Cycloaromatization of Open and Masked 1,3-Hexadien-5-ynes − Mechanistic and Synthetic Aspects

Gerhard Zimmermann[a]

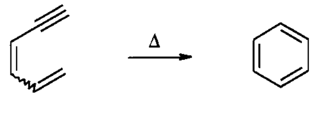
Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

Keywords: Carbenes / Cycloaromatization / Enynes / Isobenzenes / Pyrolysis / Radicals / Thermochemistry

The discovery of the net-cyclization of 1,3-hexadien-5-yne to benzene at temperatures around 250 °C was followed, particularly during the 1990s, by an increasing number of investigations of the ability of other compounds possessing a 1,3-hexadien-5-yne substructure to cycloaromatize. This has led to remarkable syntheses of compounds with very interesting molecular structures and, in particular, to pronouncedly bowl-shaped, nonalternating PAHs, the carbon skeletons of which represent fullerene subunits. Substantial insights into the three mutually exclusive cycloaromatization mechanisms, operating in distinct temperature ranges, are presented in this paper, together with the development of the method that has made it possible, when the temperature range used results in competition between the entirely different mechanisms, to analyze the complex reaction behavior.

1. Introduction

The formation of aromatic six-membered rings by thermal cycloisomerization of 1,3-hexadien-5-ynes was first reported by Hopf and Musso in 1969 (Scheme 1),[1] more than 20 years prior to the start of an era in which a number of highly strained, bowl-shaped PAHs were synthesized by an analogous procedure.



1 **2**

Scheme 1. Net-cycloaromatization of **1** into **2**

Stimulated by the spectacular high-temperature gas-phase syntheses of medium-sized and large nonalternating PAHs − such as, for example, of **4** from **3**,[3] **6** from **5**,[4] or **8** from **7**[5] (Scheme 2) − further, analogous cycloaromatizations of different 1,3-hexadien-5-ynes or of compounds incorporating such a substructure were studied at different temperatures and in different reactor systems (ampoule, flow and flash vacuum techniques).

The results clearly show that these thermal processes not only allow scarcely conceived of routes to new compounds like **28−31**[6] (cf. Scheme 7), but they also provide insights into the details of the mechanisms operating in such reactions,[7−10] and especially into the temperature dependence of the mechanisms involved.[8]

We have been actively engaged in this research since 1989 and this Microreview summarizes selected syntheses of aromatic compounds by thermal conversion of various 1,3-hexadien-5-ynes under different thermal conditions. The results obtained allow a clear differentiation to be made between the three types of mechanism.

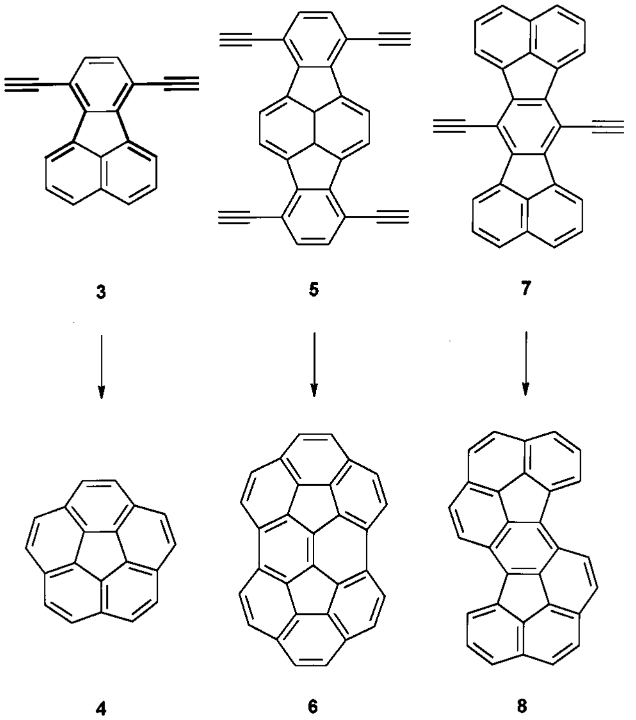
Gerhard Zimmermann was born in 1930. He studied at the University of Leipzig and completed his Ph.D. thesis on substitution reactions of alkanedioic acid derivatives under the supervision of Wilhelm Treibs in 1957. After several years during which he was at Leuna-Werke as a researcher and manager, he completed his "Habilitation" on the topic of Cope reactions of alkenylbicycloheptenes at the University of Leipzig in 1969. In the same year he received an honorary professorship at the Technical University of Merseburg. In 1974, he moved to the Academy of Sciences (Leipzig), and finally, in 1993, to the University of Leipzig, where he has been the head of the department of High-Temperature Reactions at the Institut für Technische Chemie. The main emphasis of his research is in the field of organic gas phase chemistry. Mechanistic studies using labeled compounds have been a major interest. More recent research topics include high-temperature synthesis of planar and, particularly, bowl-shaped PAHs by ring closures of compounds possessing 1,3-hexadien-5-yne substructures.

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.

---

[a] Abteilung Hochtemperaturreaktionen am Institut für Technische Chemie der Universität Leipzig,
Permoserstraße 15, 04303 Leipzig, Germany
Present address: Naunhofer Straße 14, 04299 Leipzig, Germany

1434−193X/01/0203−0457 $ 17.50+.50/0



Scheme 2. Examples of the thermal conversion of ethynylarenes into fullerene fragments

2. Alternative Precedent Mechanisms

In the days when the thermal cycloaromatization of 1,3-hexadien-5-ynes was discovered, with the simplest hydrocarbon of this family,[1] the common state of knowledge in this field was rather poor. The only conclusion that could be drawn from the reported results was the fact that the process requires a hydrogen shift either during or subsequent to the cyclization.[11] Since then, three experimentally verified mechanisms capable of rearranging the carbon skeleton of a 1,3-hexadien-5-yne into aromatic ring systems have been proposed (Scheme 3).

The type A mechanism involves the pericyclic formation of intermediates with a 1,2,4-cyclohexatriene substructure (also known as isobenzenes[12] or six-membered enallenes[13]), while during the type B process, reversible generation of vinylidenecarbenes takes place by means of 1,2-R shifts of the substituent R at the terminal carbon atom of the C−C triple bond.[14] Finally, the type C mechanism requires the generation of vinyl-type radicals by addition of chain-carrier radicals (preferably H atoms) to the C−C triple bond[8,9,15] (see also ref.[16]).

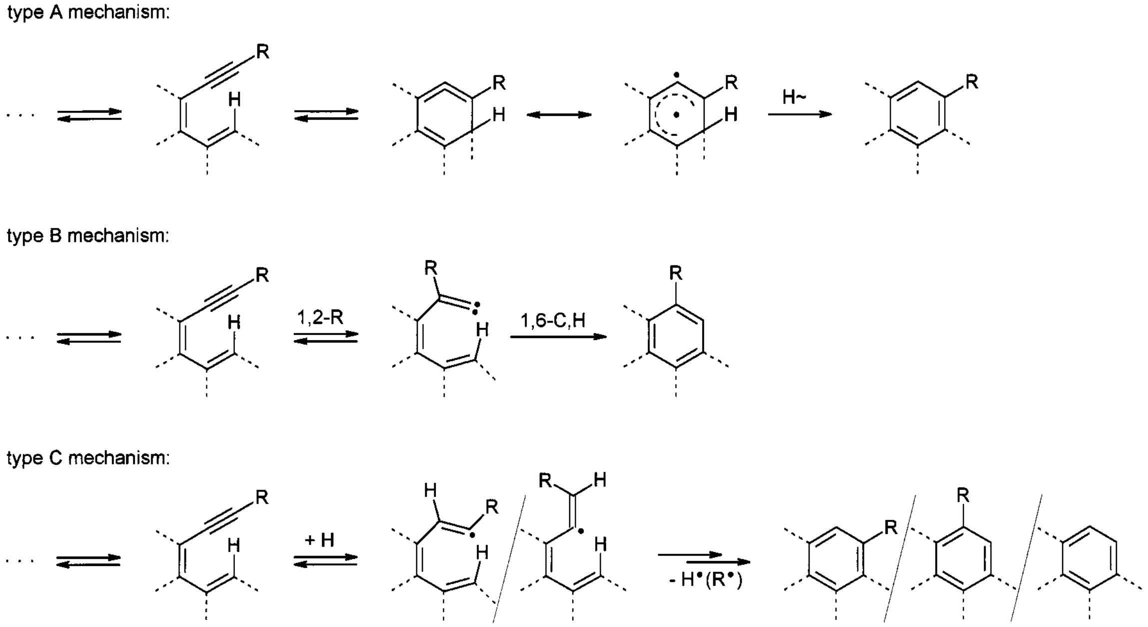
When the cycloaromatization of **1** was first announced,[1] these three alternatives were not yet the subject of serious debate. Today, however, we know that in the temperature range up to approximately 550 °C, the cycloaromatization of 1,3-hexadien-5-ynes takes place, almost without exception, by the distinct, two-stage type A mechanism. The first step of this mechanism, the so-called Hopf cyclization, is thought to be similar to the Bergman cyclization of *cis*-3-hexene-1,5-diynes.[17]

If the simplest representatives of both hydrocarbon families are considered together (Scheme 4), the cyclizations in question have some things in common:

− the six-membered ring closure proceeds by a pericyclic process at temperatures around 200/250 °C,

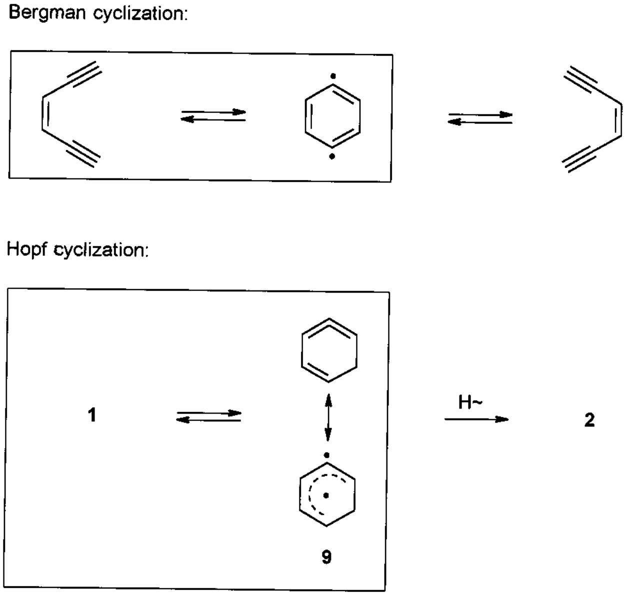
− the energies of activation have been determined to be nearly the same (32 compared with 30 kcal mol^{-1} [18]),

− the generated cyclic intermediates are either distinct diradicals (1,4-benzenediyls) or at least compounds with a strong diradical character,[18] and



Scheme 3. Alternative mechanisms of formation of aromatic rings from 1,3-hexadien-5-ynes

− both types of intermediates can be intercepted by trapping reagents before their rapid stabilization by subsequent reactions (cf. ref.[18] with ref.[6]).



