Some Developments in the High Temperature Gas Phase Chemistry of Alkynes, Arynes and Aryl Radicals

Roger F. C. Brown[a][+]

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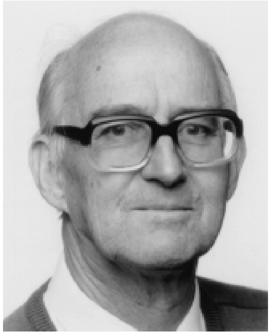
The discovery of the equilibration of alkynes with ylidenecarbenes at high temperatures has been followed by increasing use of the reactivity of such carbenes in the synthesis of polycyclic aromatic hydrocarbons. This has led to simple and elegant syntheses of fullerene fragments, and of cyclopenta-fused hydrocarbons. The related high-temperature equilibration of arynes with ring-contracted exocyclic carbenes has provided a further pathway for the transformation of polycyclic aromatic systems into less accessible cyclopenta-fused hydrocarbons. Some recent developments in the chemistry of aryl radicals have extended the scope of radical approaches to the synthesis of polycyclic hydrocarbons.

Introduction

Interest in the application of flash vacuum pyrolysis (FVP) to moderately complex organic compounds developed in a number of laboratories around the world in the mid-1960s. The work of the Monash pyrolytic group was begun at the Australian National University, and the first full paper[1] described the generation of benzyne by FVP of indantrione. Much of the early Monash pyrolytic chemistry (1968−1974) involved heterocyclic compounds, whereas the present account describes the discovery after 1972 of some key reactions which have recently been used by other groups to quite remarkable effect in the pyrolytic synthesis of polycyclic hydrocarbons, including fullerene fragments. Such chemistry involves pyrolytic reactions of acetylenes, and of precursors of arynes and aryl radicals. The coverage of recent pyrolytic chemistry is selective rather than exhaustive; in many cases examples have been chosen to fit the theme of development from earlier work rather than for their intrinsic importance.

Acetylenes and Methylenecarbenes

Our involvement with acetylenic chemistry began with our interest in the generation of cumulenones such as propadienone, $CH_2=C=C=O$, which were not then known (1972). Pyrolysis of the condensation product of benzaldehyde and Meldrum's acid (unlabelled **1**) at 430 °C generated the cumulenone (unlabelled **2**) but at 560 °C decarbonylation to the carbene occurred and phenylacetylene was formed.[2] The labelled precursor **1** at 560 °C yielded the phenylacetylene isotopomers **3** and **4** (75:25) (Scheme 1) and FVP of the single isotopomer **3** at 700 °C gave a 50:50 mixture of **3** and **4**.[2] Evidently acetylenes and methylenecarbenes, $R_2C=C$:, could equilibrate at high temperatures.



Roger Brown was born in Sydney in 1931. His B.Sc. Honours and Masters degrees from the University of Sydney were supervised by G. K. Hughes and E. Ritchie. He moved to Cambridge for his Ph.D. (1958) with V. M. Clark and Lord Todd, and spent a postdoctoral year in 1959–60 with George Büchi at M.I.T. His first teaching appointment in 1961 was to the Department of Chemistry, S.G.S., Australian National University. In 1968 he was appointed to a Readership at Monash University, and was awarded a Personal Chair from 1992 until his retirement in 1996. The main thrust of his research has been in pyrolytic chemistry, and he is the author of a standard monograph, "Pyrolytic Methods in Organic Chemistry" (1980), but he has also worked extensively in heterocyclic chemistry, and on synthesis.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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[a] Department of Chemistry, Monash University,
Clayton, Victoria 3168, Australia
[+] Present address: School of Chemistry, University of Melbourne,
Parkville, Vic. 3052, Australia
Fax: (internat.) +61-3/9347-5180
E-mail: r.brown@chemistry.unimelb.edu.au

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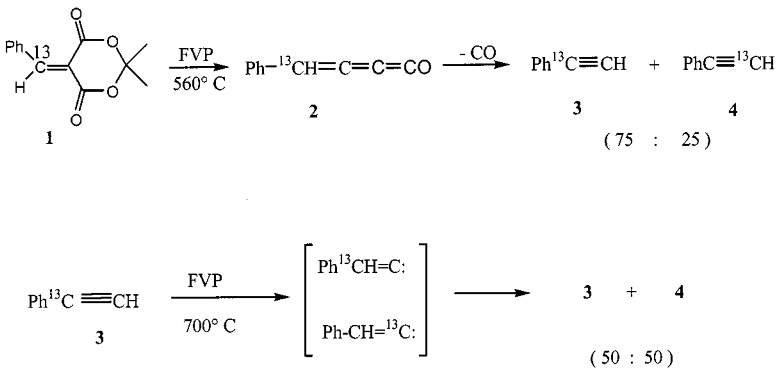


Scheme 1. Equilibration of acetylenes and methylenecarbenes

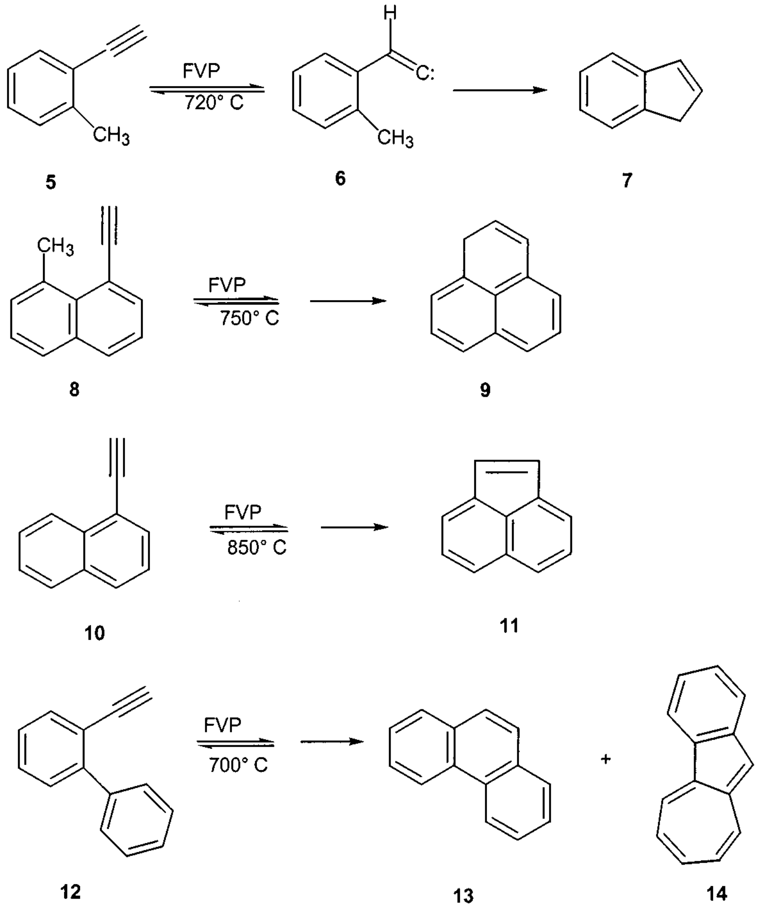
The synthetic potential became evident when it was found that this equilibration was shown by a range of acetylenes, from the labelled parent system HC = 1^{3}CD[3] to cycloalkynes[4] and various arylacetylenes. Generation of a carbene adjacent to a substituent bearing C−H bonds offered the possibility of synthetically useful insertion reactions, and this was confirmed by the behaviour of *o*-tolylacetylene **5**, which at 720°C formed indene **7** (75%) via the carbene **6**.[2] 1-Ethynyl-8-methylnaphthalene **(8)** at 750°C yielded phenalene **9** (ca 50%) by similar insertion to form a six-membered ring.[5] Pyrolysis of 1-ethynylnaphthalene **(10)** led to carbene insertion into an aromatic C−H bond with formation of acenaphthylene (**11**, 80%).[5] The pyrolysis of 2-ethynylbiphenyl **(12)** (or of the equivalent derivative of Meldrum's acid) afforded the mechanistically ambiguous apparent insertion product phenanthrene (**13**, 72%) and also 1,2-benzazulene (**14**, 28%), a product formed from an addition of the carbene to the 1′,2′ bond of the biphenyl system.[2] In Scheme 2 below the intermediate carbene is shown only for the first case.

