Scheme 37 [70]. Their synthesis emanated from tribenzo[*afk*]trindenone (truxenetrione) **141**, readily available from the trimerization of indane-1,3-dione **140** [71] or from 2-methyl acetophenone through a *de novo* synthesis [72]. Dichloromethylation of the three carbonyl groups in **141** furnished **142.** The FVP of tris(dichlorovinyl)compound **142** at 1000°C resulted in the formation of hemibuckminsterfullerene **129**, but it was contaminated with other products derived from extensive incorporation of chlorine and further dechlorination proved to be unproductive. Partial dechlorination of **142** with *n*-butyllithium resulted in a mixture of *tri*- and *tetra*-chloro derivatives and these proved to be more promising and on FVP furnished **129** in 10-15% yield. The ^{1}H NMR spectrum exhibited four resonances (a singlet, two doublets and a double doublet) expected for **129** and in conformity the ^{13}C NMR spectrum exhibited four C-H aromatic and six quaternary aromatic carbons. Theoretical studies on **129** reveal that it exists in a rigid cup-shaped structure [70] and the maximum pyramidalization angle is 11.1° which compares well with that in C_{60}. While **128** and its symmetry related C_{30} sibling **129** have similar curvatures, it is interesting to note that **128** is more stable than **129** by 16 kcal mol^{-1} according to molecular mechanics and by 18 kcal mol^{-1} by *ab initio* methods [70]. The hemibuckminsterfullerene **129** has been considered as a potential candidate for dehydrogenative dimerization leading to C_{60}- either by a concerted pathway [73] or under metal catalysis [74].



Scheme 37, *Rabideau's synthesis of C_3-hemibuckminsterfullerene*

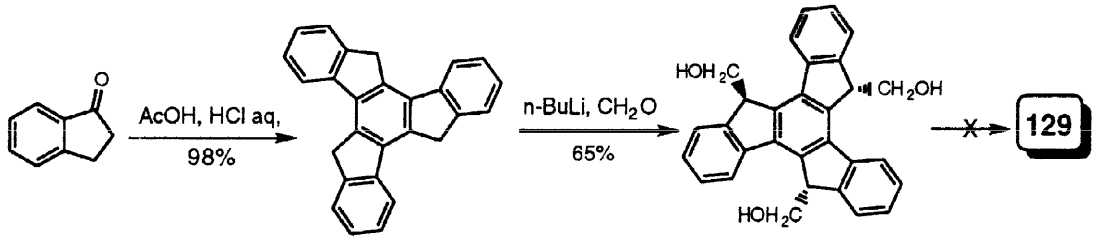
Several others have pursued similar tribenzo[*afk*]trindane **143** based approaches to **129** although somewhat less successfully and these are briefly discussed here. Before Rabideau *et al.*'s success in making **129**, De Lucchi *et al.* considered truxenene **143**,



Scheme 38, *De Lucchi's attempted synthesis of C_3-hemibuckminsterfullerene*

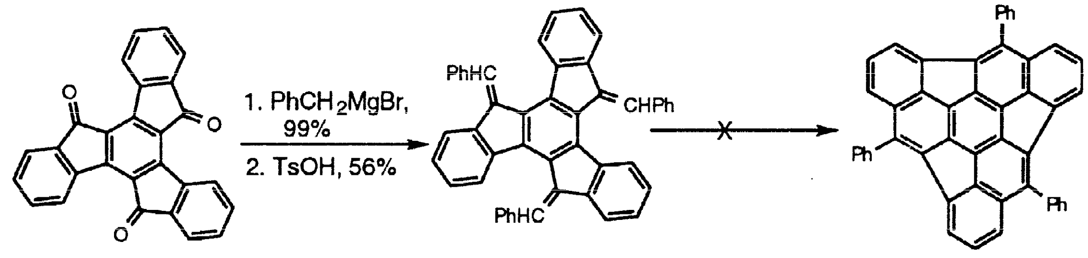
readily available from indane-1,3-dione **140** as the immediate precursor of C3-hemibuckminsterfullerene, Scheme 38 [71]. However, attempted ring closure of **143** by thermal and photochemical methods failed.

Dehmlow and Kelle have recently reported the synthesis of several truxene derivatives as possible precursors for fullerene fragments [63]. Truxene **145** was prepared in high yield from the condensation of 1-indanone **144** and it was subsequently converted to tri(hydroxymethyl)truxene **146**. But attempted three-fold ring closure *via* a Friedel-Crafts reaction did not result in any useful products (Scheme 39). Alternatively, truxenetrione **141** was transformed to tribenzaltruxene **147** (triphenyltruxenene) by both Dehmlow *et al.* [63] and Plater *et al.* [75], but, this compound also could not be coerced to undergo triple cyclization to the triphenyl derivative **148** of C3-symmetric semibuckminsterfullerene and representing a C_{48} fullerene fragment (Scheme 40) [63].



144 **145** **146**

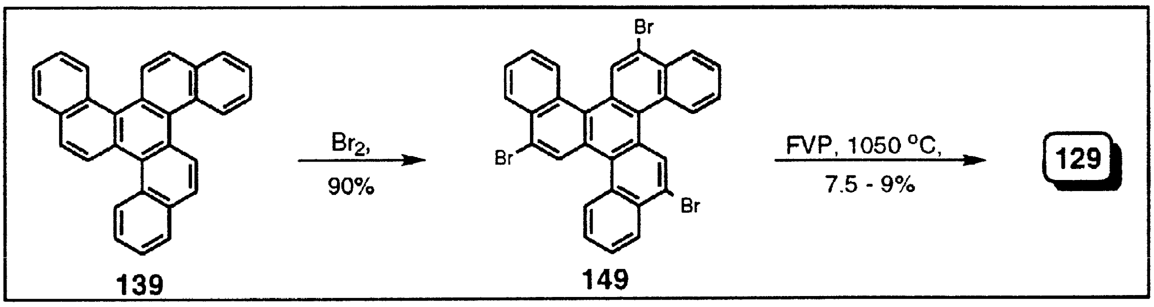
Scheme 39, *Dehmlow's attempted synthesis of C3-semibuckminsterfullerene*



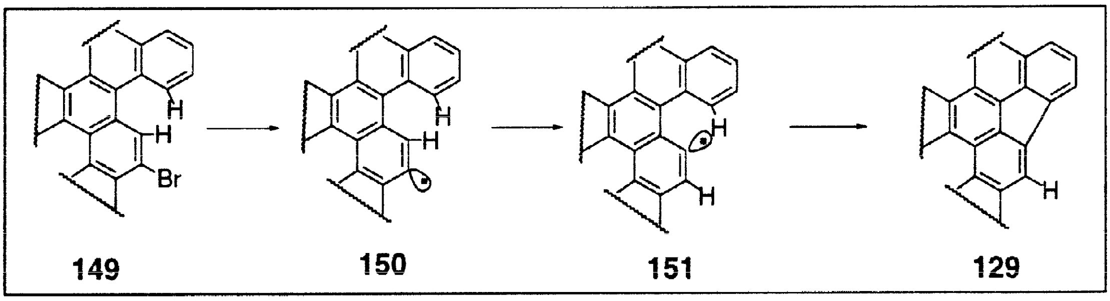
141 **147** **148**

Scheme 40, *Dehmlow and Plater's attempted synthesis of triphenyl-C3-hemibuckminsterfullerene*

Scott and Zimmermann have reported a short synthesis of C3-buckminsterfullerene **129** from C3-tribenzo[*cio*]triphenylene **139** *via* its tribromo derivative **149** (Scheme 41) [30]. The success in this case could be attributed to the high yielding regioselective bromination of the precursor tribenzotriphenylene **139** to **149**. Previously, Scott *et al.* had reported an efficient synthesis of **139** from α-tetralone [76]. The loss of bromine atoms through homolysis during FVP leads to an aryl radical of the type **150** in which the neighbouring hydrogen migrates out of the sterically hindered fjord region through a 1,2-shift to give a new aryl radical **151** which is well poised for transannular closure to **129** (Scheme 42).

