Addition and Cyclization Reactions in the Thermal Conversion of Hydrocarbons with an Envne Structure,  $5^{[\diamondsuit]}$ 

## High-Temperature Ring Closures of 1,3-Hexadien-5-ynes to Naphthalenes – Competing Reactions via Isoaromatics, Alkenylidene Carbenes, and Vinyl-Type Radicals

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The 4-substituted 1-phenyl-1-butene-3-ynes 1a-c and the 2ethynylstyrenes 7a-c were subjected to high-temperature pyrolysis. The cycloisomerization products isolated suggest that these are formed by three competing processes: by (i) an electrocyclic or a molecule-induced, (ii) an alkenylidene carbene controlled, and (iii) a radical-controlled ring-closure process. To estimate the relative importance of these three

Highly unsaturated acetylenes – among them 1,3-hexadiene-5-ynes - are known to be formed as reactive intermediates in fuel-rich hydrocarbon flames.<sup>[2][3]</sup> They have been considered as an important source of the formation of aromatic hydrocarbons in the hot waste gases from combustion, but there is little experimental evidence about the details of the actually occurring processes. Under conditions similar to those in the down-stream section of combustion, concerning a temperature range from 1000 down to < 500 °C, it is quite likely that unimolecular reactions, like electrocyclic<sup>[4][5][6][7]</sup> or molecule-induced ring closure<sup>[7b]</sup> and cycloisomerizations by reaction cascades initiated by 1,2-R shifts of the substituents of the C-C triple bonds and terminated by 1,x-C,H insertions<sup>[5][7][8][9][10][11][12][13]</sup> and by [2 + 1] cycloadditions<sup>[7][9]</sup> of the corresponding intermediate alkenylidene carbenes, are able to compete with radical-driven decomposition and cyclization reactions.<sup>[1][5][7][14][15]</sup> Among the experimental studies on the cycloisomerization of 1,3-hexadien-5-ynes our earlier publication<sup>[5]</sup> on the formation of phenyl-substituted naphthalenes from 1,4-diphenyl-1-buten-3-yne in the presence of different carrier gases is of particular importance since it allowes the determination of the relative importance of the three reactions in the cycloisomerization prozess.

In order to learn more about these competing reactions, we decided to study the cycloisomerization of the hexadienreactions here mentioned, the substrates have been isomerized in oxygen-free nitrogen and in nitrogen proportionally substituted by toluene at 700 and 650 °C, respectively. The relative contributions of these isomerizations depend not only on the conversion temperature but also on the substituent R in 1 or 7.

ynes 1a-1c (Scheme 1) and 7a-7c (Scheme 2) to the corresponding naphthalenes at 700 and 650 °C, respectively, and additionally the temperature dependence of the naphthalene formation from 1a at temperatures between 625 and 750 °C in greater detail. From our previous studies we knew that the unimolecular electrocyclic (molecule induced) ring closures and those involving alkenylidene carbenes are independent of the nature of the diluent gas whereas the corresponding radical reactions can be significantly influenced by chemically modified diluents.

In this paper, we describe a procedure which allows one to calculate the proportions in which electrocyclizations/ molecul induced ring closures as well as reaction cascades via alkenylidene carbenes and vinyl-type radicals take part in the cyclization of substituted 1,3-hexadien-5-ynes.

#### Results

#### Thermal Conversion of 1-Phenyl-1-buten-3-ynes 1a-1c

Trimethylsilyl-substituted *cis/trans*-1-phenyl-1-buten-3yne (1c) was prepared by Pd-catalyzed coupling of  $\beta$ bromostyrene and trimethylsilylacetylene as described in ref.<sup>[16]</sup>. It served as a starting compound for pyrolysis runs and also for the synthesis of **1a**. For the latter purpose, **1c** was almost quantitatively desilylated by treatment with an alcoholic sodium hydroxide solution, <sup>[14][15]</sup> and the resulting 1-phenyl-1-buten-3-yne was converted into **1a** by deuterium exchange with a 5% solution of NaOD in D<sub>2</sub>O.