These four reactions indicate the scope of the carbene cyclizations which have been used in a great many syntheses of higher, frequently cyclopenta-fused, polycyclic hydrocarbons. These syntheses have often required the initial preparation of bis-ethynyl hydrocarbons but, although such compounds are synthetically accessible, they tend to behave poorly on FVP because of decomposition to nonvolatile materials on attempted sublimation. This problem becomes acute with increasing size of the system. Thus Scott and Warren[6] successfully used 1,5-diethynylnaphthalene **(15)** as a pyrolytic precursor of pyracylene **16**, and at Monash we made 9,10-diethynylphenanthrene **(17)** and on FVP obtained cyclopent[*hi*]acephenanthrylene **(18)** in 43% yield, but with 50% formation of involatile residue.[7] Finally, 6,12-diethynylchrysene **(19)** oligomerized completely on attempted sublimation for FVP.[8]

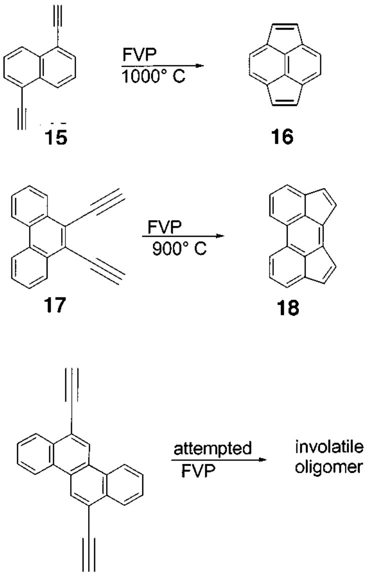
The solution to this difficulty has been to use precursors of the type Ar−CX=CH_2 which, on FVP, lose HX to give the required ethynylarene in the gas phase. Such groups are much more robust at sublimation temperatures and large multiply-substituted systems can be handled; for example, the problem of oligomerization of **19** was solved by FVP of the corresponding bis(1-chlorovinyl) compound.[8] In a pioneering approach to the construction of fullerene fragments, Scott's group in 1991 announced a spectacular synthesis of corannulene **23** by FVP of 7,10-diethynylfluoranthene **(20)** or, better, of the bis-2,2-dibromovinyl compound **21**.[9] In the full paper (1997)[10] compound **22** was described and the 1-chorovinyl group was used as a pyrolytic source of the ethynyl group; the yield of the bowl-shaped hydrocarbon **23** rose to 35−40%. Two extensions of this approach to cyclopentacorannulene **25** (from **24**)[11] and to a semibuckminsterfullerene $C_{30}H_{12}$, **(27)** (from **26**),[12] shown in Scheme 4, are due to Rabideau's group. Most workers in this field now use the 1-chlorovinyl group as an ethynyl group precursor, but Liu and Rabideau[13] have pointed out that hindered methyl ketones may fail to give 1-chlorovinyl compounds on treatment with PCl_5, and that the corresponding trimethylsilyl enol ethers, prepared with Me_3SiCl/LDA, are effective pyrolytic precursors. For a detailed account of synthetic strategies aimed at fullerene fragments and, ultimately, fullerenes see the review by Mehta.[14]

Secondary Reactions and Rearrangements

Because so many pyrolytic hydrocarbon syntheses are carried out at very high temperatures (900−1200°C) the primary products expected from the foregoing account are often transformed through secondary reactions. A concise summary of their scope is given by Scott.[15] The two examples which follow illustrate several of these processes. Scott and Necula[16] attempted to generate the benzopyracylene **(29)** by FVP of the 9,10-, 1,5- and 1,4-bis(1-chlorovinyl) derivatives of anthracene. The latter compound could eliminate HCl to give the diethynyl anthracene **28** and this, by carbene rearrangement and insertion, would be expected to form the required benzopyracylene **(29)** unambiguously. FVP at 1100°C, however, gave no **29**; the products were instead the isomers **31** and **32** (Scheme 5). It is proposed[16] that breaking of a C−C bond in **29** (dotted line) occurs with extrusion of a carbene (deinsertion) to give **30** (in equilibrium with the corresponding ethynyl compound). Reinsertion of the carbene function of **30** into the left hand ring gives the observed cyclopent[*hi*]aceanthrylene **(31)**. The



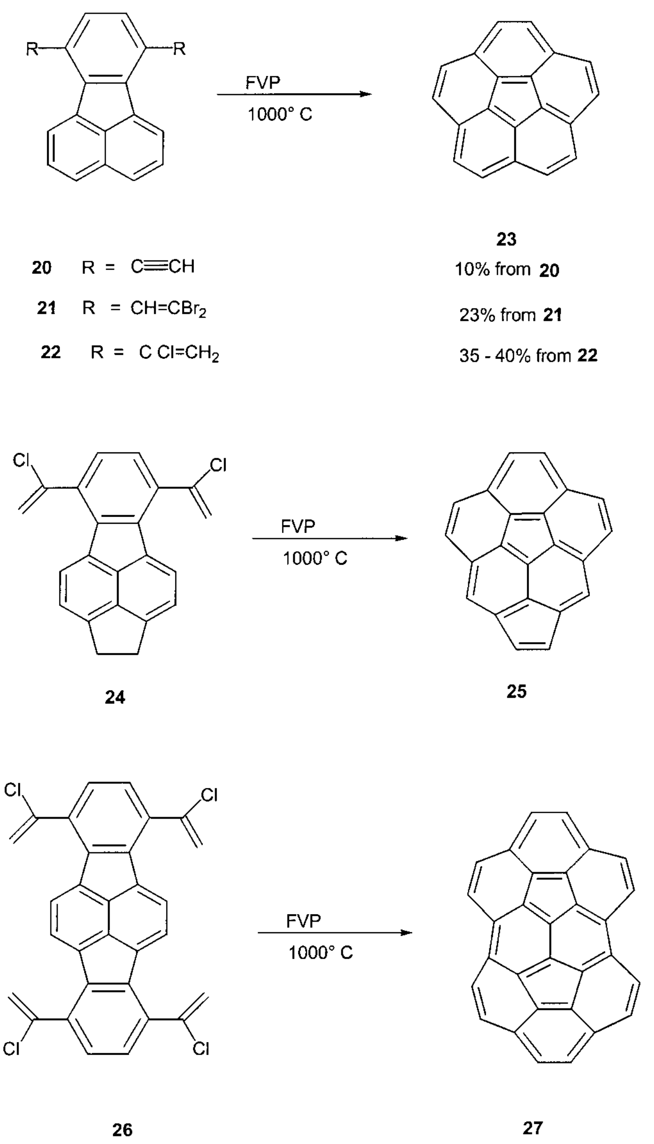
Scheme 2. Intramolecular trapping of methylenecarbenes