Scheme 4. Essential steps of the Bergman and the Hopf cyclization

Above the temperature boundary at approximately 550 °C, each of the three mechanisms may be involved in the net-cycloaromatization process of compounds possessing a 1,3-hexadien-5-yne substructure if the necessary conditions − such as the reversible rearrangement of terminal alkynes to vinylidenecarbenes,[14,19,20] and the formation of chain-carrier radicals by thermal decomposition of the employed starting compounds − are fulfilled.[7−9,15,21]

The three competing mechanisms differ from one another not only in the intermediates involved, but particularly in their rate-determining steps. These are:

− the Hopf cyclization for the type A mechanism,

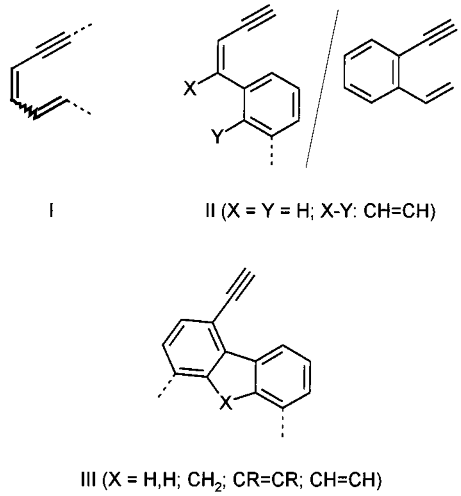
− the reversible generation of vinylidene-type carbenes (type B), and

− the formation of chain-carrier radicals by destructive adsorption of the employed hexadienynes at the externally heated reactor walls (type C).

It is hence not very surprising that, above 550 °C, the three mechanisms show completely different temperature dependences (cf. Section 5 and ref.[8]), resulting firstly in a significant increase in importance of the type B mechanism with increasing temperature. Since, simultaneously, the type C mechanism gradually decreases in importance with increasing temperature, because of the displacement of the equilibrium according to $R{-}C{\equiv}C{-}R + H^{\bullet} \rightleftarrows R{-}CH{=}C^{\bullet}{-}R$, to the disadvantage of the vinyl-type radicals, most authors tend to interpret high-temperature cycloaromatization processes in terms of the type B process (cf. Section 6).[2,22,23]

3. Substrate Properties and Reaction Engineering Aspects

Besides cycloaromatization, the hexadienynes so far studied can form by-products by intermolecular reactions. These side reactions occur to different extents, however. Therefore, the substrates can be roughly subdivided into three categories (Scheme 5).



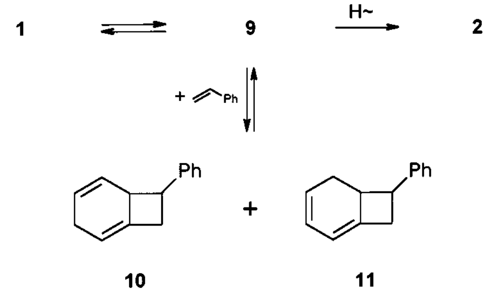
Scheme 5. Categories of 1,3-hexadien-5-ynes of different structures

Hexadienynes of type I can be cycloaromatized in acceptable yields only if the applied reaction conditions are suitable for repressing bimolecular reactions, since they otherwise usually tend to behave like acyclic, conjugated dienes. Thus, upon heating at 200 °C in an ampoule reactor, they react to give cyclic di- and oligomers preferably, by [4+2] cycloaddition.[6] Hexadienynes of type II, on the other hand, behave more or less like styrenes; they polymerize within minutes when heated. The extent of these undesired polymerizations, however, is limited, and the yields of cycloaromatization products formed are reasonable.[24] Unlike hexadienynes of type I and II, those of type III can be cycloaromatized in high yields when heated in closed vessels (cf., for example, the conversion of compounds **12** to **15** in Section 4). In general, however, hexadienynes of type I and II are best converted into products with a single or multiply annelated aromatic ring system when monomolecular reaction conditions (high dilution techniques) are used. Therefore, in many cases, gas phase pyrolysis, either in flow systems [flow pyrolysis (FP); cf. ref.[8]] or under reduced pressure [flash vacuum pyrolysis (FVP)[22,25]], has proven to be the most effective method for optimization of hexadienyne cycloaromatizations.

4. Syntheses Based on 1,2,4-Cyclohexatriene Intermediates

After many years of speculation concerning the structures of intermediates formed in the process of the cycloaromatization of 1,3-hexadien-5-ynes under conditions similar to those used by Hopf for the rearrangement of **1** into **2**

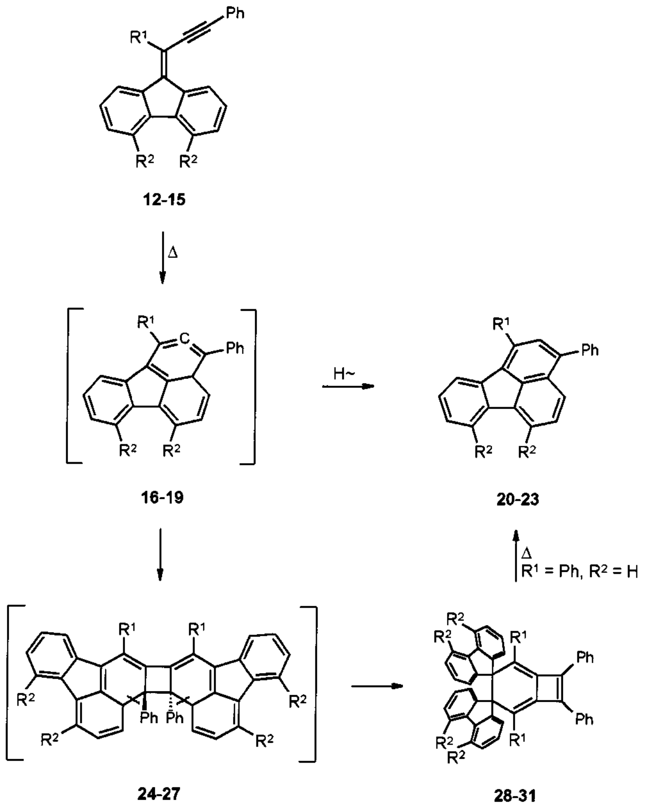
(Scheme 1),[1] Christl et al.[12a] were able to show that 1,2,4-cyclohexatriene (**9**), the assumed intermediate in the conversion of **1**, is formed. This was done by treating the dibromocarbene adduct of 1,3-cyclopentadiene with methyllithium at −30 °C. Simultaneously, they succeeded in identifying this unstable hydrocarbon by the use of trapping reactions. This immediately led to the question of whether **9** (and other compounds with 1,2,4-cyclohexatriene substructures) may also be detected in an analogous way when 1,3-hexadien-5-ynes thermally rearrange into corresponding aromatic hydrocarbons. It was indeed possible to substantiate this, and thus we were able to show that **9** is formed from **1** even at 200 °C, if the conversion is carried out in the presence of styrene (Scheme 6).[6]



Scheme 6. Trapping products of thermally generated 1,2,4-cyclohexatriene (**9**)

Under the conditions used, 7-phenylbicyclo[4.2.0]-1,4-octadiene (**10**) and 7-phenylbicyclo[4.2.0]-1,3-octadiene (**11**) were formed, besides benzene (**2**) and large amounts of higher boiling homo- and heterodimers and -trimers of **1** and styrene; this is considered to be consistent with the results of earlier investigations into the thermal conversion of acyclic conjugated dienes.[26−29] Although **10/11** and **2** were formed in a total yield of less than 10%, the ratio of (**10** + **11**)/**2** ≈ 2 clearly indicated that there was a chance that thermally generated compounds with 1,2,4-cyclohexatriene substructures might be usable as participants in unusual syntheses before they could rearrange into fully aromatic compounds. In other words, the formation of **10** and **11** from **9** was considered to be merely a representative example from a family of trapping reactions of other intermediates with such a substructure, in which 1,2,4-cyclohexatriene derivatives may not only undergo [2+2] cycloadditions with styrene but also with other compounds possessing at least one activated C−C double bond (cf. also ref.[12b]).

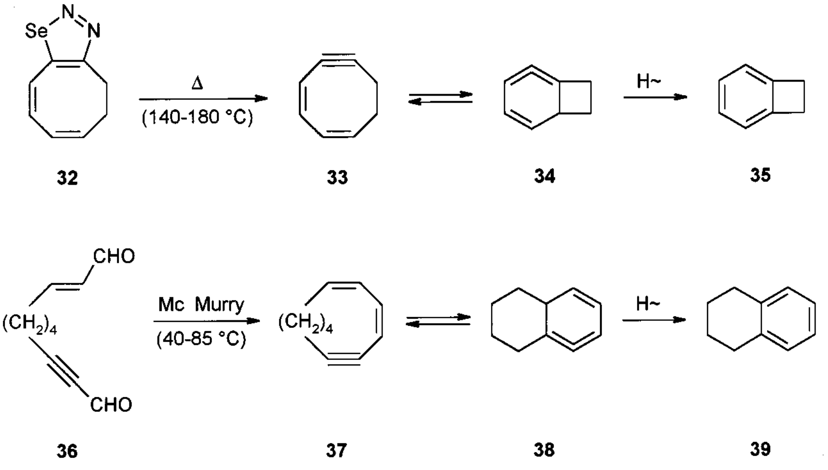
A convincing illustration of this concept is provided by the thermal conversion of the β-ethynyl-substituted styrene derivatives **12−15** (Scheme 5). These belong to category III. Therefore, the formation of di- and oligomers can virtually be ignored when they are heated in neat form or dissolved in an inactive solvent at 350 °C in an ampoule reactor. Under these conditions, the Hopf cyclization becomes the clearly dominating reaction.[6] In this manner, **12** gives the fluoranthene **20** in a 70% yield, for example (Scheme 7), although in this case the cyclization is impeded for thermodynamic (incorporation of the terminal C−C double bond into an aromatic ring system) and steric (space-filling phenyl group at the terminal carbon atom of the C−C triple bond) reasons.



