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Geodesic Polyarenes by Flash Vacuum Pyrolysis

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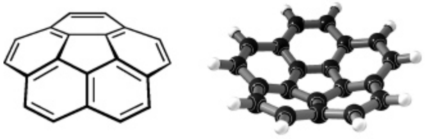
1. Introduction

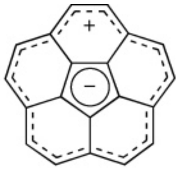
Geodesic polyarenes constitute a rapidly growing family of polycyclic aromatic hydrocarbons (PAHs) that resemble the geodesic domes of the great 20th century American architect Buckminster Fuller (Figure 1). Though differing in scale by more than 10^9, the molecules and the domes have several distinctive features in common. Both classes of structures define surfaces that curve in the same sense as the surface of the earth (hence the term “geodesic”). Those surfaces, in both cases, are built from assemblies of interconnected polygonal faces that share edges and vertices with one another. In geodesic polyarenes, trigonal carbon atoms sit at the vertices, carbon−carbon bonds form the edges, and rings of carbon atoms make up the faces.

Fullerenes comprise a set of geodesic polyarenes that can be classified as “closed”; that is, they represent complete, 3-dimensional polyhedra, every face of which is either a 5-membered ring or a 6-membered ring. Subunits of fullerenes that lack one or more of the rings but remain curved are classified as “open” geodesic polyarenes.[1] The latter have been referred to at various times in the chemical literature as bowl-shaped PAHs, fullerene fragments, and buckybowls; the terms can be used interchangeably.

The factors responsible for the bowl shape geometries of geodesic polyarenes are readily apparent from an inspection of corannulene (**1**), the smallest curved subunit of C_{60}. This PAH can be viewed as a 5-membered ring core from which five spokes radiate outward to a 15-carbon rim. The bowl shape results from the fact that the rim is too snug to accommodate the interior rings and bonds in a two-



corannulene (**1**)



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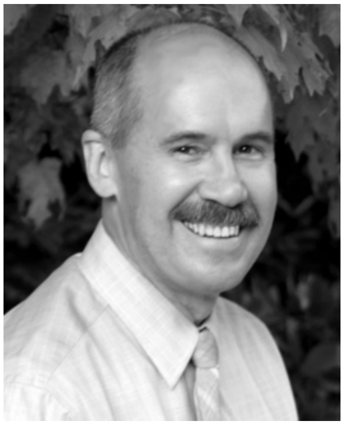
Vikki M. Tsefrikas was born in 1979 in Worcester, MA. She received her B.S. degree in 2001 and her M.S. degree in 2002 in chemistry at Worcester Polytechnic Institute, where she worked on the synthesis and photochemistry of several aromatic heterocycles under the direction of Prof. James W. Pavlik. She is currently a Ph.D. candidate in the laboratory of Professor Lawrence T. Scott at Boston College and is engaged in research aimed at the rational chemical synthesis of single walled carbon nanotubes that have uniform diameter and controlled chirality.



Lawrence T. Scott was born on June 11, 1944, in Ann Arbor, MI, and grew up in central Illinois, where he graduated from Urbana High School in 1962. As a chemistry major at Princeton University, he carried out research for his senior thesis on highly unsaturated polycyclic hydrocarbons of theoretical interest in the laboratory of Professor M. Jones, Jr., and was awarded an A.B. degree with honors in 1966. He continued to work on the synthesis and properties of unusual hydrocarbons as a graduate student under the direction of Professor R. B. Woodward at Harvard University and earned his Ph.D. degree in 1970. He then joined the chemistry faculty at UCLA as an Assistant Professor. In 1975, he moved to the University of Nevada—Reno, where he served as department chairman for 3 years and was appointed Foundation Professor. In 1993, Professor Scott moved to Boston College, where he now occupies the Louise and Jim Vanderslice and Family Chair in Chemistry. He has received senior scientist awards from NATO, the Japan Society for the Promotion of Science, and the Alexander von Humboldt Foundation. In 2003, he served as chairman of the Gordon Research Conference on Physical Organic Chemistry and was elected a Fellow of the American Association for the Advancement of Science.

dimensional plane without compressing them severely. The same is also true for all of the larger geodesic polyarenes.[2−7]

Prior to the discovery of fullerenes in 1985, the world knew only one geodesic polyarene, and that was corannulene (**1**). Richard Lawton, as an assistant professor at the University of Michigan, conceived of this $C_{20}H_{10}$ hydrocarbon and, assisted by Wayne Barth, worked out a 16-step synthesis that the two reported as a communication in 1966.[8] The full details of this landmark synthesis were published 5 years later.[9] Annulene chemistry was enjoying a golden age in those days, and the father of this first geodesic polyarene gave it the name "corannulene", in recognition of the concentric zwitterion "annulene-within-an-annulene" resonance structure (**1a**) that he speculated might contribute to the electronic properties of **1**. Several papers on the spectra and properties of corannulene followed, including an X-ray crystal structure that confirmed the bowl-shaped geometry,[10] but the length of the synthesis discouraged everyone from undertaking more extensive studies on corannulene. The first chapter of the geodesic polyarene story thus came to an end in the 1970s, and the field went into dormancy for many years.

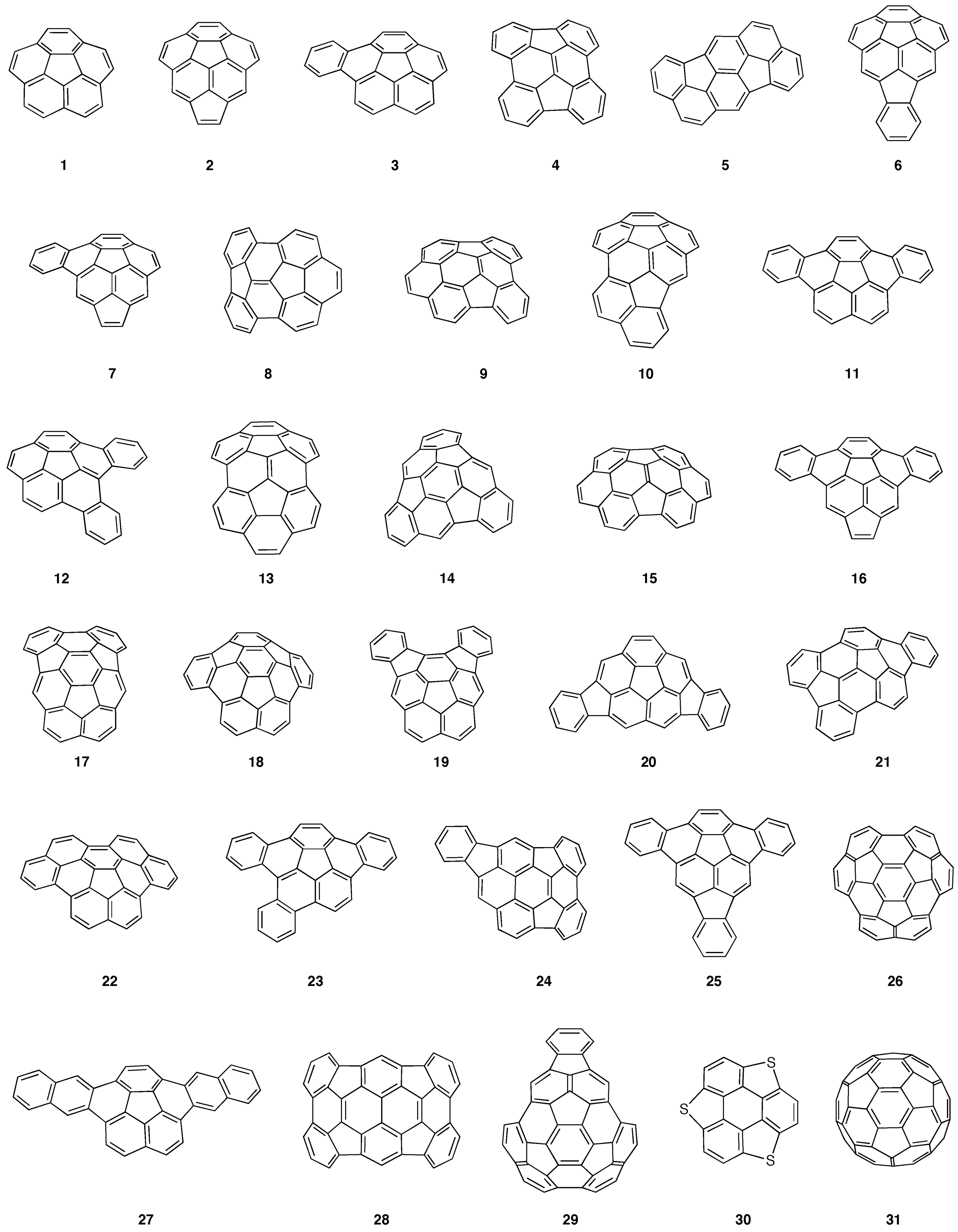
Then came the fullerenes! In 1985, Kroto, Heath, O'Brien, Curl, and Smalley rocked the world with their discovery of the first closed geodesic polyarene, C_{60}.[11] Many, many papers followed.[12] The goal of obtaining isolable quantities of C_{60} and determining whether or not it had the proposed soccer ball structure, however, eluded the scientific community for the rest of that decade.

It was during that time, in 1989, when one of the authors of this review heard a riveting lecture by Harry Kroto on the (then still elusive) fullerenes[13,14] and was instantly inspired to begin thinking about methods that might be suitable for the chemical synthesis of fullerenes in the laboratory. As described in the sections that follow, flash vacuum pyrolysis (FVP)[15−17] quickly emerged as a particularly effective synthetic tool for constructing geodesic polyarenes from derivatives of planar PAHs. A convenient new synthesis of corannulene (**1**) in 1991 launched this unconventional application of FVP into the spotlight.[18] By the next year, the synthesis of corannulene had been shortened to just three steps from commercially available starting materials,[19−21] and open geodesic polyarenes that had previously been considered unrealistic targets for synthesis soon outnumbered the known fullerenes.

This review summarizes all of the syntheses of geodesic polyarenes published before January 2006 that rely on flash vacuum pyrolysis, plus a number of unpublished examples from the authors' laboratory. The sections of the review are organized according to the size of the geodesic polyarene synthesized, from smallest (corannulene, $C_{20}H_{10}$) to largest (buckminsterfullerene, C_{60}). Only one geodesic heterocycle has been synthesized, and it is described after the last open geodesic hydrocarbon. This is not the chronological order in which the field developed, but it makes the material easily accessible. We have attempted to sort out the history at various points within the review. Most of our general comments about the FVP method and why it has proven so useful for the synthesis of geodesic polyarenes will be found at the beginning of section 2 on corannulene.

