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Perspective

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Exotic Chemistry and Rational Organic Syntheses at 1000 °C

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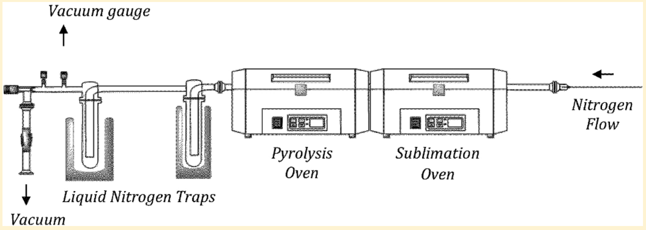
S Supporting Information

ABSTRACT: Subliming organic compounds into a stream of nitrogen gas and passing the vapors rapidly through a very hot oven (flash vacuum pyrolysis) promotes high-temperature thermal reactions in the gas phase that are generally difficult to achieve in solution under ordinary laboratory conditions. Exploring, exposing, and exploiting gas-phase organic chemistry at temperatures of 1000 °C and above has uncovered some extraordinary reactions and led to some landmark syntheses.



INTRODUCTION

My research students and I did not start out by pyrolyzing organic compounds at 1000 °C. Surely such high temperatures would decompose virtually any organic compound, even in the absence of oxygen, or at least that was the prevailing view 50 years ago. Our entry into this field actually began with studies on the mechanism of a fascinating thermal isomerization that had been reported to occur at temperatures closer to 400 °C in the gas phase (Figure 1[1]).

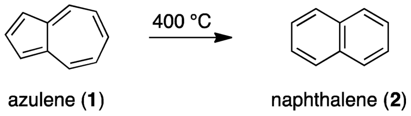


Figure 1. Thermal isomerization of azulene (**1**) to naphthalene (**2**).[1] What is the mechanism?

As so often happens in research, however, one idea led to another, and we soon found ourselves subjecting ^{13}C-labeled benzenoid aromatic hydrocarbons to temperatures of 1000 °C and even higher, albeit for only very short periods of time. To our delight, most of the aromatic hydrocarbons survived, and ^{13}C NMR spectroscopy revealed that the isotopic labels had scrambled their positions in precisely the manner that we had predicted they would (e.g., Figure 2[2]).

Then one day, it suddenly occurred to us that flash vacuum pyrolysis (FVP) could also be used as a synthetic tool to make curved polycyclic aromatic hydrocarbons (geodesic polyarenes) out of planar precursors (e.g., Figure 3[3]). That work culminated in the first chemical synthesis of C_{60}, uncontaminated by other fullerenes,[4] and the first chemical synthesis of a short, rigid, isomerically pure carbon nanotube.[5]

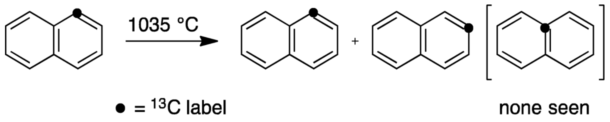


Figure 2. Thermal scrambling of carbon atoms in ^{13}C-labeled naphthalene.[2] What is the mechanism?

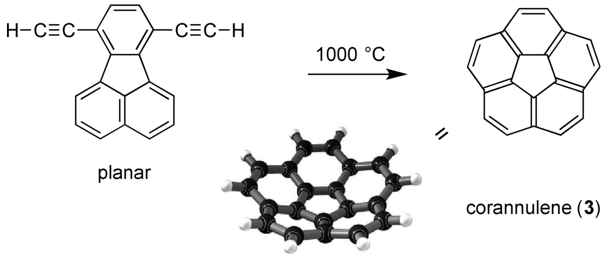


Figure 3. First use of flash vacuum pyrolysis to synthesize a bowl-shaped ("geodesic") polyarene from a planar polyarene.[3]

Many short stories comprise this Perspective. Within each section that follows, these accounts are arranged in roughly chronological order, although some of the projects actually unfolded concurrently.

THERMAL REACTIONS: CHEMISTRY WITHOUT REAGENTS OR CATALYSTS

First, I must compliment the late Professor Hamish McNab (University of Edinburgh, Scotland) for having conceived the clever title "Chemistry Without Reagents" to describe his extensive work in gas-phase thermal reactions.[6] The pioneering work,[7] classic book,[8] and warm friendship of the late Professor Roger F. C. Brown (Monash University, Australia) also served as a perennial source of inspiration to me.

R. B. Woodward Poses a Mechanism Problem in His Research Group Meeting. On Thursday evenings at Harvard

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in the late 1960s, Professor R. B. Woodward presided regally over his famous research group meetings, which started at 8:00 p.m. and rarely finished before midnight. Those in attendance included not only the graduate students and postdocs from the Woodward laboratories (about a dozen of each when I was in the group) but also throngs of onlookers from other laboratories at Harvard, MIT, and elsewhere, who came to see the legendary R.B.W. in action.

After the speaker of the evening had concluded his/her formal presentation, it was not uncommon for Professor Woodward to stand up and begin lecturing spontaneously on some aspect of the work that had just been presented or on some intriguing chemistry that he had recently come to appreciate in the course of writing his soon-to-be-published book with Roald Hoffmann on "The Conservation of Orbital Symmetry."[9] One night, he posed the long-standing mechanism problem shown above in Figure 1; he drew the structures on the blackboard, challenged us collectively to come up with a reasonable mechanism, and then walked out, leaving us all scribbling structures and scratching our heads.

Eventually, I came up with the mechanism depicted in Figure 4 and showed it to my lab partner, Jim Whitesell. He agreed that it looked appealing and convinced me to draw it on the board. In the absence of any other proposals, everyone decided that my mechanism must be good enough, and, since the hour was late and the boss had already left, we all went home.

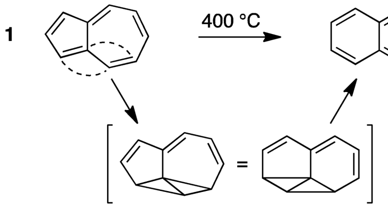

Figure 4. Mechanism proposed to account for the thermal isomerization of azulene (**1**) to naphthalene (**2**).

The next morning, I shared this mechanistic proposal with Professor Woodward, and he acknowledged that it coincided with his own thinking about the problem. Thus was solidified my life-long infatuation with thermal chemistry.

Launching My Own Independent Research Program as an Assistant Professor. We are all the products of our upbringing. In my case, working as an undergraduate research student with Professor Maitland Jones, Jr. at Princeton (A.B. degree 1966), I had become enthralled very early with syntheses and interconversions of highly unsaturated polycyclic hydrocarbons.[10] Then, as a graduate student with Professor Woodward at Harvard (Ph.D. degree 1970), I found myself working in the same general area, motivated by predictions rooted in the Woodward–Hoffmann rules.[11] When I started my independent career as an assistant professor at UCLA in the summer of 1970, however, it seemed prudent to branch out, so my first two Ph.D. students initiated projects unrelated to hydrocarbon chemistry. Nevertheless, I was unable to resist the urge to tackle the azulene-to-naphthalene rearrangement problem myself in the laboratory. A ^{13}C-labeling experiment had occurred to me (Figure 5) that would prove whether or not one of the CH units in the 7-membered ring of azulene actually migrates to the 5-membered ring, leaving the two quaternary carbon atoms at the ring junctions unaffected, as predicted by the proposed mechanism.

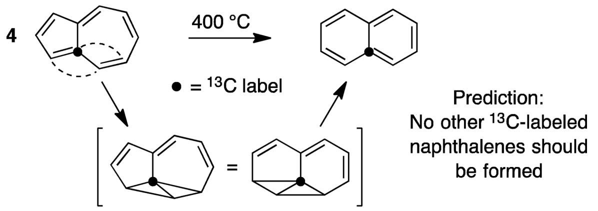

Figure 5. Predicted outcome of a ^{13}C-labeling experiment designed to test the mechanism proposed in Figure 4 for the thermal isomerization of azulene to naphthalene.