	R¹	R²		%
12	Ph	H	**28**	87
13	H	H	**29**	43
14	≡−Ph	H	**30**	50
15	≡−Ph	R^2=R^2 HC=CH	**31**	58

Scheme 7. Steps in the thermal conversion of dibenzofulvenes

These disadvantages, however, can obviously be compensated for by the reaction time, which inevitably must last at least for minutes, since the ampoule technique is used. Surprisingly, a quite different result was obtained when **12** was subjected to rearrangement conditions at only 250 °C. In this case, the crowded hydrocarbon **28**, a homodimer of **12**, was formed as the main product (87%), while the yield of **20** decreased to trace-level quantities. We therefore argued that **28** must be a subsequent product of **24**, the original [2+2] cycloaddition product of **16**. The dimer **24**, however, is obviously just as unstable as its precursor **16**. Consequently, we think rather that **24** must stabilize itself by bond reorganization immediately after it is generated, with initial breaking of the weakest C−C bonds (see wave lines in **24**). If compound **28** is heated at 350 °C, however, it rearranges smoothly and gives **20** in an 80% yield.[6] In view of this and of the analogous behavior of **13−15**, there is much evidence in favor of a so far insufficiently substantiated hypothesis, according to which, thermally generated intermediates with 1,2,4-cyclohexatriene substructures might be the compounds of choice for further syntheses of aro-



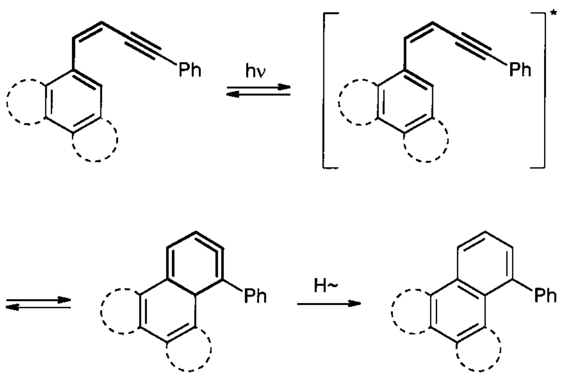
Scheme 8. Rapid stabilization of bridged 1,3-hexadien-5-ynes

matic compounds with interesting molecular structures, provided that the reaction conditions allow the intermediates to be trapped before they can dimerize or be stabilized by 1,5-H-shifts.

Two special cases of the hexadienyne cycloaromatization are the syntheses of benzocyclobutene (**35**) and the tetrahydronaphthalene **39** from the non-isolable 1,3-hexadien-5-ynes **33**[30] and **37**,[31] respectively (Scheme 8).

The thermal fragmentation of the selenodiazole **32** between 140 and 180 °C actually generates **33**, but it rearranges immediately into **35**.[30] Similar observations were made by Hopf et al.[31] for the McMurry reaction of the dialdehyde **36**, which gives not **37**, but **39** as the sole detectable reaction product, even between 40 and 80 °C. This surprisingly fast reaction is obviously facilitated by the oligomethylene bridge that spans C-1 and C-6 of the original hexadienyne system and is thought to support the establishment of the *cis*-configured isomer as the actual precursor of the electrocyclic ring closure.

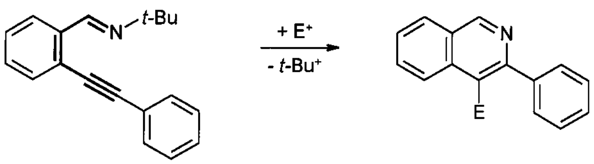
Relatively little attention has so far been paid to the photolytic ring closure of 1,3-hexadien-5-ynes. However, the photolytic conversion of some 1,4-diaryl-1-buten-3-ynes into PAHs with an additional six-membered ring shows (Scheme 9) that, even in such cases, cycloaromatization very probably proceeds according to the type A mechanism.[32]



Scheme 9. Photolytic cyclization/cycloaromatization of 1,4-diaryl-1-en-3-ynes

The formation of 1,2,4-cyclohexatriene derivatives from the singlet-state excited *cis*-isomers is also thought to be the primary reaction step in the photocyclization. The Hopf cyclization of 1,3-hexadien-5-ynes is apparently not restricted to thermally initiated processes.

The very recently published electrophilic cyclization of *N*-*tert*-butyl-substituted 2-(iminomethyl)diphenylacetylenes into the corresponding isoquinolines (Scheme 10) makes clear that there is no end in sight for the addition/cyclization reactions of compounds with 1,3-hexadien-5-yne structures as described above.[33]



Scheme 10. Electrophilic ring closure of (1-aza-)1,3-hexadien-5-ynes

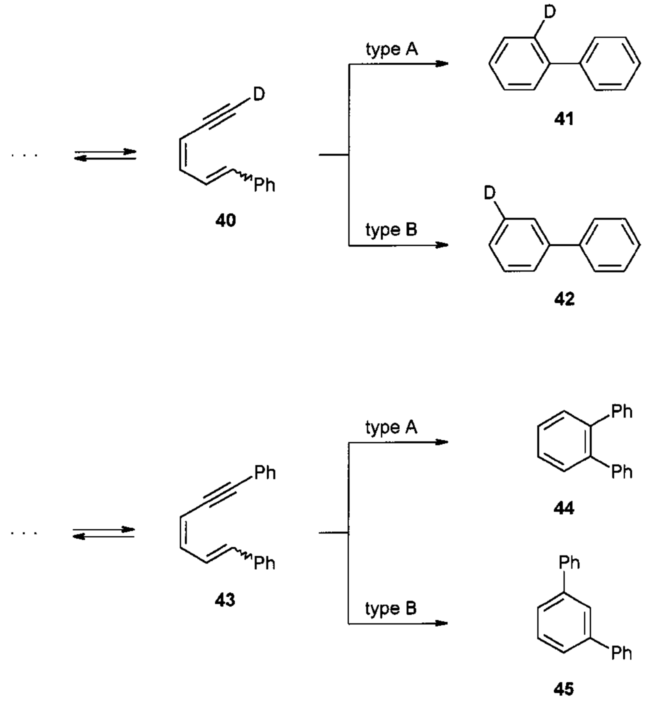
It demonstrates that even hetero-1,3-hexadien-5-ynes are convertible into heteroaromatic compounds if electrophilic reactants are available and if the nitrogen atom is substituted by suitable nucleofuges. In these cases, the intermediacy of aza-1,2,4-cyclohexatriene species appears less likely.

The previously reported thermal, photoinduced, and electrophile-assisted cyclization reactions of hexadienynes clearly show that the potential of pericyclic ring closures of compounds with 1,3-hexadien-5-yne substructures has yet to be fully exploited. Apparently, no metal-catalyzed cyclizations of the above type have been reported in the chemical literature.

5. Cycloaromatization in the Range of Competing Mechanisms

If the starting 1,3-hexadien-5-ynes are stable enough to be used in the gas phase, flow pyrolysis techniques (FP) in the presence of inert diluent gases are best suited for synthesizing aromatic compounds from these highly unsaturated precursors. Even thermally labile or hardly sublimable starting compounds can often successfully be used in the streaming gas phase when special care and techniques (spray[34] or solvent-assisted sublimation techniques[35]) are applied.

Because of the short reaction times (normally less than 2 s), reasonable degrees of conversion necessitate temperatures at least above 500 °C. Under these conditions, benzene (**2**) was formed from **1** in a yield of only 17% at 500 °C (0.3 s),[36] but at 630 °C the yield amounted to about 77%.[21,36] As expected, [6-D]-1,3-hexadien-5-yne behaves similarly, but as well as [D$_1$]benzene, trace amounts of undeuterated benzene could be detected in the pyrolyzate, indicating the beginning of accompanying radical reactions.[21]

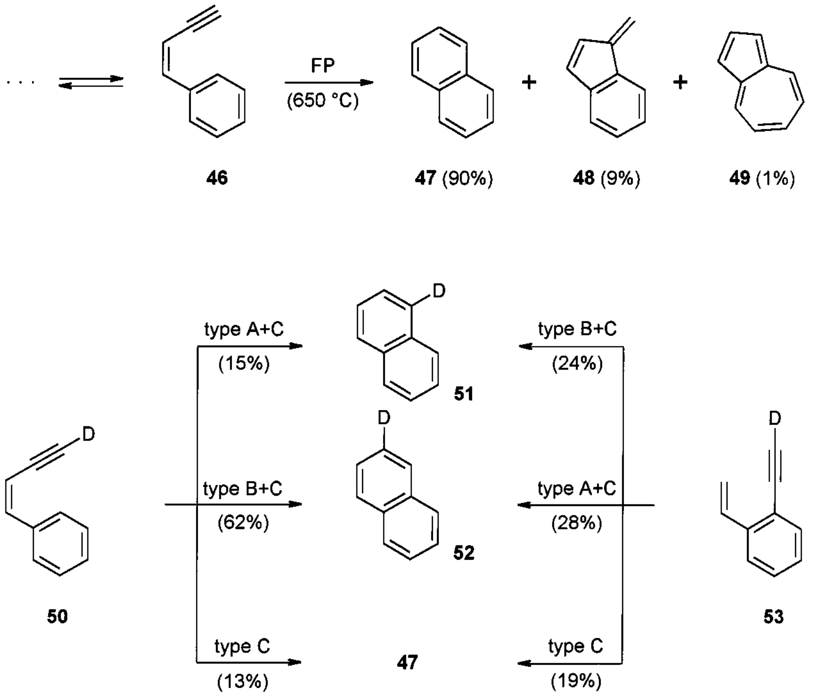


Scheme 11. Cycloaromatization products from 1,6-disubstituted 1,3-hexadien-5-ynes

Further mechanistic details were revealed when doubly substituted hexadienynes were examined. At 650 °C, [6-D]-phenyl-1,3-hexadien-5-yne **40** gave a mixture of **41** and **42** in a ratio of about 1:2 (Scheme 11), as well as other products, the origin of which was based on reactions competing with those by which the carbon atoms of the 1,3-hexadien-5-yne skeleton were converted into the newly formed aromatic ring.[21]

The substitution patterns of **41** and **42** were unequivocally predetermined by the cycloaromatization mechanisms, which resulted in the formation of **41** in the type A mechanism and of **42** in the type B one. Since the yield ratio of **41**/**42** was determined to be roughly 1:2, the B mechanism seemed to be clearly favored. Any contribution to this ratio by products formed according to the type C mechanism could be ruled out, since undeuterated biphenyl was detected only in trace amounts. FP of 1,6-diphenyl-1,3-hexadien-5-yne (**43**) showed a similar picture, but the yield ratio of the expected 1,2- and 1,3-terphenyls (**44** and **45**) was determined to be 1:10. In this case, cycloaromatization according to the type A mechanism was clearly disfavored.[21] Apparently, the Hopf cyclization was impeded by the bulky phenyl substituent at C-6.