Scheme 3. Difficulty in sublimation/FVP of large bis(ethynyl) systems

key deinsertion reaction is favoured by the strain energy of the pyracylene system of **29**. The further isomerization of **31** to cyclopent[*hi*]acephenanthrylene **(32)** is an example of Scott's now well-known hydrogen-shift/benzene ring contraction[17][18] which interconverts five- and six-membered rings in cyclopentarenes, and which is also involved in the automerization of naphthalene.[19] The formation of **31** in two steps from the 1,5-bis(chlorovinyl) compound, and the isomerization of **31** to **32**, had previously been reported by Sarobe et al.[20] The type reaction of the H/6/5 rearrangement is the conversion of aceanthrylene to acephenanthrylene and, ultimately, to fluoranthene. This was originally studied by Scott's group by flow pyrolysis,[18] but the order of stability of these compounds has been changed by the FVP work of the Utrecht group and is supported by AM1 calculations.[21] Selectivity in the direction of H/6/5 rearrangements in polycyclic systems has been observed, and has been rationalised with the help of theoretical calculations.[22][23]

In the preceding example a C_2 substituent migrated from one ring to an adjacent ring, but the Jenneskens group has observed migration of an ethynyl group to an adjacent position in the same ring.[20] 8-Ethynylfluoranthene **(33)** cannot undergo direct isomerization/insertion to give a cyclopentarene, but on FVP at 1100−1200°C benzo[*ghi*]fluoranthene **35** was a significant product (12−17%). Another important reaction was loss of C_2 to give fluoranthene **34** (28−31%) although the nature of this process is uncertain. It is proposed[24] that ethynyl migration occurs by insertion of the



Scheme 4. Synthesis of corannulene and related systems by methylenecarbene insertions

carbene into the adjacent position, followed by the alternative deinsertion reaction of the cyclobutarene **36** (Scheme 6,dotted line) and insertion of the new carbene into the adjacent ring to form **35**. A similar reaction due to Necula and Scott[25] is the FVP of 2-ethynylnaphthalene at 1100°C to give some acenaphthylene, derived from 1-ethynylnaphthalene formed by ethynyl migration.

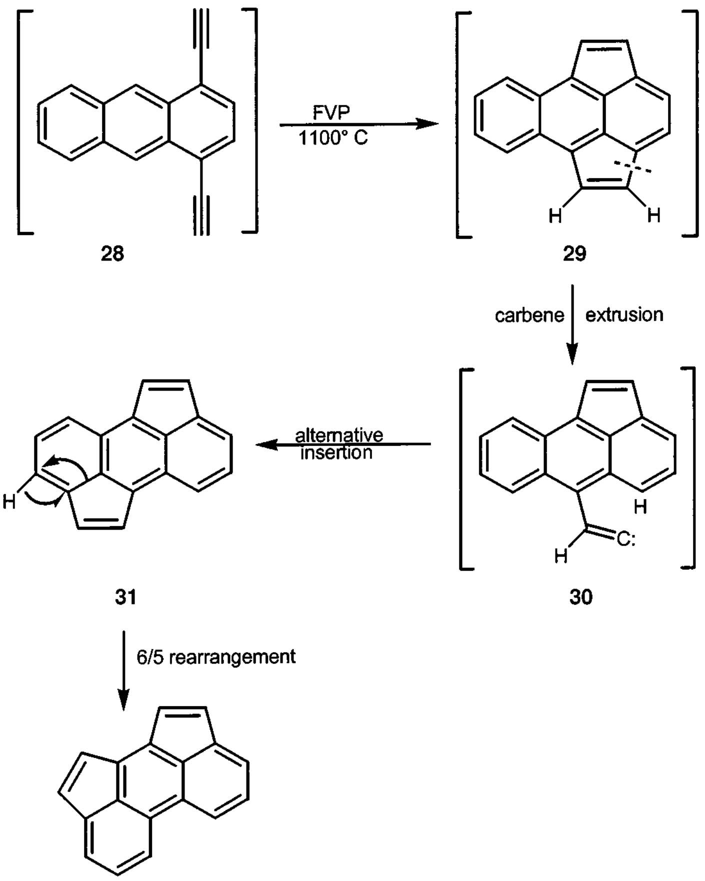
Sarobe et al.[26] have reported a very different mode of cyclization on FVP of 2,2′-diethynylbiphenyl (**37**). The expected consecutive insertions to give pyrene **41** were a minor process (< 5%); the major product was acephenanthrylene **40** (50% of pyrolysate at 900−1000°C) accompanied by fluoranthene formed by further 6/5 rearrangement, and some phenanthrene formed by loss of C_2. The pathway proposed involves initial cyclization to cyclobuta[*l*]phenanthrene **38**, deinsertion (dotted line on **38**) to give carbene **39**, and alternative insertion to form acephenanthrylene (**40**). The mechanism of the initial cyclization is uncertain, but relevant models are known.[27][28] The first stage in the production of the minor product pyrene **41** is formation of 4-ethynylphenanthrene, but pyrene can also be formed from 2- and 3-ethynylphenanthrene.[29] This is a further example of the migration of redundant ethynyl substituents to a position where both carbene formation and insertion into another ring can occur.