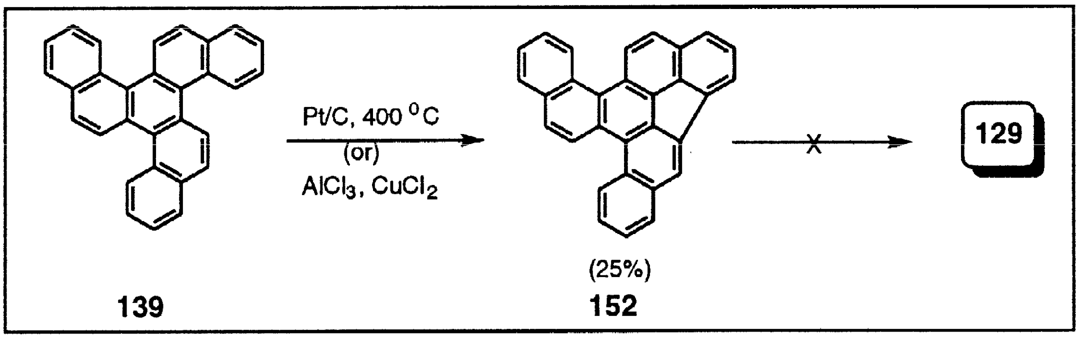


Scheme 41, *Zimmermann and Scott's synthesis of C3-semibuckminsterfullerne*



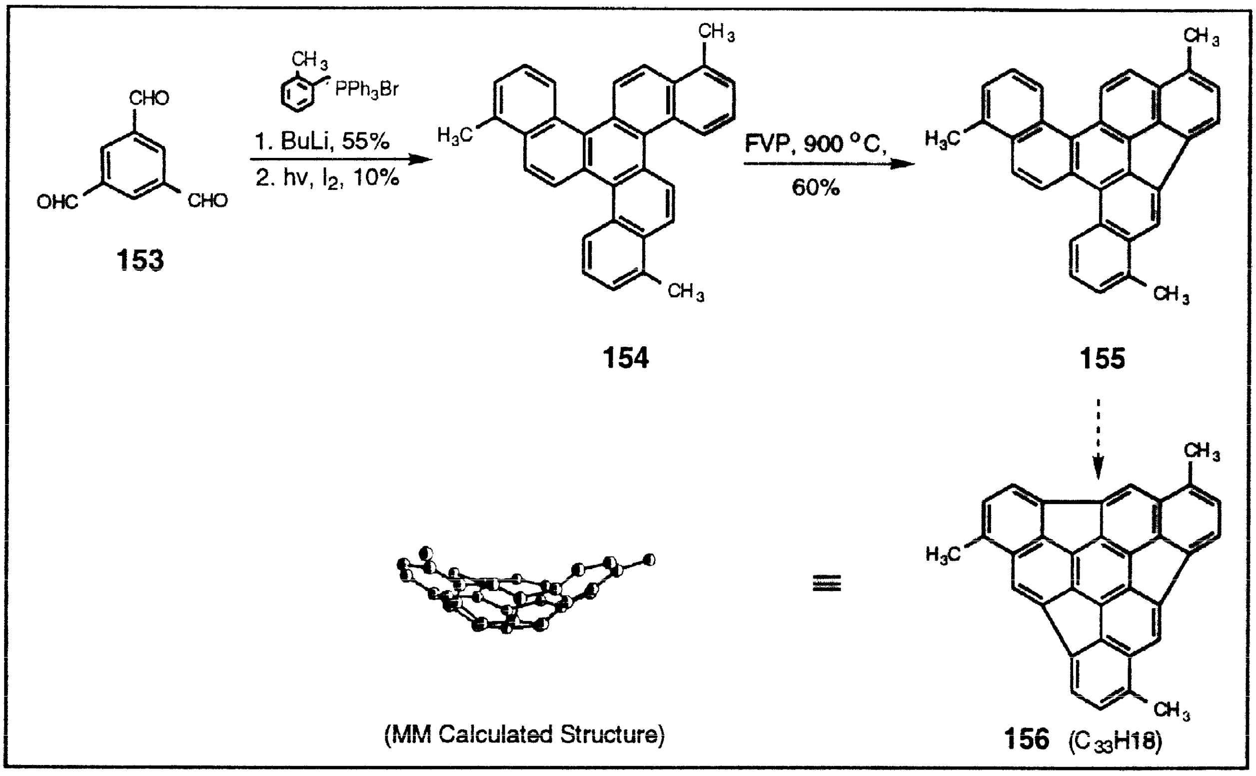
Scheme 42, *Proposed pathway for the cyclization of **149** to **129**.*

Earlier, Faust and Vollhardt too had considered dehydrogenative cyclization of C3-tribenzotriphenylene **139** as a possible route to C3-hemibuckminsterfullerene **129**, but various attempts in this direction led to the isolation of only the monobridged compound **152** as the major product (Scheme 43) [77, 78].



Scheme 43, *Faust and Vollhardt's attempted synthesis of C3-semibuckminsterfullerene*

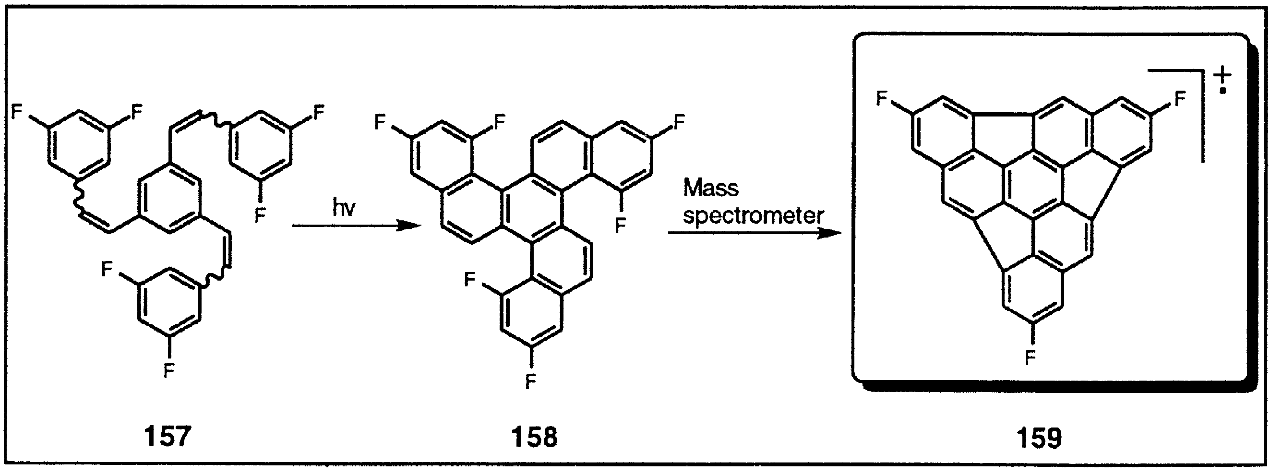
Concurrently, Mehta *et al.* devised a synthesis of a trimethyl derivative of C3-hemibuckminsterfullerene **156** *via* FVP on trimethyltribenzotriphenylene **154** [79]. The interesting feature of this approach was the projected exploitation of symmetrically disposed benzylic methyl groups in **154** and **156**, through appropriate functionalization, for further annulations to higher order fullerene fragments. For accessing the precursor **154**, a new, short and simple synthesis was devised from readily available starting materials, maintaining the C-3 symmetry all through. Thus, three-fold Wittig olefination of 1,3,5-triformylbenzene **153** with the ylide generated from 2-methylbenzylphosphonium bromide, and successive three-fold oxidative photocyclization



Scheme 44, *Mehta's attempted synthesis of trimethyl-C3-semibuckminsterfullerene*

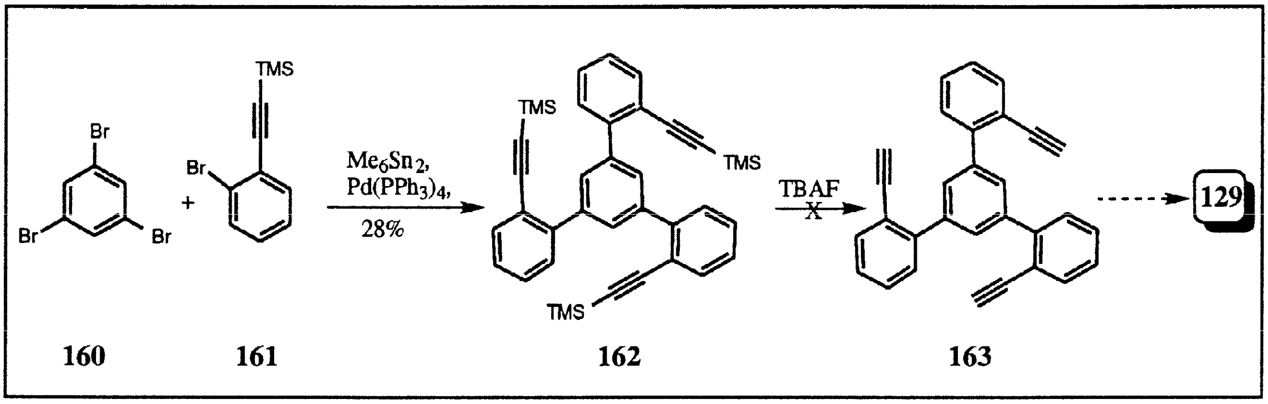
furnished the desired **154**. The heptacylic PAH **154** on FVP furnished a mixture from which only the mono-bridged product **155** could be isolated (Scheme 44) [79]. Not unexpectedly, extensive loss of the methyl groups was encountered during the pyrolysis stage.

Plater *et al.* have reported an approach to C3-trifluorohemifullerene **159**. The precursor hexafluorotribenzotriphenylene **158** was synthesized through three-fold oxidative photocyclization of **157** as shown in Scheme 45 [80]. While the difficulty in the separation of the photo products from **157** precluded a study of FVP on pure **158**, gas phase Argon ion mass spectrometric fragmentation of the photolysate from **158** showed a mass peak at m/z 425 (35%) attributable to **159** through sequential loss of three HF molecules.