FP also turned out to be effective in hexadienyne cycloaromatization when one of the C−C double bonds of the



Scheme 12. Products from **46**, **50**, and **53**

dienyl skeleton was incorporated in a phenyl ring. Thus, when the pyrolysis was carried out at 650 °C, the partially "masked" 1-phenyl-1-buten-3-yne (**46**) gave naphthalene (**47**) in a 90% yield, but 1-methylene-1*H*-indene (**48**) (9%) and trace amounts of azulene (**49**) were also formed (Scheme 12).[8]

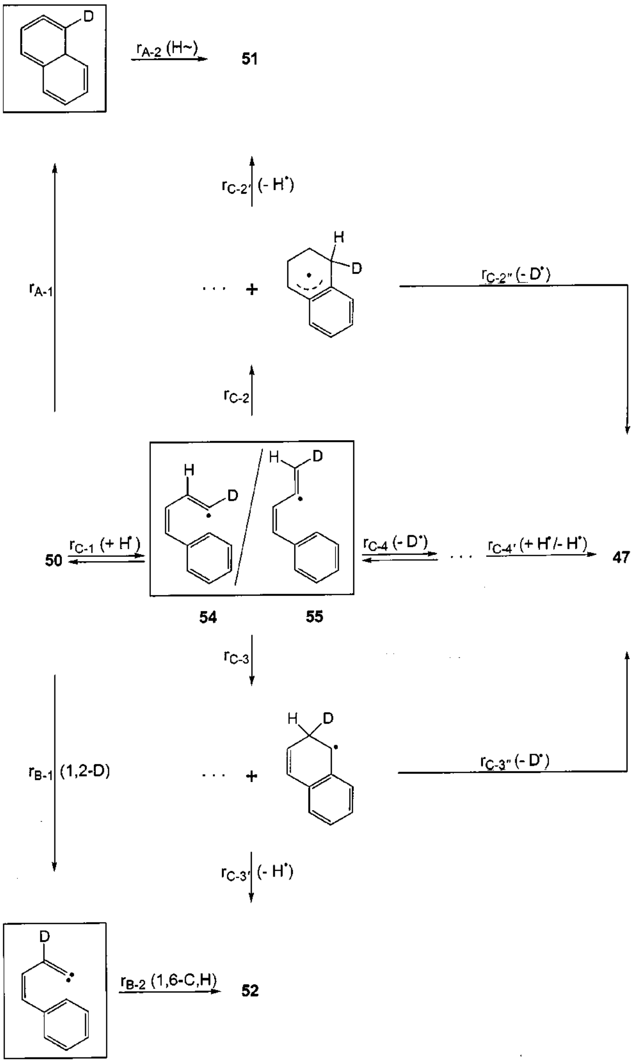
Painstaking supplementary experiments[7] revealed in addition that **48** was exclusively formed by radical pathways, but **49** by the vinylidenecarbene route only (cf. Scheme 15 in Section 6).

Furthermore, compounds **48** and **49** were proven to rearrange into **47** exclusively by radical-driven steps;[7] therefore the percentage contributions of the A, B, and C mechanisms to the formation of **47** so far remain shrouded in mystery. Only the FP of [4-D]-1-phenyl-1-buten-3-yne (**50**) shed any more light on this process (Scheme 12).[8] The formation of about 13% of **47** clearly indicates operation of the type C mechanism, but the monodeuterated naphthalenes **51** and **52** that were also detected are also partially formed by this mechanism, although not in a higher percentage than **47** (for more details, see ref.[9]). Consequently, the cycloaromatization of **50** is judged to proceed predominantly according to the carbene route.

The monodeuterated *ortho*-ethynylstyrene **53** (Scheme 12) differs from **50** inasmuch as the central double bond, rather than the terminal one, is an integral part of a phenyl group. This favors the Hopf cyclization, because there is no necessity to overcome the phenyl resonance stabilization energy during the key step of the C−C bond formation between C-1 and C-6. The results, summarized in Scheme 12 (bottom), confirm this assumption[8] and show that the three mechanisms are able to compete successfully with one another. From these experimental findings, we derive the following mechanistic proposals.

Mechanistic Analysis − Fundamental Aspects and Results: Assuming that [4-D]-1-phenyl-1-buten-3-yne (**50**) can serve as an example for other disubstituted 1,3-hexadien-5-ynes and that H atoms serve as chain-carrier radicals, Scheme 13 shows the interrelationships between the mechanisms that lead to the formation of the cycloaromatization products **47**, **51**, and **52**.

In this scheme, the reaction sequence r_A represents the pathway by which **51** is exclusively formed via 1,2,4-cyclohexatriene (or isobenzene) intermediates. Similarly, r_B describes the exclusive formation of **52** via carbene intermediates. Unlike these, the more complex reaction cascade r_C (for details see ref.[9]) starts only if radicals, particularly H atoms, are available in the reactor volume, so that vinyl-type radicals like **54/55** can be generated by addition to the C−C triple bond. Under flow conditions, these prerequisites are in general fulfilled at temperatures above 550 °C.[8,9,15,19]



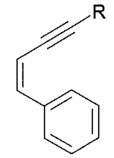
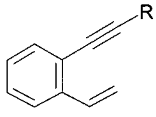
Scheme 13. Competing mechanisms for the cycloaromatization of **50** − a simplified portrait

When, for example, **50** was treated at 700 °C in nitrogen as diluent, the degree of conversion amounted to 42% and the yield ratio of the cycloaromatization products **47**, **51**, and **52** was determined to be $n_{47}/n_{51}/n_{52} \approx 1:2:7$. When, however, nitrogen was proportionally replaced by toluene, conversion decreased to about 25% and the yield ratio changed significantly to $n_{47}/n_{51}/n_{52} \approx 1:3:20$.[8] Since the unimolecular formation of **51** by $r_{A\text{-}1} + r_{A\text{-}2}$, and also of **52** via $r_{B\text{-}1} + r_{B\text{-}2}$, cannot in principle be influenced by the nature of the diluent, the results show that the presence of toluene causes a lowering of the steady state concentration of the highly reactive chain-carrier radicals, thanks to their partial conversion into less reactive, resonance-stabilized benzyl radicals, in accordance with $C_6H_5{-}CH_3 + H^{\bullet}(R^{\bullet}) \rightleftarrows C_6H_5{-}C^{\bullet}H_2 + H_2(RH)$.[37] Hence a reduction of the yield of **47** is observed, as well as of the proportion of **51** and **52** formed via radical intermediates. Although the quantities of **47**, **51**, and **52** formed via radical intermediates essentially depend on the nature and concentration of the chain-carrier radicals (see above), the corresponding yield ratio $n_{47}/n_{51}/n_{52}$ always remains constant at a given temperature, for kinetic reasons.

As detailed in ref.[8] these facts have enabled us to calculate the percentage values by which **50** reacts, in parallel, by electrocyclization (r_A), via the corresponding carbene (r_B), and via the vinyl-type radicals **54/55** (r_C), by means of basic arithmetical methods from analytically determined pyrolysate compositions.

In this way, we succeeded in showing (Table 1) that differently substituted 1-phenyl-1-buten-3-ynes (**50**, **56**, **57**) and *ortho*-ethynylstyrenes (**53**, **58**, **57**) cyclize predominantly by means of radical-driven reactions (r_C).

Table 1. The degrees (in percentages) to which mechanisms A, B, and C are involved in the cycloaromatization of the phenylbutenynes **50**, **56**, and **57** at 700 °C and of the 2-ethynylstyrenes **53**, **58**, and **59** at 650 °C[8]

mechanism		A	B	C
starting compounds:				
	**50** (R = D)	2	46	52
	56 (R = Ph)	1	10	89
	57 (R = TMS)	tr [a]	16 [a]	84 [a]
	**53** (R = D)	28	29	43
	58 (R = Ph)	8	2	90
	59 (R = TMS)	7 [a]	2 [a]	91 [a]

[a] Values with a low level of accuracy caused by degrees of conversion below 10%.

Furthermore, it follows from Table 1 that in the cases of **50**, **56**, and **57**, the reaction sequence r_A via the 1,2,4-cyclohexatriene intermediates is obviously involved only to an almost negligible degree. This picture changes at least partially, though, when the cycloaromatization of the *ortho*-ethynylstyrenes **53**, **58** and **59** is considered. The fact that there is no necessity to overcome the phenyl resonance stabilization energy in the actual cyclization step apparently favors this mechanism, relative to the cases of phenylbutenyne cyclization. This advantage, however, is partly offset once again by bulky substituents (cf. **58**, **59**), which are thought to impede cyclization by r_A thanks to steric hindrance.