Azulene (**1**) was first synthesized in 1937[12] and is generally recognized as the premier nonbenzenoid aromatic hydrocarbon.[13] A variety of new and improved azulene syntheses emerged between 1937 and 1970; however, none was amenable to a synthesis of the [3a-^{13}C]-azulene (**4**) needed for my experiment. Consequently, I worked out a new synthetic route to azulenes that would permit site-specific ^{13}C-labeling of the ring-junction position (Figure 6).[14]

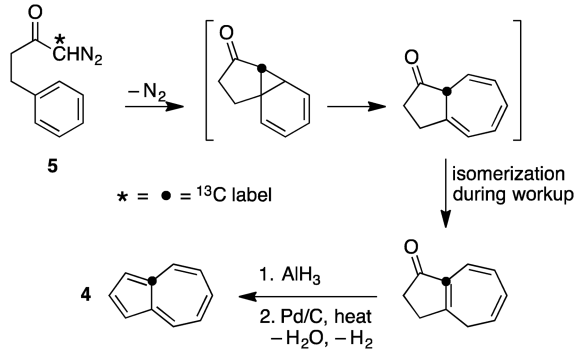

Figure 6. New synthesis of azulenes, developed for the preparation of [3a-^{13}C]-azulene (**4**).[14]

Diazoketone **5** was synthesized from the corresponding acid chloride and $^{13}CH_2N_2$, employing conditions tailored specifically to avoid the customary use of diazomethane in excess to quench the HCl produced in the reaction.[14d,15]

While this work was underway, an easier experiment occurred to us, and we actually executed it start to finish before we could get our hands on usable quantities of the desired ^{13}C-labeled azulene (**4**). The mechanism proposed in Figure 4 predicts that if naphthalene could be made to isomerize endothermically to azulene and then back to naphthalene, then the α- and β-carbon atoms of naphthalene ought to become scrambled with each other (**6** ⇆ **7**). Furthermore, the α- and β-carbon atoms of naphthalene ought not to exchange places with the carbon atoms at the ring junctions (Figure 7).

A synthesis of [α-^{13}C]-naphthalene (**6**) had already been reported and was easily replicated. To our delight, subliming this material through a hot quartz tube gave a significant amount of [β-^{13}C]-naphthalene (**7**), together with unchanged [α-^{13}C]-naphthalene (**6**) and no trace of [γ-^{13}C]-naphthalene (**8**),[2] just as we had predicted (compare Figure 2 and Figure 7)! We had anticipated that extreme temperatures would be required to drive the highly endothermic isomerization of naphthalene to azulene, and 1035 °C gave good results. By extending the contact time of the material in the hot zone, we were able to achieve nearly complete equilibration of [α-^{13}C]- and [β-^{13}C]-naphthalene (final ratio **6**/**7** = 53:47), still with no formation of [γ-^{13}C]-naphthalene (**8**).[2] This gratifying result did not "prove" the

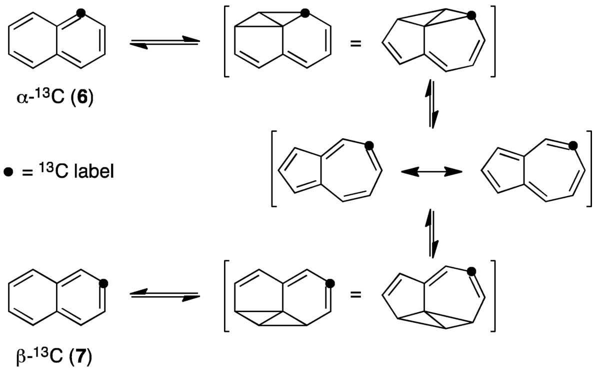

Figure 7. Predicted scrambling of ^{13}C-labeled naphthalene by isomerization of naphthalene to azulene and back, following the pathway proposed in Figure 4.

mechanism proposed in Figure 4 for the azulene-to-naphthalene rearrangement, of course, but it gave us great confidence that we were on the right track.

It was actually some time later when we finally completed the more demanding synthesis of [3a-^{13}C]-azulene (**4**) and subjected that material to FVP conditions, fully expecting the result predicted in Figure 5. Our confidence in our understanding of the thermal behavior of azulene and naphthalene was instantly shattered, however, by the discovery that FVP of [3a-^{13}C]-azulene (**4**) gives not only the predicted product, **8**, but all three possible isomers of ^{13}C-labeled naphthalene (**6**, **7**, and **8**, Figure 8).[14c,d,16,17]

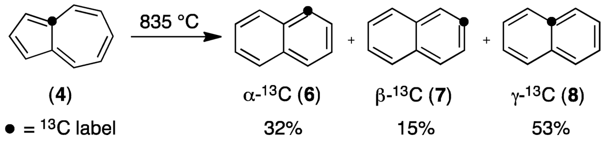

Figure 8. FVP of [3a-^{13}C]-azulene (3) does ***not*** give exclusively [γ-^{13}C]-naphthalene (**8**), contrary to the outcome predicted by the mechanism in Figure 5.[14c,d,16,17]

We were completely wrong about the mechanism of the azulene-to-naphthalene thermal rearrangement.

As students of physical organic chemistry learn at an early age, no number of successful experiments can ever "prove" a reaction mechanism, but it takes only one experiment to absolutely disprove a mechanism. Our experimental results summarized in Figure 8 unambiguously disprove the mechanism proposed in Figures 4 and 5. At least, it cannot be the sole pathway, if it is followed at all. Contrary to the predictions, some of the hydrogen atoms do not remain paired up with the carbon atoms to which they were originally attached during this isomerization.

Regardless of whether or not the mechanism of the azulene-to-naphthalene thermal rearrangement is every elucidated,[14c,17−19] the mechanism shown in Figure 7 for the thermal scrambling of ^{13}C-labeled naphthalene must be wrong! Azulene cannot lie on the pathway for that reaction. If it did, the principle of microscopic reversibility demands that some of the starting [α-^{13}C]-naphthalene (**6**) would rearrange to [3a-^{13}C]-azulene (**4**) and some of that would rearrange to [γ-^{13}C]-naphthalene (**8**), yet no [γ-^{13}C]-naphthalene is ever formed. Thus, instead of solving one mechanism problem, we uncovered a previously invisible reaction of a different compound and created a second mechanism problem (Figure 2): how do the α- and β-carbon atoms of naphthalene become scrambled at high temperatures, while the ring junction carbon atoms (γ) remain stationary?

■ UNPRECENTED ORGANIC REACTIONS AT 1000 °C

Thermal Isomerizations. The concept of pericyclic reactions as a unified class of chemical transformations and the role of orbital symmetry conservation in controlling their stereochemistry had pretty much crystallized by the late 1970s. It bothered me, however, that aromatic hydrocarbons never seemed to participate in thermal pericyclic reactions. Does aromaticity somehow protect these conjugated π-systems and render them immune to electrocyclic reactions, sigmatropic reactions, and all the other types of pericyclic processes? It should not. Aromatic hydrocarbons, such as benzene and naphthalene, enjoy a substantial amount of thermodynamic "aromatic stabilization," which means that they lie at the bottom of deep energy wells; however, every well has exit channels, no matter how high the walls. High barriers to escape from a deep energy well simply mean that higher than normal temperatures will be required to see the onset of any thermal chemistry.

The more I thought about this, the more intrigued I became with investigating the intrinsic chemistry of aromatic hydrocarbons at high temperatures in the gas phase. As a community, organic chemists have learned an enormous amount about the chemistry of organic compounds at room temperature ± 100 °C in the last 200 years, but the rules of structure and bonding and chemical reactivity do not end at the temperatures of dry ice/acetone baths or of refluxing toluene; the laws of nature apply at all temperatures (and all pressures, etc.). What other new chemical processes might we find at 1000 °C that have no counterparts under ordinary laboratory conditions? Unexplored corners of science hold many secrets. I had innocently taken the first step down this path with the pyrolysis of ^{13}C-labeled naphthalene, and now I was hooked.