High Temperature Chemistry of Arynes

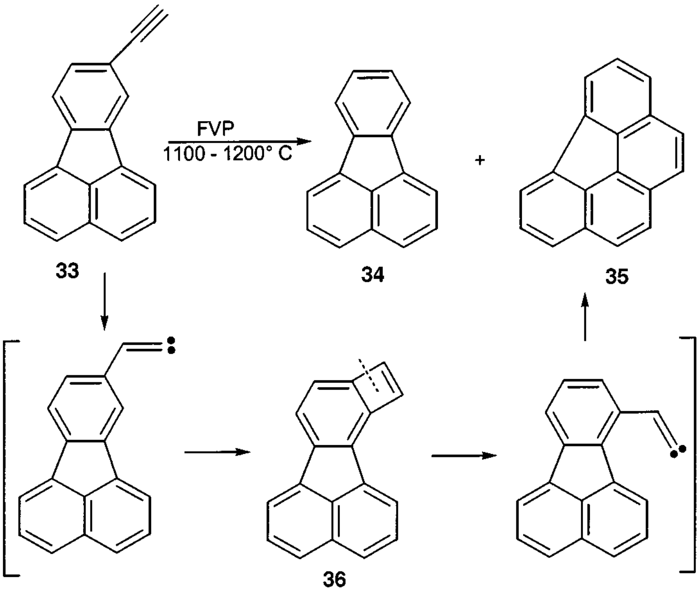
In the early 1980s we realised that the acetylene−methylenecarbene equilibration should also be shown at high temperatures by benzyne and other arynes, considered as bent acetylenes. In the case of the benzyne precursors indantrione[1] and phthalic anhydride[30] the decomposition temperatures were already in a range which might lead to equilibration of benzyne with an exocyclic carbene. Our initial approach was to look for scrambling of ^{13}C labels in biphenylene formed from high-temperature benzyne, and later we explored the synthetic consequences of interaction of the exocyclic carbene with neighbouring substituents. For the key experiment the doubly-labelled phthalic anhydride **42** was synthesised by an intramolecular Diels−Alder route from labelled acetylene, and then diluted with unlabelled anhydride to give 5% of the $^{13}C_2$ species.[31] FVP of this sample gave a pyrolysate containing biphenylene in which the major labelled isotopomer was $^{13}C_2$-biphenylene, but ^{13}C NMR spectroscopy showed that in this biphenylene **47** one ^{13}C label was distributed approximately equally between two quaternary positions. This result was explained (Scheme 8) in terms of alternative ring contractions of benzyne **43** leading to exocyclic carbenes **45** and **46**, to benzyne **44**, and ultimately to scrambling of one label in biphenylene **47**.

Further experiments included FVP of the dione **48** at 650−830°C[31] and of the doubly-labelled 2-(3′,3′-dimethyltriazenyl)benzoic acid (**49**) at 400−850°C; in the latter case scrambling of the label in the biphenylene product was clearly shown to increase with temperature.[32]

This interpretation of the labelling results of Scheme 8 has been challenged by Wentrup[33] who proposed that scrambling is due to the symmetry of loss of carbon dioxide from anhydride **42**. Wolff ring-contraction of the resulting carbenes **50** and **51** to ketenes **52** and **53** would lead on decarbonylation to the same exocyclic carbenes **45** and **46** (Scheme 9) and thus to scrambling in the biphenylene product **47**. This type of pathway has been proved in the case of cyclohexene-1,2-dicarboxylic anhydride,[33] but attempts to detect the formation of the unlabelled ketene corresponding to **52**/**53** by IR spectroscopy of pyrolysates from phthalic anhydride have not produced fully convincing results.[33] It is plausible that both types of mechanism operate,[34] but at present the nature of the decomposition of phthalic anhydride on FVP has not been fully clarified. The aryne contraction pathway has been established only in the case of the 8-methylnaphthalene system (**62**) (see below).

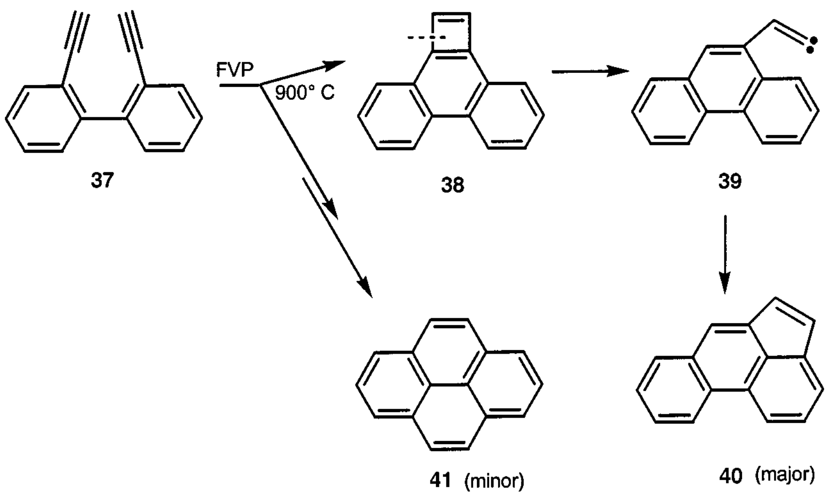


Scheme 5. The insertion/deinsertion/reinsertion sequence leading to cyclopent[*hi*]aceanthrylene **31**

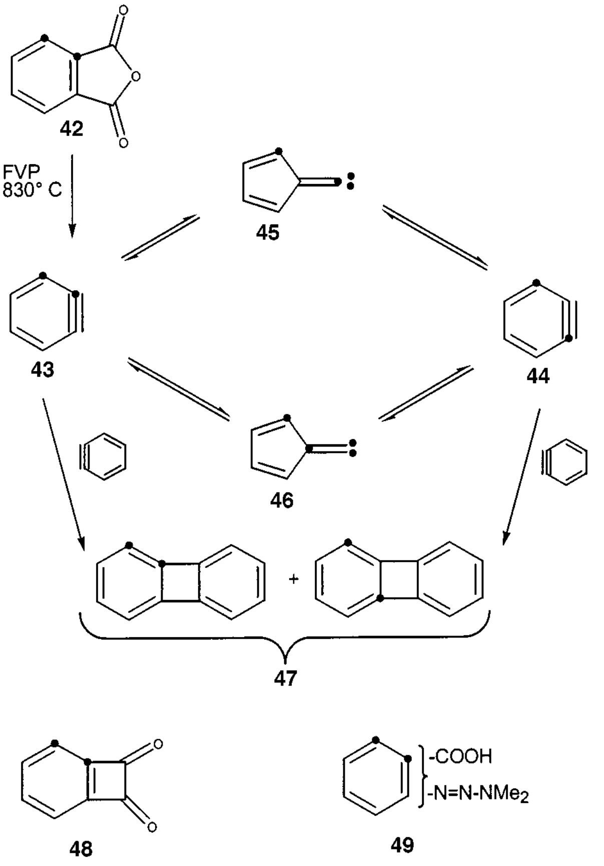


Scheme 6. Migration of the HC_2 group through a cyclobutarene

Irrespective of particular pathways, the pyrolysis of an aromatic anhydride is likely to generate an exocyclic carbene which can be trapped by insertion into a neighbouring group. In the benzene series an *ortho*-phenyl substituent in **54** efficiently traps the carbene in **55** to give cyclopent[*a*]indene (benzopentalene) **56** as the major product.[35] Simi-