A fact of greater importance than conversion in a small temperature interval consists of the temperature dependence of the degree (given as percentage contributions) to which the different mechanisms compete with one another. Figure 1 illustratively demonstrates this dependence for the conversion of **50** into **47**, **51**, and **52** in the range between 625 and 750 °C.[8]

As can be seen, the reaction sequences r_B and r_C change significantly with changing temperature, while the sequence r_A does not. At 625 °C, route r_C clearly dominates the cycloaromatization event, but it gradually decreases in importance as the temperature rises. In contrast, sequence r_B increases steadily in importance with increasing temperature, and accounts for approximately 60% of cycloaromatization at 750 °C. Extrapolation of these dependencies to temperatures above 750 °C reveals clearly that, at very high temperatures, cycloaromatization is almost exclusively governed by the carbene mechanism (r_B). Syntheses according to this pathway are the subject of the following section.

6. Cycloaromatizations Preferably Based on Carbene Insertions

Two fundamental discoveries opened up the pathway for the preparation of numerous cyclopenta- and cyclohexa-annelated PAHs that previously had either been unknown or could only be synthesized by extended routes:

– At higher temperatures, terminal alkynes equilibrate with the corresponding isomeric vinylidenecarbenes,[38] and

– such carbenes stabilize themselves by intramolecular 1,*x*-C,H insertions if the necessary structural prerequisites for such intramolecular ring closure are fulfilled.[14a]

While 1,5- and 1,6-C,H insertions have been proven to occur experimentally (see the examples in Scheme 14, top),[14a] it is still controversial whether 1,4-C,H insertions have a real existence, although this seems to be the simplest interpretation for the formation of benzo[*ghi*]fluoranthene (**61**)from 8-ethynylfluorcenthene (**60**) during FVP at 1100 °C (Scheme 14, middle;[39] compare also ref.[40]).

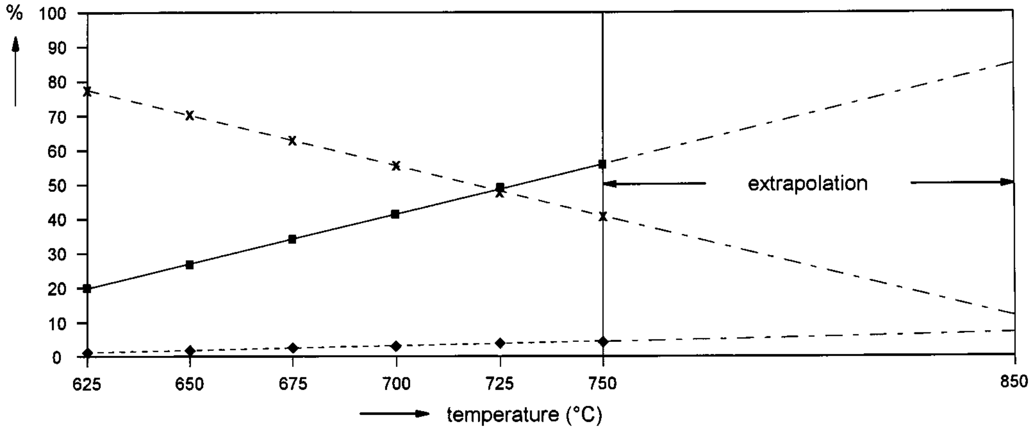
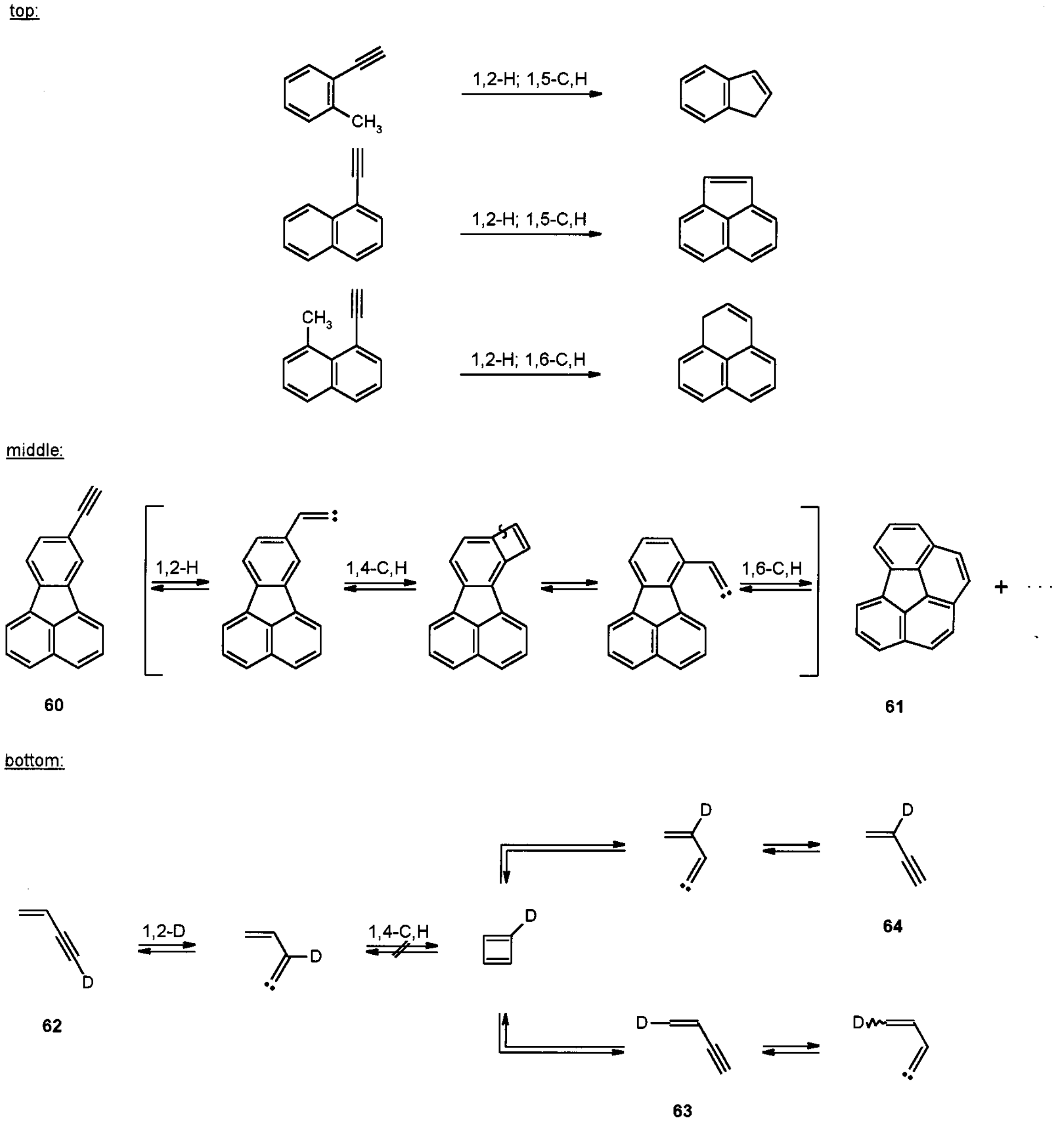


Figure 1. Temperature dependence of the mechanisms competing in the cycloaromatization of **50** (× radical, n carbenic, u electrocyclic)



Scheme 14. 1,x-C,H insertions of vinylidenecarbenes

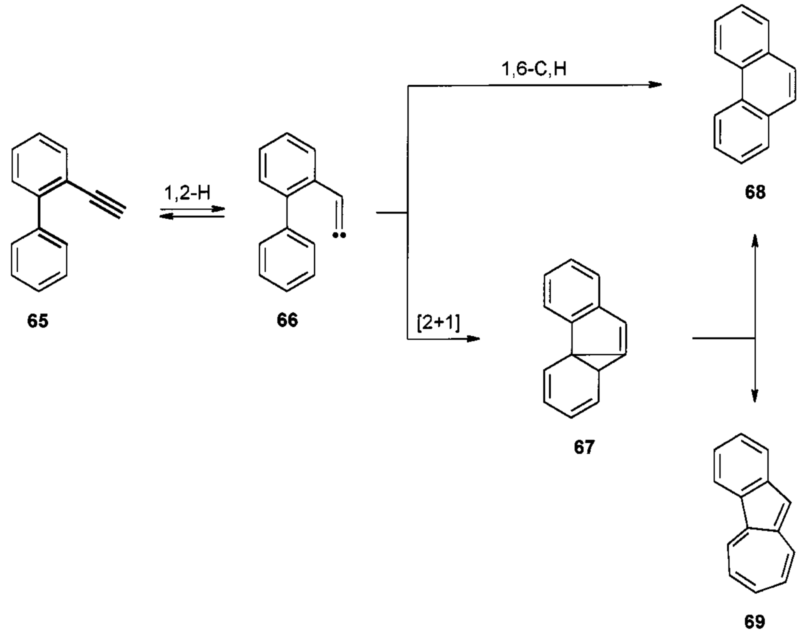
The proposed mechanism involves not only 1,4-C,H insertions, but also the reverse of this reaction. When, in a painstaking experiment,[41] we tried to find support for this picture, we failed to find any indications that such a mechanism was indeed operating. Pyrolysis (FP and FVP) of [4-D]-1-buten-3-yne (**62**) between 800 and 1000 °C resulted in the formation neither of **63** nor of **64**, which would have been expected on the basis of the mechanism depicted in Scheme 14 (bottom).

Leaving these mechanistic details out of consideration, the remainder of this review is focussed only on the formation of aromatic ring systems from compounds with a 1,3-hexadien-5-yne substructure. Therefore, the following remarks refer to 1,6-C,H insertions only as an outstanding synthetic tool for the rearrangement of masked 1,3-hexadien-5-ynes under FVP conditions (500−1100 °C, 0.3 s to 50 ms), while ignoring the also useful synthesis of cyclopenta-annelated PAHs[42] (cf. also ref.[43]).

Although, even under such conditions, the formation of cycloaromatized products according to the type A and C mechanisms cannot completely be ruled out[7] (cf. also Figure 1), the majority of the reactions outlined in the following section are considered to take place as carbene insertions.

