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Microwave Flash Pyrolysis

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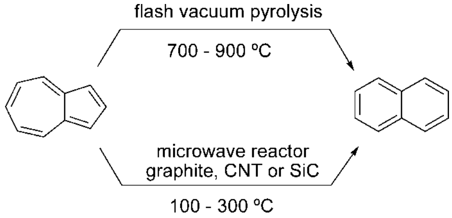

In a microwave reactor, graphite heats rapidly to high surface temperatures; applications of graphite thermal "sensitization" have been described previously. We report here that microwave thermal sensitization with graphite, carbon nanotubes, or silicon carbide can be used to carry out reactions more typically accomplished by flash vacuum pyrolysis (FVP) and which usually require temperatures much higher than the nominal limit of a microwave reactor. The graphite-sensitized microwave reaction of azulene in the solid phase at temperatures of 100 to 300 °C affords rapid rearrangement to naphthalene, a reaction typically observed by FVP at 700−900 °C. Multiwall carbon nanotubes give similar results when used as a thermal sensitizer. Other graphite-sensitized reactions that we have observed include the following: conversion of 2-ethynylbiphenyl to phenanthrene, fragmentation of phthalic anhydride to benzyne, cleavage of iodobenzene to phenyl radical, aryl−aryl bond cleavage, and a variety of cycloaromatizations. An advantage is seen for less volatile substrates. Rearrangement of azulene and generation of benzyne from phthalic anhydride have also been observed on powdered silicon carbide. Because of the high temperature, rapid heating, and frequent ejection of material from the irradiation zone, we refer to this general method as microwave flash pyrolysis (MFP).

Introduction

Microwave-assisted organic synthesis (MAOS) has advanced at a rapid pace during the past decade.[1−3] The scope of microwave reactions generally is limited by absorption characteristics of solvent, safety concerns, or the temperature range of commercial microwave reactors. Allotropes of carbon offer the potential for carrying out higher temperature processes in the solid phase. In a microwave oven, graphite[4] and carbon nanotubes[5−7] absorb radiation with high efficiency and heat rapidly to high surface temperatures. Applications of graphite as a thermal susceptor or "sensitizer" in microwave chemistry have been reviewed by Laporterie, who developed this method,[8] and more recently by Besson.[9] At present, few reported graphite sensitized reactions venture toward the more extreme regime of flash vacuum pyrolysis.[10−13] Some notable examples (Scheme 1) include the ene cyclization of citronellal (**1**),[14] "microwave assisted pyrolysis" of urea to give cyanuric acid (**2**),[15] and ketodecarboxylation of adipic acid (**3**).[16] There is also a growing body of literature on the generation of biofuels by sewage pyrolysis by using graphite as a microwave absorber.[17] Silicon

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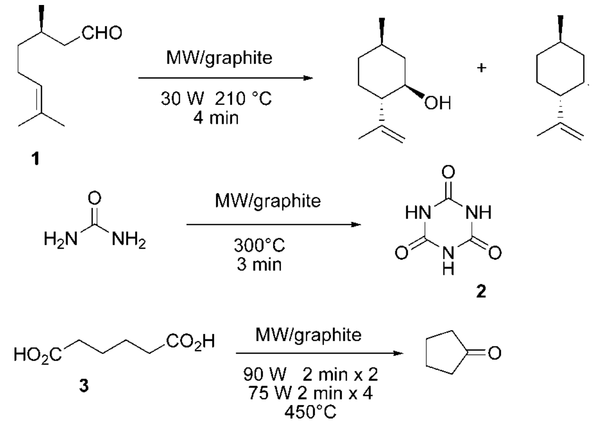
SCHEME 1. Microwave Reactions on Graphite



carbide absorbs efficiently and has been used as a "passive heating element" in microwave reactions.[18,19] In principle, powdered SiC might function like graphite as a sensitizer for high-temperature chemistry.