"Automerization" is the name often used to classify molecular rearrangements from which the products formed are structurally identical to the starting materials, in the absence of isotopic labels.[20] The Cope rearrangements of bullvalene[21] and the Wagner−Weerwein rearrangements of the 2-norbornyl cation[22] stand out as two classic examples. "Homomerization" might be a more proper term for such "degenerate rearrangements," but by any of these names, our atom scrambling in ^{13}C-labeled naphthalene (Figure 2) qualifies.

We began investigating the FVP of other ^{13}C-labeled polyarenes, and those studies revealed a remarkable conclusion:

> *The 1,2-swapping of carbon atoms at high temperatures is a universal reaction of benzenoid polycyclic aromatic hydrocarbons.*

Figure 9 shows the cases that we have documented. In every case, the ^{13}C-label migrates only to the adjacent position and never migrates to a ring junction position. We have found no benzenoid polycyclic aromatic hydrocarbons that fail to exhibit the 1,2-swapping of carbon atoms at high temperatures.[23]

Even benzene, the aromatic hydrocarbon that reigns as the supreme standard to which all others are compared,[24] shows the same behavior. We synthesized [1,2-$^{13}C_2$]-benzene (**9**), starting from $K^{13}CN$ (not a trivial task), and subjected it to FVP at 1110 °C. Direct analysis of the recovered benzene by ^{13}C NMR spectroscopy was useless, of course, because all of the ^{13}C NMR signals were singlets at essentially the same chemical shift; however, we devised a postpyrolysis derivatization method to determine the relative amounts of *ortho-*, *meta-*, and *para-*$^{13}C_2$-labeled benzene. Under the conditions we employed, complete

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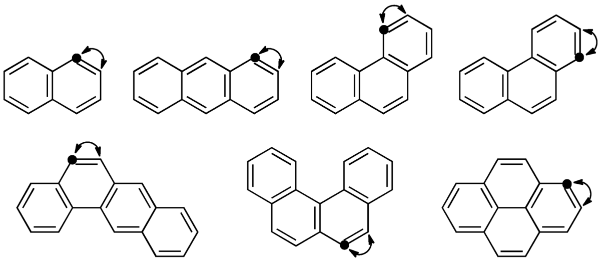

Figure 9. 1,2-Swapping of carbon atoms at high temperatures is a universal reaction of benzenoid polycyclic aromatic hydrocarbons.[23] What is the mechanism?

equilibration of the three isomers was not achieved, fortunately, and that allowed us to see that [1,3-$^{13}C_2$]-benzene (**10**) is formed as the primary product of rearrangement, in agreement with the 1,2-swap precedents. As the amount of **10** increases, its subsequent rearrangement by another 1,2-swap of carbon atoms gives rise to small quantities of the secondary product, [1,4-$^{13}C_2$]-benzene (**11**, Figure 10).[23e,25]

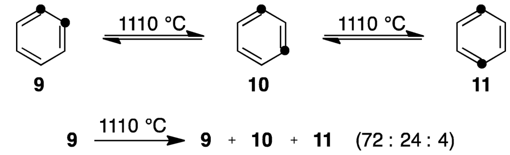

Figure 10. 1,2-Swapping of carbon atoms occurs even in benzene.[23e,25]

Reversible double electrocyclization of benzene to benzvalene represents the simplest mechanism to explain the 1,2-swapping of carbon atoms in benzene (Figure 11). High-level theoretical calculations on the C_6H_6 energy surface actually find this pathway to be the most favorable, albeit by only a small margin.[26] On the other hand, the benzvalene mechanism is inconsistent with experimental data for the 1,2-swapping of carbon atoms in larger, *cata*-condensed, polycyclic benzenoid hydrocarbons (see below) and may be restricted to the parent benzene and possibly to some *peri*-condensed aromatics, such as pyrene.[27]

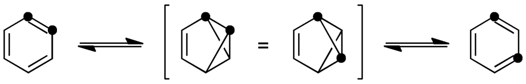

Figure 11. Mechanism believed to account for 1,2-swapping of carbon atoms in benzene.[26,27]

The mechanism for 1,2-swapping of carbon atoms at high temperatures in benzenoid aromatic hydrocarbons larger than benzene remained a mystery for many years; however, we noticed that the scrambling occurs more rapidly in some polyarenes and more slowly in others under comparable conditions. Specifically, the more olefinic the bond between two carbon atoms located *ortho* to each other (i.e., the higher the π-bond order) the more readily the two carbon atoms swap positions (Figure 12).[23f,28]

This realization, supported by theoretical calculations, led us to the mechanism depicted in Figure 13 to account for the thermal 1,2-swapping of carbon atoms in benzenoid polyarenes.[29]

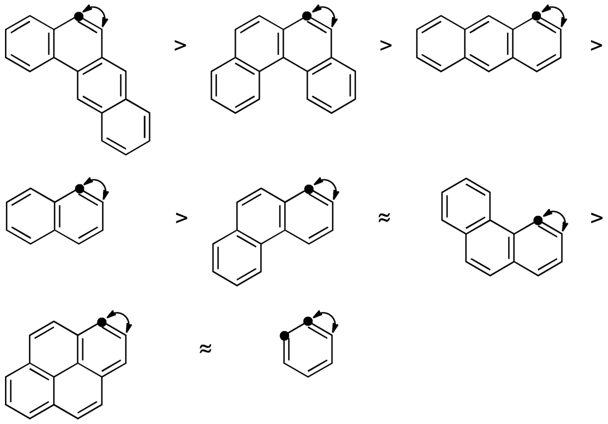

Figure 12. Ease of thermal 1,2-swapping of carbon atoms in benzenoid polyarenes correlates with the π-bond order between the two carbon atoms that swap positions.[23f,28]

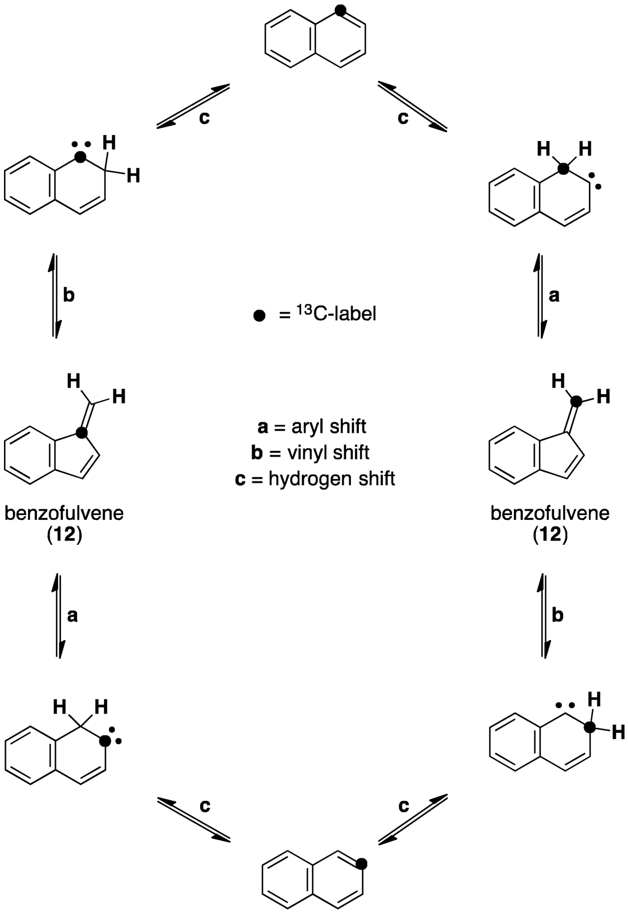

Figure 13. Mechanism believed to account for 1,2-swapping of carbon atoms in naphthalene and other benzenoid aromatic hydrocarbons at high temperatures.[29]

Isomerizations of carbenes to alkenes by 1,2-shifts of hydrogen or carbon atoms have been well-known for many years. The highly endothermic reverse processes are not observed at ordinary temperatures, however, and the greater the aromaticity of the benzene ring, the higher the energetic cost for disrupting the cyclic conjugation. As predicted by this mechanism, independent FVP of benzofulvene (**12**) gives naphthalene as the sole product.[29a,30] Further support for this mechanism comes from the results of the double-labeling experiment shown in Figure 14. In agreement with the calculations, the 1,2-swapping of hydrogen atoms in naphthalene is faster than the 1,2-swapping of carbon atoms[31] because the activation energies for the