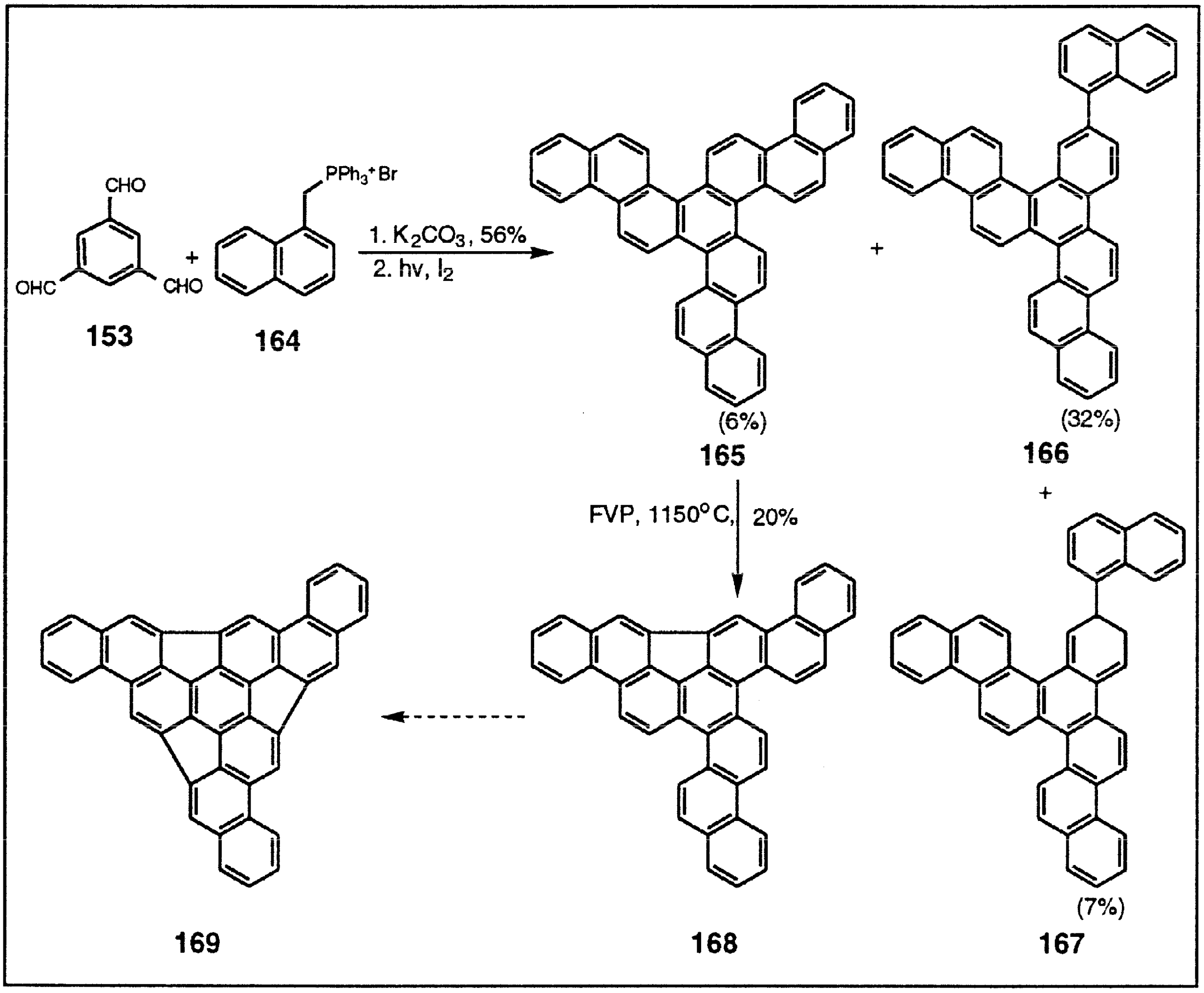


Scheme 45, *Plater's approach to C3-trifluorohemifullerene*

A conceptually different approach to C_3-hemibuckminsterfullerene **129**, has been explored by Faust and Vollhardt in which they considered 1,3,5-tris(2'-ethenylphenyl)benzene **163** as a suitable precursor. In this ambitious scheme, a triple 4+2 cycloaddition followed by dehydrogenation was expected to deliver **129**, Scheme 46 [77]. However, in reality only the *tris*-trimethylsilyl protected derivative **162** of **163** could be prepared from 1,3,5-tribromobenzene **160** and TMS protected 2-bromophenylacetylene **161**. Attempted deprotection of **162** only resulted in polymerization (Scheme 46). FVP of **162** also did not lead to any anticipated product.



Scheme 46, *Faust and Vollhardt's approach to C_3-hemibuckminsterfullerene*

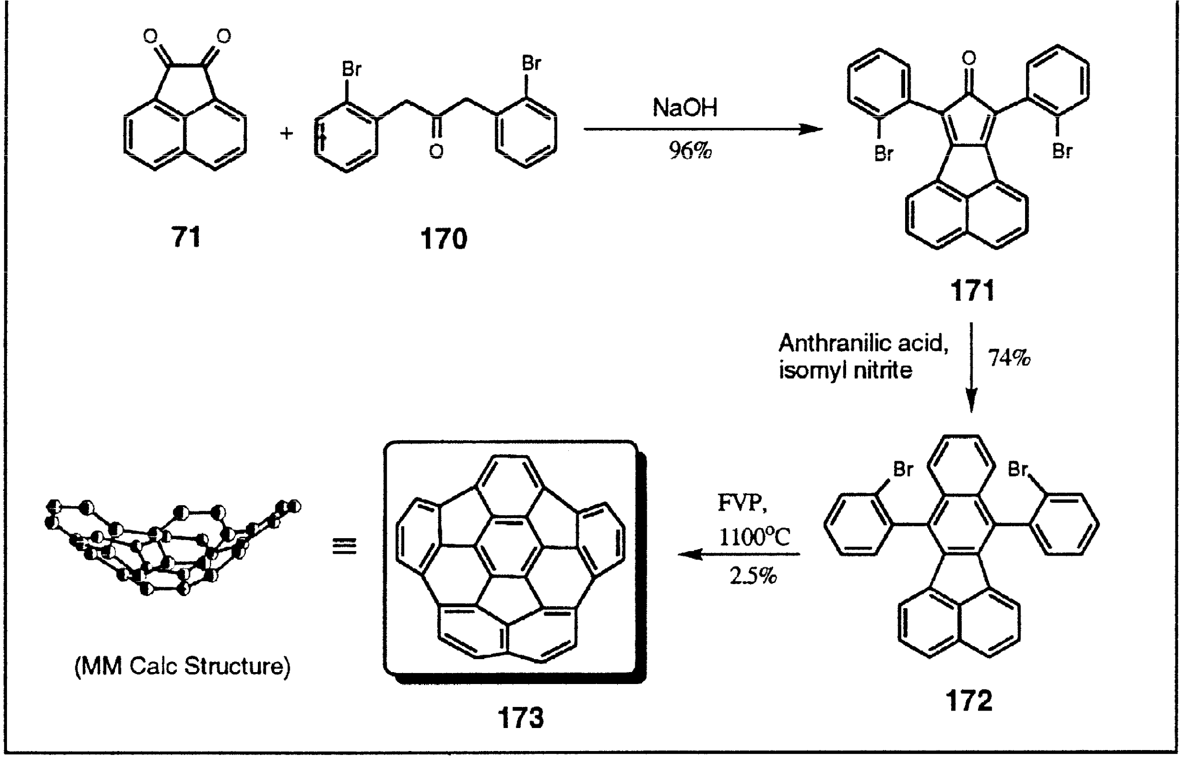


Scheme 47, *Mehta's attempted synthesis of tribenzo-C_3-hemibuckminsterfullerene*

Mehta and co-workers have extended their approach towards **156** to C_3-tribenzohemibuckminsterfullerene **169** , a $C_{42}H_{18}$ fragment of C_{60} (Scheme 47) [81]. Three- fold Wittig olefination of 1,3,5-triformylbenzene **153** and the ylide generated from 1-naphthylmethyl(triphenyl)phosphonium bromide and oxidative photocyclization furnished PAHs **165**, **166** and **167**. When the C_3 symmetric **165** was subjected to FVP at 1150°C, only a mono-bridged product **168** could be realized. This experiment further demonstrated that the dehydrogenative cyclizations in unsubstituted PAHs are not always successful for generating buckybowls and the presence of appropriate substituents, such as halogen is desirable to facilitate the cyclization process.