2. $C_{20}H_{10}$ Corannulene (1)

Flash vacuum pyrolysis (FVP) is a method for heating molecules in the gas phase to very high temperatures for a very short time.[15−17] The hot zone typically consists of a horizontal quartz tube heated by an electric furnace to temperatures in the range of 500−1100 °C (Figure 2). Under vacuum, the sample is sublimed; the vapors pass through a hot zone, and the products are collected in a cold trap. A gentle stream of nitrogen carrier gas is commonly used to facilitate the flight of large molecules that have low vapor pressures through the hot zone. In the authors' laboratory, with a mechanical vacuum pump and nitrogen "leaking in" through a short piece of glass capillary tubing, the final



1 **2** **3** **4** **5** **6**

7 **8** **9** **10** **11**

12 **13** **14** **15** **16**

17 **18** **19** **20** **21**

22 **23** **24** **25** **26**

27 **28** **29** **30** **31**

Figure 1. Geodesic polyarenes that have been prepared by flash vacuum pyrolysis (FVP).

pressure typically falls in the range of 0.1−1.0 mmHg. To minimize bimolecular reactions in the gas phase, a slow rate of sublimation is generally desirable. This requirement does limit the amount of material that can be put through the hot zone in a reasonable period of time, though it is possible to prepare corannulene (**1**), for example, on a scale of 1.0 g or more in a single FVP run.[21] The other major limitation of the method is that starting materials must be sufficiently robust to survive whatever heating is required to sublime them into the gas phase. For syntheses of geodesic polyarenes by FVP, yields in the 20−35% range are not uncommon, and higher yields are rare. More details on the apparatus and its operation have been published elsewhere.[22]

Scheme 1 shows the first application of flash vacuum pyrolysis (FVP) to the synthesis of a geodesic polyarene.[18] Scott's choice of diyne **32** as a precursor to corannulene (**1**)

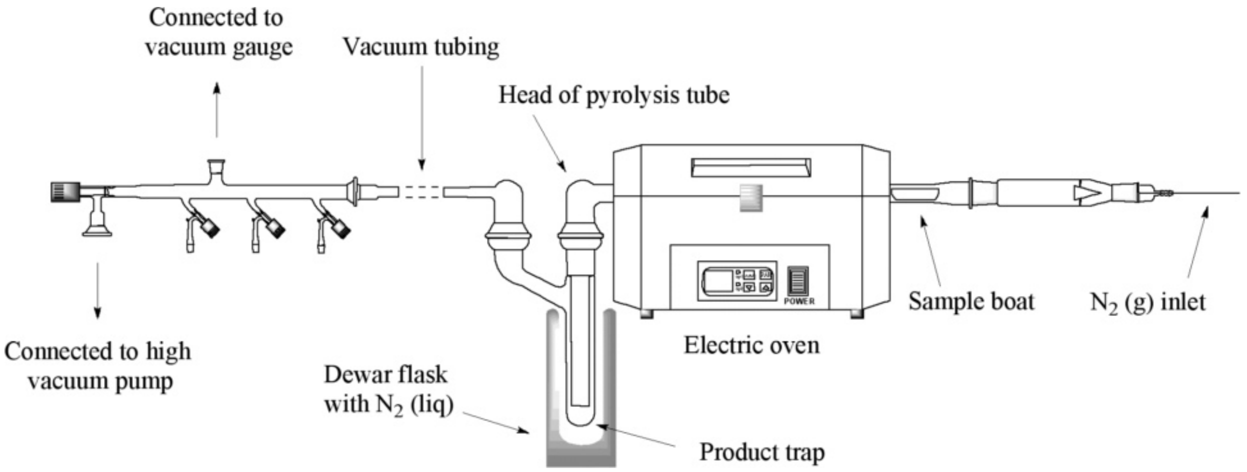
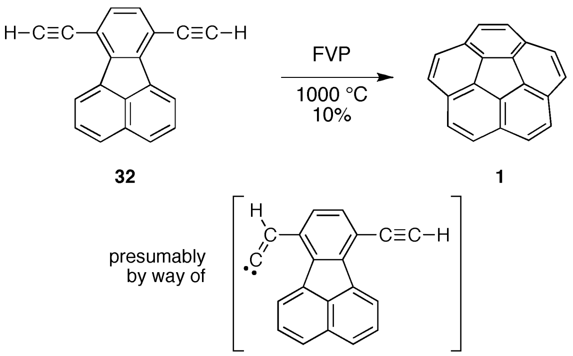


Figure 2. Schematic view of the FVP apparatus in the authors' laboratory.

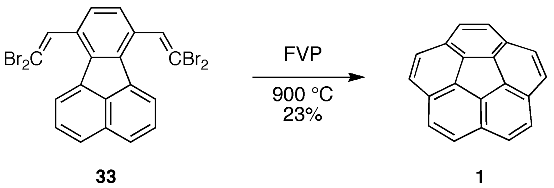
was predicated on two considerations. First, he was well aware of the early reports by R. F. C. Brown that terminal alkynes isomerize reversibly under FVP conditions by 1,2-shifts of hydrogen atoms and that the resulting vinylidenes can be trapped by insertion into nearby C−H bonds.[23,24] In addition, however, he reasoned that the high temperatures should temporarily populate bent geometries of the fluoranthene nucleus that would ordinarily be inaccessible, thereby allowing the carbene to approach within bonding distance of the carbon atom across the wide bay region. Earlier attempts by others to close 6-membered rings across the bay region of the fluoranthene nucleus by conventional methods in solution had always failed.[25]

The synthesis of corannulene illustrated in Scheme 1 provided a striking first validation of the strategy that Scott had envisioned for preparing geodesic polyarenes by distorting flat PAHs with heat and then "catching" the deformed ring systems by C−C bond-forming reactions at the rim. Unfortunately, the proclivity of diyne **32** for polymerization when heated during the sublimation kept the yield of this particular isomerization to no more than 10%. It was quickly discovered, however, that FVP of tetrabromide **33**, the synthetic precursor to **32**, also gives corannulene (Scheme 2),[3] and this modification not only improved the yield of corannulene from the FVP significantly, but it also shortened the synthesis by another step.

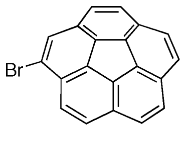
Scheme 1



Scheme 2



Originally, these investigators entertained the notion that the FVP in Scheme 2 might involve vinylidene intermediates analogous to those in Scheme 1 or that electrocyclic reactions might precede the loss of bromine. Subsequent work in other systems, however, suggests that these cyclizations probably involve vinyl radicals generated by homolysis of C−Br bonds (cf. section 7.1, for example). The isolation of bromocorannulene (**34**) and 1,6-dibromocorannulene (**35**) as byproducts in varying amounts when the FVP is run at lower temperatures[3] supports this view.



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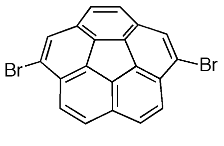

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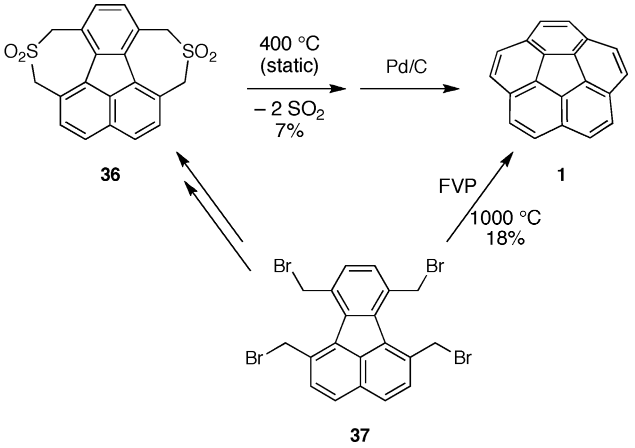
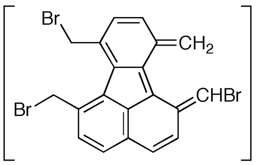
Scheme 3 outlines two high-temperature syntheses of corannulene reported by Siegel and co-workers in 1992.[4] Professor Siegel, then at the University of California, San Diego, had been unaware of the activities in the Scott laboratory at the University of Nevada, Reno (and *vice versa*) until the synthesis in Scheme 1 was published. The two research groups quickly began exchanging information, and the syntheses shown in Schemes 2 and 3 were published back-to-back less than a year later.[3,4]

Scheme 3



Siegel's routes likewise build two bridges across the bay regions of a fluoranthene nucleus, but they start out with one carbon atom on each side of each bay. The pyrolysis of sulfone **36** was actually conducted under static vacuum, rather than in a flow system; however, the benefits of the high temperature were felt nonetheless. The initial mixture of corannulene, dihydrocorannulene, and tetrahydrocorannulene isolated from the crude product mixture was aromatized with Pd/C. The idea to pyrolyze tetrabromide **37** directly was inspired by the pioneering work of Boekelheide on the FVP synthesis of strained benzocyclobutenes;[26] a series of four HBr elimination reactions, intermingled with electrocyclic reactions of intermediates such as **38**, presumably accounts for the overall transformation.[27]



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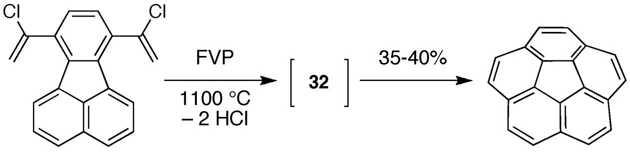
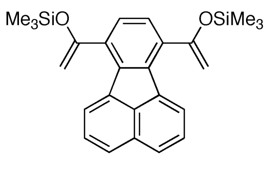


Scheme 4

The best precursor found to date for synthesizing corannulene by FVP is the bis(1-chlorovinyl)fluoranthene **39**. This "masked" version of dialkyne **32** sublimes cleanly without polymerization and loses 2 mol of HCl in the hot zone to generate **32** *in situ*,[28] which then cyclizes twice in 35−40% overall yield (Scheme 4). This route to **1** and a two-step synthesis of **39** from commercially available starting materials were first reported in 1992,[19,20] and the full details were published in 1997.[21]

Several other side chains have subsequently been tested as "masked acetylenes" for this reaction, and they all work to some extent, but no variation has proven superior to FVP of 7,10-bis(1-chlorovinyl)fluoranthene (**39**). Silylation of the ketone from which **39** is made produces the bis(trimethylsilyl)enol ether **40**, and FVP of **40** gives corannulene in 8% yield.[29] Attempts to prepare tetrabromide **41** by direct bromination of the very easily accessible 7,10-diethylfluoranthene invariably yield mixtures of polybrominated materials. FVP of those mixtures, however, does give usable quantities of corannulene in just three steps from simple starting materials using cheap reagents.[30,31] Surprisingly, even 7,10-diisopropenylfluoranthene (**42**) gives small amounts of corannulene upon FVP, presumably by loss of 2 mol of methane.[32,33] Wittig olefination of the dialdehyde precursor to **33** can also be used to prepare 7,10-bis(2-chlorovinyl)fluoranthene (**43**), FVP of which gives corannulene in 32% yield.[34]



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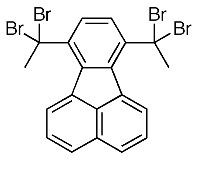

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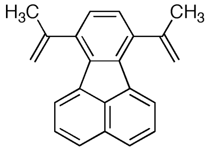

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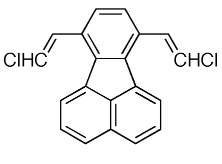

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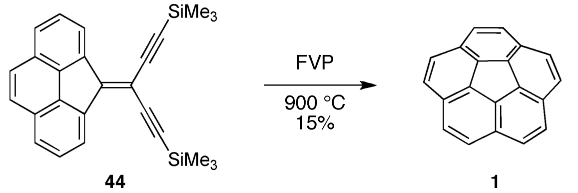
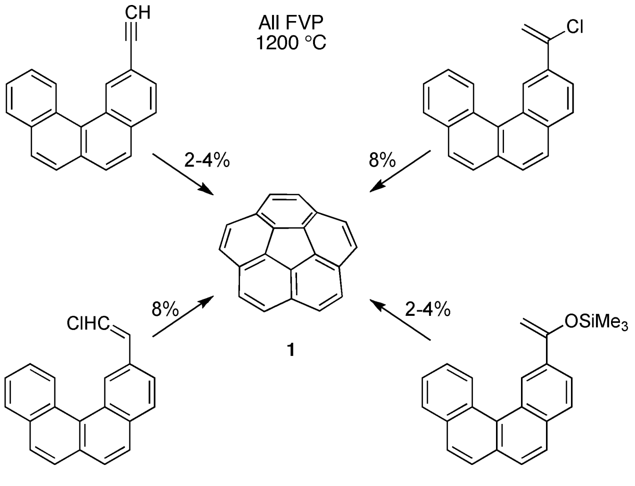
Scheme 5



Scheme 5 shows the first FVP route to corannulene that does not start from a preformed fluoranthene nucleus.[35] Zimmerman *et al*. found that the parent diyne of **44**, without the trimethylsilyl protecting groups, is even more prone to polymerization than diyne **32**. Fortunately, the TMS groups seem to fall off during the FVP. Most likely, free Si−OH groups on the surface of the hot quartz tube actually effect the desilylation.