The first reported intramolecular carbene insertion was the synthesis of phenanthrene (**68**) from the monoethynyl-substituted biphenyl **65** (Scheme 15).[14a]

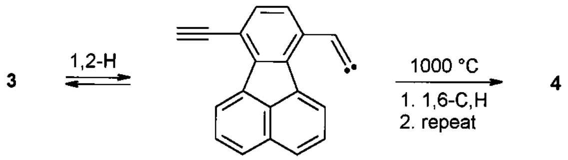
Benzazulene (**69**), formed in parallel from the same carbene **66**, is considered to be a confirmation of the existence of carbene intermediates rather than to call this into question. It corresponds with the pattern of cyclopropane formation by intermolecular [2+1] cycloaddition of carb-



Scheme 15. Mechanism of formation of aromatic hydrocarbons and azulenes from vinylidenecarbenes

enes to olefinic and aromatic C−C double bonds.[44] Wentrup, Zeller, and co-workers[45] interpreted the formation of naphthalene (**47**) and azulene (**49**) from **46** in a manner analogous to Brown et al.'s explanation of the formation of **68** and **69**.

In the period following, the discovery of this principle led to the development of an efficient synthetic tool for the preparation of bowl-shaped PAHs, the enormous geometric strain of which has to be built up during ring closure by 1,6-C,H insertion. This necessitated high-energy conditions, which are provided in FVP only at high temperatures. Numerous PAHs, up to that point unavailable or not effectively accessible by conventional routes, have been prepared by FVP of 1,3-hexadien-5-ynes possessing dienyl skeletons completely incorporated in aromatic structures. The most spectacular example of this was the short and convenient synthesis of corannulene (**4**) from 7,10-diethynylfluoranthene (**3**) by Scott et al.[3] (Scheme 16).



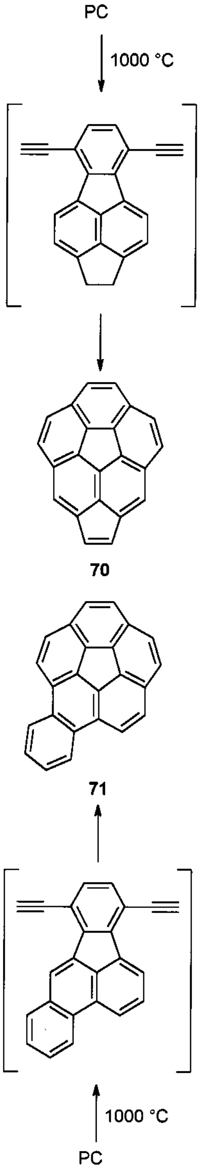
Scheme 16. Scott's first high-energy approach to corannulene (**4**)

This route to a hydrocarbon, possessing the minimal structure of a C_{5v}-symmetrical fullerene subunit, was an incentive to prepare further PAHs of this kind, such as, for example, the fullerene fragments **6**,[4] **8**[5] (see Scheme 2), **70**,[47] and **71**[48] (Scheme 17), albeit that **8** is a planar PAH.

Yamamoto et al. found this last-mentioned hydrocarbon was formed in a futile attempt to synthesize the corannulene derivative **72** from **7**. Instead of the bowl-shaped **72**, the nearly planar **8** was isolated in 20% yield and calculated to be more stable than **72** by 28 kcal mol^{-1} (Scheme 18, top).[5]

Similar observations were made by Rabideau et al.[49] Their unsuccessful efforts to synthesize the dimethylbenzcorannulene **74** from **73** at 1000 °C resulted predominantly in the formation of the planar **75** (Scheme 18, bottom). Both examples clearly show that the formation, by means of 1,6-C,H insertions of vinylidenecarbenes, of highly strained compounds with curved, bowl-like architecture only has a chance of occurring if alternative cyclizations to more or less planar cycloaromatization products can be precluded by a lack of structural prerequisites.

It soon turned out that multiply ethynyl-substituted precursors, as required for the synthesis of large, bowl-shaped PAHs, are relatively unstable on attempted sublimation and that this phenomenon becomes gradually more significant, the larger the size of such precursors becomes.[20] The search for stable precursors that can be sublimed without unacceptable polymerization or decomposition in the sublimation chamber, and attempts to convert these precursors into the unprotected ethynylarenes only inside the reactor chamber at the reaction temperature, resulted in the application of precursor compounds differing from the parent ethynylarenes in that their ethynyl groups were substituted with modified acetylenic substituents. As such, 1-chloroethenyl,[4,47,48,50–52] 1-trimethylsilylethenyl ether,[49] and 2-trimethylsilylethynyl groups[53] turned out to be the most effective (Scheme 19).



Scheme 17. Further high-temperature syntheses of the fullerene fragments **72**, **74**; PC: pre-parent compounds (see Scheme 19)

Although numerous PAHs could successfully be prepared by FVP of compounds masked in such a way, the yields of the target PAHs were comparatively low (2−40%). This is essentially caused by two undesired radical reactions: the formation of aryl- and vinyl-type radicals, respectively. These were initiated by the chain-carrier radicals that are unavoidably generated from any hydrocarbon species at the overheated reactor walls. The aryl radicals are formed by bimolecular radical H abstraction from the rim positions of the polyaromatic fragments of the starting materials, as well as the target compounds.[54,55] They contribute to the enlargement of aromatic clusters, promoting the formation of nonvolatile, coke-like material,[56,57] and hence to a decreased yield. Unlike the aryl radicals, the vinyl-type radicals can cause a loss of ethynyl substituents by β(C−C) scission of ethen-2-yl radicals (Scheme 20).

This side reaction also lowers the chances of forming the target compounds in higher yields, and contributes to the formation of further undesired aryl radicals.

7. Cycloaromatization Starting from Trimethylsilyl-Protected Acetylenes

In a manner almost parallel to Faust's ambitious, though futile, approach to synthesizing C_3-symmetric hemibuckminsterfullerene (**78**) from 1,3,5-tris(2′-ethynylphenyl)benzene (**77**) (Scheme 21),[58] we succeeded in preparing corannulene (**4**) from the doubly trimethylsilyl-protected cyclopentaphenanthrenepentadiyne **79**.[53]

Although we could not obtain **80** by desilylation of **79**, for the same reason that Faust failed to prepare **77** from **76**, we were able to show that the FP of **79** in the presence of nitrogen gave **4** only in trace amounts, but that the replacement of nitrogen by hydrogen furnished **4** in 15% yield at 900 °C (1.6 s).[53] As shown in Scheme 22, the trimethylsilyl-substituted corannulenes **81** and **82**, as well as the benzo[*ghi*]fluoranthenes **83** and **84**, were also formed, besides **4** and some further PAHs considered to be products of consecutive radical reactions.

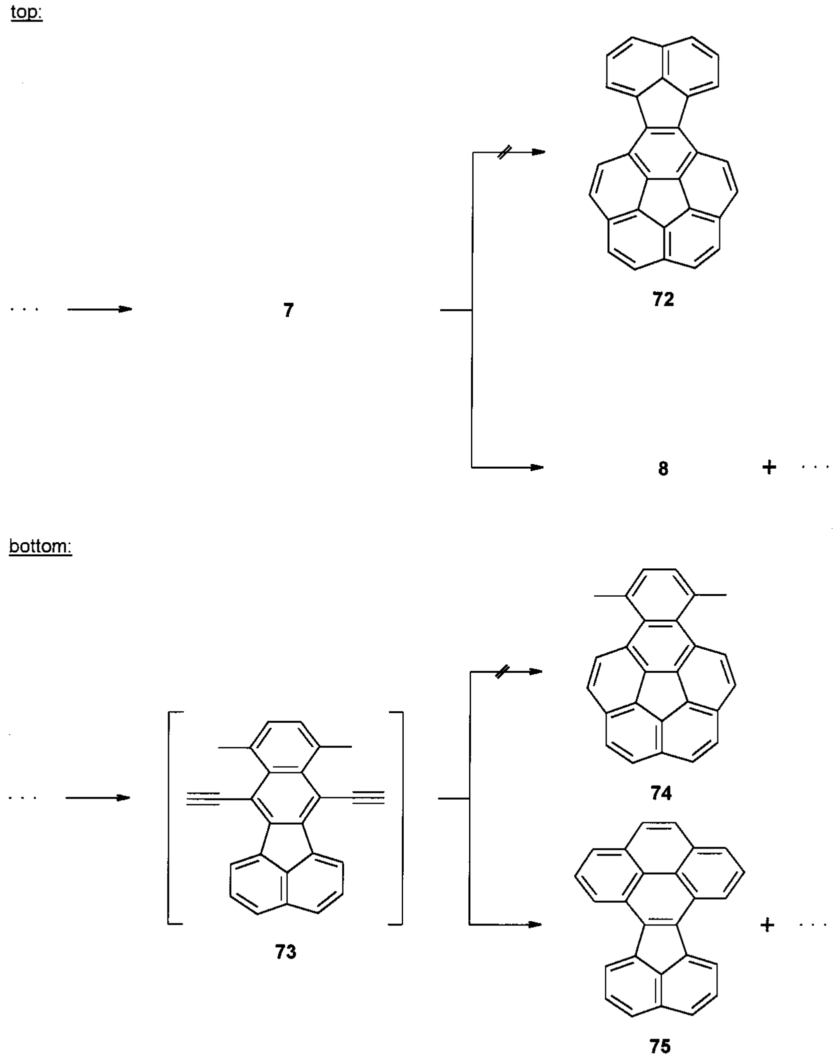
In this experiment, the steady state concentration of the chain-carrier radicals was deliberately increased by generation of additional H atoms through thermal dissociation of molecular hydrogen.

This supports the formation of vinyl-type radicals according to $R{-}C{\equiv}C{-}R' + H^{\bullet} \rightleftarrows R{-}C^{\bullet}{=}CH{-}R'/R{-}CH{=}C^{\bullet}{-}R'$, as well as release of **80** by stepwise cleavage of the TMS substituents from the corresponding Markovnikov-type radicals. On the other hand, the *anti*-Markovnikov-type radicals also generated can cyclize by 1,6-cycloaddition (resulting eventually in **81** and **82**) and eliminate ethynyl substituents by β(C−C) scission. Taken together, these reactions can adequately explain the variety of products formed in the hydropyrolysis of **79**.