The potential for higher energy microwave chemistry is suggested by a variety of literature. Microwave irradiation has been used to exfoliate graphite[20] and graphite intercalation compounds.[21] Tour[5] and more recently Varma[6] have shown that in a microwave field, carbon nanotubes can undergo structural changes, glow, or even ignite in air. Clearly, the limits and preparative applications of chemistry under these extreme conditions bear further exploration. The question posed in the present work was whether many higher temperature reactions that have typically been accomplished by flash vacuum pyrolysis (FVP)[10-13] might be carried out in a microwave reactor through thermal sensitization with graphite or other substances. FVP reactions often generate radicals, arynes, and other reactive intermediates; thus, the chemical inertness of graphite is a further advantage. As our work progressed, silicon carbide emerged as another good candidate for a thermal sensitizer.[18,19]

We report here that with high power, solid-phase graphite or carbon nanotube sensitization extends the range of microwave reactions to include broad classes of high-energy processes. Powdered silicon carbide shows similar behavior but does not seem to reach as extreme temperatures. Because of the high temperature, rapid reaction, and frequent ejection of material from the heated reaction zone, we refer to this general method as microwave flash pyrolysis (MFP).

Methodology Development. Two general microwave methods were employed in this work. Additional details are provided in the Supporting Information. A CEM Discover reactor was used for all reactions. Substrates were mixed with graphite, carbon nanotubes, or silicon carbide by light grinding prior to reaction. Although some earlier studies employed precoating of graphite by solvent evaporation,[8,9] we prefer to avoid residual solvent impurities and find that reactants are rapidly redistributed during pyrolysis.

Our first method was "open vessel", i.e., ambient pressure, with mixtures of substrate and graphite irradiated under a nitrogen atmosphere with use of 100−300 W of power in quartz tubes for periods of 1−5 min. In general, higher power and temperatures differentiates our approach from earlier graphite-sensitized experiments.[8,9] A loose plug of glass wool above the graphite minimized ejection of material from the reaction zone. As noted earlier by Laporterie,[8] quartz glassware is desirable because of the potentially high surface temperatures. Sparks were seen occasionally during irradiation and a nitrogen atmosphere minimizes explosion hazards. Products were collected by rinsing the cooled reactor and graphite with several portions of solvent. The CEM microwave reactor uses an infrared sensor to limit temperatures to a default value of 300 °C; we did not modify this upper limit. Measurements of the graphite temperature with a thermocouple immediately after microwave irradiation showed temperatures only slightly above this limit. High initial power is essential; lower power microwave irradiation tends to cause more sublimation than chemical reaction.

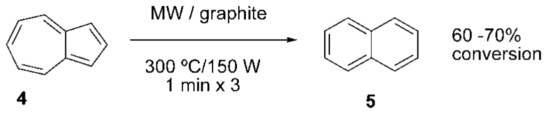
In a second "closed vessel" method, pyrolyses were carried out in 10 mL capped Pyrex tubes lined with a smaller quartz tube (12 × 70 mm; glassblower fabrication) and purged with nitrogen. The quartz insert minimizes thermal risk to the Pyrex tube and is commonly reusable. Reaction tubes were cooled prior to opening and products were isolated by rinsing the tube and graphite with $CDCl_3$. Samples were filtered and analyzed directly by NMR, TLC, or GC. Control experiments with pure graphite heated by microwave to 300 °C showed minimal pressure buildup from outgassing.

Under these high-power conditions, reaction tubes usually fill with aerosols, while solid product is deposited above the heated zone. Tubes may look charred but mass balances are good in most cases. MFP reactions are not stirred but most reactants are rapidly redistributed by vaporization. With their low density (<0.6 g/cm^3), graphite and nanotubes appear to undergo substantial agitation during reaction, while SiC (density 3.2 g/cm^3) does not.

Results and Discussion

Rearrangement of Azulene. We initially investigated the thermal isomerization of azulene (**4**) to naphthalene (**5**), a reaction first reported in 1947 by Heilbronner[22] and later studied in great detail by Scott,[23] Alder,[24] and Wentrup.[25] Vapor-phase rearrangement of **4** typically is carried out in the range of 700−900 °C. Barriers to unimolecular rearrangement of azulene have been estimated to be >80 kcal/mol.[24,26] Lower energy radical initiated processes are also likely.[24]

SCHEME 2. Azulene Thermal Rearrangement on Graphite



Microwave reaction of **4** on graphite was carried out both at atmospheric pressure and in sealed tubes, with similar results. Irradiation was conducted for one to three 1 min periods initially at 300 °C/150 W, interspersed with 1 min cooling periods. Following these reaction conditions, we observe 60−77% conversion of **4** to naphthalene (Scheme 2) as the sole product seen by NMR or GC. Limitations on conversion to product seem primarily due to sublimation of reactant out of the graphite hot zone.