This same trick was used several years later by Knölker *et al*. to overcome the polymerization problem encountered in Scheme 1.[36] Building the carbon skeleton by a novel but lengthy organometallic route, these workers prepared the bis-TMS derivative of **32** and showed that it can be converted to corannulene directly in 36% yield by FVP at 1000 °C.[36]

Scheme 6



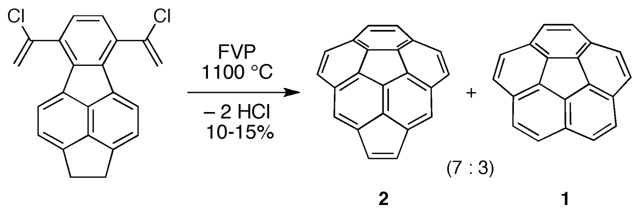
The only other published syntheses of corannulene based on FVP are those reported in 1997 by Mehta and Panda (Scheme 6).[37] These all start from substituted [4]helicenes and rely on cyclodehydrogenations to close the 5-membered ring. The resulting benzo[*ghi*]fluoranthene intermediates (not shown) that continue on to corannulene are the same as those formed above after the first cyclizations of **32**, **39**, **40**, and **43**, respectively. Unfortunately, thermal cyclodehydrogenations of [4]helicenes are not very efficient, and the yields of corannulene from these precursors never reach 10%.

As of this writing, the authors' laboratory still uses precursor **39** (Scheme 4) to synthesize corannulene by FVP.

3. $C_{22}H_{10}$ Acecorannulene (2)

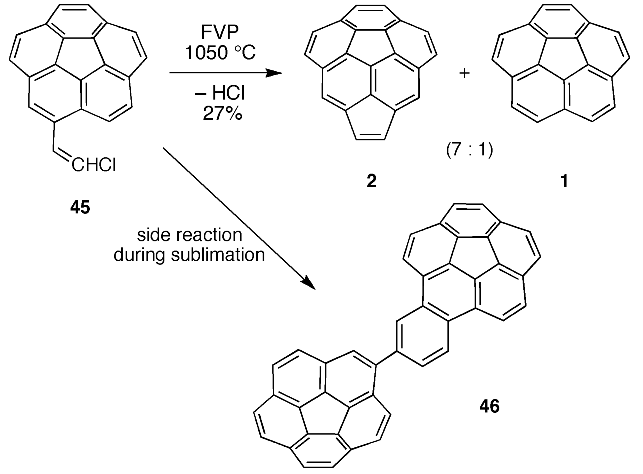
Acecorannulene (**2**) was the first derivative of corannulene to be synthesized by FVP (Scheme 7).[38,39] A starting material with the extra 5-membered ring already appended was carried through synthetic steps analogous to those that had been used previously to prepare corannulene precursor **39**. During the FVP, some of the molecules lose the two-carbon bridge, giving corannulene as a byproduct (**2**:**1** = 7:3).

Scheme 7

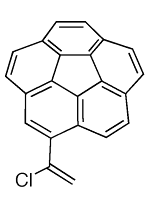


Acecorannulene has also been prepared by adding a 2-carbon bridge to connect adjacent *peri*-positions on the rim of corannulene. Thus, formylation of corannulene[33] followed by Wittig olefination[40] gives the 2-chlorovinyl derivative **45** as a mixture of geometrical isomers. FVP of **45** gives acecorannulene, contaminated by small amounts of corannulene from loss of the side chain (Scheme 8).[40] Unfortunately, compound **45** suffers from a tendency to dimerize during the sublimation, which diverts significant quantities of **45** (possibly only the *E*-isomer) to the Diels–Alder product **46**.[41]

Scheme 8



FVP of corannulene derivatives **47a**,[42,43] **47b**,[33] and **47c**[41] also gave acecorannulene, without any Diels–Alder complication, albeit in lower yields and likewise contaminated with small amounts of corannulene.



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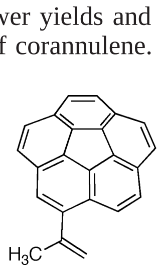
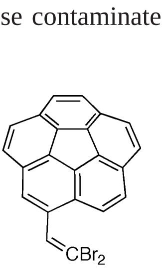


47b



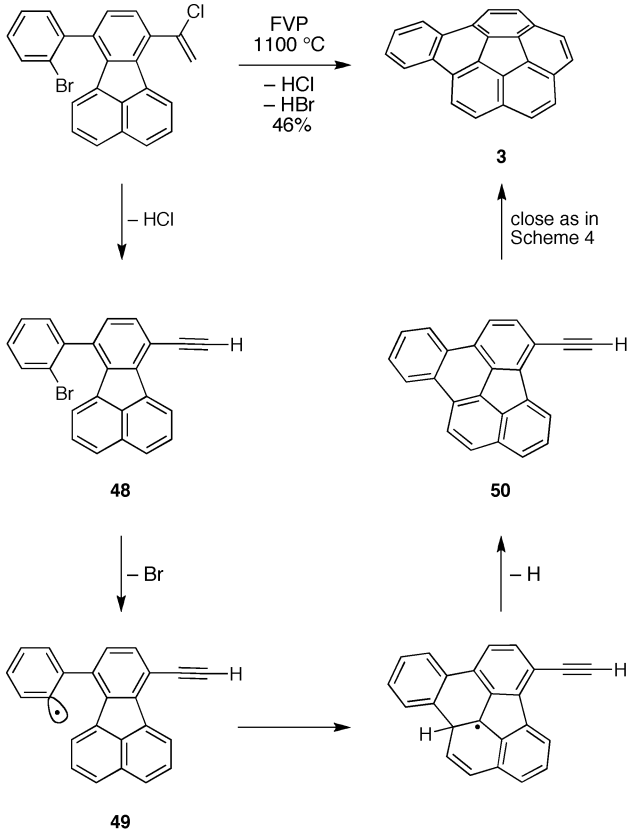
47c

The mechanism for side chain loss is not known. Nor is it clear why this fragmentation reaction should surface here, when no such problem was encountered with the same side chains in the corannulene syntheses (section 2).

4. $C_{24}H_{12}$ Benzo[a]corannulene (3)

The first synthesis of benzo[*a*]corannulene (**3**) was achieved in 1995 by an undergraduate research student at Boston College, Casey McComas, who also obtained the X-ray crystal structure.[44] As shown in Scheme 9, this synthesis again uses the 1-chlorovinyl group as a "masked acetylene" to close a ring across one bay region of the fluoranthene nucleus. Cyclization across the other fluoranthene bay region, however, was effected by an intramolecular radical addition to the naphthalene moiety. Homolysis of a C–Br bond under the FVP conditions generated the reactive aryl radical in this case.

Scheme 9

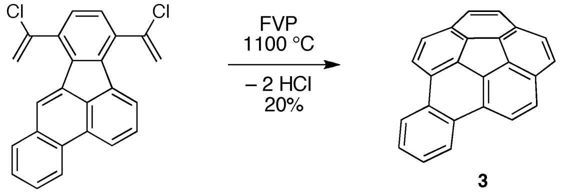


Insight into the order of events was obtained by repeating this reaction at 900 °C. Under these milder conditions, some of the molecules make it only part way through the sequence. Intermediates **48** and **50** could both be isolated in significant amounts (2:1 ratio), and their presence argues convincingly that (1) HCl loss is facile and (2) subsequent cyclization of the 2-bromophenyl group is faster than cyclization of the ethynyl group.

In principle, the conversion of **48** to **50** might occur by an electrocyclic reaction, followed by thermal loss of HBr. The simultaneous disruption of aromaticity in three separate benzene rings, however, would be energetically very costly. Evidence for the intermediacy of aryl radicals in this case (and in many other cases discussed in later sections) comes from the isolation of varying amounts of uncyclized byproducts in which the aryl radical (e.g., **49**) has scavenged a hydrogen atom. Nevertheless, detailed experimental studies on the mechanisms of these "radical cyclizations" have not been performed, and the mechanisms proposed, therefore, should be recognized simply as working hypotheses.

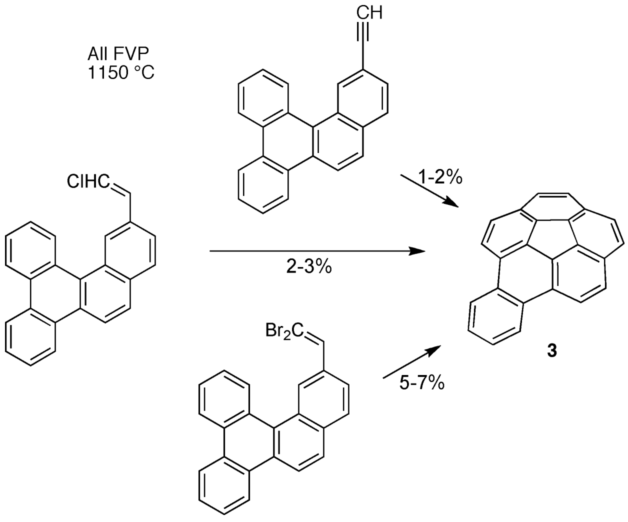
Brandon McMahon, another Boston College undergraduate, carried out the second synthesis of benzo[*a*]corannulene (Scheme 10).[45] As in the first synthesis of acecorannulene (**2**, Scheme 7), the strategy here was simply to follow the corannulene synthesis in Scheme 4, starting from a compound on which the extra ring was already attached.

Scheme 10



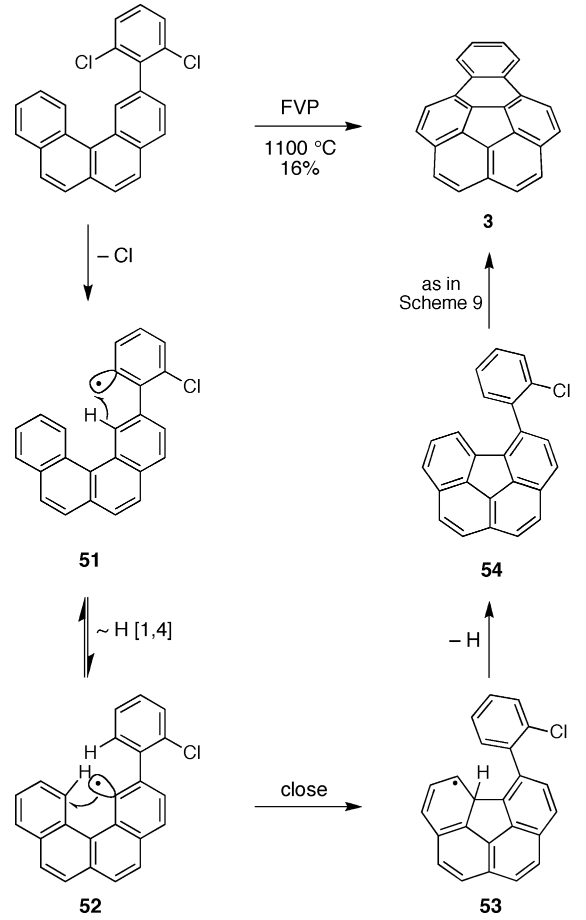
Some years later, Mehta and Srirama Sarma synthesized benzo[*a*]corannulene by FVP of the three precursors shown in Scheme 11.[46] These routes parallel the Mehta–Panda syntheses of corannulene summarized in Scheme 6 and suffer from the same low efficiency for closure of the 5-membered ring by thermal cyclodehydrogenation.

Scheme 11



Very recently, another FVP synthesis of benzo[*a*]corannulene from a [4]helicene precursor was reported by Peng and Scott (Scheme 12).[47] In this case, closure of the 5-membered ring was triggered by intramolecular abstraction of a hydrogen atom from the congested cove region by a strategically located, nearby radical center, i.e., a 1,4-shift of hydrogen (**51** → **52**). The subsequent 6-membered ring closure (**54** → **3**) is completely analogous to the aryl radical cyclization outlined in Scheme 9.