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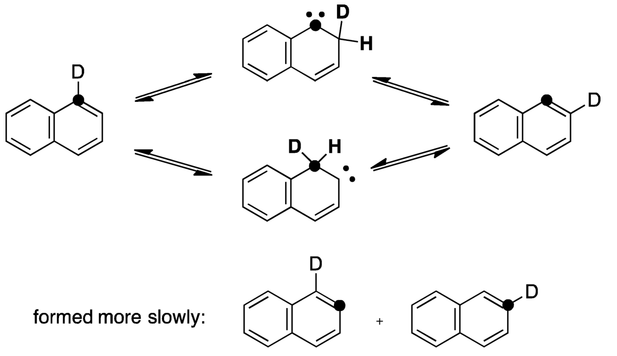


Figure 14. In agreement with calculations,[29] the 1,2-swapping of hydrogen atoms in benzenoid aromatic hydrocarbons at high temperatures is faster than the 1,2-swapping of carbon atoms.[31]

hydrogen atom shifts are lower than those for the subsequent carbon atom shifts.[29]

Another prediction of the mechanism shown in Figure 13 and the trend summarized in Figure 12 is that a ^{13}C label in the 2-position of naphthalene (β) should exchange readily with the 1-position (α) but much more slowly or not at all with the 3-position (β'). A $\beta \leftrightarrows \beta'$ swap would temporarily destroy the aromaticity of *both* rings in naphthalene, which would be prohibitively costly energetically. The experiment summarized in Figure 15 verifies this prediction.[25d]

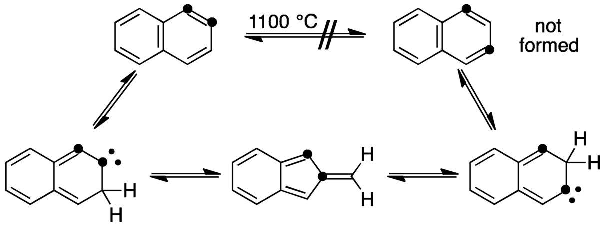
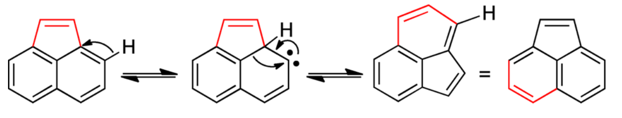


Figure 15. In agreement with calculations, the 2,3-swapping of carbon atoms in naphthalene does not occur under conditions that promote the 1,2-swapping of carbon atoms in naphthalene; the aromaticity of *two* rings would be temporarily lost.[25d]

It is always gratifying to come up with a mechanism that not only accounts for all the known facts about a reaction but also leads to new predictions that survive experimental testing. Nevertheless, we were not satisfied. The mechanism we had put forward (Figure 13) includes the borderline-heretical claim that benzene rings must suffer temporary ring contraction reactions at high temperatures (e.g., naphthalene ⇆ benzofulvene). The most convincing evidence for such ring contractions, we felt, would be to stop the rearrangement at the halfway point and actually isolate the 5-membered ring product. In light of the 24.5 kcal/mol more favorable heat of formation of naphthalene relative to benzofulvene (B3LYP/6-31G*), however, achieving that dream seemed impossible.

Then it occurred to us that by incorporating an ethylene bridge on naphthalene (thereby making acenaphthylene, **13**) we could render the highly endothermic ring contraction reaction thermoneutral because the aromaticity gained by ring expansion of the 5-membered ring would exactly balance the aromaticity lost by ring contraction of the 6-membered ring (Figure 16). In short, our mechanism predicted the never-before-seen thermal homomerization of acenaphthylene.



13 **13**

Figure 16. Benzene ring contraction in acenaphthylene (**13**) according to the mechanism shown in Figure 13 would lead to concomitant ring expansion of the 5-membered ring and a net homomerization of acenaphthylene.

To test this prediction, we synthesized two ^{13}C-labeled acenaphthylenes (**13b** and **13e**) and subjected them independently to FVP conditions. Much to our delight, **13b** gave **13a** and **13c** as the primary rearrangement products,[25d,32] whereas **13e** gave only **13d** and **13f** (Figure 17),[31] in complete agreement with the mechanism shown in Figure 16. Furthermore, when the FVP of **13b** was pushed to higher levels of conversion, isotopomer **13d** began to appear at the expense of **13c**, exactly as predicted (Figure 17).[25d,32] It is interesting to note that the ^{13}C-label eventually finds its way to every position on the rim of acenaphthylene, but it never migrates to the hub position.[28]

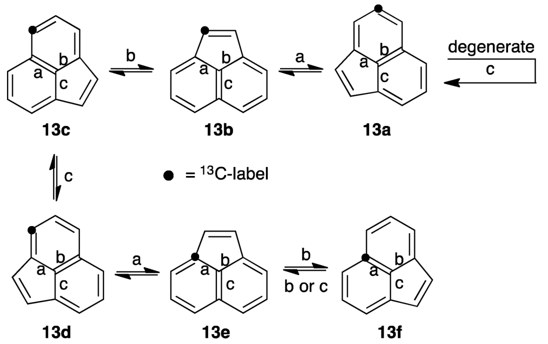


Figure 17. Homomerization of ^{13}C-labeled acenaphthylenes (**13**).[25d,31,32] The experimental results are in complete accord with the mechanism shown in Figure 16. For each step, a 1,2-shift of hydrogen to the bridgehead position precedes a 1,2-shift in the opposite direction of one of the spoke bonds connecting the hub to the rim (labeled a−c).

As an alternative to incorporating a ^{13}C-label into acenaphthylene (**13**), benzannulation can also be used to reveal this invisible reaction (Figure 18). Thus, FVP of aceanthrylene (**14**) gives acephenanthrylene (**15**); independent FVP of fluoranthene (**16**) likewise gives acephenanthrylene (**15**); and FVP of acephenanthrylene (**15**) gives both aceanthrylene (**14**) and fluoranthene (**16**).[25d,33]

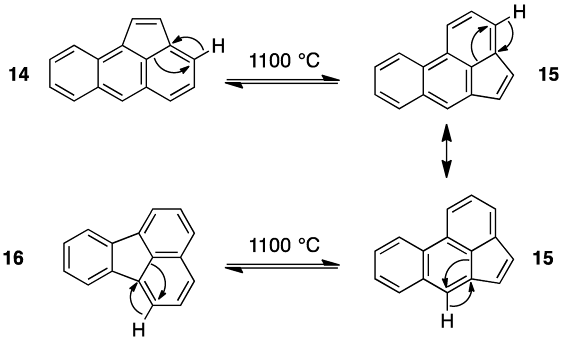


Figure 18. Thermal interconversions of aceanthrylene (**14**), acephenanthrylene (**15**), and fluoranthene (**16**).[25d,33]

The rearrangements in Figures 15−17 can be viewed conceptually as transpositions of 5- and 6-membered rings within the polycyclic frameworks of aromatic hydrocarbons ("5/6-ring switching"). Such transpositions are believed to play a key role in the thermodynamically driven "annealing" of fullerenes under the conditions of their random formation at high temperatures in the gas phase. The so-called "Stone−Wales rearrangement," proposed explicitly as a pathway for interconverting isomers of fullerenes (Figure 19),[34] is really just a special case of the 5/6-ring switching process discovered in our laboratory.