8. ACENAPHTHOINDACENOPICENE

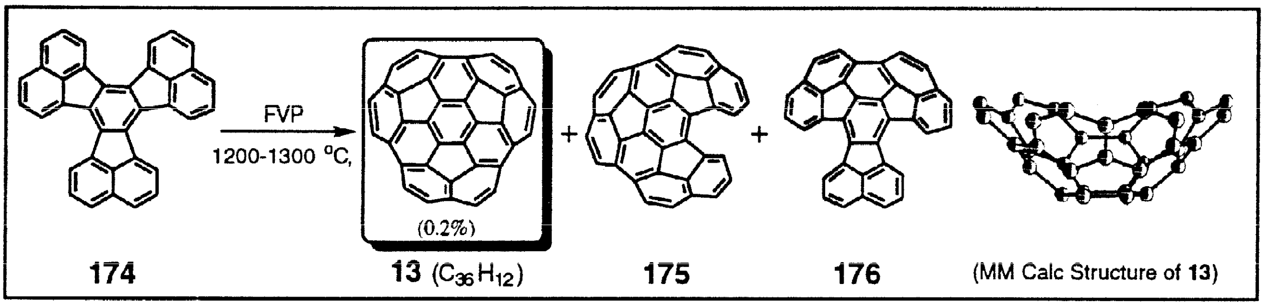
Rabideau and Clayton revealed the synthesis of acenaphtho[3,2,1,8-*fghij*]*as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picene indacenopicene **173**, a $C_{32}H_{12}$ hydrocarbon, which forms a structural motif on the surface of both C_{60} and C_{70} (Scheme 48) [82]. Acenapthenequinone **71** was condensed with the dibromo-ketone **170** to furnish **171** in almost quantitative yield. The resulting cyclopentadienone **171** was treated with benzyne and subsequent decarbonylation resulted in the benzo-annulated product **172**. FVP of **172** at 1000°C furnished acenaphthoindacenopicene **173** in about 2.5% yield. As expected from the symmetry of the molecule, the ^{13}C NMR spectrum revealed six methine carbons and the ^{1}H NMR spectrum showed a AB quartet, a singlet, two doublets and a double doublet. The mass spectrum of the crude pyrolysate revealed the presence of other interesting hydrocarbons, some of which are likely to be buckybowls.



Scheme 48, *Rabideau's synthesis of acenaphthoindecnopicene*

9. C_3-TRIACENAPHTHOTRIPHENYLENE

Scott *et al.* have disclosed the first successful synthesis of triacenaphthotriphenylene, $C_{36}H_{12}$ **13**, which constitutes 60% of the carbon framework of C_{60} and is an important fragment on its surface along the C_3 retrosynthetic route (Schemes 1 and 49) [83]. When commercially available decacyclene **174**, a trimer of acenaphthyne, was subjected to FVP at 1200-1300°C the three-fold cyclized product **13** was obtained in about 0.2% yield. Other products formed in the FVP reaction included doubly closed $C_{36}H_{14}$ **175**, singly closed $C_{36}H_{16}$ **176** and traces of C_{60}. Among these, **175** can be regarded as *bis*-fluorene annulated corannulene. In agreement with the C_3 symmetry of the molecule, the ^1H NMR spectrum of **13** showed two doublets for aromatic protons and the ^{13}C NMR spectrum had the expected seven lines. The UV absorption spectrum of **13** bears a striking resemblance to that of C_{60}.

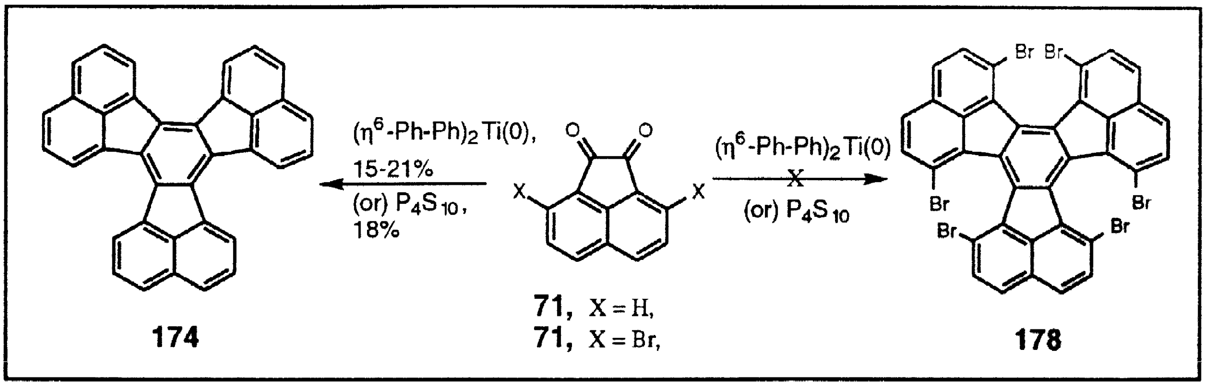


Scheme 49, *Scott's synthesis of C_3-triacenaphthotriphenylene*

The success of triple ring closure in decacyclene **174** leading to the formation of **13** has been attributed to the high potential energy imparted to the molecule at 1200-1300°C. In fact, several researchers recognized the utility of decacyclene and its derivatives as potential precursors to **13** but were not successful as they possibly did not employ the required high temperatures [67, 84]. In one case, **174** did furnish some C_{60} during the FVP conditions [15].

Balch and coworkers have determined the crystal structure of **13**, which revealed a highly ordered columnar stacking of the bowls with the insertion of the convex face of one over the concave face of the other [85]. The C-C bond distances among the core carbons in **13** found to be remarkably similar to the one found in C_{60}, with the C-C bond distances in the 6:6 ring junction was shorter (1.379A) than those in the 6:5 ring junction(1.42A). The maximum bowl depth was found to be 3.107A, which makes **13** the deepest bowl known till now. The extent of pyramidization (POAV1 angle) of the core carbons was found to be 11.91° and 12.35°, while for C_{60} it is 11.64°.

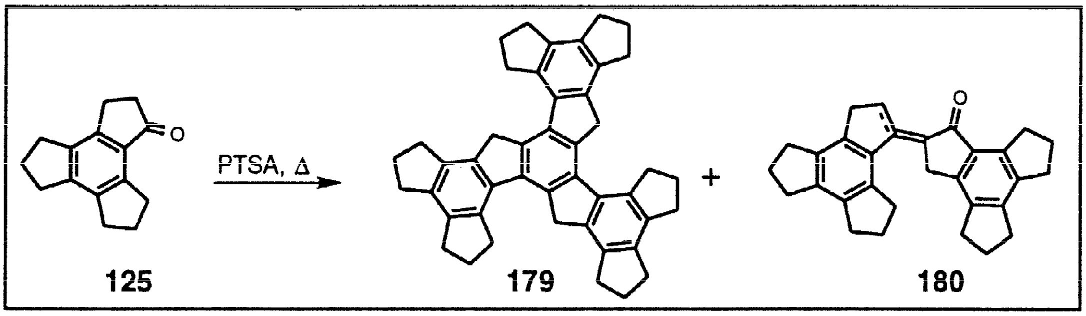
While decacyclene is commercially available, Zimmermann and Haenel explored its new preparation with the object of accessing functionalized derivatives. While the reductive cyclotrimerization of acenaphthoquinone **71** (X=H) to **174** with bis(η^6-biphenyl)titanium (0) or with phosphorus pentasulphide was successful [86], the trimerisation of 3,8-dibromoacenaphthenequinone **71** (X=Br), under the same conditions did not furnish hexabromodecacyclene **178**, Scheme 50. The product, if obtained, could serve as a better precursor for **13**.



Scheme 50

10. SYNTHETIC EFFORTS TOWARDS ASSORTED, HIGHER ORDER C_{60} FRAGMENTS

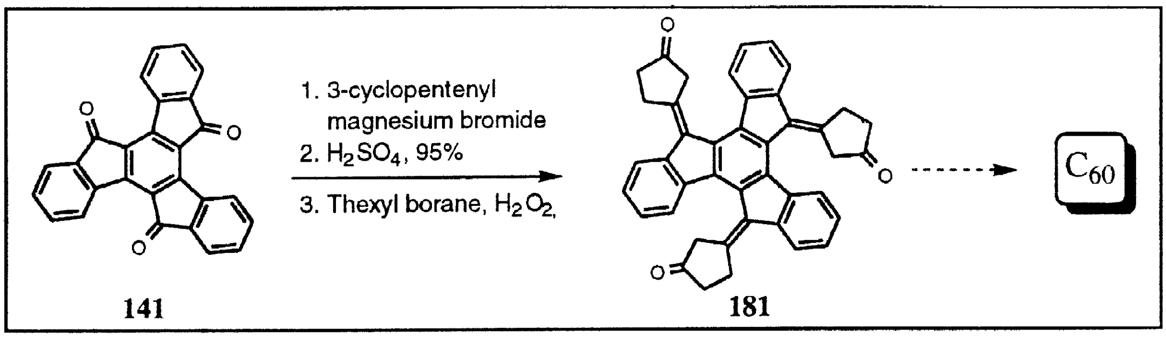
In one of the early efforts towards the synthesis of C_{60}-fullerene, Rassat *et al.*. pursued the $[C_{45}+C_{15}]$ approach and prepared fragment **179** which has 9 of the 12 pentagonal rings of C_{60}, Scheme 51 [87]. The acid catalyzed trimerization of triindanone **125** resulted in the trimeric product $C_{45}H_{48}$ **179** in 5% yield along with the dimer $C_{30}H_{30}O$ **180**. Both the trimer and dimer possess the carbon-framework found on the C_{60} surface. However, further transformations aimed at effecting appropriate cyclizations on either **179** or **180** enroute to C_{60} were not very encouraging.