Scheme 7. Cyclization and further rearrangement of 2,2′-diethynylbiphenyl



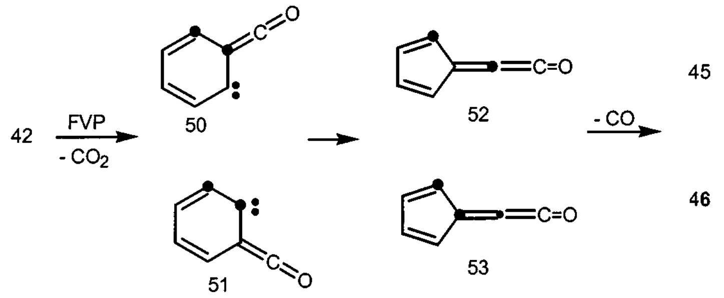
Scheme 8. Generation and rearrangement of [1,6-$^{13}C_2$]benzyne

larly the *o*-vinyl anhydride **57** gave pentalene **58**,[35] and the *o*-tolyl anhydride **59** gave both fluorene **60** (49%) and the benz[*e*]indenes **61** (1:1, 22%) by attack on the 2′-methyl group only.[36] In the naphthalene series the 8-methyl-1,2-dicarboxylic anhydride **(62)** on FVP at 750−880 °C gave exclusively 1*H*-cyclopent[*cd*]indene **(65)** by ring contraction of the 1,2 -naphthalyne **(63)** to the carbene **64** and insertion into the *peri*-methyl group.[37] In this case contraction to an intermediate ketene **66** could be ruled out, because this ketene could be generated independently[38] and it cyclised (McMullen reaction[39]) to give acenaphthylen-4-ol **(67)**, which did not decarbonylate under these conditions.[37] Insertions into phenyl rings were observed on FVP of the 8-phenyl- and 3-phenyl-naphthalene-1,2-dicarboxylic anhydrides,[40] and similarly on FVP of the 2-phenyl and 2-benzylquinoline-3,4-dicarboxylic anhydrides;[41] in the last case a probable carbene addition pathway was also detected.

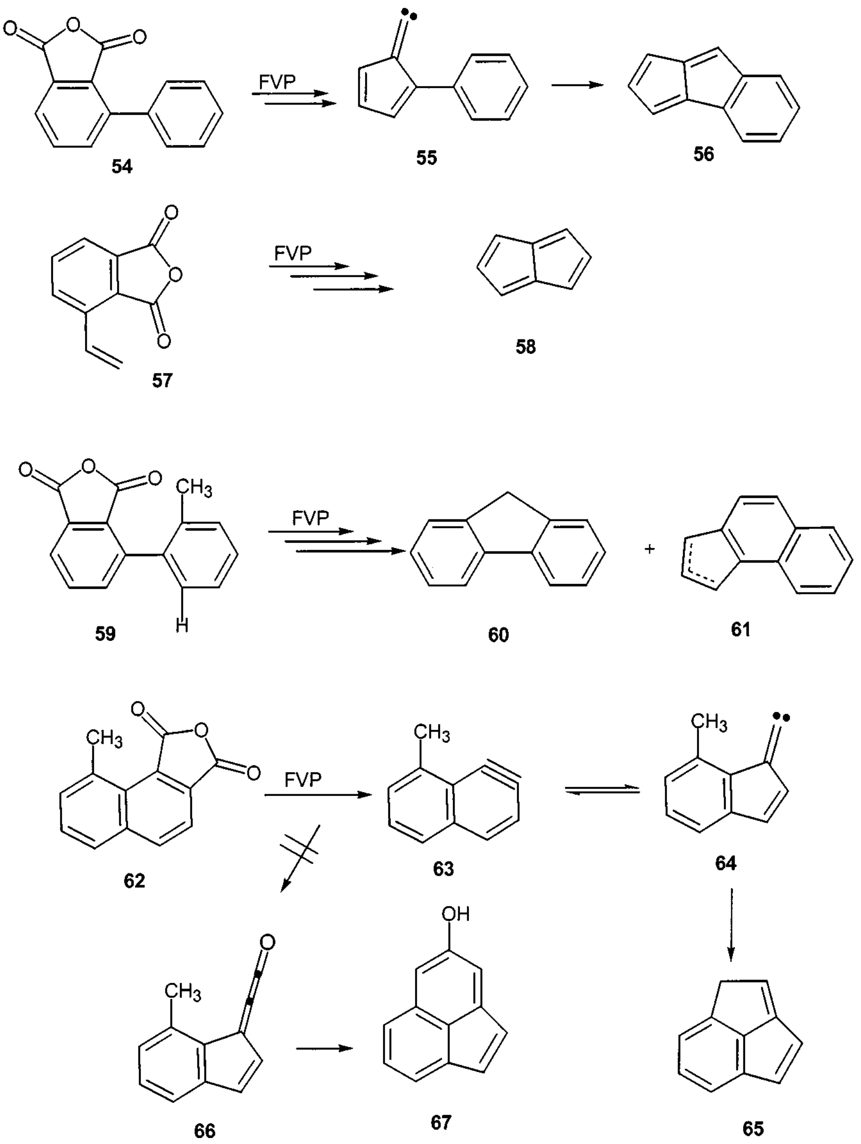
Exocyclic Carbene Insertion Across a Bay Region

Phenanthrene-3,4-dicarboxylic anhydride **(68)** was subjected to FVP to discover whether the exocyclic carbene function of **70** could insert into the C−H bond across the bay region. At 870 °C a complex mixture was obtained, with no sign of any primary product, but the two most readily identified products were 1-ethynylacenaphthylene **(72)** and 3-ethynylacenaphthylene **(73)**. Their formation was ascribed to alternative modes of cleavage, a and b, in the presumed intermediate **71** which must be highly strained.[42] This was the first observation of the deinsertion process (compare intermediates **29** and **30**[16]). Subsequently we generated the transient intermediate **71** by FVP of 1,7-diethynylnaphthalene **(74)** at 1100 °C and again observed the two alkynes **72** and **73**,[43] but we failed to recognise the formation of a third important product, pyracylene **16**, which was identified by Scott[15] and rationalised as the product of 6/5 hydrogen shift/ring contraction involving rings D and A of **71** (Scheme 11). The Utrecht group[44] has described an efficient synthesis of pyracylene **16** from 5-(1-chlorovinyl)acenaphthene on FVP at 1100 °C, involving both carbene insertion and dehydrogenation, and reported the further thermal behaviour of **16**.