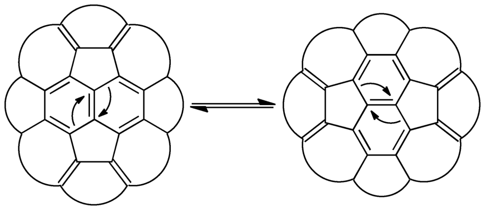
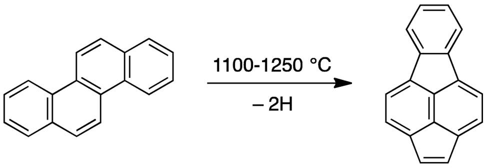


Figure 19. Stone−Wales rearrangement.[34]

Other Unprecedented Thermal Reactions. During the course of our studies on the FVP of polycyclic aromatic hydrocarbons and their ^{13}C-labeled counterparts, we periodically encountered unexpected reactions, such as the one shown in Figure 20.[28]



17 **18**

Figure 20. Thermal conversion of $C_{18}H_{12}$ chrysene (**17**) to $C_{18}H_{10}$ acefluoranthrylene (**18**).[28]

The intriguing aspects of this transformation include the permanent destruction of one benzene ring, the net loss of H_2, the creation of two new 5-membered rings, and the formation of a ring system that maps directly onto that of C_{60}. We soon discovered that other polyarenes having one or more "bay regions" suffer reactions with all these same characteristics at high temperatures (Figure 21).[23d,f,28] This thermal chemistry appears to be universal among polyarenes that have bay regions.

Experiments designed to elucidate the mechanism of this prevalent transformation, including multiple ^{13}C-labeling studies, all point to a pathway that begins with cyclodehydrogenation at the bay region, to form a reactive 4-membered ring intermediate, as shown for phenanthrene in Figure 22.[23d,f,28,35] Two C−H bonds must be broken, and one new C−C bond must be formed in the cyclodehydrogenation step, but we do not know the order of those events or whether any of them might occur in concert. The subsequent 4/6- and 5/6-ring switching steps, on the other hand, seem quite reasonable, each occurring stepwise, with a 1,2-shift of a hydrogen preceding the 1,2-shift of carbon.

In other mechanistic and reaction discovery work, we found evidence for [1,*n*]shifts of hydrogen atoms in aryl radicals (*n* = 2, 3, 4, and 5)[36] and for the migration of ethynyl groups between *peri*-positions on adjacent benzene rings in a polyarene;[37] interested readers will find more details on these and other high-temperature transformations in the relevant original publications.[2b,5d,23f,38]

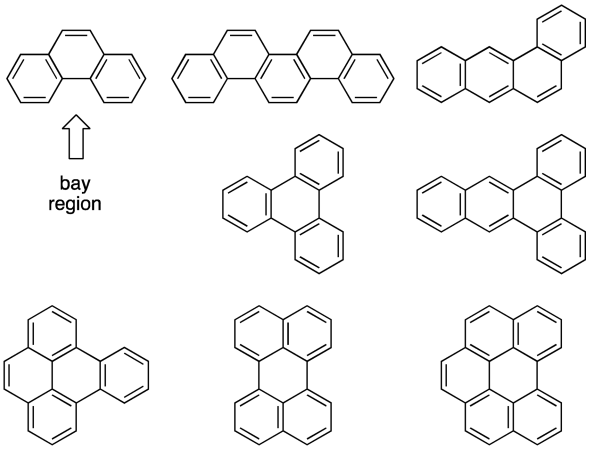


Figure 21. Other polyarenes having "bay regions" that suffer transformations similar to that shown for chrysene in Figure 20.[23d,f,28]

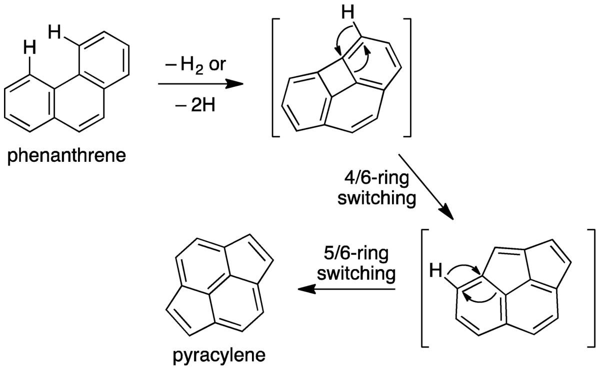


Figure 22. Mechanism believed to account for the conversion of bay region polyarenes into fullerene substructures at high temperatures, illustrated by the conversion of phenanthrene to pyracylene.[35]

■ RATIONAL ORGANIC SYNTHESIS AT 1000 °C

How It Began. When I first heard that C_{60} had been detected in fuel-rich flames, I was stunned.[39] Most organic chemists are familiar with the soot-producing flames that result from burning benzene (or even methane) with insufficient oxygen to cleanly convert the hydrocarbon all to CO_2, but how could C_{60} be formed in such flames? Clearly, many intermolecular C−C bond-forming reactions would be required in order to build up structures that contain 60 carbon atoms. Furthermore, many 5-membered rings and 6-membered rings would also have to be formed by intramolecular C−C bond-forming reactions, and many, many hydrogen atoms would have to be lost.

As I puzzled over this enigma, it dawned on me that all of the steps necessary for the formation of C_{60} in fuel-rich flames were well-precedented in gas-phase pyrolysis chemistry! The dimerization of benzene to form biphenyl at high temperatures in the gas phase had been known since the middle 1800s (Figure 23).[40] Considering this prototype, it was not difficult to imagine how terphenyls, tetraphenyls, and polyphenyls might be built up by multiple iterations of the same process. As for the intramolecular C−C bond-forming reactions, we had encountered (actually, rediscovered) various thermal cyclization reactions of phenyl-substituted arenes in our own laboratory that produced new 5- and 6-membered rings under FVP conditions (Figure 23).[41]

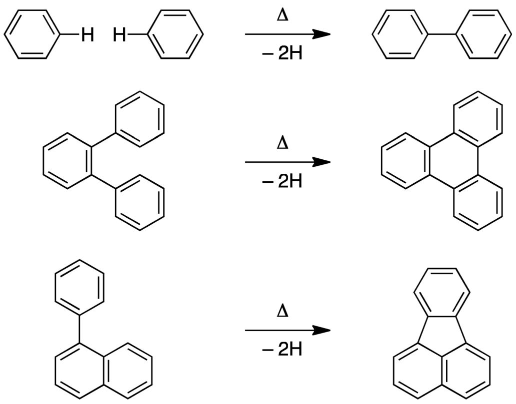


Figure 23. Known intermolecular and intramolecular C−C bond-forming reactions of the sort that might be involved in the production of C_{60} from benzene in fuel-rich flames.[40,41]

Each of the three C−C bond-forming reaction types illustrated in Figure 23 involves the loss of two hydrogen atoms. At the high temperatures in flames and in FVP experiments, the entropic cost of linking two polyatomic molecules together ($T\Delta S < 0$) is more than offset by the entropic gain of releasing two hydrogen atoms, and cyclization reactions that release two hydrogen atoms are even more favorable energetically ($\Delta G = \Delta H - T\Delta S$).

What about the strain energy of C_{60}? What pays the price of more than 500 kcal/mol for pyramidalizing all of those trigonal carbon atoms that prefer planar geometries? Again, the energetics of gas-phase organic reactions at high temperatures provide the answer. Out-of-plane deformations represent basic fundamental vibrational modes of polyarenes, and the amplitudes of these modes are accentuated at high temperatures, so the bending is a natural motion. As long as the C−C bond-forming reactions that constrain the bent structure are exergonic ($\Delta H - T\Delta S = \Delta G < 0$), the excess energy can be captured as additional strain energy in the growing geodesic polyarene.

Thus was born the idea that we might be able to harness the unique attributes of high temperature chemistry in the gas phase to develop a rational, stepwise synthesis of C_{60} using FVP to "stitch up" a relatively strain-free 60-carbon synthetic precursor. Retrosynthetic analysis of the C_{60} target quickly led us to the quasiplanar ring system **19** (Figure 24). With more than 150 years of organic chemistry to draw from, we had no doubt that this ring system could be synthesized. The transformation of a planar PAH into a geodesic polyarene by FVP, on the other hand, had never been reported before.