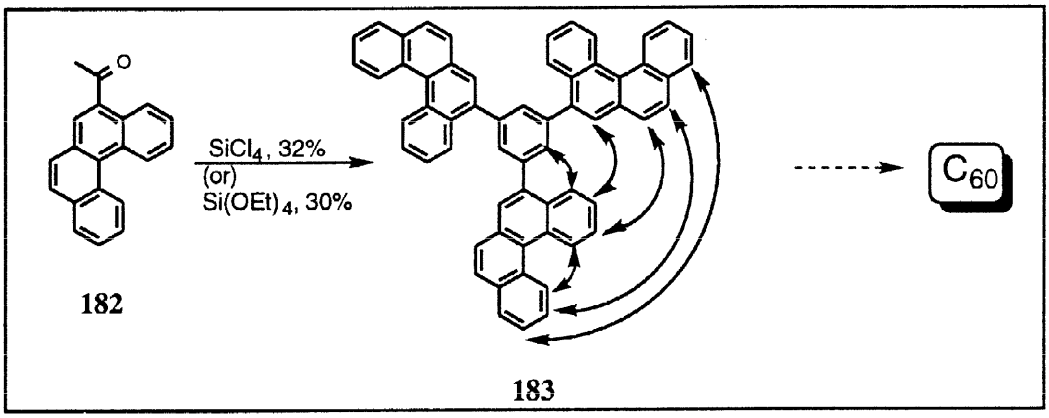
Scheme 51

Chapman and Loguercio considered the triketone **181** as a possible fullerene precursor, which has 6 of the required 12 five membered rings of C_{60}. The triketone **181** was synthesized from truxenone **141** (Scheme 52) [88]. The X-ray studies revealed that the triketone **181** is a severely distorted non-planar molecule and therefore is not amenable to further cyclizations to furnish fullerene fragments.

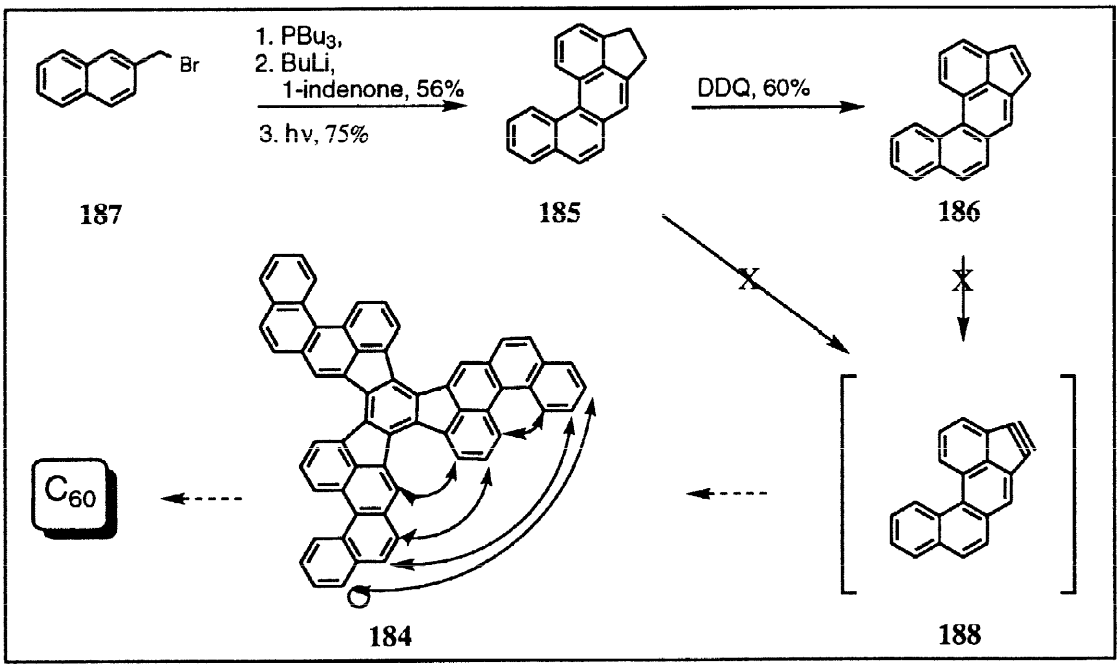
Plater reported the assembly of an array of aromatic rings **183** *via* a simple acid catalyzed trimerization of methyl ketone **182** in 32% yield (Scheme 53)[89,90]. In **182**, one can readily visualize the right kind of connectivities to generate C_{60} (see arrows, shown on only one side). Under appropriate gas phase dehydrogenative conditions, **182** could close like the petals of a flower to furnish C_{60}. Despite the conceptual simplicity of this approach, success along this route has not been forthcoming.



Scheme 52, *Chapman's strategy for the synthesis of C_{60}*

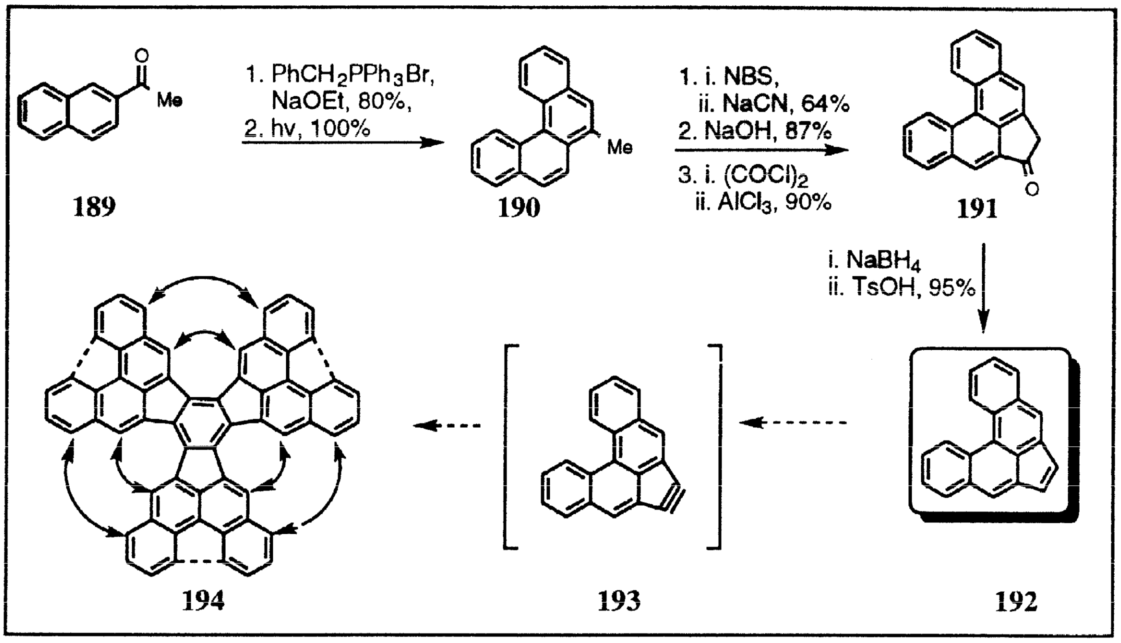


Scheme 53, *Plater's strategy for C_{60}*



Scheme 54 , *Plater's alternative plan for C_{60}*

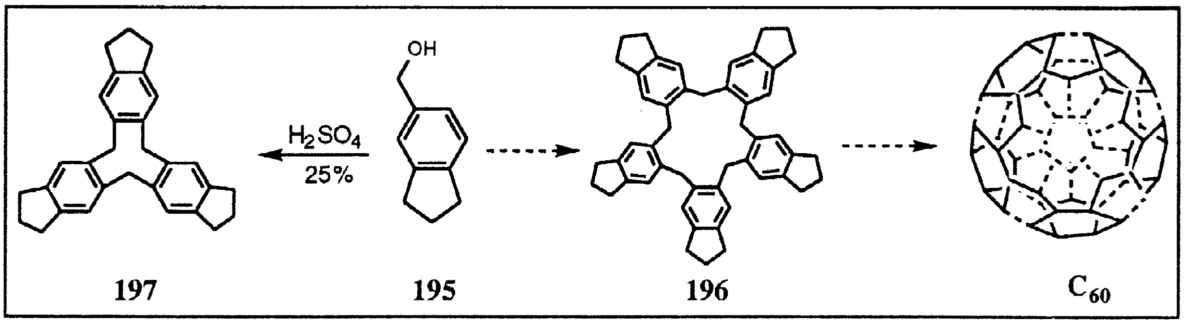
Following the success of Scott's synthesis of the C_{36}-buckybowl from decacyclene, benzo-, dibenzo-, and naphtho-annulated decacyclenes have drawn attention as attractive precursors for the generation of deeper bowls and C_{60} itself. Such derivatives can be prepared from the corresponding acenaphthyne-like intermediates. Pursuing the larger objective of the synthesis of C_{60}, Plater considered the preparation of C_3-symmetric trinaphtho-annulated decacyclene **184** enroute to C_{60} (see arrows, Scheme 54) [90]. Benzo[*l*]cyclopentaphenanthrylenes **185** and **186** were prepared from 2-naphthylmethylbromide **187** and 1-indanone following routine procedures. But, **185** and **186** failed to trimerize to **184**, *via* the pentacyclic alkyne **188**, even under stringent conditions, possibly because of the low solubility of the hydrocarbons.