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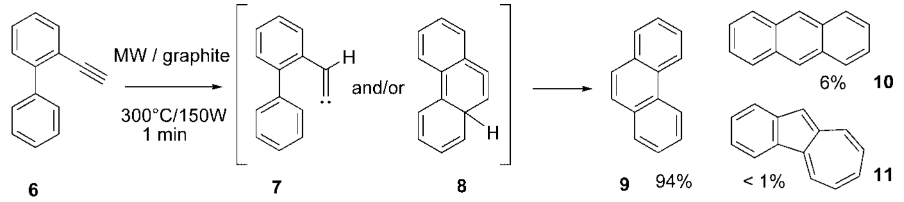
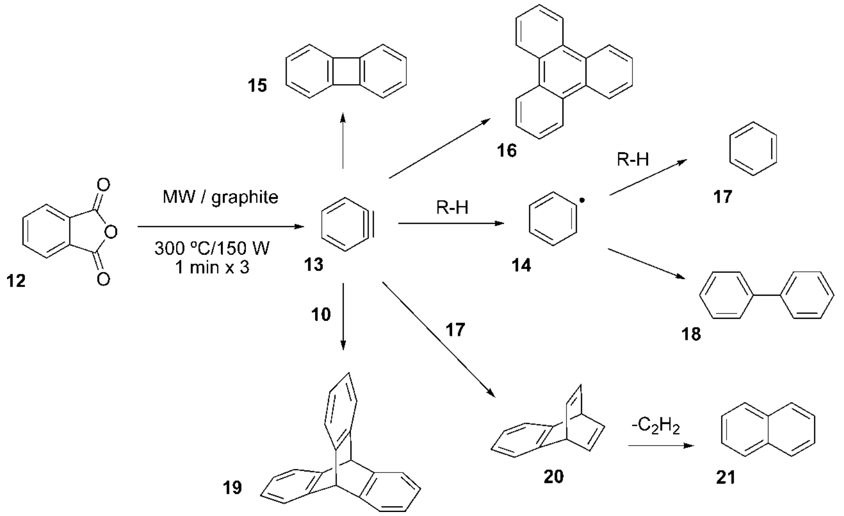
SCHEME 3. Thermal Rearrangement of 2-Ethynylbiphenyl on Graphite



SCHEME 4. Microwave Generation of Benzyne



Not surprisingly, a nearly identical reaction was observed when the graphite was replaced with inexpensive Baeyer multiwalled nanotubes (BayTubes). Amorphous carbon was less effective, giving only ca. 20% conversion under similar conditions. We conducted a series of sealed tube experiments on graphite in which the limiting temperature was stepped from 100 to 300 °C while maintaining the maximum power level at 200 W. At 100 °C, we still observed 34% conversion of **4** to **5** after only 1 min of irradiation. Control experiments showed that heating pure azulene under the same reaction conditions (150 W/300 °C) resulted only in sublimation of reactant to the upper part of the tube.

We briefly explored finely powdered silicon carbide[18,19] as a thermal sensitizer for **4**. Heating a mixture of azulene and silicon carbide for 1 min at 300 °C resulted in 16% conversion to naphthalene. The ramp time to maximum temperature was longer than with graphite, however, and most of the azulene sublimed out of the reaction zone.

Rearrangements of 2-Ethynylbiphenyl. FVP reaction of **6** (700 °C/0.01 Torr) has been reported by Brown and co-workers to give a mixture of phenanthrene (**9**) and benzazulene (**11**) in a ratio of 72:28.[27] These products (Scheme 3) may result from Brown rearrangement (1,2-H shift to vinylidene **7**)[12] although we have recently shown by computations that there is a competitive route to **9** passing through cyclic allene **8**.[28]

The reaction was carried out with graphite at 300 °C/150W maximum power in a closed vessel and the product mixture was analyzed directly by NMR. When pyrolyzed by MFP for only 1 min, ca. 80% of **6** was converted to products. The major products were phenanthrene (**9**) and anthracene (**10**) in a ratio of 94:6. Traces (<1%) of benzazulene **11** were seen by NMR. Anthracene was an unexpected product but is easily explained as a secondary product from **11**. Whittaker and Alder reported in 1975 that pyrolysis of **11** gives **9** and **10** in a 2.5:1 ratio.[29] Thus the initial reaction products apparently are **9** and **11**, with **10** a secondary product of **11**. This implies an initial product ratio (**9**: **11**) of ca. 85:15.