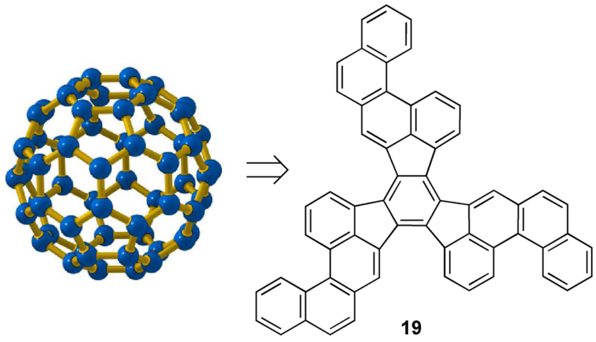


Figure 24. Retrosynthetic analysis of C_{60} leads to the relatively strain-free, quasiplanar, 60-carbon synthetic precursor **19**.

Corannulene and Other Bowl-Shaped Polyarenes.

Rather than dive directly into a synthesis of **19**, we thought it prudent first to test the hypothesis that FVP could be used to generate geodesic polyarenes from planar PAHs. The obvious "practice compound" was corannulene (**3**), the minimum subunit of C_{60} that retains the geodesic curvature of the fullerene ball. In fact, corannulene (**3**) was already a known hydrocarbon, having been synthesized (and named) by Richard Lawton and Wayne Barth almost 20 years prior to the discovery of C_{60}.[42] The high melting point of corannulene (268−269 °C, without decomposition)[42] encouraged us to speculate that corannulene might survive FVP temperatures, and we were delighted to learn that it does. FVP of 7,10-diethynylfluoranthene at 1000 °C gives corannulene (Figure 3).[3] Subsequent refinements and optimization of this route eventually shortened it to a three-step gram-scale synthesis of corannulene (**3**).[3b,43,44]

The attentive reader will have noticed that the cyclization reactions shown in Figure 3 do not release any hydrogen atoms; the starting material and product are both $C_{20}H_{10}$ hydrocarbons. Thus, the overall reaction is an isomerization, and therefore, it does not owe its success to any favorable entropic effects at high temperatures. In this case, the gain of two strong $(sp^2)C-(sp^2)C$ bonds and two additional aromatic rings far outweighs the loss of two relatively weak acetylenic π-bonds and the trade-off of two strong $(sp)C-H$ bonds for two weaker $(sp^2)C-H$ bonds. At the B3LYP/6-31G(d,p) level of theory, the isomerization shown in Figure 3 is exothermic ($\Delta H_{rxn} < 0$) by 68 kcal/mol (see the Supporting Information).

The isomerization in Figure 3 was originally conceived as a thermal process involving vinylidiene intermediates that insert into C−H bonds on the lower portion of the fluoranthene core (Figure 25). The reversible 1,2-shift of hydrogen atoms in terminal alkynes to generate reactive vinylidenes is known as the Roger Brown rearrangement and occurs at temperatures well below 1000 °C.[7,45]

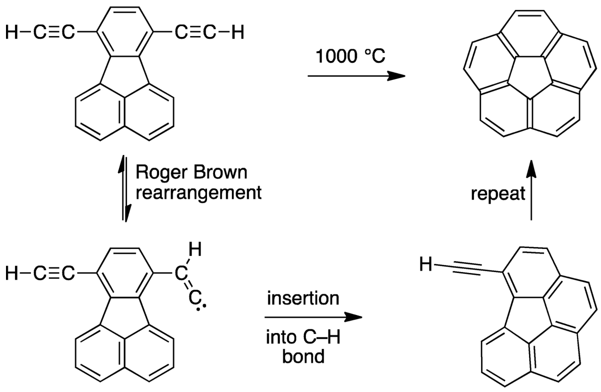


Figure 25. Mechanism for the isomerization shown in Figure 3 is believed to involve two Roger Brown rearrangements.[7,45]

In the spirit of full disclosure, I must confess that we also attempted to prepare 1,6-diazacorannulene (**20**) by an analogous FVP procedure (Figure 26), but that synthesis failed completely.[43e] At every temperature we tried, starting material was recovered, and no cyclization reactions were seen. Subsequent calculations revealed the folly of these experiments; at the B3LYP/6-31G(d,p) level of theory, the isomerization shown in Figure 26 is actually *endothermic* ($\Delta H_{rxn} > 0$) by 18 kcal/mol (see the Supporting Information). The lower aromaticity of pyridine rings, compared to that of benzene

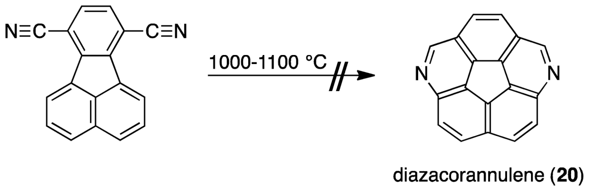


Figure 26. Unsuccessful attempts to prepare 1,6-diazacorannulene (**20**) by an FVP route analogous to that for the synthesis of corannulene (**3**, Figure 3).[43e]

rings,[46] undoubtedly diminishes the driving force for these cyclizations. To make the situation worse, both π-bonds of nitriles are quite strong, unlike the π-bonds of acetylenes,[47] and that disfavors the cyclization reactions proposed in Figure 26 even further.

Nevertheless, our success with the synthesis of corannulene (**3**, Figure 3) started us down a path that led to the synthesis of more than two dozen larger geodesic polyarenes by FVP (Figure 27).[28,36f,38i,43e,48] Other research groups also adopted this methodology, and their contributions have been summarized, together with those from my laboratory, in a comprehensive publication in *Chemical Reviews*.[49]

Early in the course of this work, we learned the importance of strategically incorporating chlorine or bromine substituents, in place of hydrogen atoms, at the sites where we hoped to form new C−C bonds.[48] The C−Cl and C−Br bonds in such synthetic intermediates are weaker than all of the C−H and C−C bonds in the molecules,[50] which makes them the most vulnerable to homolytic cleavage at temperatures in the range of 1000 °C. The resulting aryl radicals are then able to add to the π-systems of remote benzene rings, thereby closing additional cycles. Figure 28 shows one example of this principle.[48g,i]

This lesson taught us that hydrocarbon **19** itself would probably be a poor precursor for the synthesis of C_{60} by FVP