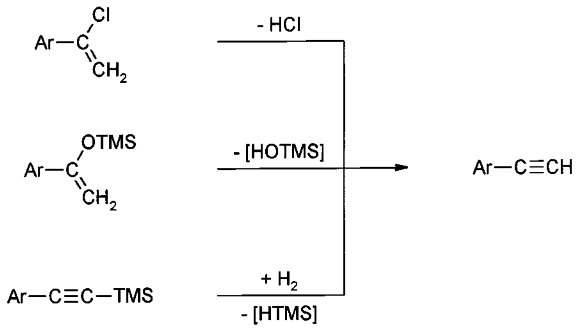
The results outlined above, together with those obtained in Scott's attempt to prepare **4** by FVP of 7,10-bis(2,2-dibromoethenyl)fluoranthene,[3,59] clearly show that even vinyl-type radicals can contribute valuably to the preparation of PAHs from compounds with a 1,3-hexadien-5-yne substructure, provided that the reaction conditions are adapted to the problem to be addressed and the ethynyl substituents of the starting compounds are suitably modified in each case.

For syntheses of this kind, it is not decisive, but still worth bearing in mind, that at temperatures above 550 °C the carbon skeleton of 1,3-hexadien-5-ynes is subjected to automerization involving 1,2-C switches. This could clearly be shown by thorough studies with doubly labeled [4-^{13}C,4-D]-1-phenyl-1-buten-3-yne (**85**).[10,20] The automerization of **85** gives **86** (Scheme 23).

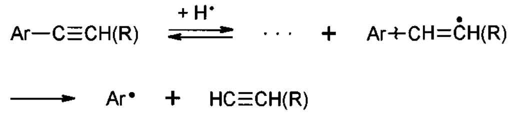
This normally hidden process occurs prior to naphthalene formation by 1,6-C,H insertion, and involves not only 1,2-D but also 1,2-styryl shifts.[10]



Scheme 18. Ring closures to the planar PAHs **8**, **75** outperform those to the bowl-shaped PAHs **72** and **74**, respectively



Scheme 19. Masked ethynyl groups commonly used to effect 1,*x*-C,H insertions of vinylidenecarbenes at high temperatures



Scheme 20. From ethynylarenes to aryl radicals by ethyne elimination from *anti*-Markovnikov vinyl-type radicals

8. Concluding Considerations

Compounds possessing a 1,3-hexadien-5-yne structure or substructure are known to be present

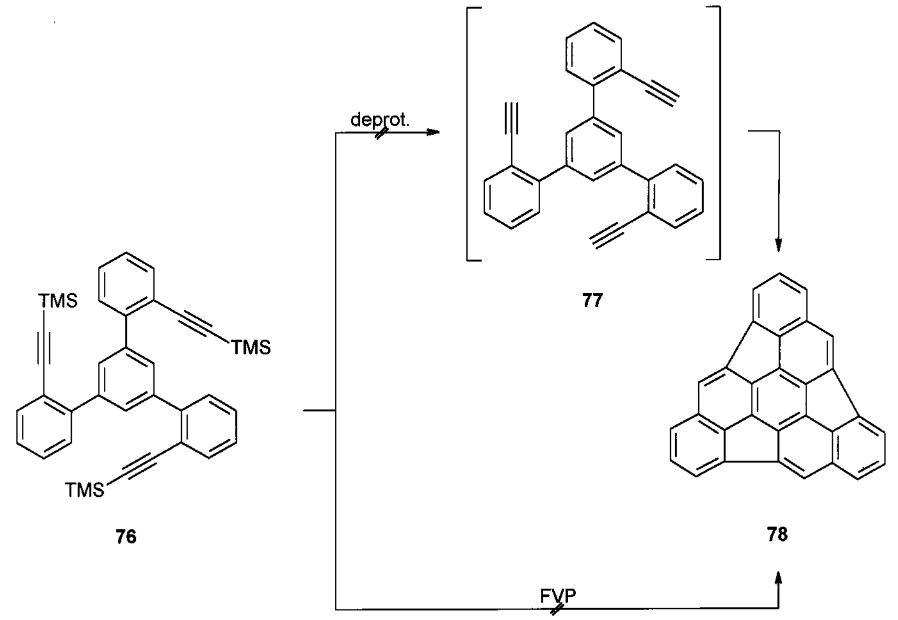
– in natural products (e.g. prymnesins[60]), or they act as intermediates

– in acetylene pyrolyses,[61] and

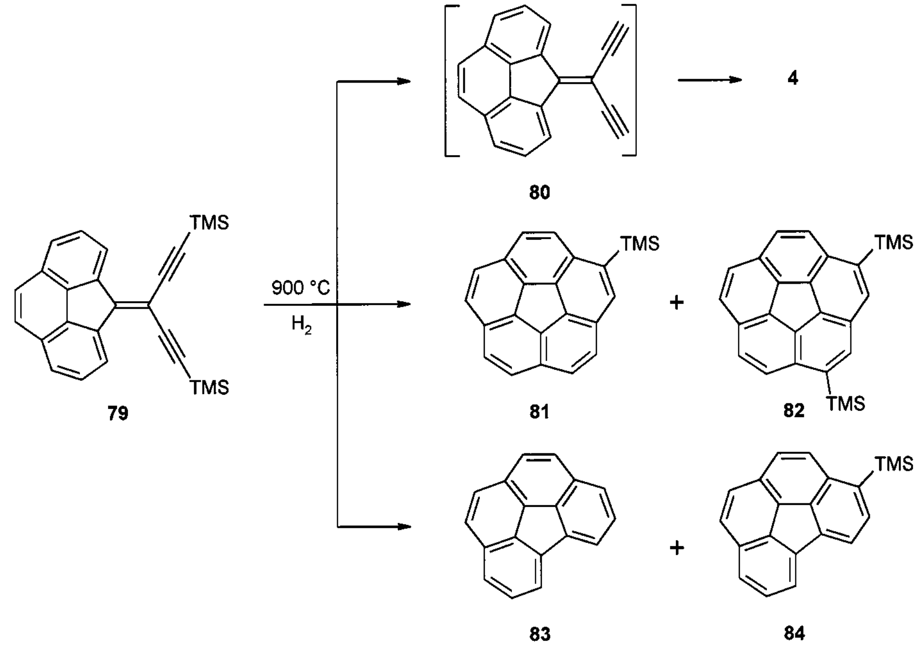
– in combustion processes, especially in fuel-rich flames and the corresponding hot waste gases.[15,54,62,63]

Additionally, hexadienynes of this type have been synthesized and used as precursors for the thermal generation of 1,2,4-cyclohexatriene derivatives by the Hopf cyclization (see Section 4) and high-temperature syntheses of specially designed PAHs by FP and FVP techniques (see Sections 5–7). Finally, hexadienynes, as well as other enynes,[43a] have been used as model compounds to develop building blocks for kinetically based combustion models.[4,54,62,63]

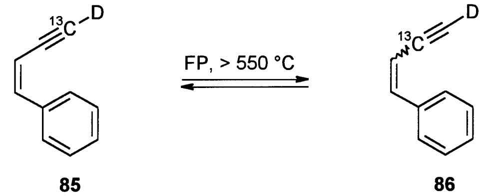
The previously studied cycloaromatizations during which the carbon skeleton of each considered 1,3-hexadien-5-yne substructure is converted into members of the newly formed aromatic six-membered ring, can essentially take place by



Scheme 21. Faust's unsuccessful approach to C_3-symmetric hemibuckminsterfullerene (**78**)



Scheme 22. Corannulene (**4**) synthesis by hydropyrolysis of the cross-conjugated enediyne derivative **79**



Scheme 23. Automerization within the enyne skeleton

the three alternative mechanisms A, B, and C (see Scheme 3), which operate in distinct temperature ranges. Two of them are pronouncedly endothermic,[27,64,65] and proceed through unimolecular reactions (A, B). The third (C) represents a cluster of radical reactions consisting of exothermic, and slightly endothermic steps. To trigger such reaction clusters, chain-carrier radicals from other sources are needed. In the process of FP and FVP, they are unavoidably generated at reactor wall temperatures well above 550 °C.

Irrespective of exceptional cases, reactive radicals reduce the yields of the aromatized target compounds.

For synthetic purposes, pathways by the A and B mechanisms are therefore at the center of interest. Both make it possible to synthesize compounds which are either completely inaccessible by means of other strategies or only accessible by extended synthetic routes. Cycloaromatization at temperatures below approximately 500 °C is now reasonably well understood. The Hopf cyclization of 1,3-hexadien-5-ynes to intermediates with a 1,2,4-cyclohexatriene (isobenzene or cyclic enallene) substructure is proposed as a major means of access to the generation of such reactive molecules. It also offers opportunities for the synthesis of novel compounds, by using these intermediates as co-reactants in the nascent state.

Unlike the synthesis by the type A mechanism, the FVP of structurally well-designed and appropriately masked ethynylarenes has proven to be the most useful tool for preparing medium-sized and large, nonalternating PAHs representing fullerene fragments.

Acknowledgments

I would like to thank my former co-workers and partners in scientific cooperation whose names are cited in the references. Over the years, the work has been supported by the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, and the Fonds der Chemischen Industrie.

---

[1] H. Hopf, H. Musso, *Angew. Chem.* **1969**, *81*, 704; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 680.

[2] G. Mehta, H. S. Prakash Rao, *Tetrahedron* **1998**, *54*, 13325−13370. Further literature: see refs. [1−7] therein.

[3] L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082−7084.

[4] P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marzinow, A. Sygula, R. J. Sygula, *J. Am. Chem. Soc.* **1994**, *116*, 7891−7892.

[5] M. Matsuda, H. Matsubara, M. Sato, S. Okamoto, K. Yamamoto, *Chem. Lett.* **1996**, 157−158.

[6] H. Hopf, H. Berger, G. Zimmermann, U. Nüchter, P. G. Jones, J. Dix, *Angew. Chem.* **1997**, *109*, 1236−1238; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1187−1190.

[7] K. Schulz, J. Hofmann, G. Zimmermann, *Liebigs Ann./Recueil* **1997**, 2535−2539.