Generation of Benzyne from Phthalic Anhydride. In 1965, Fields and Meyerson reported evidence that benzyne is generated by FVP of phthalic anhydride.[30a] Other benzynes have been generated from anhydrides and similar precursors under similar conditions.[30,31] We can find only one published example of benzyne generation in a microwave reactor; this was carried out by base-promoted elimination.[32]

MFP reactions of phthalic anhydride (**12**) were carried out at atmospheric pressure or in sealed tubes, resulting in high conversions of starting material but only a modest mass balance. Sealed-tube reactions of **12** (with careful monitoring of pressure!) gave the best results. The product mixture (Scheme 4) consisted of unreacted **12** (34%), benzene (38%), biphenyl (**18**, 17%), naphthalene (**21**, 9%), biphenylene (**15**, 0.8%), and triphenylene (**16**, 0.5%). Addition of 1 equiv of anthracene to the mixture in open vessel experiments produced a low yield

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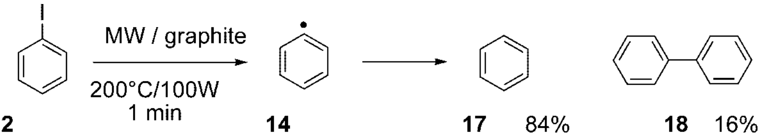
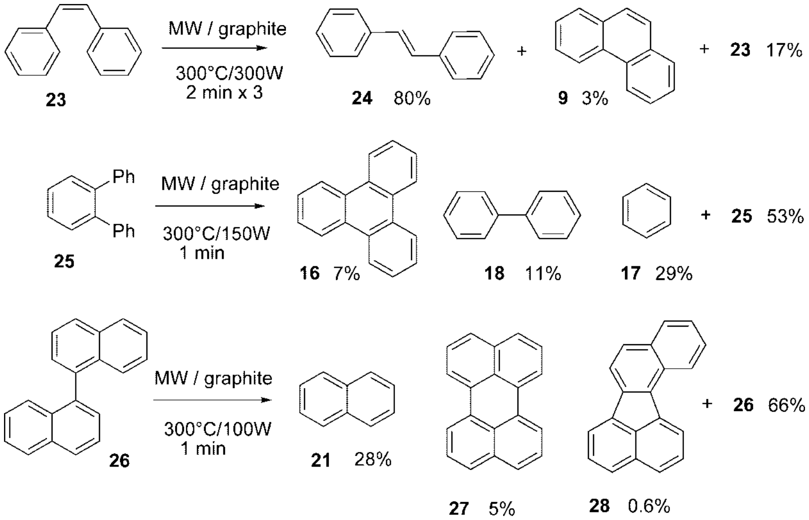
SCHEME 5. Aryl Iodide Cleavage on Graphite



SCHEME 6. Microwave Cycloaromatizations on Graphite



of trypticene (**19**), as seen by NMR. These observations support the intermediacy of *o*-benzyne (**13**), presumably formed through loss of CO and CO_2 from **12**. Hydrogen abstraction leads to phenyl radical (**14**) and then **18** through dimerization. Although metal-catalyzed trimerization of benzyne is well-known,[33] thermal trimerization is rare.[30] This suggests a high concentration of reactive intermediates, consistent with the rapid reaction we observe. Naphthalene is likely to be a secondary product arising from cycloreversion of benzobarrelene (**20**), itself formed from cycloaddition of **13** and **17**. This sequence was noted earlier from pyrolysis of benzyne precursors in benzene.[34] We found that graphite-sensitized pyrolysis of benzobarrelene (**20**)[35] under similar conditions yielded naphthalene.

Again, we briefly explored replacing graphite with powdered silicon carbide. With use of comparable reaction parameters, the SiC + **12** mixture heated more slowly but the same collection of products appeared in similar ratios, including **15**–**18** and **21**. The similarity of product distributions observed with graphite and SiC suggests that the source of hydrogen atoms in these experiments must be other molecules of substrate. This would also explain the poor mass balances.

Aryl Iodide Cleavage to Aryl Radicals. Aryl iodides undergo facile thermal homolysis[36] thus a direct MFP route to phenyl radical is the pyrolysis of iodobenzene (**22**). In a sealed tube, this reaction proceeded smoothly (82% conversion), affording (Scheme 5) benzene and biphenyl in a ratio of 84:16. Molecular iodine is also generated in these reactions as judged by the deep purple coloration of the reaction mixture. As noted above, hydrogen atoms are likely to derive from other molecules of substrate.