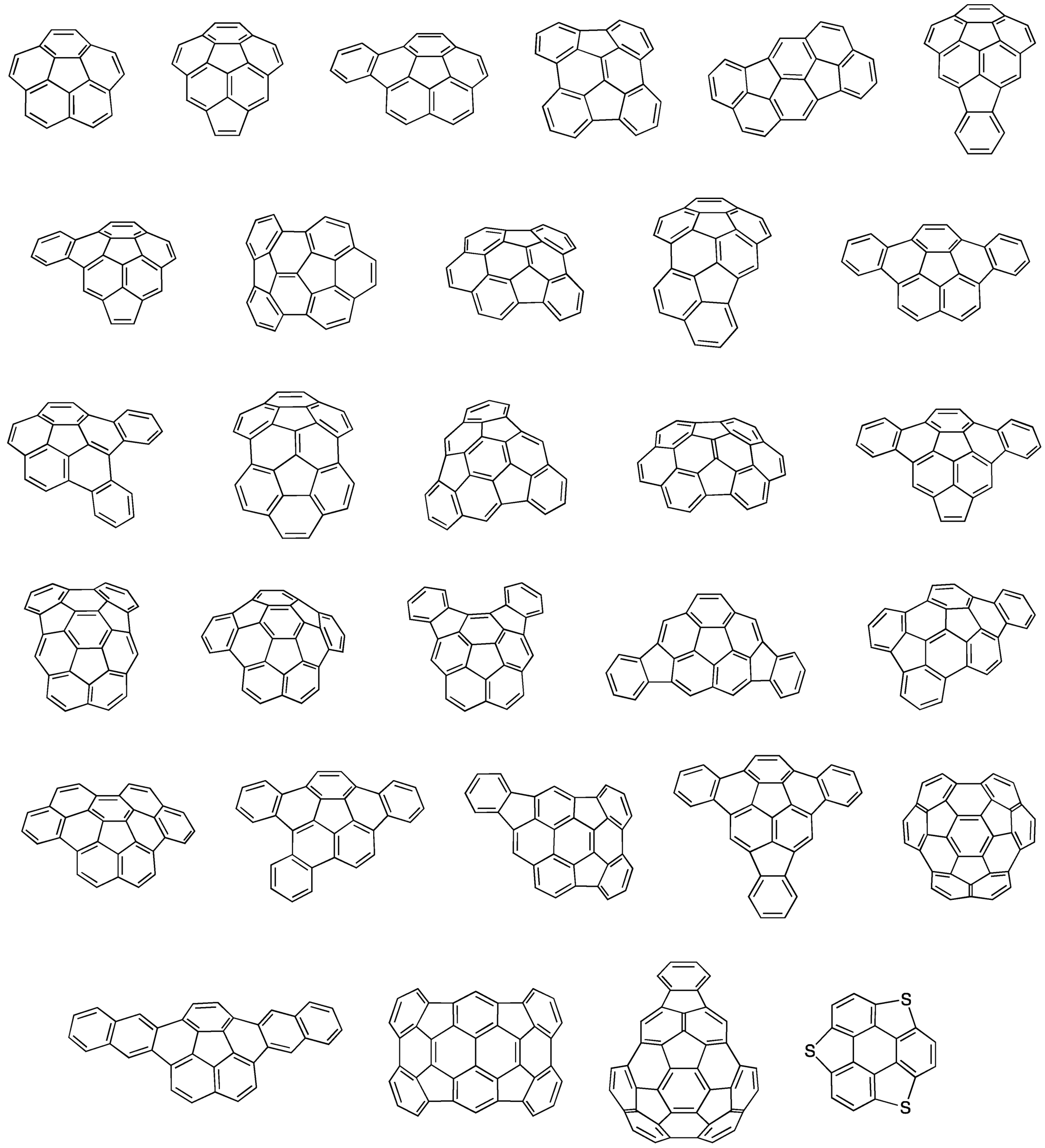


Figure 27. Geodesic polyarenes synthesized by FVP as summarized in ref 49.

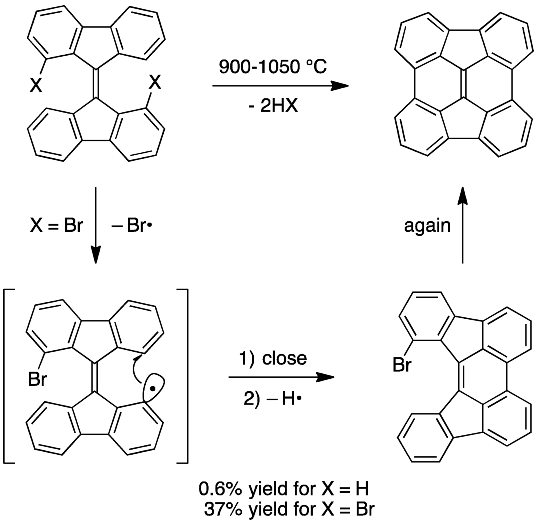


Figure 28. Strategically placed halogen atoms typically improve the yields of geodesic polyarenes synthesized by FVP by 10- to 50-fold, compared to FVP of the corresponding unfunctionalized hydrocarbon.[48g,i]

without the incorporation of some halogen atoms. A bit later, we learned that aryl radicals can actually rearrange by 1,2-shifts of hydrogen atoms at temperatures in the range of 1000 °C,[36a,b] and that meant we could reap the benefits of incorporating chlorine or bromine substituents even if they were one position away from the site of the intended C−C bond formation (e.g., Figure 29).[48]

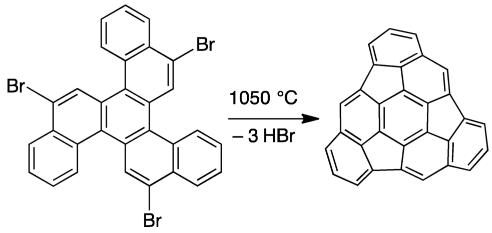


Figure 29. Ability of aryl radicals to rearrange by 1,2-shifts of hydrogen atoms at high temperatures[36a,b] makes it unnecessary to incorporate halogen substituents (radical precursors) at highly hindered positions to promote cyclization reactions.[48]

We also discovered that once the introduction of curvature begins in a developing geodesic polyarene, thermal cyclodehydrogenations become easier, and additional 5- and 6-membered rings will form spontaneously, even without the help of a strategically placed halogen (e.g., Figure 30).[36e]

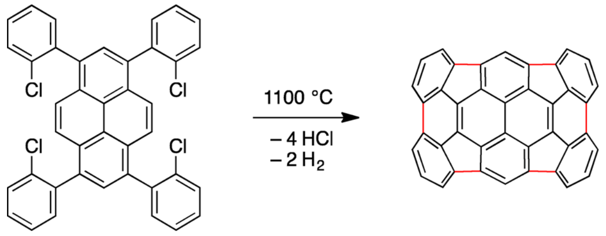


Figure 30. Six new C−C bonds are formed in this geodesic polyarene synthesis, even though the FVP precursor contained only four radical-generating chlorine substituents. Spontaneous thermal cyclodehydrogenations gave the two new 6-membered rings.[36e]

Rational Synthesis of C_{60}. Reveling in all our success at making new geodesic polyarenes, I lost track of our original objective, until one day when Meg Boorum, a graduate student in my laboratory, spoke up and asked, "Why are we still making bowls? Why don't we synthesize C_{60}, now that we know all the rules of FVP chemistry that we need?" She was right, of course, and we immediately began putting together a quasiplanar 60-carbon molecule with the same skeleton as the one shown in Figure 24. Rather than attempt to close up the naked hydrocarbon (**19**) by brute force, however, Meg put three chlorine atoms at positions strategically chosen to introduce the initial curvature, taking advantage of the ability of aryl radicals to rearrange by 1,2-shifts of hydrogen atoms at high temperatures. We were hopeful that spontaneous thermal cyclodehydrogenations would continue the process of stitching up the three seams of the developing ball and give all the remaining 5- and 6-membered rings.

Meg's synthesis of our C_{60} precursor required 11 steps, and the 12th step was the FVP. Subliming such a heavy organic molecule (MW > 850 Da) into the gas phase and getting it through a hot quartz tube, however, was quite challenging with the apparatus we had been using. Fortunately, my long-time collaborator, Armin de Meijere, in Göttingen, Germany,[51] had inherited an excellent vacuum system with a high capacity vacuum pump. One of his graduate students, Hermann Wegner, had just spent a year in my laboratory, and when Hermann returned to Göttingen, he set up an FVP system there using Professor de Meijere's high-capacity vacuum pump. Meg sent her $C_{60}H_{27}Cl_3$ compound (**21**) to Göttingen. Hermann ran the FVP there and succeeded in detecting C_{60} in the crude pyrolysate by HPLC, which showed a peak at the same retention time as authentic C_{60}. Furthermore, the diode array UV detector on his HPLC gave a UV spectrum matching that of authentic C_{60}. Hermann sent the crude product back to us in Boston, and we ran the HPLC again, this time collecting the C_{60} peak, together with the effluent that came out after that, where C_{70} and any higher fullerenes would emerge. After removal of the solvent, electrospray mass spectral analysis of the isolated product showed a prominent peak at m/z 720 for C_{60}. Importantly, we saw no peak at m/z 840 for C_{70} or any higher mass peaks for higher fullerenes. Our synthesis gave C_{60} as the only fullerene formed (Figure 31).[4]

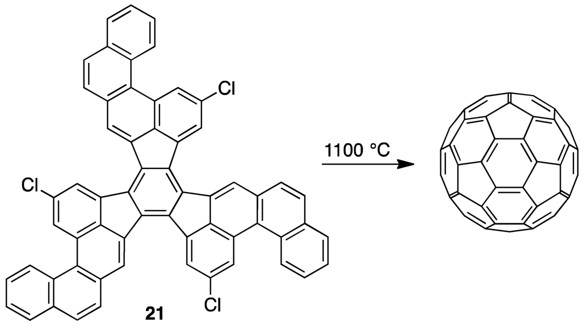


Figure 31. First size-specific synthesis of a fullerene in isolable amounts.[4]

The smidgen of C_{60} we synthesized in this manner proves that fullerenes can indeed be prepared in the laboratory in a targeted way, but it hardly represents a practical route to useful amounts of material. Other research groups have pushed this methodology toward targeted syntheses of higher fullerenes,[52] but the development of rational methods for the preparative-scale synthesis of isomerically pure fullerenes remains a daunting challenge for future generations of organic chemists.