Scheme 12



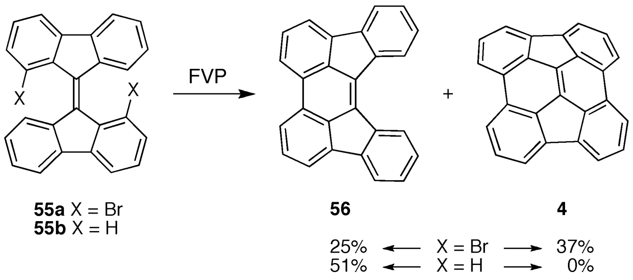
5. C$_{26}$H$_{12}$

At 26 carbon atoms, we begin to see several different geodesic polyarenes with the same molecular formula, i.e., isomeric bowls.

5.1. C$_{26}$H$_{12}$ Tetrabenzopyracylene (4)

Although solution-phase methods have started appearing as alternatives to FVP for syntheses of the corannulene ring system and a few of the larger geodesic polyarenes,[48–50] the tetrabenzopyracylene ring system (**4**) has been prepared only by FVP of bifluorenylidenes (**55**). The dibromobifluorenylidene **55a** works best, giving hydrocarbon **4** in 37% isolated yield;[42,51] brute force pyrolysis of unfunctionalized bifluorenylidene (**55b**), by contrast, gives only the singly closed hydrocarbon **56** without a trace of **4** (Scheme 13).[52]

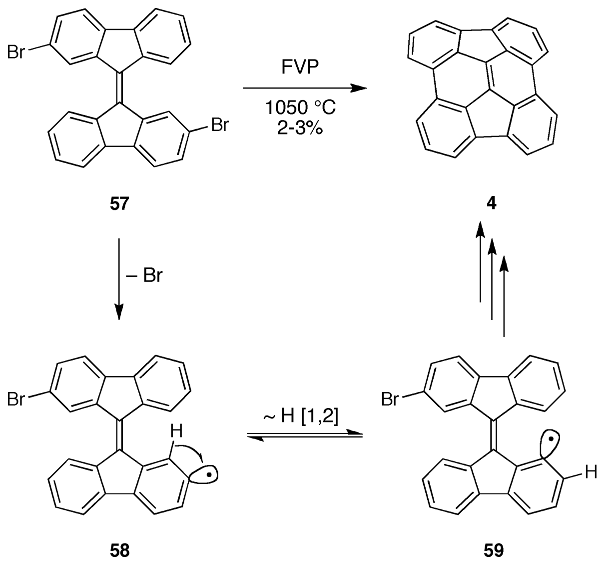
Scheme 13



If **56** is isolated and resubjected to FVP, it cyclizes to tetrabenzopyracylene (**4**) in 0.6% yield.[52]

Presumably, the bromides in **55a** serve as precursors to aryl radicals, which are then responsible for the cyclizations, as in Scheme 9. Interestingly, even dibromide **57**, an isomer of **55a**, gives small amounts of **4** by FVP (Scheme 14).[51] In this case, 1,2-shifts of hydrogen atoms (**58** → **59**) would be required in the aryl radicals in order to promote the cyclizations. Such shifts have been documented in other systems under FVP conditions[53] (see also, for example, sections 7.1, 8.1, 8.2, and 20).

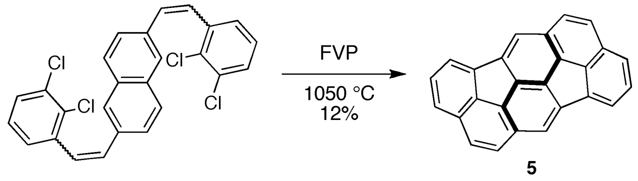
Scheme 14



5.2. $C_{26}H_{12}$ Yin–Yang Fluoranthenes (5)

A new FVP route to benzo[*ghi*]fluoranthenes[54] has been employed in a 2-fold manner to produce hydrocarbon **5**, in which two fluoranthene units nestle together in a head-to-tail fashion resembling the Chinese yin–yang symbol (Scheme 15). Mechanistic studies in simpler systems[33,54] suggest that these cyclizations begin with electrocyclic reactions to form the 6-membered rings, which quickly aromatize by loss of HCl. The subsequent 5-membered ring closures probably involve aryl radical intermediates, generated by homolysis of the strained C–Cl bond in the newly formed cove regions.

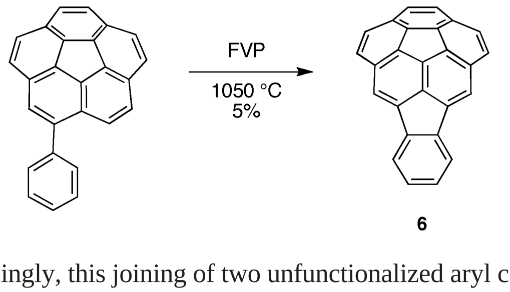
Scheme 15



5.3. $C_{26}H_{12}$ Indeno[1,2,3-*bc*]corannulene (6)

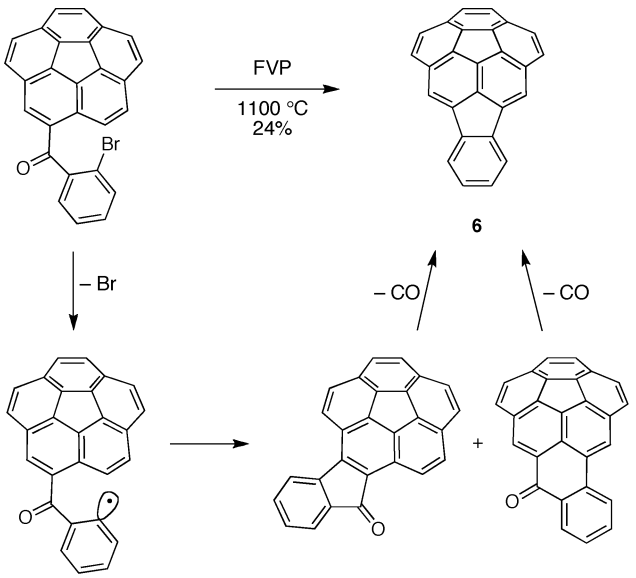
The first synthesis of indenocorannulene (**6**) was achieved by direct FVP of phenylcorannulene (Scheme 16).[55] Not surprisingly, this joining of two unfunctionalized aryl carbon atoms by cyclodehydrogenation is not at all efficient, and other products are also found.[55]

Scheme 16



Some years later, a convenient two-step method for the indenoannulation of corannulene was developed that involved Friedel–Crafts acylation with 2-bromobenzoyl chloride followed by FVP (Scheme 17).[33] From studies in other systems,[56] it is known that the radical generated by bromine atom loss cyclizes to make both 5- and 6-membered ring ketones, both of which then decarbonylate. Owing to the special symmetry of corannulene, these two pathways reconverge to form a single hydrocarbon product (**6**). Both isomers of diindenocorannulene have been prepared in the same manner by pushing the Friedel–Crafts reaction to bis(2-bromobenzoyl)corannulene (section 11.1), but the second acyl group deactivates the ring system too much to permit further acylation.[33,43]

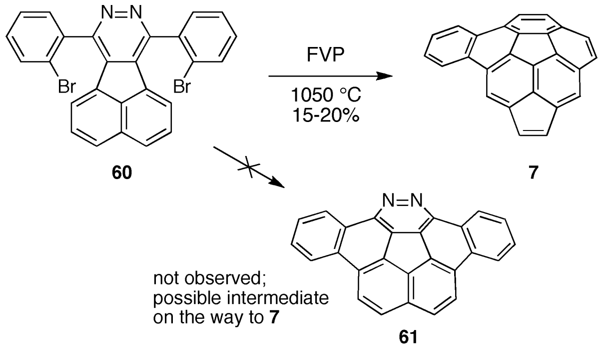
Scheme 17



5.4. $C_{26}H_{12}$ Benzo[*g*]acecorannulene (7)

Heterocycle **60** was synthesized by Bodwell *et al.* in the hope that it could serve as a precursor to the first aza-bowl (**61**).[57] An earlier synthesis of the hydrocarbon corresponding to **61**, dibenzo[*a*,*g*]corannulene (**11**), from a dibromide analogous to **60** provided the impetus for this project (see section 7.1). FVP of **60**, however, gives benzo[*g*]acecorannulene (**7**) as the only identifiable product; no trace of **61** could be found (Scheme 18).[58] The mechanism for formation of **7** from **60** is certainly not obvious, but one plausible route passes through **61** as an intermediate that fails to survive under the FVP conditions.

Scheme 18

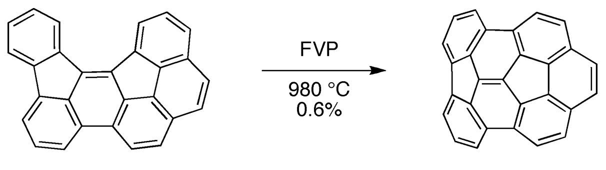


6. $C_{28}H_{12}$

6.1. $C_{28}H_{12}$ Fluoreno[1,9,8-*abcd*]corannulene (8)

Hydrocarbon **8**, a benzannulated derivative of tetrabenzopyracylene (**4**), has been prepared only once (Scheme

Scheme 19



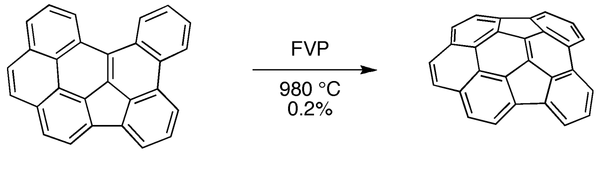
62 **8**

19).[59] As in the cyclodehydrogenation of **56** to **4**, the cyclodehydrogenation of **62** to **8** barely yields enough of the geodesic polyarene to allow isolation and characterization.

6.2. $C_{28}H_{12}$ Difluoreno[1,9,8,7-*cdefg*:2′,1′,9′,8′-*klmno*]anthracene (9)

In the same papers,[52,59] Hagen *et al*. report FVP of the isomeric hydrocarbon, **63**, which gives tetrabenzopyracylene with a benzene ring fused in the other bay region (**9**, Scheme 20). The yield in this case is even lower than that for the synthesis of isomer **8**. Hydrocarbon **9** has recently been isolated in multi-milligram quantities as a secondary product in the synthesis of the $C_{40}H_{14}$ bowl **28** by FVP (see section 17).

Scheme 20

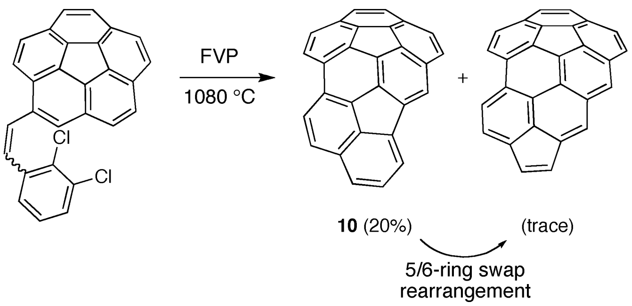


63 **9**

6.3. $C_{28}H_{12}$ Acenaphtho[1,2,3-*bcd*]corannulene (10)

The annulation method used to prepare the yin−yang fluoranthenes (**5**) in Scheme 15 has been applied also to the annulation of corannulene (Scheme 21).[33] Under the high-temperature conditions, the initial product (**10**) begins to rearrange to acenaphtho[4,5,6-*bcd*]corannulene, a less strained isomer, by what is now a well-known 5/6-ring swap process.[60−62]

Scheme 21



10 (20%)

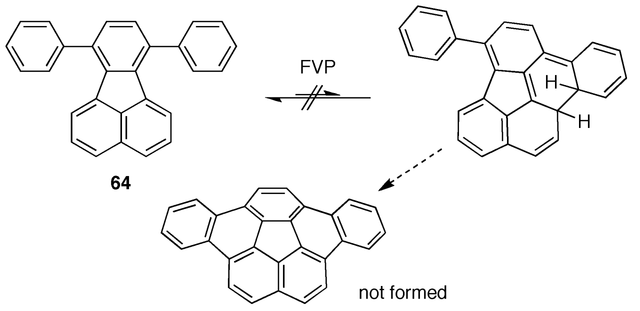
7. $C_{28}H_{14}$

With 28 carbon atoms, we begin to see geodesic polyarenes having the same number of carbon atoms but different numbers of hydrogens.