Our interest in bay region systems was extended by the reports of Neilen and Wiersum[45−47] who found that FVP of triphenylene at 1000 °C gave cyclopent[*hi*]acephenanthrylene **(80)**. This was attributed to dehydrogenation to 1,2-triphenylyne **(76)**, followed by the familiar sequence of ring

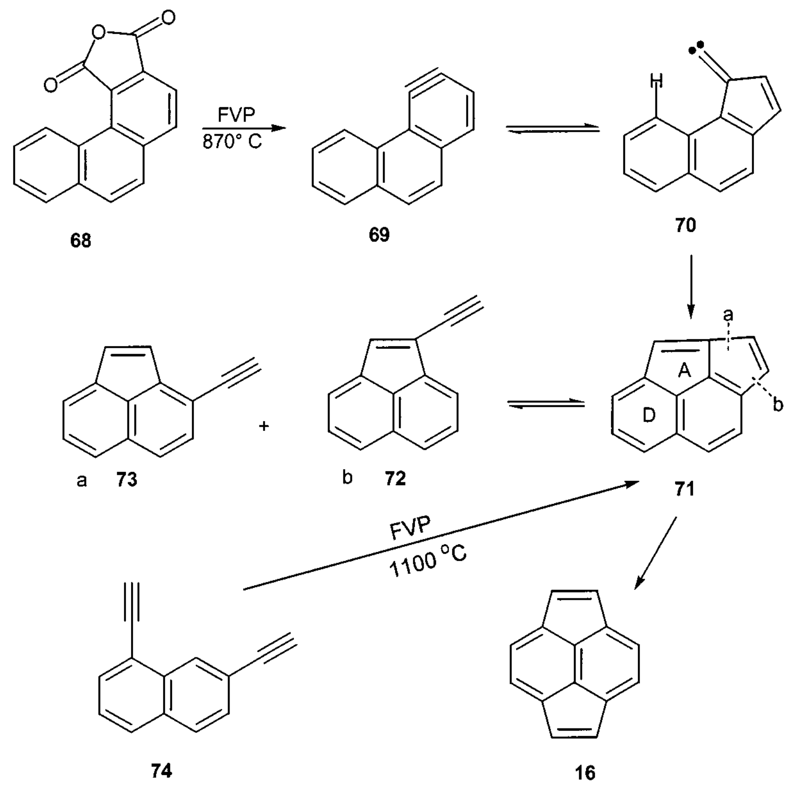


Scheme 9. Wentrup's mechanism for the scrambling of ^{13}C labels by Wolff ring-contraction

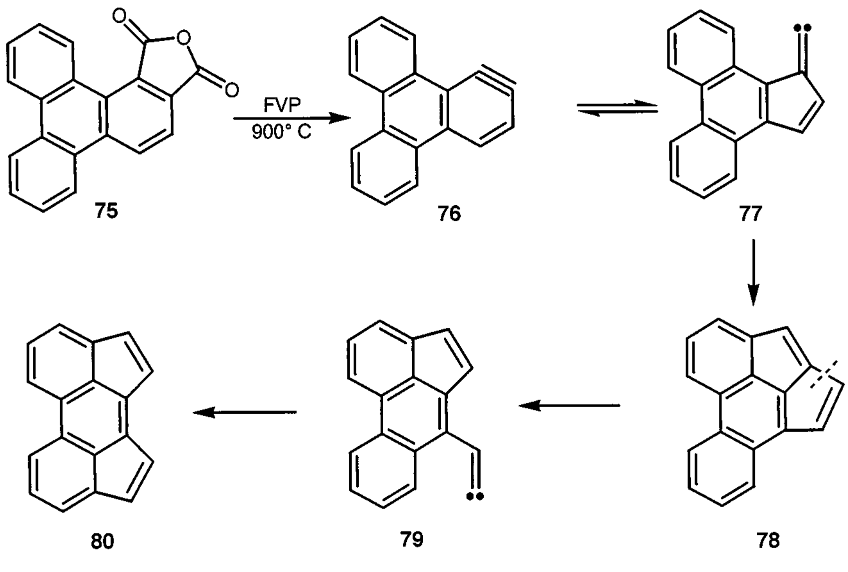


Scheme 10. Intramolecular trapping of exocyclic carbenes

contraction to **77**, insertion to give **78**, alternative deinsertion to **79**, and final insertion to give **80**. When we pyrolysed triphenylene-1,2-dicarboxylic anhydride **(75)** at 900 °C, **80** was formed in 66% yield, together with some triphenylene (Scheme 12).[7] This appeared to provide confirmation of the Neilen and Wiersum pathway, but further work showed that the 1,2-, 1,3-, 1,4- and 2,3-didehydrotriphenylenes all formed cyclopent[*hi*]acephenanthrylene **(80)** at 900−1100 °C but by distinct mechanisms.[7][42] Such an interpretation implies initial maintenance of a diradical structure at high temperatures; it could be complicated by hydrogen migration, which is considered next.



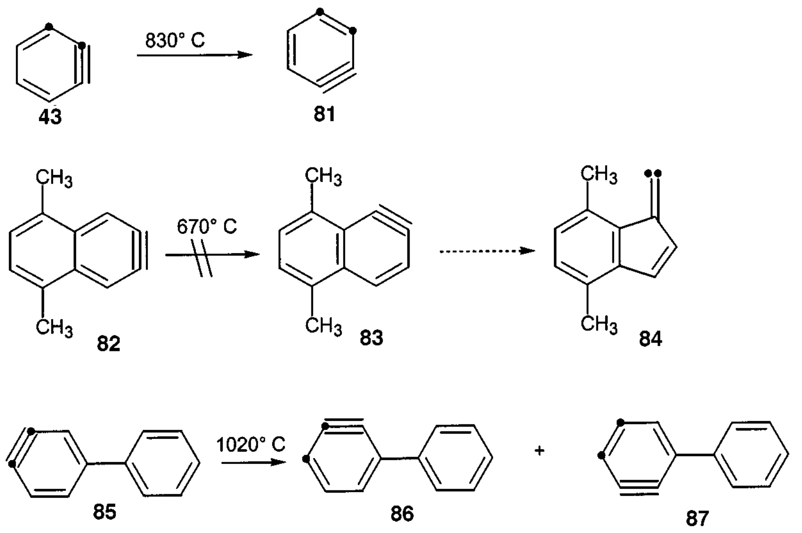
Scheme 11. Rearrangement products of 3,4-phenanthryne



Scheme 12. Rearrangement of 1,2-triphenylyne

Hydrogen Migrations and Hydrogen Abstractions

In the early work[31] on the scrambling of ^{13}C in benzyne derived from [1,6-$^{13}C_2$]-phthalic anhydride **(42)** it was noted that a minor process was hydrogen migration in the aryne ring; the initial aryne **43** formed the isotopomer **81**. However, an attempt[49] to detect hydrogen migration in the dimethyl-2,3-naphthalyne **(82)** (to give the 1,2-naphthalyne **83**) by trapping the related exocyclic carbene **84** with an internal methyl group was not successful. In the biphenyl series, biphenyl-2,3-dicarboxylic anhydride **(54)** formed the primary product cyclopent[*a*]indene **(56)** via the initial 2,3-aryne[35] (Scheme 10), but the corresponding 3,4-anhydride on FVP at 1020 °C yielded a similar pyrolysate containing **56**. $^{13}C_2$ Labelling and the occurrence of complete scrambling of a (2-^{2}H) label suggest that labelled 3,4-aryne **85**