Cycloaromatizations. Gas phase pyrolysis of aromatic compounds often yields highly complex mixtures in which rings are broken, formed, rearranged, or joined together.[37] Polycyclic aromatic ring synthesis has been widely studied because of its relationship to soot formation in combustion chemistry.[38,39] This is also a critical area of materials science where many high-temperature cycloaromatizations have been described.[10,40,41]

We have carried out a series of model cycloaromatization reactions (Scheme 6). Stilbenes are known to cyclize under FVP conditions, although cis–trans isomerization is clearly faster.[42,43] MFP reaction of *cis*-stilbene (**23**) on graphite afforded primarily cis–trans isomerization to **24**, with only a low yield of **9**. Similar results occurred with stereoisomer **24**. Better success was observed with pyrolysis of *o*-terphenyl (**25**) on graphite, which gave 7–15% efficiency in cyclization to **16**. Sealed tube pyrolyses of **25** showed that biphenyl and benzene are the major reaction products. As expected, 1,1′-binaphthyl (**26**) cyclized in both directions to give **27** and **28**; unexpectedly, the major reaction product was naphthalene. Sublimation from the hot zone is a major limiting factor in these reactions.

Perhaps most astonishing is the observation that MFP of both **25** and **26** on graphite gives major products arising from cleavage of aryl–aryl bonds. Indeed, naphthalene is the major product from MFP of **26**. Aryl–aryl bonds have dissociation energies of >115 kcal/mol,[44] thus direct dissociation seems unlikely. Lower activation barriers have been reported for bond cleavage in biphenyl, with radical addition to the ipso carbon

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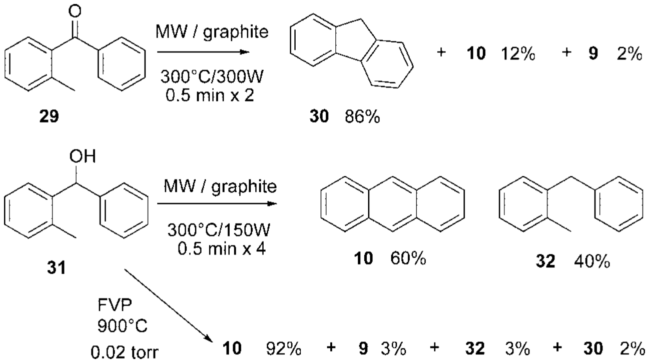
SCHEME 7. Elbs Cyclizations and Related Reactions



suggested as a mechanism.[45] Thus it is possible that radical processes are occurring in these MFP reactions.

We explored a variety of cycloaromatization reactions related to the Elbs cyclization, a venerable route to aromatic compounds.[46−48] Atmospheric pressure MFP reaction of 2-methylbenzophenone (**29**) on graphite (Scheme 7) afforded primarily fluorene (**30**) with smaller amounts of **10** and **9**; these products are consistent with earlier FVP results.[49] 2-Methybenzhydrol (**31**) cyclized more smoothly to **10**, presumably through initial loss of water, but also yielded **32**, from homolytic cleavage. Flash vacuum pyrolysis of **31** has not been reported previously and was explored for comparison; we find efficient conversion to anthracene and suggest this may be a useful route to some types of aromatic compounds.

Mechanism of Thermally Sensitized Pyrolysis. How can azulene rearrange at a bulk temperature of 100 °C in a 1 min reaction? There has been much discussion in the literature of thermal vs. nonthermal microwave effects.[50−53] The azulene (**4**) isomerization to naphthalene (**5**) may be an ideal reaction for studying unusual effects in microwave chemistry. As suggested previously for urea pyrolysis on graphite,[15] we believe our results with azulene provide compelling evidence for the existence of localized heating ("hot spots") created by a combination of microwave absorption by the sensitizer and polarity of the substrate. Reaction may be localized just inside the tube because deep penetration of strongly absorbing solid materials is unlikely. Hot spots have been observed to form and grow in microwave irradiation of other solid materials.[54−56] Cleavage of phthalic anhydride to benzyne and the apparent secondary reaction of benzazulene **11** provide additional examples of polar substances reacting rapidly while nonpolar reactants such as *o*-terphenyl (**24**) undergo less efficient reaction.