7.1. $C_{28}H_{14}$ Dibenzo[*a,g*]corannulene (11)

Historically, the use of FVP as a synthetic tool to prepare geodesic polyarenes had its beginnings here in 1989, with an attempted synthesis of dibenzo[*a,g*]corannulene (**11**). Diphenylfluoranthene **64** was the first compound examined in the Scott laboratory. High temperatures were (naively) expected to promote endothermic electrocyclic reactions that would be driven by irreversible thermal dehydrogenations to deliver the previously unknown dibenzo[*a,g*]corannulene (**11**). All attempts failed completely (Scheme 22)![30,63] No trace of **11** could be detected. Nevertheless, from this disappointing first venture grew the idea to examine diyne **32**, from which FVP gave the prototype PAH bowl, corannulene (**1**, Scheme 1).

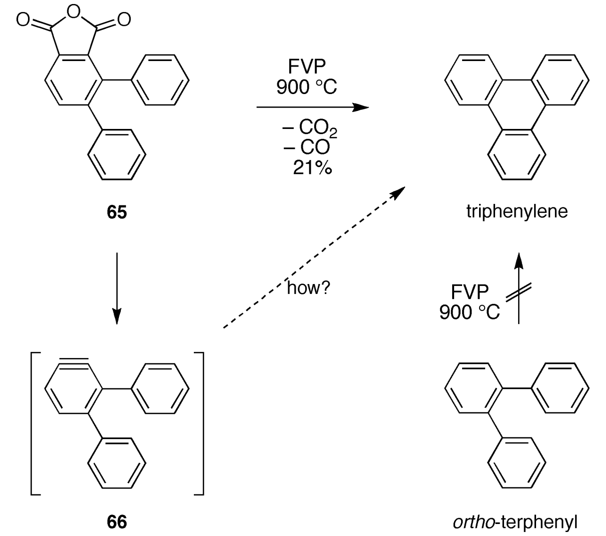
Scheme 22



64 **11**

Attempts to synthesize dibenzo[*a,g*]corannulene (**11**) again did not resume until interest was rekindled by a discovery in the laboratory of R. F. C. Brown in Australia that FVP of 3,4-diphenylphthalic anhydride (**65**) gives triphenylene as the major product (Scheme 23).[64,65] This report was surprising because FVP of the parent hydrocarbon, *o*-terphenyl, gives no triphenylene under the same conditions (Scheme 23). Earlier work by Brown on the FVP of aromatic anhydrides suggested that benzyne **66** must be the initial intermediate generated in this pyrolysis,[66] but no pathway from there to triphenylene was immediately apparent at the time. It was difficult to understand how a C−C bond could be formed at a site so remote from the most reactive part of the benzyne and how hydrogen atoms could find their way to sites where they were needed from sites where they were superfluous.

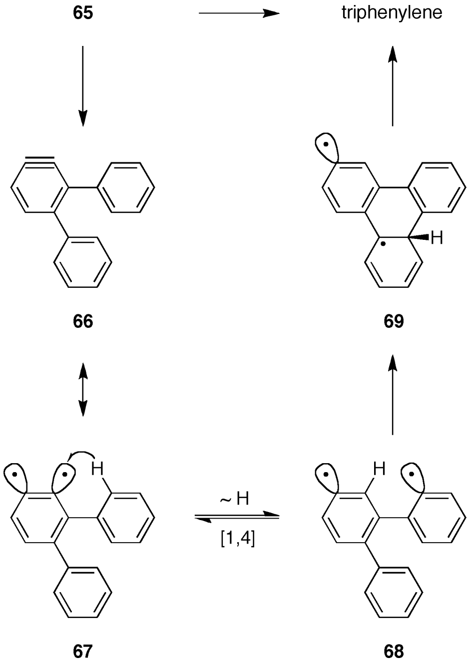
Scheme 23



65 **66**

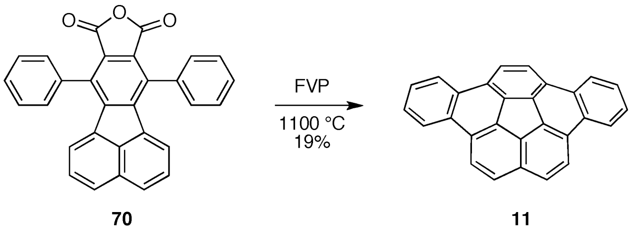
To rationalize the observed transformation, Brown postulated that benzyne **66** might be displaying chemistry of the sort expected for a 1,2-diradical (**67**) and engage in intramolecular hydrogen abstraction reactions, as suggested in Scheme 24 (**67** → **68**, cf. Scheme 12, **51** → **52**). The newly formed radical center on one phenyl substituent could then swing around and cyclize onto the other phenyl ring (**68** → **69**, cf. Scheme 9, **49** → **50**).

Scheme 24



Recognizing that the cyclizations previously envisioned for **64** (Scheme 22) involved nothing more than *o*-terphenyl moieties imbedded in a somewhat more complex ring system, Bratcher and Scott[67] prepared anhydride **70** and subjected it to FVP. This experiment was stimulated largely by empirical speculation, since the mechanism of Brown's "remote activation" of sites for cyclization was still unclear. Gratifyingly, FVP of **70** does indeed give dibenzocorannulene **11** as the major product at temperatures in the range 850−1000 °C (Scheme 25)![68,69]

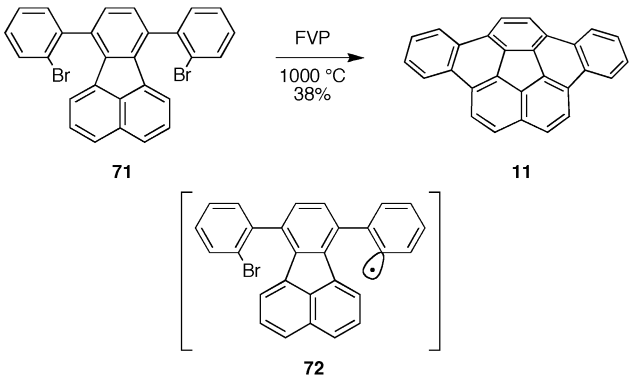
Scheme 25



There is a clear parallel between these two anhydride pyrolyses (Schemes 23 and 25); however, there is also a major distinction between them that supports Brown's explanation for the "remote activation" of sites for cyclization. Note in Scheme 23 that the cyclization represents an isomerization of the benzyne: two hydrogens are lost at the site of C−C bond formation, and two hydrogens are acquired by the benzyne carbon atoms; there is no net change in the number of hydrogen atoms. The analogous transformation starting from anhydride **70**, therefore, should promote *only one* cyclization, but no product was found that had only one ring closed. Apparently, each half of the benzyne is capable of initiating a separate hydrogen transfer/radical cyclization sequence.

Regardless of the mechanism, this success stimulated Bratcher and Scott to think of more direct ways to introduce radical centers at the *ortho*-positions of the phenyl groups in **64**. Their earlier observation that C−Br bonds of aryl bromides do not survive FVP at 1000 °C (e.g., **34** and **35**, see Scheme 2) prompted them to synthesize 7,10-bis(2-bromophenyl)fluoranthene (**71**) and subject it to FVP at 1000 °C. Under these conditions, dibenzo[*a*,*g*]corannulene (**11**) was obtained in 38% isolated yield (Scheme 26).[63,67,70]

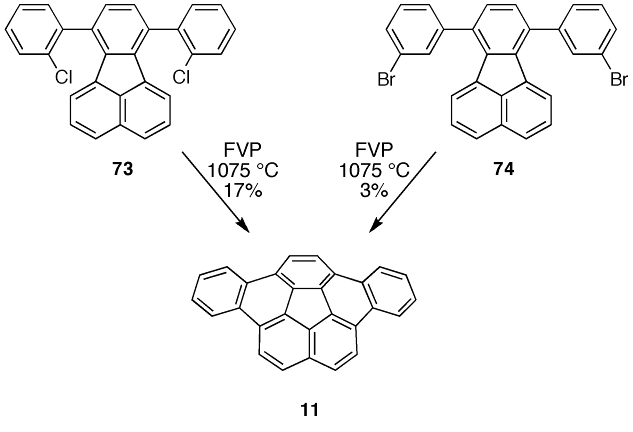
Scheme 26



Presumably, these cyclizations involve initial formation of reactive aryl radicals (starting with **72**), which close the rings as detailed in Scheme 9. As an historical point, this synthesis of **11** predates the synthesis of benzo[*a*]corannulene (**3**) shown in Scheme 9 and represents the first preconceived use of aryl radicals as alternatives to vinylidenes for the synthesis of geodesic polyarenes by FVP.

The corresponding dichloro precursor (**73**) also gives dibenzocorannulene, but higher temperatures are required, and the yield drops (Scheme 27).[63] Even 7,10-bis(3-bromophenyl)fluoranthene (**74**), with the radical precursors in the wrong positions, gives small amounts of **11** (Scheme 27),[63] presumably by 1,2-shifts of hydrogen atoms in the initial aryl radicals[53] (cf. Scheme 14).

Scheme 27

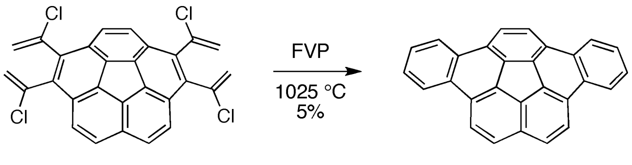


Most recently, hydrocarbon **11** has been synthesized in low yield also by annealing two benzene rings onto a preformed corannulene (Scheme 28).[71]

7.2. $C_{28}H_{14}$ Dibenzo[*a*,*d*]corannulene (12)

The other isomer of dibenzocorannulene (**12**) has been synthesized only once. Mehta and Srirama Sarma report that FVP of **75** at 1150 °C gives **12** in 5−7% yield (Scheme

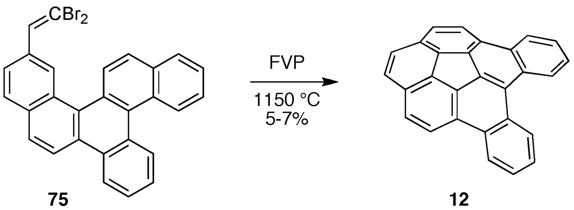
Scheme 28



11

29).[46] Precursor **75** is a benzannulated derivative of a precursor used by the same authors to synthesize benzo[*a*]corannulene (Scheme 11), and the reaction presumably follows the same course.

Scheme 29



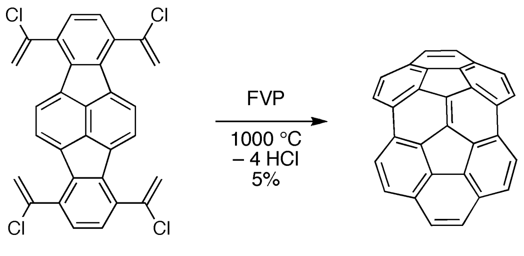
75 **12**

8. $C_{30}H_{12}$

8.1. $C_{30}H_{12}$ [5,5]Circulene (13)

Extending the FVP synthesis of corannulene in Scheme 4 simultaneously to both ends of the indeno[1,2,3-*cd*]fluoranthene nucleus (**76**), Rabideau, Sygula, and co-workers prepared [5,5]circulene (**13**), the first geodesic polyarene comprising 50% of the C_{60} skeleton (Scheme 30).[72,73] The yield in the final FVP step, though only 5%, is surprisingly good, considering how much strain is introduced and how many new C−C bonds had to be formed around the rim.