Scheme 13. Hydrogen shifts in arynes

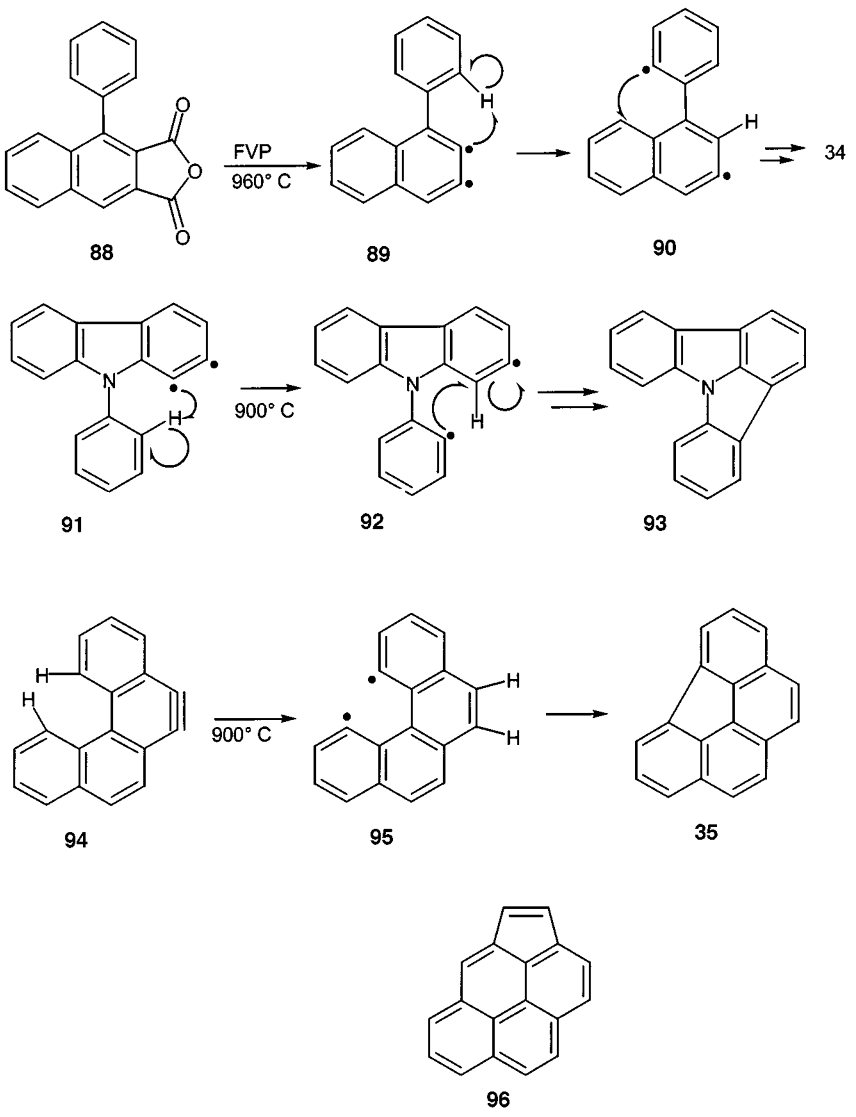
might undergo hydrogen shifts to produce the 2,3- and 5,6-arynes **86** and **87**[50] (Scheme 13) which then rearrange to form cyclopent[*a*]indenes, but this is an over-simplified view of a complex system. All of the four cyclopent[*a*]indene isotopomers formed contained adjacent ^{13}C atoms, whereas a carbene mechanism would form one isotopomer from **86** with labels separated. For this reason the possibility of ring contraction in an aryl radical mode was proposed.[50] For a simpler example of this radical hypothesis see the account of biphenylyl radicals below.

In cases where the aryne/exocyclic carbene equilibrium is less likely to lead to trapping of the carbene, the aryne itself may be involved in hydrogen abstraction. It is convenient to represent such a reaction as a radical abstraction, as in the case of FVP of 1-phenylnaphthalene-2,3-dicarboxylic anhydride **(88)**,[40]where the major product was fluoranthene **34**. The key step appears to be the hydrogen abstraction shown on **89**, followed by rotation of the C_6H_4 ring and radical attack at C-8 of the naphthalene ring in **90**. Formation of **34** requires further hydrogen shifts of uncertain mechanism. Similar pyrolytic behaviour was shown by a group of N-substituted carbazole-1,2-dicarboxylic anhydrides.[51] The *N*-phenyl system, which should generate the aryne **91**, gave a ca. 80% yield of indolo[3,2,1-*jk*]carbazole **(93)**; a plausible pathway involves hydrogen abstraction from C-1 of **91** and radical cyclization to C-1 of **92**, followed by a [1,2]-H shift. In the corresponding *N*-methyl series hydrogen transfer occurred from the *N*-methyl group to the aryne function, and the major outcome was ring expansion to phenanthridine.[51] Sarobe,Jenneskens and Wiersum[52] examined the FVP of benzo[*c*]phenanthrene-5,6-dicarboxylic anhydride and obtained as the major product benzo[*ghi*]fluoranthene **(35)**. They proposed that the initial 5,6-aryne **94** undergoes shifts of the hydrogen atoms of the bay region, again of uncertain mechanism, to give the 1,12-diradical **95**, followed by coupling to **35**. This result should be considered with the earlier observation[53] that FVP of benzo[*c*]phenanthrene itself at moderate pressures gave, by dehydrogenation, both benzo[*ghi*]fluoranthene **(35)** and cyclopenta[*cd*]pyrene **(96)** in significant yields. Both radical coupling and aryne/carbene insertion/ 6/5 rearrangement pathways were proposed[53] to explain this cyclization to **96**.

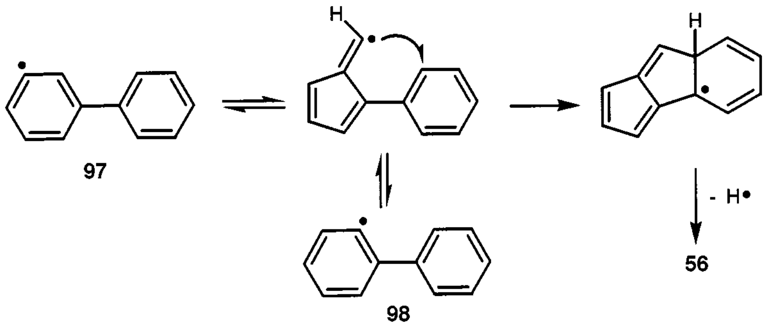
Aryl Radicals and Radical Rearrangement

We had tended to regard the pyrolytic formation of cyclopent[*a*]indene **(56)** as evidence for the probable involvement of the exocyclic carbene **55** (Scheme 10) and the related biphenyl-2,3-yne, until we found that 2-, 3- and 4-biphenylyl radicals gave significant yields of **56** at 1000−1100°C. The radicals were generated by FVP of allyl esters; the twelve diesters behaved similarly.[50] In the case of the phenyl radical loss of a hydrogen atom to give benzyne did not occur under these conditions. Interconversion of the three biphenylyl radicals could occur by 1,2 hydrogen shifts (see below), but a further possibility was that both this interconversion and the cyclization to **56** involved reversible ring contraction to exocyclic radical species. Scheme 15 shows as an example[50] the possible conversion of biphenyl-3-yl **(97)** to biphenyl-2-yl **(98)** and to cyclopent[*a*]indene **(56)**; a similar approach could be applied to Scheme 16. However, in the absence of definitive $^{13}C/D$ labelling experiments Scheme 15 is only a hypothesis.