Conclusions

Graphite-sensitized microwave reactions were first developed by Laporterie and co-workers.[8] Many types of graphite-sensitized chemistry have been reported earlier,[8,9,14−16] but the upper limits of this method remained to be explored. We have found that with higher initial power, graphite sensitization extends easily to reactions that have previously been accomplished at high temperature (>500 °C) by flash vacuum pyrolysis[10−13] even though the bulk graphite temperature remains much lower. Formation of surface "hot spots" seems the most likely explanation for our results, but much further study is required to understand processes in these extreme regions of microwave chemistry.

Microwave flash pyrolysis experiments use no solvents or expensive reagents, can be run in minutes, apply readily to nonvolatile substrates—an advantage over FVP methods in some cases—and appear to generate high concentrations of reactive intermediates. This technique is rapid and simple but requires quartz glassware and careful attention to safety concerns. In general, results are similar to other methods for thermal reactions but novel chemistry has been observed in some cases.

Graphite clearly is not unique as a thermal sensitizer but may provide the best combination of properties and economy. Solid phase reaction on carbon nanotubes yielded similar chemistry but nanotubes are less inert and more expensive than graphite. Powdered silicon carbide offers another alternative. We were able to effect rearrangement of azulene and generation of benzyne from phthalic anhydride on silicon carbide and suggest that this inert solid deserves further exploration, not just as a "passive heating element"[18,19] but as a high-temperature thermal sensitizer.

We have developed a simple method for small-scale closed-vessel microwave pyrolysis, but caution that such reactions should be carried out under inert atmosphere and with careful monitoring of pressure. In our closed-vessel pyrolytic method, *all* reaction products are captured in the reaction tube. This clearly has preparative applications where volatile products are created. Additionally, this method is ideal for reactions requiring headspace analysis and may be useful in analytical method development where decomposition of samples is desirable.

Solid phase thermal sensitization with graphite, carbon nanotubes, silicon carbide—and almost certainly other substances yet to be explored—greatly extends the range of chemistry that can be accomplished in a common microwave reactor. We are continuing to explore novel applications of this simple technique.

Experimental Section

Caution! Graphite, carbon nanotubes and silicon carbide heat rapidly in a microwave field, generating high surface temperatures and occasional sparks. **To minimize explosion hazards, thermally sensitized experiments should be conducted in quartz glassware under nitrogen.** An external explosion shield is recommended for open vessel experiments. For closed-vessel experiments, the pressure should be monitored closely; tubes may hold residual pressure after cooling.

Product analyses were carried out by a combination of 400 MHz ^{1}H NMR, TLC, or GCMS. Representative NMR spectra are reproduced in the Supporting Information. Unless otherwise stated, quoted percentages represent product ratios not absolute yields.

Pyrolysis of Azulene on Graphite: Closed Vessel. Azulene (20 mg, 0.16 mmol) and graphite (50 mg; Aldrich synthetic graphite, 20 μm) were mixed with a mortar and pestle and transferred to a quartz tube (12 × 70 mm). A small plug of glass wool was placed

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above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. The reaction was run "closed vessel" in a CEM Discover reactor at 300 °C/150 W for 1 min hold time. Product was isolated by washing the cooled tube with small volumes of $CDCl_3$ and filtering through neutral alumina. Analysis by 400 MHz ^{1}H NMR showed the mixture to be 35% azulene and 65% naphthalene.

Pyrolysis of Azulene on Graphite: Open Vessel. To a quartz test tube (25 × 200 mm) were added 1.00 g of graphite and 40 mg (0.31 mmol) of powdered azulene. The tube was mixed well, purged with nitrogen, sealed with a rubber septum, and vented to a nitrogen line. The mixture was heated by microwave for 1 min (hold time) at 150 W/ 300 °C, then cooled for 2 min. The same heating process was repeated twice more. After cooling, the tube was rinsed several times with hexane. The solution was filtered through neutral alumina, eluting with hexane. The eluate (250 mL) was concentrated to yield 32.5 mg (81% mass recovery) of blue solid. NMR and GC analysis showed the product to be 23% of azulene and 77% of naphthalene.