Scheme 30

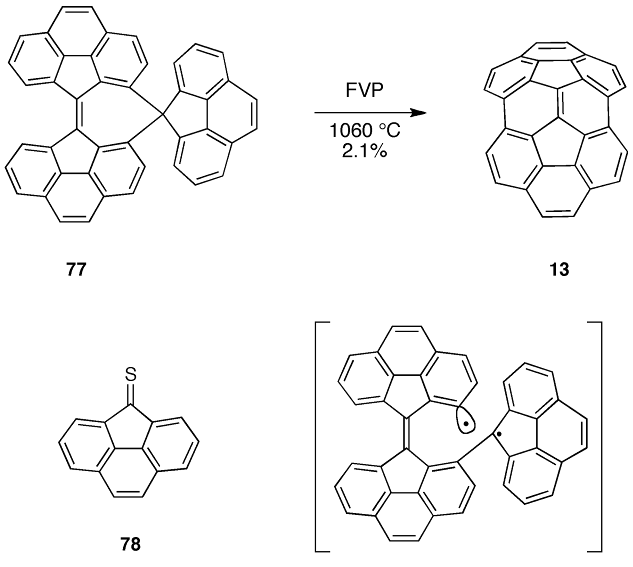


76 **13**

FVP of hydrocarbon **77** also gives [5,5]circulene, albeit in even lower yield (Scheme 31).[74] The synthesis of this precursor, unlike that of **76**, was not planned but was discovered as an unexpected side reaction in the reductive coupling of thioketone **78** by Stefan Hagen, a Ph.D. student in the laboratory of G. Zimmermann in Leipzig.[75] Later, as a postdoc in the Scott laboratory, Hagen examined the FVP of **77**, after he realized that cleavage of a relatively weak benzylic bond might generate aryl radical **79** and start the molecule on a pathway toward **13**. A 180° rotation around the central C=C bond in **79** prior to cyclization would presumably favor the production of **13**, but that should be facile at FVP temperatures.[76a]

Mehta and Panda reported a conceptually new route to **13** in 1997 with the FVP of dibromoarene **80** (Scheme 32).[76b] The 5-membered ring closures in this case were modeled after those reported earlier the same year[74] for the synthesis of an isomeric $C_{30}H_{12}$ bowl and involve 1,2-shifts of hydrogen atoms in the intermediate aryl radicals[53] (cf. Scheme 34). The necessity for a final cyclodehydrogenation, with no additional radical precursor to promote formation of the third C−C bond, may contribute to the low yield.

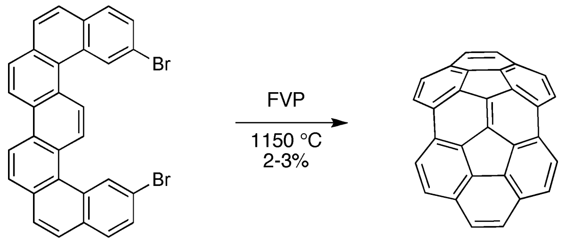
Scheme 31



77 **13**

78 **79**

Scheme 32

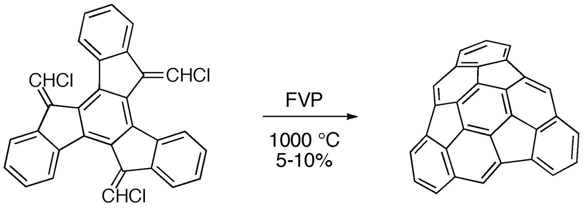


80 **13**

8.2. $C_{30}H_{12}$ Hemifullerene-C_3 (14) (Triindenotriphenylene)

Rabideau, Sygula, and co-workers were also the first to prepare the C_3-symmetric "hemifullerene" **14**.[77] From truxenone, they synthesized the chlorinated tris-fulvene **81** as a mixture of geometric isomers, and FVP of **81** gives **14** in 5−10% yield (Scheme 33).[77] The simplest mechanistic picture for this transformation is homolysis of a C−Cl bond and cyclization of the resulting methine radical, three times over, but the actual pathway might well be more circuitous.

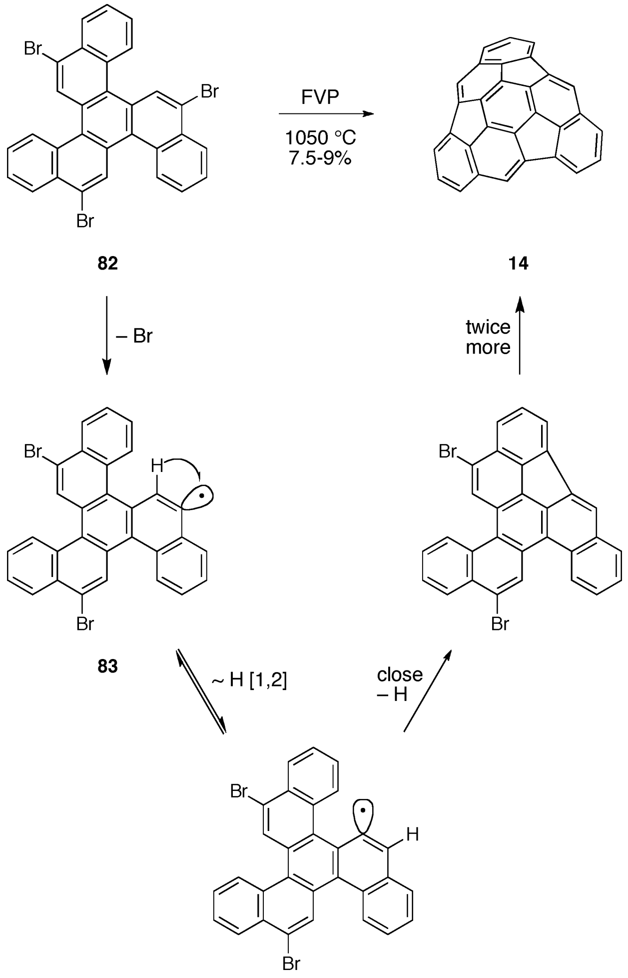
Scheme 33



81 **14**

An alternative FVP synthesis of **14** developed in the authors' laboratory is summarized in Scheme 34.[74] This was

Scheme 34

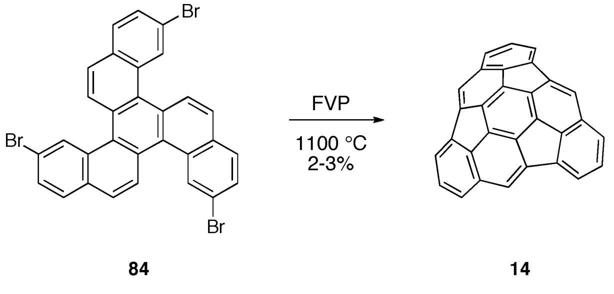


the first FVP synthesis reported that incorporates obligatory 1,2-shifts of hydrogen atoms in the intermediate aryl radicals[53] prior to C−C bond formation. Since then, the strategy has been exploited several times (see, for example, sections 5.1, 8.1, and 20).

Although it has not been possible to push the yield for this triple ring closure above 10%, the starting material (**82**) is relatively easy to prepare on a large scale,[74] and the FVP can be performed on a 1.0 g scale, or even larger, to yield >50 mg of **14** in a single run.

The isomeric tribromide **84** also gives **14** under conditions of FVP; however, the yield from this regioisomer is significantly lower (Scheme 35).[78] The superiority of **82** as a precursor to **14** may lie in the fact that the aryl radicals formed by homolysis of its C−Br bonds (e.g., **83**) have only one 1,2-shift of hydrogen available.

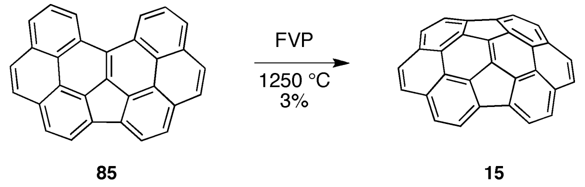
Scheme 35



8.3. Difluoreno[2,1,9,8,7-*defghi*:2′,1′,9′,8′,7′-*mnopqr*]naphthacene (15)

Hydrocarbon **15**, a third isomer of $C_{30}H_{12}$, has been synthesized only once. Stefan Hagen prepared the $C_{30}H_{14}$ hydrocarbon **85** during his graduate studies in Leipzig but had been unsuccessful in promoting the final cyclodehydrogenation to **15** by FVP. As a postdoc in the Scott laboratory, however, he was able to reinvestigate this FVP at higher temperatures and found that the cyclodehydrogenation could be achieved in low yield at 1250 °C (Scheme 36).[74]

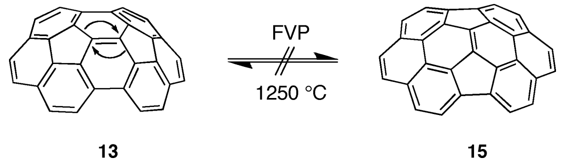
Scheme 36



Hydrocarbon **15** is significant for two reasons. First, it is the only geodesic polyarene encountered in this review so far that does *NOT* map onto the ring system of C_{60}. The smallest stable fullerene that contains a naphthacene ("tetracene") moiety is C_{70}, but the smallest stable fullerene that contains the full 30-carbon skeleton of **15** is C_{78}.

The other interesting aspect of **15** stems from its structural relationship to [5,5]circulene (**13**). Both hydrocarbons contain a pyracylene core annulated by two phenanthrenes; they differ only in the orientation of the pyracylene core. A so-called "Stone−Wales" rearrangement[79,80] would interconvert **13** with **15**. Despite the extreme temperatures of these FVP experiments, however, no trace of **15** was seen as a byproduct in the synthesis of **13**, and no trace of **13** was seen as a byproduct in the synthesis of **15** (Scheme 37). To the best of our knowledge, the so-called "Stone−Wales" rearrangement has *never* been observed under FVP conditions, despite deliberate attempts to find examples of it.[42,81]

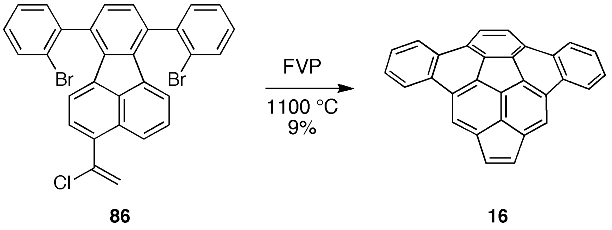
Scheme 37



9. $C_{30}H_{14}$ Dibenz[*f,l*]acecorannulene (16)

The synthesis of dibenz[*f,l*]acecorannulene (**16**) by FVP of **86** (Scheme 38)[82,83] is simply a composite of the syntheses of dibenzo[*a,g*]corannulene (**11**) and acecorannulene (**2**) from **71** and **47a**, respectively. As in all the acecorannulene

Scheme 38



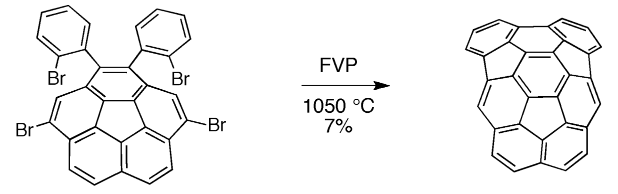
syntheses (section 3), loss of the 2-carbon side chain presents a serious problem here, too.

10. $C_{32}H_{12}$

10.1. $C_{32}H_{12}$ Acenaphtho[3,2,1,8-*ijlkm*]diindeno[4,3,2,1-*cdef*:1′,2′,3′,4′-*pqra*]triphenylene (17)

FVP of the corannulene derivative **87** closes three C−C bonds to give hydrocarbon **17** (Scheme 39).[84] Although the starting material has four precursors for radical centers on the rim, 1,2-shifts of hydrogen atoms are required for two of them to be useful. Compound **17** can be viewed as a relative of *o*-diindenocorannulene (**19**) in which the two proximal indeno rings have formally been joined by a cyclodehydrogenation.