Examples of 1,2-shifts of hydrogen in naphthyl radicals were reported by Necula and Scott.[25] Radicals were generated from bromonaphthalenes at 850°C/0.1−0.5 Torr in the presence of a 100-fold excess of maleic anhydride, a precursor of acetylene at this temperature. 2-Bromonaphthalene **(99)** gave a substantial yield of 2-ethynylnaphthalene **(101)** by addition of the 2-naphthyl radical **100** to acetylene, and loss of hydrogen, but the major product was acenaphthylene **(11)**, formed by the carbene insertion route (see Scheme 2) from 1-ethynylnaphthalene **(10)** (Scheme 16). Control

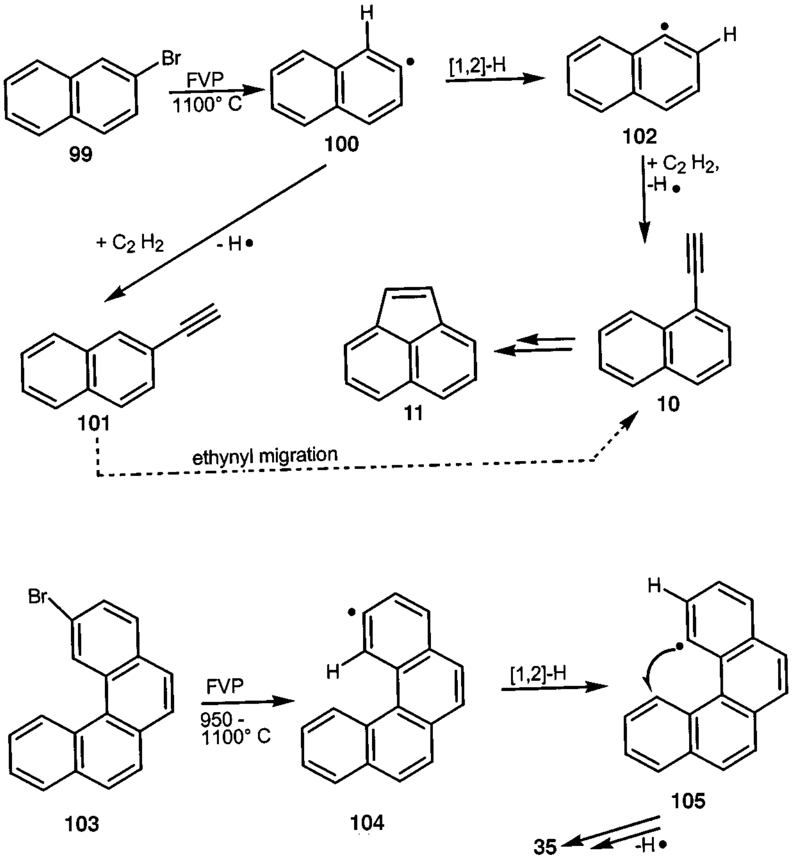


Scheme 14. Intramolecular hydrogen abstractions and migrations in arynes

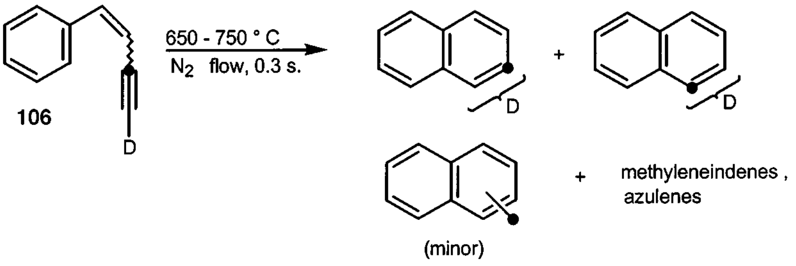


Scheme 15. Proposed ring contraction of a 3-biphenylyl radical

experiments suggested that the major pathway to **10** involved isomerization of the 2-naphthyl to the 1-naphthyl radical **102** and that direct isomerization of **101** to **10** by ethynyl migration was less important. A similar hydrogen shift was proposed for the biphenyl 2-yl/3-yl system.[25] An even clearer example, where trapping of the new radical is intramolecular rather than intermolecular, has been observed by Brooks and Scott.[54] FVP of 2-bromobenzo[*c*]phenanthrene (**103**) at 950−1100°C generated the 2-benzo[*c*]phenanthryl radical **104** which was converted by a 1,2-shift of hydrogen into the 1-radical **105**. Radical attack on the neighbouring bay position 12 and loss of hydrogen



Scheme 16. Hydrogen migration in the 2-benzo[*c*]phenanthryl radical and subsequent cyclization



Scheme 17. Scrambling of D and ^{13}C labels in the cyclization of 1-phenyl-1-buten-3-yne to naphthalene

then gave benzo[*ghi*]fluoranthene (**35**) (Scheme 16). This interpretation is supported by deuterium labelling studies and by BP/DN** calculations leading to an activation energy of 58.4 kcal/mol for the 1,2-[H] shift. An aryne mechanism[54] was ruled out because the very stable cyclopenta[*cd*]pyrene was not detected.

Many of the previous reactions have shown fairly clear involvement of either carbenes, arynes or radicals in the reaction pathway, but the work of Zimmermann's group on the apparently straightforward cyclization of 1-phenyl-1-buten-3-yne to naphthalene at 650−750°C has emphasised the importance of careful labelling studies. This work[55][56] showed that under flow conditions (reaction time 0.3 s, N_2) the cyclization of the deuterated and ^{13}C-labelled enyne **106** shown in Scheme 17 involves electrocyclic reaction, 1,6-cyclization via a methylenecarbene, 1,2-styryl migration, and a complex series of radical cyclizations induced by addition of hydrogen atoms to the triple bond.

Conclusion

Flash vacuum pyrolysis is now a mature technique in organic chemistry. The excitements of the exploratory phase of high temperature organic chemistry which were prominent from the mid-1960s to the late 1980s are not now so evident in the rapid-publication literature. FVP remains a major technique for generating and handling transient and sensitive molecules, and the latter class includes pyracylene **16** and cyclopent[*a*]indene **(56)**. Recent work has been concentrated in areas of synthesis where FVP offers striking advantages (fullerene fragments, polycyclic aromatic hydrocarbons) or in detailed elucidation of pyrolytic pathways through labelling and computational studies. Future work may yield many surprises, but the element of surprise is likely to be concealed in a complex mechanistic pathway, to be revealed only by painstaking study of labelled substrates.

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