Pyrolysis of Azulene on Silicon Carbide: Closed Vessel. Azulene (20 mg, 0.16 mmol) and silicon carbide (500 mg; Alfa Aesar, 2 μm powder, alpha-phase) were ground lightly together and transferred to a quartz tube (12 × 70 mm). Reaction was run "closed vessel" as above at 300 °C/150 W for a 2 min hold time. Blue solid sublimed into the upper part of the tube. NMR analysis of the product showed 84% azulene and 16% naphthalene.

Pyrolysis of 2-Ethynylbiphenyl on Graphite: Closed Vessel. 2-Ethynylbiphenyl[27] (**6**, 23 mg, 0.13 mmol) and graphite (68 mg) were mixed and pyrolyzed as above. NMR analysis showed ca. 90% conversion to products, with formation of phenanthrene (**9**) and anthracene (**10**) (ratio 17:1), as well as traces (<1%) of benzazulene **11** and several unidentified products.

Pyrolysis of Phthalic Anhydride on Graphite: Closed Vessel. Phthalic anhydride (**12**, 27 mg, 0.18 mmol) and graphite (100 mg) were mixed with a mortar and pestle and pyrolyzed as above at 200 °C/100 W for 1 min. Product analysis by NMR showed the following composition: phthalic anhydride (34%), benzene (38%), biphenyl (17%), naphthalene (9%), biphenylene (0.8%), triphenylene, (0.5%).

Pyrolysis of Phthalic Anhydride on Silicon Carbide: Closed Vessel. Phthalic anhydride (**12,** 27 mg, 0.18 mmol) and silicon carbide (100 mg) were mixed with a mortar and pestle and pyrolyzed as above at 200 °C/100 W for 1 min. Products were isolated by washing the quartz tube with small volumes of $CDCl_3$ and filtering through neutral alumina directly into an NMR tube. Analysis by NMR showed the following composition: phthalic anhydride (26%), benzene (45%), biphenyl (21%), naphthalene (7%), biphenylene (1.2%), and triphenylene, (0.5%).

Pyrolysis of *o*-Terphenyl on Graphite: Closed Vessel. *o*-Terphenyl (**25**, 23 mg, 0.010 mmol) and graphite (80 mg) were mixed with a mortar and pestle and pyrolyzed as above at 300 °C/150 W for 1 min. Products were isolated by washing the tube with small volumes of $CDCl_3$ and filtering through neutral alumina directly into an NMR tube. NMR analysis showed the mixture to be composed of starting material (53%), triphenylene (7%), biphenyl (11%), and benzene (29%).

Pyrolysis of 1,1′-Binaphthyl on Graphite: Closed Vessel. 1,1′-Binaphthyl (**26**, 25 mg, 0.100 mmol) and graphite (100 mg) were mixed with a mortar and pestle and pyrolyzed as above at 300 °C/100 W for 1 min. Product analysis by NMR showed the following: 1,1′-binaphthyl (**26**, 77%), perylene (**27**, 5%), naphthalene (27.5%), and benzo[*j*]fluoranthene (**28**, 0.6%).[57]

Pyrolysis of 2-Methylbenzophenone on Graphite: Open Vessel. To a quartz test tube (25 × 200 mm) were added 1.0 g of graphite and 300 mg (1.53 mmol) of 2-methylbenzophenone (**29**). The tube was stirred well and an additional 1.0 g of graphite was added on top. The tube was purged with nitrogen, sealed with a rubber septum, vented by needle to a nitrogen line, and heated in the microwave for 30 s at 300 W/300 °C, then cooled for 2 min. This cycle was repeated. After cooling, the product was isolated to yield 170 mg (57% mass recovery) of yellow oil. No starting material remained. NMR analysis showed fluorene (86%), anthracene (12%), and phenanthrene (2%).

Flash Vacuum Pyrolysis of 2-Methylbenzhydrol. 2-Methylbenzhydrol (**31,** 100 mg, 0.507 mmol) was subjected to flash vacuum pyrolysis by flow through a quartz reaction tube maintained at 900 °C and 0.02 Torr. The product (59 mg, 66%) was obtained within 5 min. NMR analysis showed no starting material. GC and NMR analysis showed anthracene (91.6%) along with phenanthrene (3.1%), fluorene (**30**, 2.2%), and 2-benzyltoluene (**32**, 3.1%). Pyrolysis at 700 °C and 0.02 Torr yielded similar products but only ca. 30% conversion.

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Supporting Information Available: General procedures, additional experimental descriptions, and NMR spectra of product mixtures for microwave flash pyrolysis reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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