Scheme 39

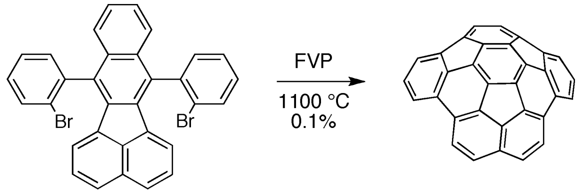


87 **17**

10.2. $C_{32}H_{12}$ Acenaphth[3,2,1,8-*fghij*]-*as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picene (18)

The bis(2-bromophenyl) compound **88** can be viewed as a benzannulated derivative of **71** (Scheme 26), a previously known precursor to dibenzo[*a,g*]corannulene (**11**). FVP of **88** likewise forms the dibenzocorannulene ring system, but two additional ring closures in this case take the molecule all the way to the deeper bowl **18** (Scheme 40).[85] Analysis of the original product mixture in this case revealed the presence of several additional geodesic polyarenes in small amounts ($C_{32}H_{14}$, $C_{32}H_{16}$, etc.), but only **18** was isolated and characterized.

Scheme 40



88 **18**

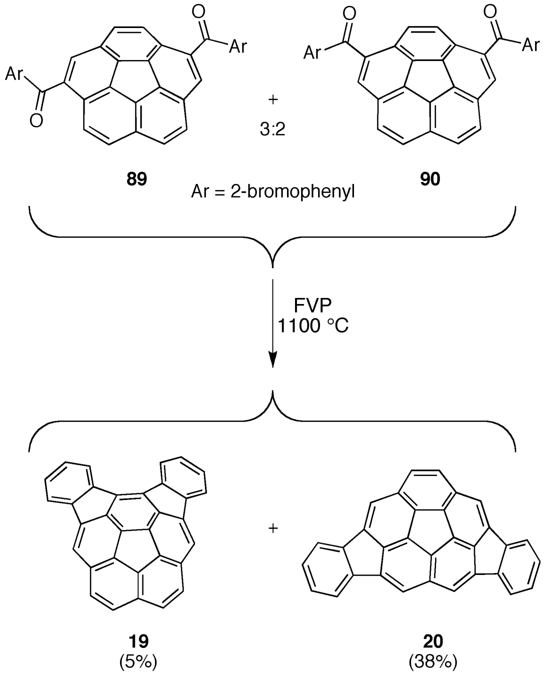
It is worth noting here that precursor **88** has only two radical precursors on the rim, yet four new C−C bonds get formed. Apparently, the cyclizations involving the 2-phenyl radicals stimulate a "cascade" process, wherein uncharacteristically facile cyclodehydrogenations continue stitching up the molecule until no additional aryl−aryl linkages are possible (contrast with Scheme 22). This cascade effect had been observed earlier by McMahon and Scott (section 11.2)[45] and was exploited in a major way in the first chemical synthesis of C_{60} (section 20).[86,87]

11. $C_{32}H_{14}$

11.1. $C_{32}H_{14}$ *o*-Diindenocorannulene (19) and *p*-Diindenocorannulene (20)

As discussed in section 5.3, FVP of (2-bromobenzoyl)corannulene produces indenocorannulene by two distinct pathways (Scheme 17). Pushing the acylation of corannulene with 2-bromobenzoyl chloride past the first substitution gives a mixture of two bis(2-bromobenzoyl)corannulenes. A 3:2 mixture of the 1,5- and the 1,8-isomers (**89** and **90**, respectively) is obtained as a result of the directing effect of the first acyl group.[88] FVP of this mixture, without separation, gives *o*-diindenocorannulene (**19**) and *p*-diindenocorannulene (**20**) in 5% and 38% yield, respectively (Scheme 41).[33,88]

Scheme 41

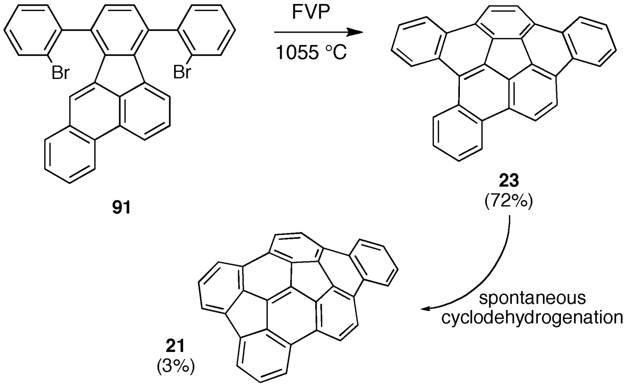


The great predominance of **20** in this reaction is consistent with earlier findings[33,56] that cyclizations of 2-benzoyl radicals give more 5-membered ring ketones in the initial closure than 6-membered ring ketones (cf. Scheme 17).

11.2. $C_{32}H_{14}$ Benzo[*a*]fluoreno[1,9,8-*ghij*]corannulene (21)

Compound **91**, like its isomer, **88**, can be viewed as a simple benzannulated derivative of the disubstituted fluoranthene used to prepare dibenzo[*a,g*]corannulene (cf. **71** → **11**, Scheme 26). FVP of **91** was expected to yield tribenzo[*a,d,j*]corannulene (**23**, Scheme 42), and it does, but a fraction of the molecules also close a third ring to give **21**.[45] This

Scheme 42

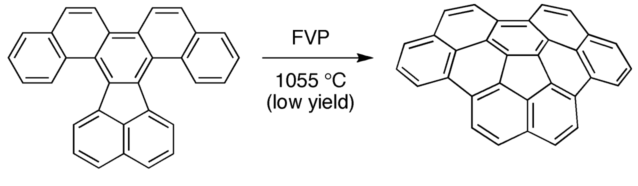


was the first example of the “cascade” effect discovered in the Scott laboratory (cf. section 10.2).

11.3. $C_{32}H_{14}$ Acenaphtho[3,2,1,8-*efghi*]peropyrene (22)

In 1997, Klumpp *et al*. reported a two-step synthesis of the crowded hydrocarbon **92** from acenaphthenequinone.[89] Recognizing that double cyclodehydrogenation of **92** would give a new geodesic polyarene, they sent a sample of the material to the Scott laboratory, where it was subjected to FVP. At 1055 °C, a small amount of **92** does indeed close twice to give the doubly fused corannulene, acenaphtho-[3,2,1,8-*efghi*]peropyrene (**22**, Scheme 43).[90] As with most brute force cyclodehydrogenations, however, the yield is quite low (cf. Scheme 22). Hydrocarbon **22** was characterized by ^{1}H NMR spectroscopy and mass spectrometry, but it was not rigorously purified, so a precise yield could not be determined.

Scheme 43

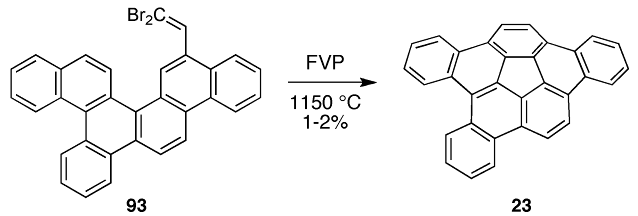


92 **22**

12. $C_{32}H_{16}$ *Tribenzo[a,d,j]corannulene* (23)

The first synthesis of tribenzo[*a*,*d*,*j*]corannulene (**23**) is the one shown above in Scheme 42.[45] Several years later, Mehta and Srirama Sarma prepared the same compound again by FVP of **93** (Scheme 44).[46] As with Mehta’s other syntheses of geodesic polyarenes by FVP of [4]helicene precursors, the yield is quite low (cf. Schemes 6, 11, and 29).

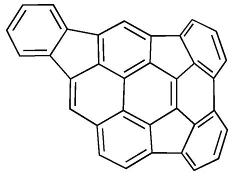
Scheme 44



93 **23**

13. $C_{34}H_{14}$ *Benzo[e]triindeno[1,2,3-cd:1′,2′,3′-fg:1″,2″,3″-jk]pyrene* (24)

Hydrocarbon **24**, an indeno-annulated derivative of **9**, was obtained as a secondary product in the synthesis of the $C_{40}H_{14}$ bowl **28** by FVP (see section 17).

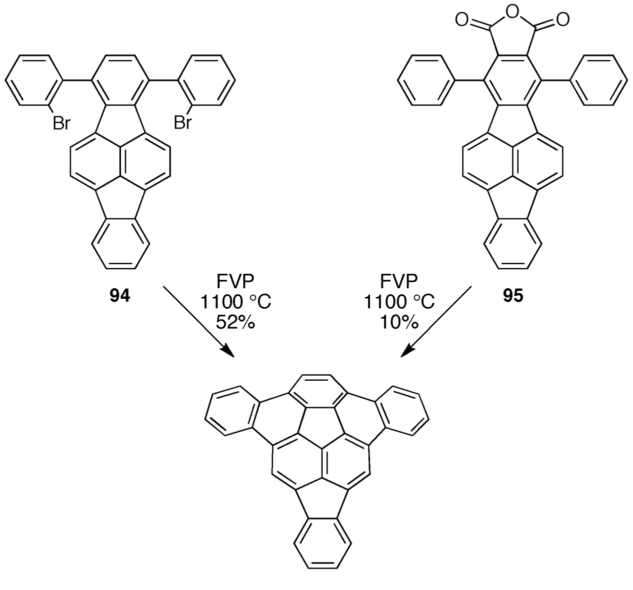


24

14. $C_{34}H_{16}$ *Dibenz[a,j]indeno[ef]corannulene* (25)

The synthesis of dibenz[*a*,*j*]indeno[*ef*]corannulene (**25**) by FVP of **94** (Scheme 45)[91] parallels the syntheses of dibenzocorannulene (**11**) and tribenzocorannulene (**23**) in Schemes 26 and 42, respectively. The anhydride variant of this route was also examined[91] (Scheme 45, cf. Scheme 25); FVP of **95** does afford **25**, but the yield is lower, as is the case in the parent system. In both routes, the indeno moiety was incorporated by standard synthetic methods and simply carried through the FVP step. It survives intact.

Scheme 45



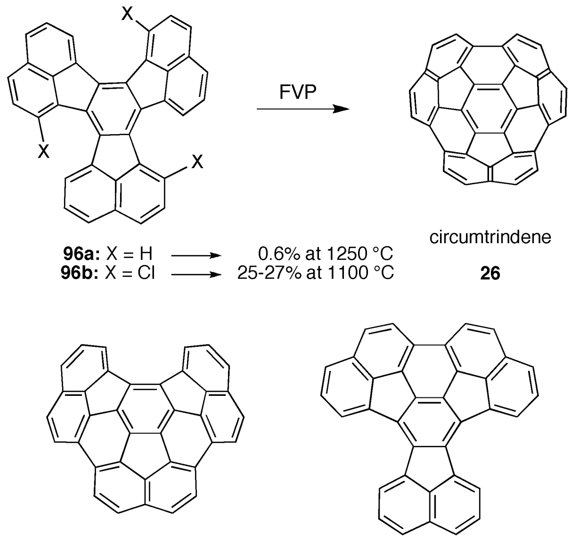
94 **95**

25

15. $C_{36}H_{12}$ *Circumtrindene* (26) *(Triacenaphtho-[3,2,1,8-cdefg:3′,2′,1′,8′-ijklm:3″,2″,1″,8″-opqra]-triphenylene)*

FVP of decacyclene (**96a**) at 1100 °C gives recovered decacyclene and no detectable quantities of any geodesic polyarenes. At 1200−1300 °C, on the other hand, very small amounts of circumtrindene (**26**) are formed, along with comparable quantities of materials having only two or one new aryl−aryl bond (**97** and **98**, respectively, Scheme 46).[92] Since the original report of this triple cyclodehydrogenation,

Scheme 46



26

97 **98**

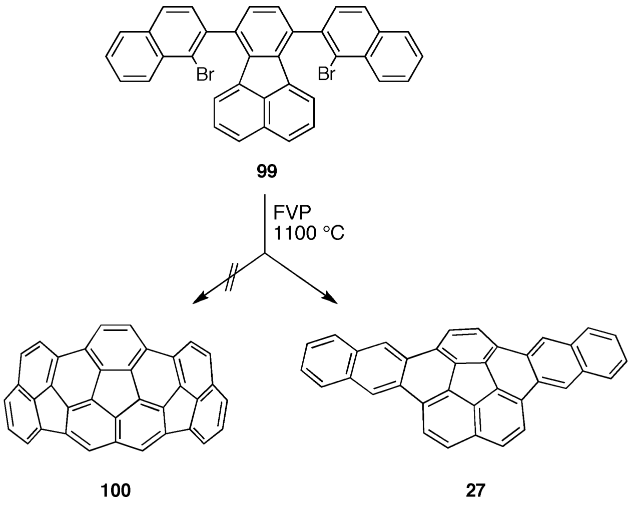
the yield of circumtrindene (**26**) from **96a** has been improved from 0.2% to 0.6%,[93] but it is still abysmally low. On the positive side, this transformation constitutes a one-step synthesis of 60% of C_{60} from commercially available material; decacyclene is inexpensive, and the FVP can be performed on a 5 g scale.