Scheme 55

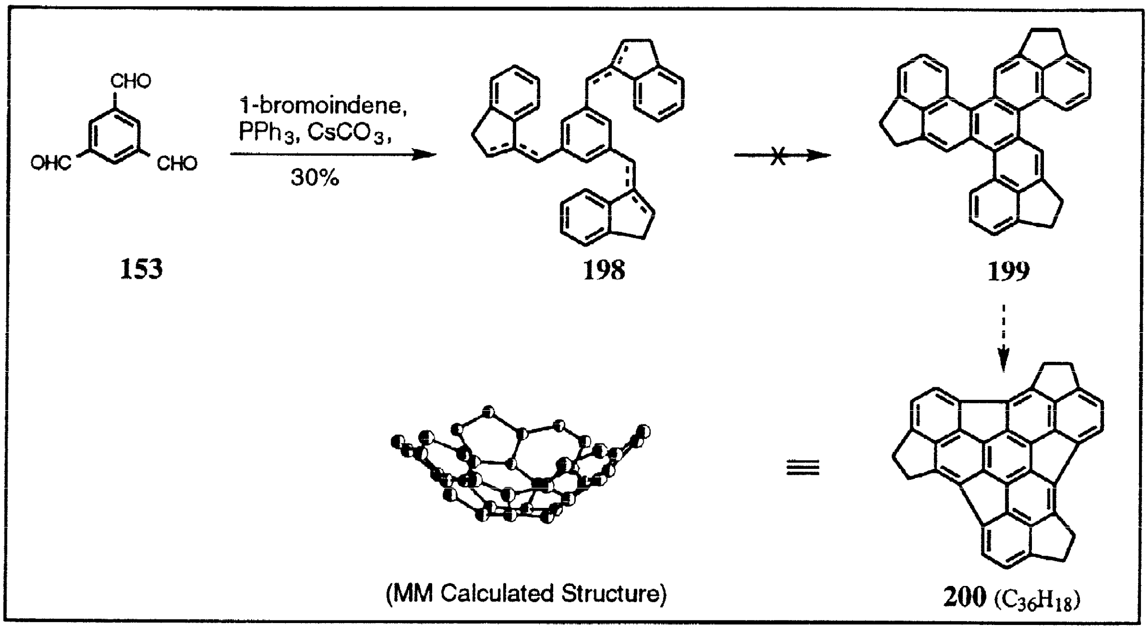
Magnus *et al.* reported the synthesis of 6,7-benz[*c*]acephenanthrylene **192**, which is a fullerene sub-structure and a potential precursor for buckybowls (Scheme 55) [91]. Naphthannulation on 2-acetylnaphthalene **189** *via* Wittig olefination and oxidative photocycloaddition resulted in 6-methylbenzo[*c*]phenanthrene **190**. Cyclopenta-annulation through one carbon homologation and intramolecular Friedel-Crafts acylation furnished the pentacyclic ketone **191**. Reduction and dehydration resulted in the desired compound **192** which was found to photo-dimerize on standing or on photolysis. Efforts directed towards trimerization of **192** to **194** *via* the alkyne **193** are awaited.

Earlier, Magnus *et al.* conceived an impressive but far-fetched synthetic route for C_{60}-fullerene in which *ortho*-cyclophanes with indenyl systems such as **196** could serve as advanced precursors, Scheme 56 [92]. However, in practice, cyclo-oligomerization of indan-5-carbinol **195** with aqueous sulfuric acid furnished the rigid cup-like trimerization product, **197**, in 25% yield (Scheme 56).



Scheme 56, *Magnus's strategy towards C_{60}-fragment*

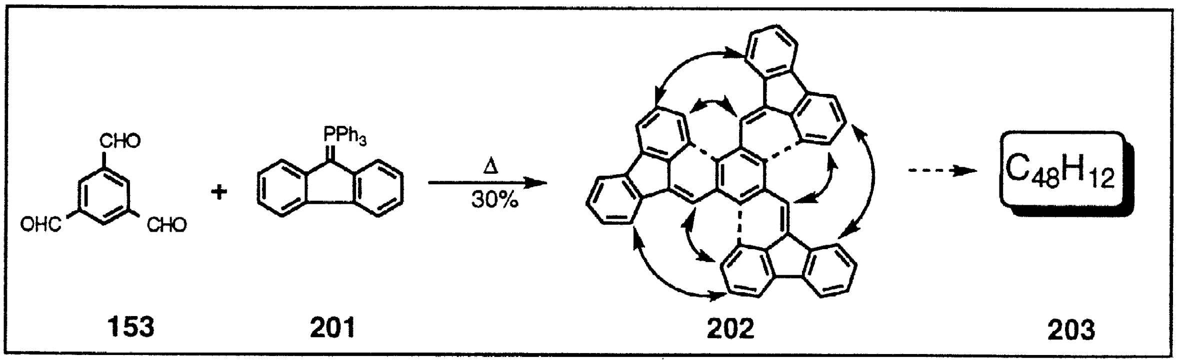
Mehta and co-workers recognized the C_3-symmetric 1,3,5-triformylbenzene **153** as an appropriate starting material for quick assembly of the carbon framework present in several C_{60}-fullerene fragments. Three-fold Wittig olefination with an ylide generated from the appropriately substituted arylalkylphosphonium bromides followed by oxidative photocyclization, could furnish PAH's with the prospect for establishing the correct C-C connectivities. A further dehydrogenative cyclization reaction under FVP conditions was expected to yield buckybowls.



Scheme 57, *Mehta's attempted synthesis of $C_{36}H_{18}$*

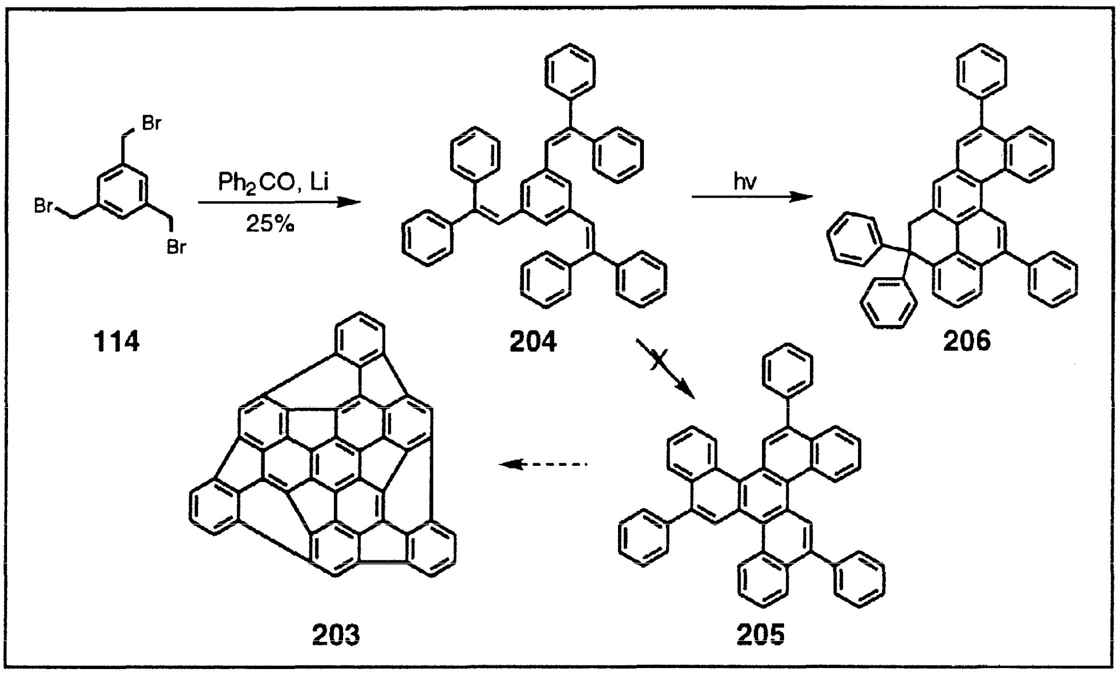
For example, in an approach to the buckybowl $C_{36}H_{18}$ **200**, Mehta and Rao carried out a three-fold Wittig olefination on 1,3,5-triformylbenzene **153** with the ylide derived from 1-bromoindene to generate a C_{36}-hydrocarbon **198** (Scheme 57) [93]. However, further cyclization in **198** to **199** could not be forced under a variety of reaction conditions.

In an analogous pathway directed towards the deep-bowl $C_{48}H_{12}$ **203**, a three-fold Wittig condensation between trialdehyde **153** and the ylide derived from 9-bromofluorene **201** led to $C_{48}H_{30}$ **202** (Scheme 58) [94]. However, further oxidative cyclization was not successful. An X-ray crystal structure determination on **202** revealed that the three fluorenyl units remained out of the plane of the central benzene ring and the molecule had a propeller like structure.



