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# Trapping Aryl Radicals with Acetylene: Evidence for $C_2$-Accretion as a Mechanism for Polycyclic Aromatic Hydrocarbon Growth[1]

Atena Necula and Lawrence T. Scott*

*Department of Chemistry*
*Merkert Chemistry Center, Boston College*
*Chestnut Hill, Massachusetts 02467-3860*

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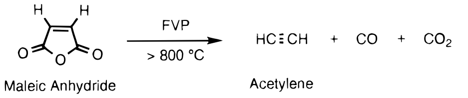
The formation of polycyclic aromatic hydrocarbons (PAH),[2] fullerenes,[3] soot,[2,4] and other carbonaceous materials during the combustion or pyrolysis of low-molecular weight hydrocarbons requires, at a minimum, that small molecules and/or reactive intermediates somehow become joined to make larger ones. Most likely, more than one type of intermolecular C−C bond-forming reaction plays a role. The accretion of $C_2$-units has long been considered a probable pathway for the stepwise growth of PAH in flames,[5] but evidence also points to the operation of bimolecular processes in which both partners can be relatively large.[6] The experiments reported here address the former paradigm and provide clear support for a specific $C_2$-accretion pathway in which the key C−C bond-forming step involves the simple trapping of aryl radicals by acetylene ($C_2H_2$), both of which are abundant species in flames.[4,5]

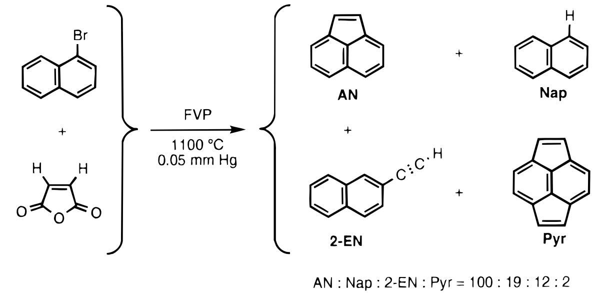
Flash vacuum pyrolysis (FVP) of aryl bromides is known to generate transient aryl radicals in the gas phase (eq 1).[7] Under the same conditions, maleic anhydride decomposes very cleanly to acetylene, carbon monoxide, and carbon dioxide (eq 2).[8] Thus, co-pyrolysis of aryl bromides with a large molar excess of maleic anhydride provides a convenient and relatively safe means of producing aryl radicals in an acetylene-rich environment.

$$\mathrm{Ar{-}Br} \xrightarrow[> 800\ °\mathrm{C}]{\mathrm{FVP}} \mathrm{Ar}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}: \qquad (1)$$

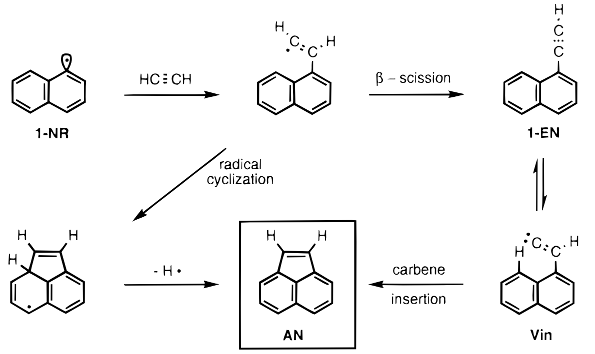


(2)

**Scheme 1**



**Scheme 2**



Co-pyrolysis of 1-bromonaphthalene ($C_{10}H_7Br$) and maleic anhydride in a flow system at 1100 °C/0.05 mmHg[9] gives acenaphthylene (**AN**, $C_{12}H_8$) as the dominant product, accompanied by minor amounts of naphthalene (**Nap**, $C_{10}H_8$) and 2-ethynylnaphthalene (**2-EN**, $C_{12}H_8$), plus traces of pyracylene (**Pyr**, $C_{14}H_8$), in a ratio of approximately 100:19:12:2[10] (Scheme 1). A material balance of 75−80% was achieved, and no starting material survived. In a control experiment, co-pyrolysis of unsubstituted naphthalene ($C_{10}H_8$) and maleic anhydride under the same conditions gave almost entirely recovered naphthalene and only insignificant amounts of the products shown in Scheme 1.