Rational Synthesis of Uniform Carbon Nanotubes. The laboratory synthesis of single-index (*n*,*m*)carbon nanotubes (CNTs) likewise stands as one of the grand challenges in our era.[53] Semiconducting CNTs are characterized by a finite energy band gap between the valence band and the conduction band (i.e., the HOMO−LUMO gap), but the size of the gap varies according to the (*n*,*m*) indices of the nanotubes and drops to zero for some tubes, which gives them "metallic" conductivity properties.[54] Thus, some CNTs could serve as ultrathin molecular wires in nanoelectronic devices, whereas others should be ideal for applications as nanoscale alternatives to semiconducting silicon. Unfortunately, all known methods for preparing CNTs yield mixtures of tubes having different (*n*,*m*) indices.[55] Specific applications of CNTs in nanoscale electronics will require access to nanotubes with identical properties; however, no methods have yet been found that allow uniform, single-index CNTs to be separated from the available mixtures on a useful scale. How can scientists solve this dilemma?

We see this problem as a challenge for the synthetic organic chemistry community. When an organic synthesis works as it is designed to, it delivers molecules that are all identical, not mixtures of molecules that have many different structures. Why not synthesize single-index (*n*,*m*)carbon nanotubes "from the bottom up," instead of by uncontrollable empirical methods?

Our idea was to synthesize the hemispherical $C_{50}H_{10}$ hydrocarbon **22** and to use it as a template from which to "grow" pure (5,5)carbon nanotubes (Figure 32). The diameter and the (*n*,*m*) index of the resulting CNTs would be dictated, respectively, by the diameter of the template and the "armchair" structure of its rim.

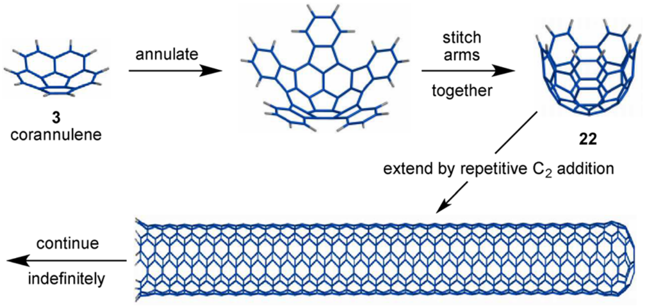


Figure 32. Proposed synthesis of pure (5,5)carbon nanotubes from a small hydrocarbon template (**22**).[56]

One can imagine elongating the CNT end-cap **22** by attaching it to a transition-metal nanoparticle of the sort commonly used to catalyze the growth of CNTs using traditional methods, but purely organic, noncatalytic methods can also be envisaged.[38g,56] The fact that individual CNTs have been grown by traditional methods to lengths of more than 20 cm (!)[57] underscores one of the most appealing aspects of this plan: If the CNT end-cap **22**, which is approximately 1 nm in length, could be elongated to a length of just 1 mm, that would correspond to an increase in size of 10^6, which means that 1 mg of **22** could yield up to 1 kg of pure (5,5)carbon nanotubes! This huge size amplification means that our synthesis of CNT end-cap **22** would need to provide only milligram amounts of material, and we were confident that we could accomplish that.

In the end, we succeeded in synthesizing intermediate **23** in just two steps from corannulene (**3**), and FVP of **23** gives milligram amounts of pure CNT end-cap **22** (characterized by X-ray crystallography, Figure 33).[5] Corannulene itself (**3**) is now available on a kilogram scale, thanks to the beautiful work of Jay Siegel,[44] and our synthesis of **23** is readily amenable to scale-up, so CNT end-cap **22** could be prepared in multigram quantities, in principle.

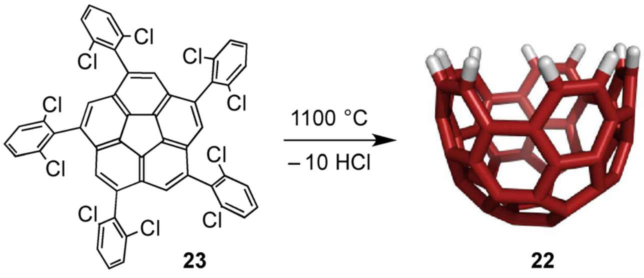


Figure 33. FVP synthesis of pure (5,5)carbon nanotube end-cap **22**.[5]

As of this writing, CNT end-cap **22** has not been elongated to full-length (5,5)CNTs. We are encouraged, however, by the recent growth of (6,6)CNTs from a 90-carbon end-cap that was generated in situ on a platinum metal surface from a quasiplanar precursor by surface-catalyzed cyclodehydrogenations.[58] The growth of single-index (*n*,*m*)carbon nanotubes in useful amounts from small hydrocarbon templates is not yet a solved problem, but it is a problem that can and will be solved by organic chemists.

Further Reading and Concluding Comments. Further examples of unusual chemistry at 1000 °C from our laboratory that were not presented in this Perspective are listed here with literature references for anyone interested in reading more about organic chemistry without reagents or catalysts at very high temperatures.

- The thermal conversion of triquinacene to azulene[2b,38a]
- An unusual ground-state di-π-methane rearrangement[38b]
- Experimental evidence against the occurrence of Stone−Wales rearrangements in ^{13}C-labeled pyracylene[28]
- Trapping aryl radicals with acetylene in the gas phase: experimental evidence for C_2-accretion as a mechanism for polycyclic aromatic hydrocarbon growth in flames[38c]
- Phenyl migrations in dehydroaromatic compounds: a new mechanistic link between alternant and nonalternant hydrocarbons at high temperatures[38d,i]
- 1,2-Shifts of phenyl and naphthyl groups in aryl radicals[36f]
- Thermal cyclodehydrogenations to form 6-membered rings: mechanistic studies on cyclizations of [5]-helicenes[38e,k]
- Aryl−aryl bond formation by flash vacuum pyrolysis of benzannulated thiopyrans[38f,j]
- Gas phase Diels−Alder cycloaddition of benzyne to an aromatic hydrocarbon bay region[38g,56f]
- Probing mechanisms of aryl−aryl bond cleavages under flash vacuum pyrolysis conditions[38h,k]

From an innocent curiosity about a thermal rearrangement reaction for which nobody has ever foreseen any possible application (Figure 1), a research program evolved that uncovered a host of unprecedented organic reactions, gave birth to dozens of geodesic polyarenes, and made early strides down the long road toward directed chemical syntheses of isomerically pure fullerenes and single-index (*n*,*m*)carbon nanotubes. The challenges that are timely today did not even exist when this program began, but channeling the research in directions of emerging opportunities has made the journey increasingly relevant while keeping the “fun” in fundamental.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02113.

B3LYP/6-31G(d,p) calculations for the starting materials and products shown in Figures 3 and 23 (PDF)

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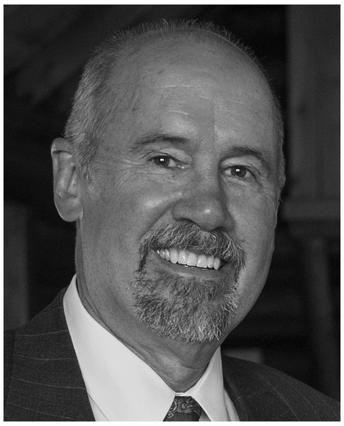
Notes

The author declares no competing financial interest.

Biography



Lawrence T. Scott grew up in Urbana, IL. He graduated from Princeton University in 1966 and earned his Ph.D. degree in 1970 at Harvard University under the direction of the late Professor R. B. Woodward. He then accepted an Assistant Professor position at the University of California, Los Angeles. In 1975, he moved to the University of Nevada, Reno and served as department chairman there from 1988 to 1991. In 1993, he moved to Boston College, where he held the Louise and Jim Vanderslice Chair in Chemistry until he retired in 2014 at the age of 70.

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