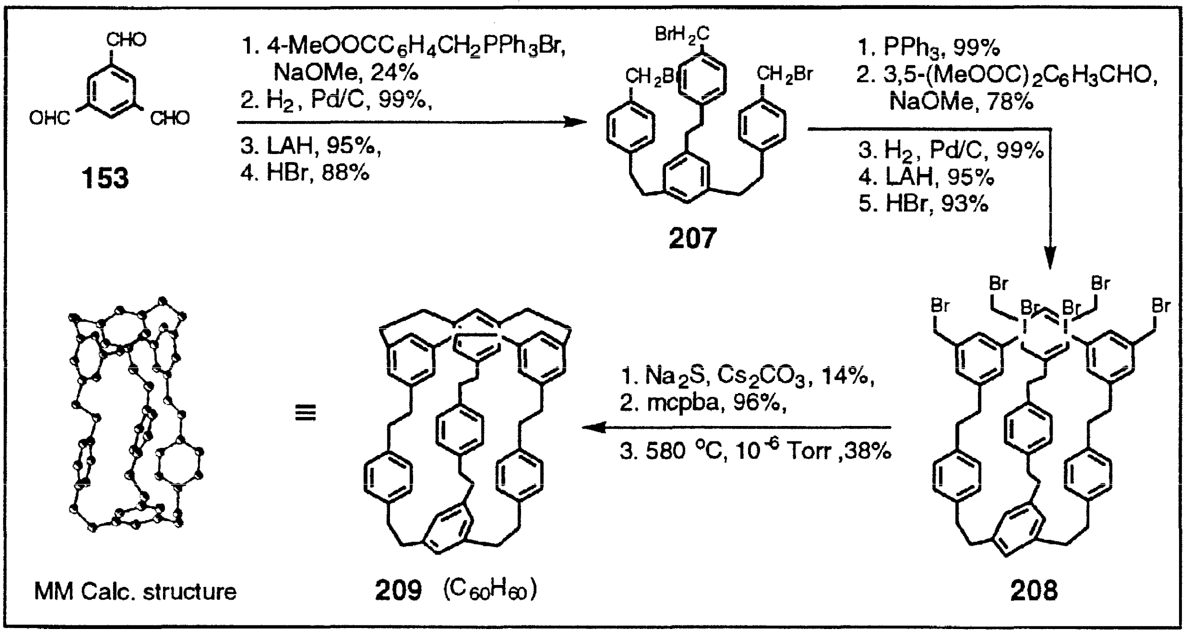
Scheme 58, *Mehta's attempted synthesis of $C_{48}H_{12}$*

The same authors also reported an alternative strategy for assembling the C_{48}-buckybowl **203** starting from 1,3,5-tris(bromomethyl)benzene **114**. Reaction of **114**with benzophenone in the presence of lithium metal and dehydration furnished the $C_{48}H_{36}$ hydrocarbon **204**. Further oxidative-photocyclization did not take place in the desired manner to yield **205**, but resulted in the rearranged product **206** (Scheme 59) [95].



Scheme 59, *Mehta's attempted synthesis of $C_{48}H_{12}$ buckybowl*

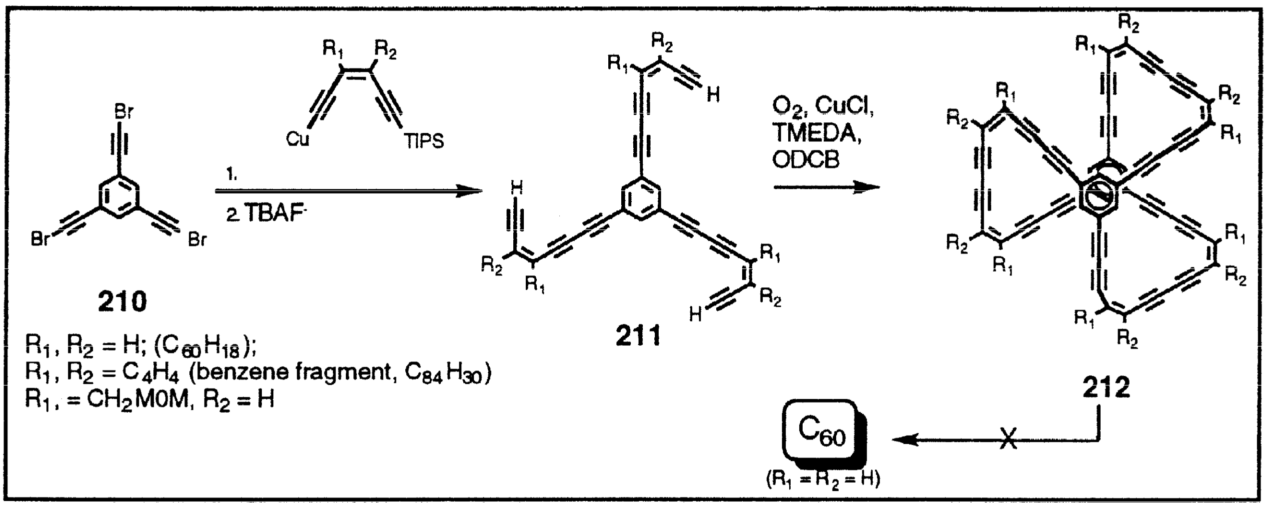
A conceptually different approach to fullerene precursors is to synthesize cage molecules having connectivities as found on the fullerene surface. Such rigid cage structures are expected to offer several advantages. For example, being pre-organized structures, with little conformational mobility for its constituents, they could undergo



Scheme 60, *Vogtle's synthesis of $C_{60}H_{60}$, a possible precursor for C_{60}*

the required cyclizations to generate spheroidal fullerenes more efficiently. Since the cavity they encompass can accommodate metal ions and other neutral molecules, final cyclization reactions could result in filled fullerenes.

Vogtle *et al.* disclosed the synthesis and complexation studies on the cyclophane-based hydrocarbon cage molecule, $C_{60}H_{60}$ **209** (a spherephane) [96]. The spheroidal hydrocarbon **209** was synthesized in a multi-step sequence starting from 1,3,5-triformylbenzene **153** *via* tribromo **207** and hexabromo **208** intermediates and involving repetitive Wittig olefination, catalytic hydrogenation and functional group alterations. The terminal cage cyclization was accomplished using the sulphoxide elimination methodology generally employed in cyclophane syntheses, Scheme 60.



Scheme 61, *Rubin's attempted fullerene synthesis*

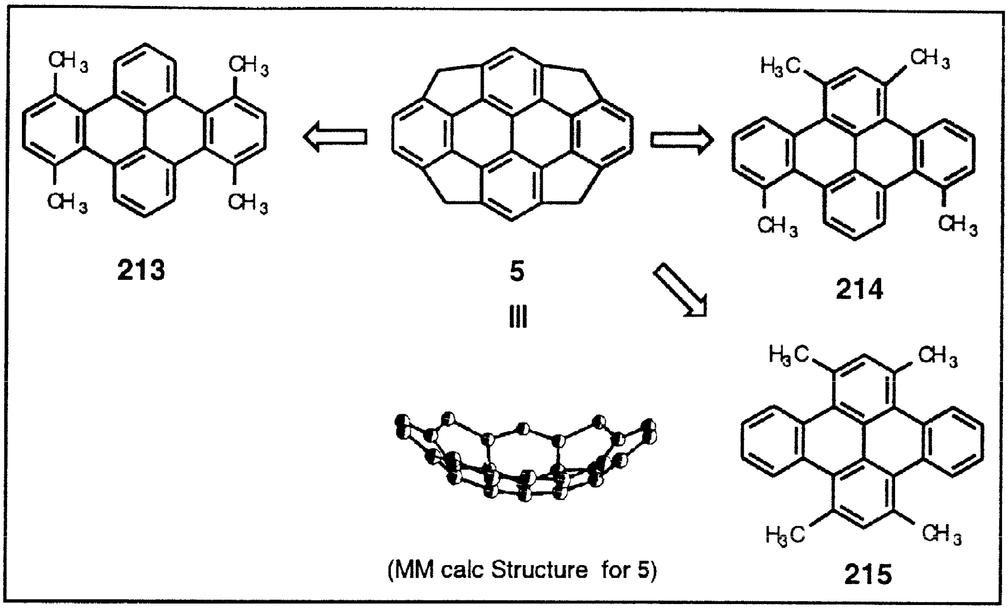
Rubin *et al.* reported the synthesis of cyclophane based polyacetylenic compounds as potential precursors for C_{60} and other higher order fullerenes (Scheme 61) [97,98]. They synthesized C_3-enediyne precursors **212** from tristribromoalkyne **210** *via* enetriyne intermediate **211**. However, **212** failed to undergo required dehydrogenative ring closure either under MALDI mass spectral conditions or under FVP conditions to give fullerenes.

11. C70-FULLERENE FRAGMENTS

Several curved PAHs which are unique to C_{70}-fullerene **2** can be identified as structural motifs (Schemes 2), and the synthetic efforts directed towards them have begun to surface only recently.