The major product (**AN**) obtained from the reaction in Scheme 1 results from the efficient trapping of the 1-naphthyl radical (**1-NR**) by acetylene. Two distinct routes to **AN** can be envisaged from the vinyl radical formed in the intermolecular C−C bond-forming step: (1) direct radical cyclization followed by rearomatization and (2) $\beta$-scission followed by cyclization of the resulting 1-ethynylnaphthalene (**1-EN**) (Scheme 2). Isotopic-labeling studies (discussed below) argue against the former mechanism but are compatible with the latter. Thermal cyclization of **1-EN** to **AN** has been known for many years[11] and is believed to occur by way of a vinylidene intermediate (**Vin**),[12] although a concerted alternative has been proposed.[13] The great exothermicity of the **1-EN** → **AN** isomerization[13] accounts for the absence of any **1-EN** in the product mixture.[14]

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[9] For a detailed description of the apparatus and the procedure, see: Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744.

[10] The product ratios, normalized to a relative value of 100 for the dominant product, were determined by integration of the $^1$H NMR spectra of the crude pyrolysates; errors are estimated to be ±5%.

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[14] In cases where no further isomerization is possible, the arylacetylene survives, e.g., copyrolysis of bromobenzene and maleic anhydride at 1100 °C gives phenyl acetylene and benzene as the only significant products. The volatility of these two hydrocarbons precluded an accurate determination of their relative abundances in our apparatus.

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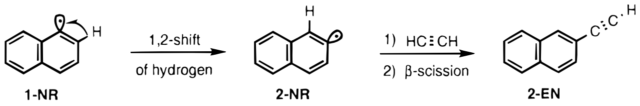
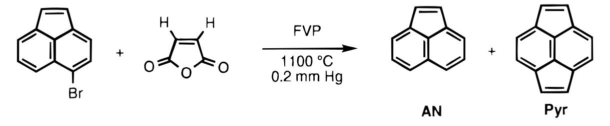
**Scheme 3**



**Scheme 4**



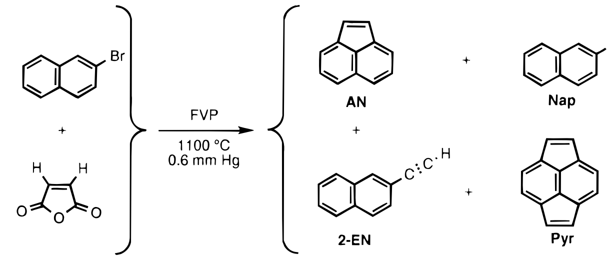
AN : Pyr = 100 : 50

Naphthalene (**Nap**), the second most abundant product obtained from the 1-naphthyl radical (**1-NR**), can be readily explained by the abstraction of hydrogen atoms from other organic species in the gas phase or on the walls of the pyrolysis tube. Hydrogen atom abstraction represents a common fate of aryl radicals at high temperatures in the gas phase.[15,16]

The 2-ethynylnaphthalene (**2-EN**) obtained from co-pyrolysis of 1-bromonaphthalene and maleic anhydride (Scheme 1) presumably arises by a 1,2-shift of hydrogen and trapping of the 2-naphthyl radical (**2-NR**) with acetylene, followed by $\beta$-scission (Scheme 3). The alternative pathway involving migration of the ethynyl group[17] (**1-EN** → **2-EN**) can be ruled out, since FVP of 1-ethynylnaphthalene (**1-EN**) at 1100 °C gives only acenaphthylene (**AN**) and does not lead to 2-ethynylnaphthalene (**2-EN**).[18] The 1,2-shift of hydrogen atoms in aryl radicals, on the other hand, although observed only recently for the first time,[16] is probably a universal reaction of aryl radicals in the gas phase at high temperatures. Evidence for the same 1,2-shift of hydrogen in the reverse direction is described below (**2-NR** → **1-NR**).