[8] J. Hofmann, K. Schulz, A. Altmann, M. Findeisen, G. Zimmermann, *Liebigs Ann./Recueil* **1997**, 2541−2548.

[9] K. Schulz, J. Hofmann, M. Findeisen, G. Zimmermann, *Eur. J. Org. Chem.* **1998**, 2135−2142.

[10] K. Schulz, J. Hofmann, G. Zimmermann, *Eur. J. Org. Chem.* **1999**, 3407−3412.

[11] J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*, Academic Press, New York, **1981**.

[12] [12a] M. Christl, M. Braun, G. Müller, *Angew. Chem.* **1992**, *104*, 471−473; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 473. − [12b] B. Miller, X. Shi, *J. Am. Chem. Soc.* **1987**, *109*, 578−579. − [12c] M. Christl, S. Groetsch, *Eur. J. Org. Chem.* **2000**, 1871−1874.

[13] Compare, for example, the review on allene dimerizations: H. Hopf, in: *The Chemistry of the Allenes* (Ed.: S. R. Landor), Academic Press, London, **1982**.

[14] [14a] R. F. C. Brown, F. W. Eastwood, K. J. Harrington, G. L. McMullen, *Aust. J. Chem.* **1974**, *27*, 2393−2402. − [14b] R. F. C. Brown, F. W. Eastwood, G. P. Jackman, *Aust. J. Chem.* **1977**, *30*, 1757−1767.

[15] J. Hofmann, G. Zimmermann, K.-H. Homann, *Liebigs Ann.* **1995**, 841−848.

[16] [16a] A. L. J. Beckwith, D. J. O'Shea, *Tetrahedron Lett.* **1986**, *27*, 4525−4528. − [16b] A. L. J. Beckwith, S. Gerba, *Aust. J. Chem.* **1992**, *45*, 289−308.

[17] [17a] R. R. Jones, R. G. Bergman, *J. Am. Chem. Soc.* **1972**, *94*, 660−661. − [17b] R. G. Bergman, *Acc. Chem. Res.* **1973**, *6*, 25−31.

[18] W. R. Roth, H. Hopf, C. Horn, *Chem. Ber.* **1994**, *127*, 1765−1779.

[19] B. Ondruschka, G. Zimmermann, M. Remmler, U. Ziegler, F.-D. Kopinke, B. Olk, M. Findeisen, *Chem. Ber.* **1989**, *122*, 715−719.

[20] K. Schulz, J. Hofmann, G. Zimmermann, M. Findeisen, *Tetrahedron Lett.* **1995**, *36*, 3829−3830.

[21] U. Nüchter, G. Zimmermann, V. Franke, H. Hopf, *Liebigs Ann./Recueil* **1997**, 1505−1515.

[22] R. F. C. Brown, *Eur. J. Org. Chem.* **1999**, *12*, 3211−3222 and refs. cited therein.

[23] L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291−300 and refs. cited therein.

[24] G. Zimmermann, unpublished results, Leipzig, **1995**.

[25] [25a] G. Seybold, *Angew. Chem.* **1997**, *89*, 377−385; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 365−374. − [25b] R. F. C. Brown, *Pyrolytic Methods in Organic Chemistry* (Organic Chemistry Series, vol. 1), Academic Press, New York, **1980**. − [25c]P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235−242.

[26] W. v. E. Doering, M. Franck-Neumann, D. Hasselmann, R. L. Kaye, *J. Am. Chem. Soc.* **1972**, *94*, 3833−3844.

[27] Ch. Duschek, W. Höbold, W. Pritzkow, B. Rothenhäusser, H. Schmidt, W. Engler, D. Estel, H.-G. Hauthal, J. Korn, G. Zimmermann, *J. Prakt. Chem.* **1970**, *312*, 15−29.

[28] K. Kahlert, W. Pritzkow, G. Zimmermann, *J. Prakt. Chem.* **1976**, *318*, 627−634.

[29] C. E. Döring, D. Estel, J. Weber, G. Zimmermann, D. Zschummel, *J. Prakt. Chem.* **1971**, *313*, 1081−1091.

[30] H. Meier, N. Hanold, H. Kolshorn, *Angew. Chem.* **1982**, *94*, 67−68; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 66−67.

[31] H. Hopf, personal communication, **1999.**

[32] R. J. F. M. van Arendonk, P. F. de Violett, W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 256−262 and refs. cited therein.

[33] J. A. Hunter, K. R. Roesch, R. C. Larock, *219th ACS National Meeting*, San Francisco, **2000** (March 26−30), poster 19.

[34] Y. Rubin, S. S. Lin, C. B. Knobler, J. Anthony, A. M. Boldi, F. Diederich, *J. Am. Chem. Soc.* **1991**, *113*, 6943−6949.

[35] J. Magrath, F. W. Fowler, *Tetrahedron Lett.* **1988**, *29*, 2171−2174.

[36] U. Nüchter, Ph. D. Thesis, University of Leipzig, **1996**.

[37] J. A. Kerr, M. J. Parsonage, *Evaluated Kinetic Data on the Gas Phase Addition Reaction: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds*, Butterworth, London, **1976**.

[38] [38a] R. F. C. Brown, K. J. Harrington, *J. Chem. Soc., Chem. Commun.* **1972**, 1175. − [38b] R. F. C. Brown, F. W. Eastwood, *Synlett* **1993**, 9−19 and references cited therein.

[39] A. Necula, L. T. Scott, *9th International Symposium on Novel Aromatic Compounds*, Hong Kong, **1998** (August 2−7), poster 62.

[40] M. Sarobe, L. W. Jenneskens, A. Kleij, M. Petroutsa, *Tetrahedron Lett.* **1997**, *38*, 7255−7258.

[41] J. Hofmann, G. Zimmermann, M. Findeisen, *Tetrahedron Lett.* **1995**, *36*, 3831−3832.

[42] [42a] L. T. Scott, H. B. Warren, *7th International Symposium on Novel Aromatic Compounds*, Victoria, Canada, **1992** (July 19−24), poster 65. − [42b] M. D. Banciu, R. F. C. Brown, K. J. Coulston, F. W. Eastwood, C. Jurss, J. Mavropoulos, M. Stanescu, U. E. Wiersum, *Aust. J. Chem.* **1996**, *49*, 965−976.

[43] [43a] N. D. Marsh, M. J. Wornat, L. T. Scott, A. Necula, A. L. Lafleur, E. F. Plummer, *Poly. Arom. Comp.* **2000**, *13*, 379−402 and refs. cited therein. − [43b] L. T. Scott, A. Necula, *Tetrahedron Lett.* **1997**, *38*, 1877−1880.

[44] See for example, E. Vogel, *Angew. Chem.* **1960**, *72*, 4−26.

[45] J. Becker, C. Wentrup, E. Katz, K. P. Zeller, *J. Am. Chem. Soc.* **1980**, *102*, 5110−5112.

[46] [46a] R. Faust, *Angew. Chem.* **1995**, *107*, 1559−1562; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1429−1432. − [46b] J. S. Siegel, T. J. Seiders, *Chem. Br.* **1995**, *34*, 313−316.

[47] A. H. Abdourazak, A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1993**, *115*, 3010−3011.

[48] Z. Marcinow, F. R. Fronczek, Y.-H. Liu, P. W. Rabideau, *J. Org. Chem.* **1995**, *60*, 7015−7016.

[49] C. Z. Liu, P. W. Rabideau, *Tetrahedron Lett.* **1996**, *37*, 3437−3440.

[50] A. Sygula, H. E. Folsome, R. Sygula, A. H. Abdourazak, Z. Marzinow, F. R. Trautzek, P. W. Rabideau, *J. Chem. Soc., Chem. Commun.* **1994**, 2571−2572.

[51] A. Sygula, A. H. Abdourazak, P. W. Rabideau, *J. Am. Chem. Soc.* **1996**, *118*, 339−343.

[52] L. T. Scott, P.-C. Cheng, M. Hashemi, M. S. Bratcher, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1997**, *119*, 10963−10968.

[53] G. Zimmermann, U. Nüchter, S. Hagen, M. Nüchter, *Tetrahedron Lett.* **1994**, *35*, 4747−4750.

[54] J. Hofmann, G. Zimmermann, K. Guthier, P. Hebgen, K.-H. Homann, *Liebigs Ann.* **1995**, 631−636 and refs. cited therein.

[55] J. Herzler, P. Frank, *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 1333−1338.

[56] A. Hamins, D. T. Anderson, J. H. Müller, *Chem. Phys. Processes Combustion* **1987**, 4/1−4/4.

[57] Cf. also: K.-H. Homann, *Angew. Chem.* **1988**, *110*, 2572−2590; *Angew. Chem. Int. Ed. Engl.* **1988**, *37*, 2434−2451.

[58] R. Faust, *On the Role of Delocalization in Benzene: Theoretical and Experimental Investigation of the Effects of Strained Ring Fusion*, University of California, Berkeley, **1993**, cited in ref.[2]

[59] L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921.

[60] Compare for example, T. Igaraski, M. Satake, T. Yasumoto, *J. Am. Chem. Soc.* **1999**, *121*, 8500−8511.

[61] [61a] S. W. Benson, *Int. J. Chem. Kinet.* **1989**, *21*, 233−243. − [61b] S. W. Benson, *Int. J. Chem. Kinet.* **1992**, *24*, 217−237.

[62] K. Guthier, P. Hebgen, K.-H. Homann, J. Hofmann, G. Zimmermann, *Liebigs Ann.* **1995**, 637−644.

[63] M. Hausmann, P. Hebgen, K.-H. Homann, *24th Symposium (International) on Combustion*, The Combustion Institute, **1992**, pp. 793−801.

[64] [64a] M. M. Gallo, P. Hamilton, H. F. Schaefer III, *J. Am. Chem. Soc.* **1990**, *112*, 8714−8719. − [64b] B. J. Smith, R. Smernik, L. Radom, *Chem. Phys. Lett.* **1992**, *188*, 589−594.

[65] Compare also: J. Kaneti, M. Karpf, A. S. Dreiding, *Helv. Chim. Acta* **1982**, *65*, 2517−2525.

Received July 12, 2000
[I00350]