Four years after the first synthesis and characterization of circumtrindene (**26**), Ansems and Scott reported a more rational synthesis of this geodesic polyarene based on FVP of trichlorodecacyclene (**96b**, Scheme 46).[94] Not surprisingly, the yield of **26** improves dramatically when radical precursors are incorporated at the sites where new C−C bonds are to be formed.

16. $C_{36}H_{18}$ Dinaphtho[2,3-a:2′,3′-g]corannulene (27)

Facile hydrogen shifts under FVP conditions can sometimes divert aryl radical cyclization reactions from their intended course. The FVP shown in Scheme 47 provides a perfect example. Thus, the bis(1-bromo-2-naphthyl)fluoranthene **99**, an analogue of the dibenzocorannulene precursor **71**, was synthesized and subjected to FVP in an attempt to prepare the long hydrocarbon bowl **100**. The only geodesic polyarene found, however, was dinaphtho[2,3-*a*:2′,3′-*g*]corannulene (**27**).[91]

Scheme 47

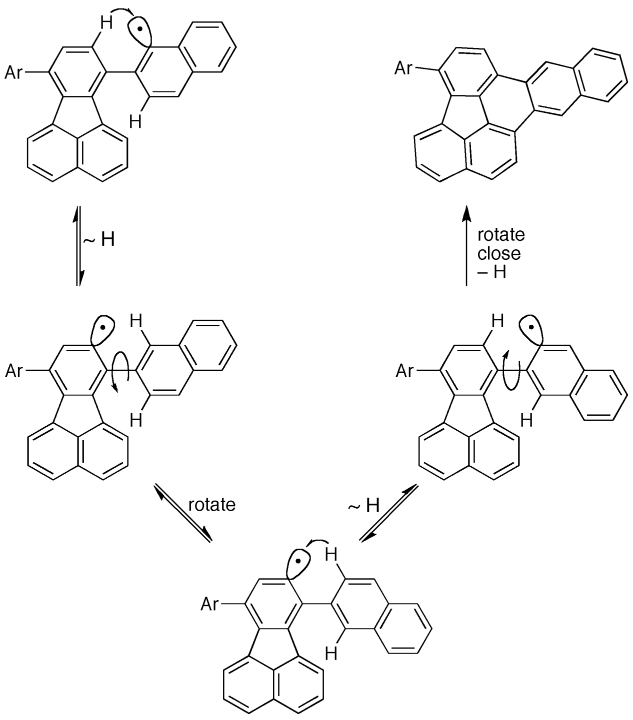


In retrospect, this synthesis was doomed from the start. Rapid 1,4-shifts of hydrogen atoms,[47] back and forth between the fluoranthene nucleus and the naphthyl substituents, at high temperatures quickly equilibrate the 1-naphthyl radicals with the 3-naphthyl radicals, and the latter are able to cyclize more easily than the former for steric reasons (Scheme 48).

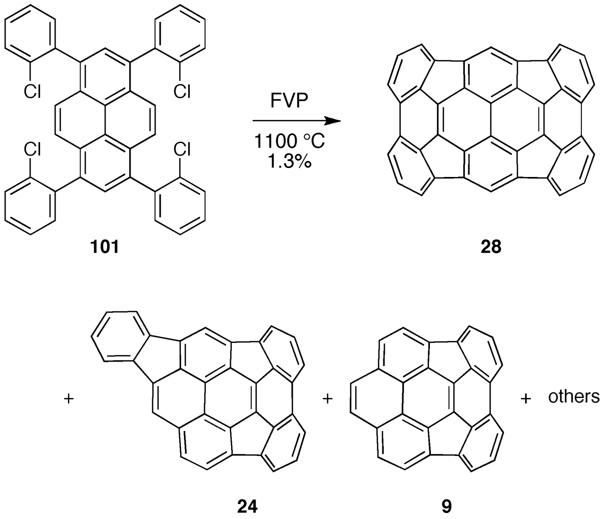
17. $C_{40}H_{14}$ Diphenanthro[1,10,9,8-abcde:1′,10′,9′,8′-jklmn]tetracyclopentapyrene (28)

An impressive example of the “cascade” effect discussed in sections 10.2 and 11.2 can be seen in Scheme 49.[95] The tetrakis(2-chlorophenyl)pyrene **101** is easily synthesized on a large scale in just two steps from pyrene by bromination and a 4-fold Suzuki−Miyaura coupling. FVP of **101** at 1100 °C gives several products, including some that are missing one or more of the aryl groups, but the most interesting is the C_{70} subunit **28**.[95]

Scheme 48



Scheme 49

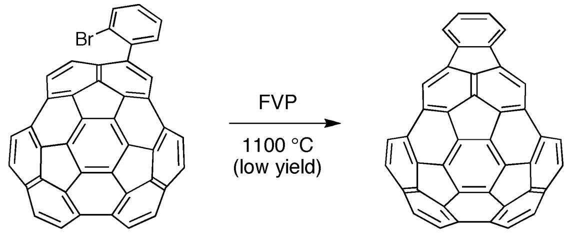


Four aryl radical closures of the sort outlined in Scheme 9 were expected to produce tetraindenopyrene. The exceedingly low solubility of that nearly flat PAH,[96] however, precluded its isolation by chromatography, if any was present at all. Fortunately, the greater solubility and chromatographic mobility of most geodesic polyarenes, compared to their planar counterparts, facilitates the isolation and purification of the orange hydrocarbon **28** in milligram amounts. Clearly, the four anticipated ring closures do occur, and two more cyclodehydrogenations accentuate the curvature of the pyrene core. The smaller fragments of **28** (**24** and **9**) presumably come from the same reaction pathway but with one or two of the aryl groups being lost in competition with cyclization.

18. $C_{42}H_{14}$ Indeno[1,2,3-bc]circumtrindene (29)

The largest open geodesic polyarene prepared to date is the indeno-annulated circumtrindene **29**.[93] Monobromination of circumtrindene (**26**) followed by Suzuki−Miyaura coupling gives the 2-bromphenyl-substituted bowl (**102**), and FVP of **102** at 1100 °C yields small amounts of the $C_{42}H_{14}$ polyarene **29** (Scheme 50). The major product in this case is circumtrindene (**26**), formed by loss of the aryl group, and repeated chromatography failed to separate **29** completely from the large amount of **26**.

Scheme 50

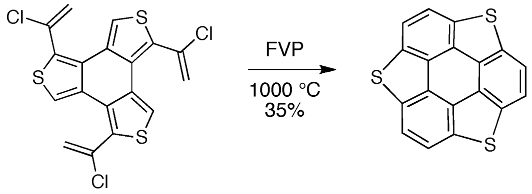


102 **29**

19. A Geodesic Heterocycle: $C_{18}H_6S_3$ Triphenyleno[1,12-bcd:4,5-b′c′d′:8,9-b″c″d″]-trithiophene (**30**)

Only one geodesic heterocycle has been reported to date, and it was synthesized by FVP. Thus, Otsubo and co-workers used 1-chlorovinyl substituents as “masked acetylenes” (cf. Scheme 4) on the trithiophene **103**. The robust thiophene rings of **103** survive FVP at 1000 °C, and the cyclization reactions give the triphenyleno trithiophene **30** in 35% yield (Scheme 51).[97]

Scheme 51

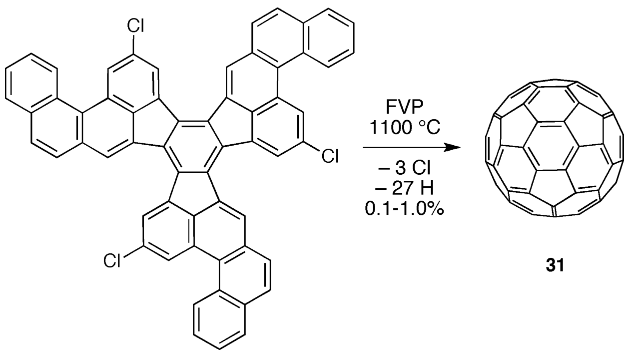


103 **30**

20. Buckminsterfullerene C_{60} (**31**)

The first chemical synthesis of buckminsterfullerene C_{60} (**31**) in isolable quantities also relied on FVP to zip up a conventional polyarene and introduce the geodesic curvature (Scheme 52).[86,87] No C_{70} or higher fullerenes were formed.

Scheme 52



104 **31**

The overall yield to C_{60} from **104** falls in the range of only 0.1−1.0%, but 15 new C−C bonds are formed, and that corresponds to an average yield of greater than 60% per bond. The presence of only three chlorine atoms to serve as radical precursors in **104** means that the “cascade” effect is responsible for closing the other twelve C−C bonds (cf. sections 10.2, 11.2, and 17). For synthetic expedience, the three chlorine atoms in **104** were attached in sterically undemanding positions, and that imposed an additional requirement for 1,2-shift of a hydrogen atom[53] following each C−Cl bond homolysis in order to set up a ring closure (cf. sections 5.1, 7.1, 8.1, 8.2, and 10.1).

21. Prospects for the Future

Extensive experimental investigation into the chemistry and properties of corannulene (**1**) and other geodesic arenes has been made possible over the last 15 years by syntheses based on flash vacuum pyrolysis. Not unlike the birth and growth of the fullerene field, this new branch of science has contemporaneously opened up and blossomed where virtually nothing was known before. As alternatives to FVP, several solution based synthetic methods have been introduced in the last 10 years,[48,49,50] and some have proven quite useful for constructing specific target molecules. The number of bowl shaped PAH ring systems that have been prepared by methods other than FVP, however, still constitutes only a small fraction of those that are known (Figure 1), and it appears unlikely that FVP will be surpassed any time soon as the most generally applicable strategy for preparing geodesic polyarenes.

22. Acknowledgments

We thank all the students and postdoctoral research fellows whose dedicated efforts in this laboratory and around the world have contributed to the scientific advances summarized in this review. Financial support from the National Science Foundation and the Department of Energy has been indispensable and is likewise gratefully acknowledged.

23. Notes and References

(1) Technically, our “open” geodesic polyarenes also represent polyhedra, if the atoms around the rim are considered to define one very large face. Within this context, “closed” geodesic polyarenes are defined as those that have no rings other than 5- or 6-membered rings.

(2) The compression of interior bonds can be seen in the calculated transition states for bowl-to-bowl inversions of such geodesic polyarenes.[3−5] It was a discussion of this phenomenon that evolved into a friendly game of designing ground state molecules with “squeezed bonds”, the outcome of which has recently been published.[6,7]

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