Pyracylene (**Pyr**), though only a minor product from the co-pyrolysis of 1-bromonaphthalene and maleic anhydride (Scheme 1), is noteworthy in that it reveals a process whereby *two* molecules of acetylene are captured. We are reluctant to speculate about the details of such a minor pathway (**1-NR** → **Pyr**) but can report that the co-pyrolysis of 5-bromoacenaphthylene ($C_{12}H_7$-Br) and maleic anhydride in a flow system at 1100 °C/0.2 mmHg[9] gives acenaphthylene (**AN**, $C_{12}H_8$) and pyracylene (**Pyr**, $C_{14}H_8$) in a ratio of approximately 100:50[10] (Scheme 4). The pyracylene (**Pyr**) in this reaction is probably formed by way of 5-ethynylacenaphthylene.[19] Co-pyrolysis of underivatized acenaphthylene (**AN**) with maleic anhydride under the same conditions gives no more than traces of pyracylene.

**Scheme 5**



AN : 2-EN : Nap : Pyr = 100 : 87 : 16 : 2

Co-pyrolysis of 2-bromonaphthalene ($C_{10}H_7Br$) and maleic anhydride in a flow system at 1100 °C/0.6 mmHg[9] gives acenaphthylene (**AN**, $C_{12}H_8$) again as the major product, accompanied by comparable amounts of 2-ethynylnaphthalene (**2-EN**, $C_{12}H_8$), lesser quantities of naphthalene (**Nap**, $C_{10}H_8$), and traces of pyracylene (**Pyr**, $C_{14}H_8$), in a ratio of approximately 100:87:16:2[10] (material balance 70−80%) (Scheme 5). At 975 °C, the product ratio changed to approximately 100:69:0:0, and at 850 °C, only starting material was recovered.

The large amount of **AN** formed in this pyrolysis indicates that the 1,2-shift of hydrogen depicted in Scheme 3 must be reversible, although a portion of the “rearrangement product” (**AN)** in this case probably does come from ethynyl group migration.[18] It is also apparent that complete equilibration was not achieved under our conditions prior to trapping of the aryl radicals with acetylene, since the ratio of the trapping products from the 1- and 2-naphthyl radicals (**AN**:**2-EN**) varies in the expected way as a function of which radical is formed first (compare Schemes 1 and 5).

To shed light on the relative importance of the two competing mechanistic pathways illustrated in Scheme 2, we repeated the co-pyrolysis of 1-bromonaphthalene with maleic anhydride using maleic anhydride-$d_2$. The direct cyclization pathway should lead to retention of both deuterium atoms in the acenaphthylene formed, whereas the $\beta$-scission pathway should give acenaphthylene in which only one deuterium atom from the $D{-}C{\equiv}C{-}D$ is retained (see Scheme 2). To suppress the known thermal automerization of acenaphthylene,[20] the experiment with maleic anhydride-$d_2$ was conducted at 1000 °C (material balance 80−85%).

$^1$H NMR analysis of the product mixture obtained from co-pyrolysis of 1-bromonaphthalene with anhydride-$d_2$ reveals that the signal for the hydrogens on the bridge of acenaphthylene does not disappear completely, as would be required by the direct cyclization mechanism (Scheme 2), but is reduced by only 50%, as expected from the $\beta$-scission pathway (Scheme 2).

From these experiments, we conclude that direct cyclization of a vinyl radical must be too slow to compete with $\beta$-scission to any significant extent under our conditions. The main steps in the $C_2$-growth mechanism, then, are (1) capture of acetylene by an aryl radical, (2) rapid $\beta$-scission of the vinyl radical to an ethynyl-PAH, and (3) subsequent cyclization[12,13] or migration of the ethynyl group[17] (e.g., Scheme 2). This pathway for $C_2$-accretion is far more favorable under our conditions than any direct reaction of an intact PAH with acetylene.

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(18) In the absence of more facile competing reactions, ethynyl group migration does occur on the naphthalene ring system: FVP of 2-ethynylnaphthalene (1100 °C, 0.2 mmHg) gives a 2:1 mixture of acenaphthylene and starting material, presumably by the sequence **2-EN** → **1-EN** → **AN**.

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