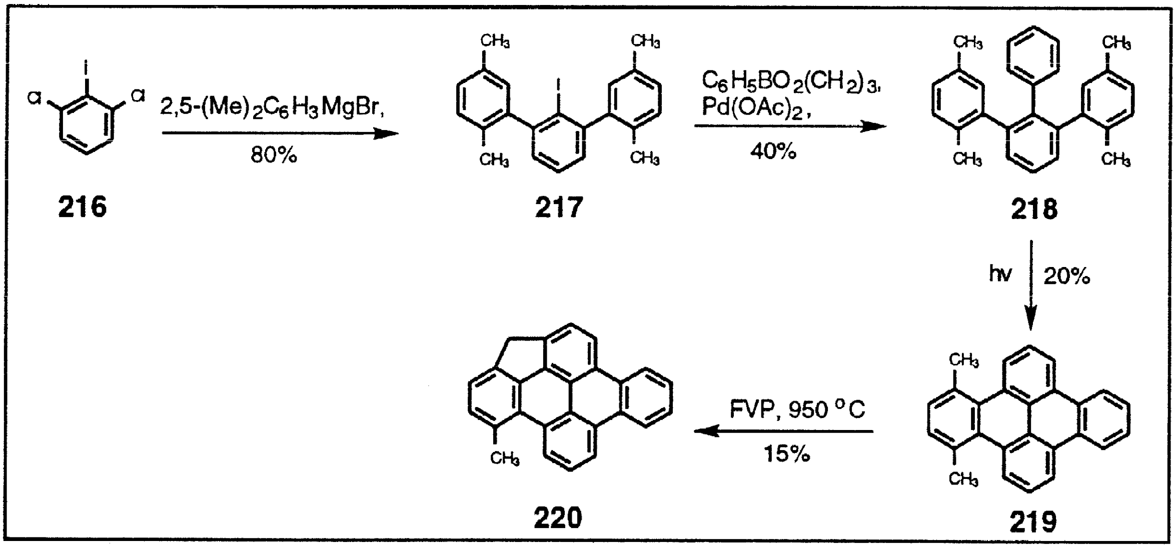
11.1 Pinakene

Pinakene, $C_{28}H_{14}$ **5** (pinak = bow; Sanskrit), a bowl-shaped hydrocarbon, is the smallest curved fragment derived through dismantling C_{70} along the C_2-**a** route (Scheme 2). Semiempirical calculations (MNDO) revealed the bowl-depth in **5** to be 2.03Å and bowl-to-bowl inversion barrier to be about 48.6 kcals mol^{-1} implying that it is a very rigid bowl [17]. Mehta and coworkers considered several synthetic strategies towards pinakene, in which tetramethyl PAHs **213, 214** and **215** could serve as immediate precursors (Scheme 62) [17].



Scheme 62

In practice, an attempt has been made to synthesize hither to unknown PAH **213**, Scheme 63 [99]. Highly crowded *m*-terphenyl derivative **218** prepared from 2,6-dichloroiodobenzene **216** *via* 2,6-diaryliodobenzene **217**, on photolysis resulted in 4,7-dimethyldibenzo[*fg,op*]naphthacene **219** instead of the expected **213**. Formation of **219** could proceed through photodearylation-rearylation process in which the p-xylene moiety in **216** is exchanged with a phenyl moiety from solvent benzene prior to cyclization. FVP reaction on **219** resulted in only monobridged product **220**.

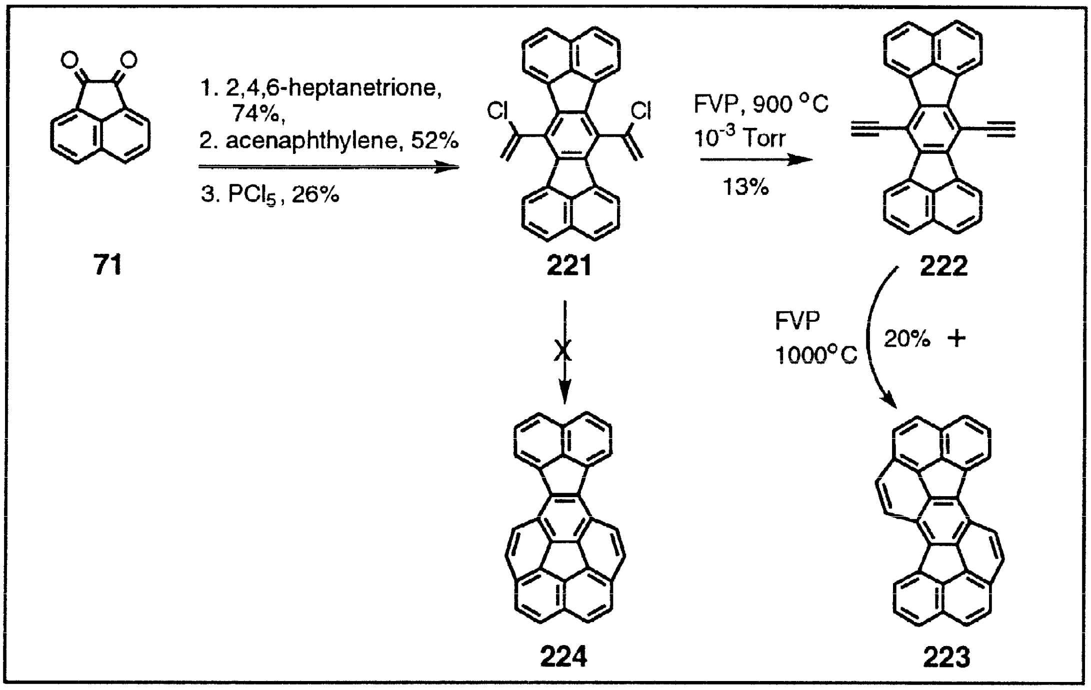


Scheme 63, *Mehta's attempted synthesis of Pinakene*

11.2 Hepta(5,5)circulene

Yamamoto *et al.* reported the synthesis of hepta(5,5)circulene **223**, which forms a structural motif on C_{70} **2** (but, not on C_{60}), Scheme 64 [100]. Acenaphthenequinone **71** was converted into *bis*(1-chlorovinyl)acenaphthofluranthene **221** by following Scott's benzoannulation protocol. Flash vacuum pyrolysis of divinylchloride **221** at 900°C resulted in diethynylacenaphthofluoranthene **222** and hepta(5,5)circulene **223** in about

6% yield. The diethynyl compound **222** also furnished **223** on FVP at 1000°C in 20% yield. These authors were aiming for an annulated corannulene derivative **224** through the FVP of **221** along the familiar Scott's route, but in actuality the reaction led to the formation of planar **223**. Molecular mechanics calculations showed that **223** is 28 kcal mol^{-1} more stable than its bowl-shaped isomer **224**.



Scheme 64, *Yamamoto's synthesis of hepta[5][5]circulene*

12. CONCLUSION

The discovery and high impact of fullerenes on the chemical sciences scene has generated a world-wide quest for a classical synthesis of C_{60} and C_{70}. As structures of newer fullerenes are delineated and a range of new siblings (nano-tubes, ropes, onion-rings) are identified, newer challenges of even higher magnitude would emerge. Despite the fact that interest in the syntheses of fullerenes and their fragments emanated only a few years ago, there has already been significant success. However, with the exception of C_{20} corannulene, buckybowls are still scarce and not yet available for a detailed scrutiny of their potentially rich chemistry. During the coming years, many exciting developments can be expected as new fullerene fragments are synthesized and their chemistry explored.

13. ACKNOWLEDGEMENTS

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Biographical sketch

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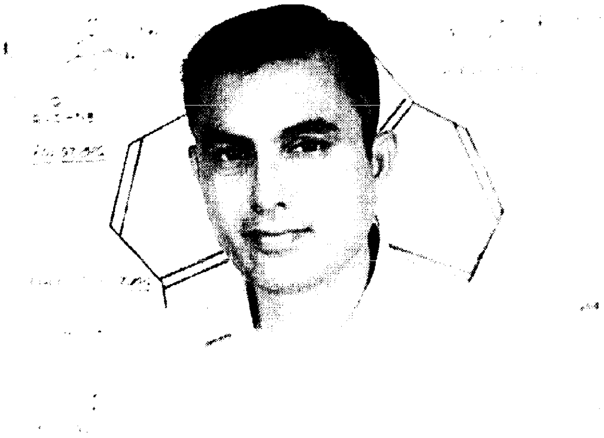

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Goverdhan Mehta was born in Jodhpur, India in 1943 and obtained his Ph.D (1966) working at the National Chemical Laboratory, Pune, under the supervision of Dr. Sukh Dev. After Post-doctoral research with Professors Don Farnum and Paul Gassman in the US, he joined in 1969 the Indian Institute of Technology, Kanpur, as a faculty member. In 1977 he moved to the University of Hyderabad as a Professor of Chemistry. Recently, he has accepted an invitation to be a Professor of Organic Chemistry at the Indian Institute of Science, Bangalore. He has been a recipient of numerous awards and honors for his research accomplishments and has extensively lectured in India and abroad. Mehta's current research interests encompass total synthesis of natural products, design of aesthetically pleasing molecular entities like prismanes, ladderanes, 'oxa-bowls', 'bucky-bowls' and devising incisive probes to study stereoelectronic control of diastereoselectivity.

Hulluru Surya Prakash Rao was born in Punganooru, A.P., India in 1953. After his undergraduation (1973) and post-graduation (1975) he received Ph.D. (1980) working with Professor S.N. Balasubrahmanyam at the Indian Institute of Science, Bangalore. Later he did post-doctoral work with Professor R.J. Parry, Rice University, Professor Edward Leete, Univesity of Minnesota and Professor Goverdhan Mehta, University of Hyderabad. He joined North Eastern Hill University, Shillong, as a lecturer in 1985 and then moved on to the Pondicherry University in 1988 where he is currently a Professor in the Department of Chemistry. His research interests include stereoselection in alkylation reactions, synthesis of heterocycles from chalcones, reactions of acyl azides and developments of new reagents and reactions.