<sup>[]</sup> Part 4: Ref. [1].

Scheme 1



<sup>[a]</sup> For example benzene, ethynylbenzene, styrene, 2-ethynylstyrenes (from **1a** in nitrogen), additionally indenes (from **1a** in nitrogen-to-luene).

Scheme 2



<sup>[a]</sup> For example twice deuterated **2** and unidentified trace compounds (from **7a** in nitrogen).

*cis/trans*-1,4-Diphenyl-1-buten-3-yne (1b) was synthesized as described in ref.<sup>[5]</sup> by copper(I) oxide catalyzed dimerization of ethynylbenzene. The substrates 1a-1c were pyrolyzed immediately after their preparation at 700 °C and a reaction time of approximately 0.3 s after their preparation.<sup>[17]</sup> In a further set of pyrolysis runs, the conversion and temperature dependence of the cycloisomerization of 1a was studied between 625 and 750 °C to determine the influence of the temperature on the competing cyclization mechanisms.

The pyrolyses were performed in the tubular quartz reactor described in ref.<sup>[5]</sup>. In each run, 0.5 ml of a 10% solution of the substrate 1 in benzene was slowly evaporated into a stream of nitrogen  $(N_2)$  and nitrogen containing ca. 5 mol-% of toluene (N<sub>2</sub>-tol), respectively, that carried the substrates in low concentrations  $(n_1/n_{N_2(N_2-tol)}, 1:50)$  through the reactor into a cold trap. The liquid pyrolyzates were dissolved in 5 ml of diethyl ether and the solution was analyzed by GC, GC/MS, and GC/FT-IR analysis. The peaks recorded were identified by comparison of their analytical data with those of independently synthesized reference compounds, if necessary. The pyrolyzate of 1a and later 7a were additionally analyzed by <sup>2</sup>H-NMR spectroscopy. The yield of the liquid pyrolyzates was in excess of 90% in each case. The degree of conversion depends not only on the temperature and the substrate structure, but also on the nature of the diluent gas. Referring to a definite temperature, the conversion in nitrogen was always significantly higher than in nitrogen-toluene but the isolated pyrolyzates consisted qualitatively of the same products (Scheme 1). Table 1 lists the selectivities  $S_i$  in mol of the corresponding products  $P_i$  formed from 100 mol of the converted substrate 1i at 700 °C. The corresponding naphthalenes 2, 3j, and 4j are considered to be the main products followed by 1-methylene-1H-indenes 6j (in N2) and azulenes 5j (in N2-tol), cf. also the results described in ref.<sup>[1]</sup>. The composition of the naphthalene fraction shows unambiguously that the concentration of 1- and 2-R-substituted naphthalenes and unsubstituted naphthalene (2) differ enormously when the product selectivities obtained in N<sub>2</sub>-tol are compared with those obtained in the presence of  $N_2$  only.

Table 1. Conversion and selectivities  $S_j^{[a]}$  of the reaction products from 1i at 700 °C in nitrogen (N<sub>2</sub>) and nitrogen-toluene (N<sub>2</sub>-tol) mixtures

Substrate E:	1a 1b		10			
Diluent gas	$N_2$	N <sub>2</sub> -tol	N <sub>2</sub>	N <sub>2</sub> -tol	N <sub>2</sub>	N <sub>2</sub> -tol
Conversion [%]	42	25	40	6	4	1
Products:						
naphthalene (2)	9	4	26	9	4	19
[1-R]naphthalenes 3j	19	12	26[b]	17[b]	22	10
[2-R]naphthalenes 4j	64	79	27	61	21	60
azulenes 5j	1	3	tr.	tr.	-	tr.
1-methylene-1H-indenes 6j	8	tr.	2	< 1	< 1	tr.
others [c]	ca. 3	ca. 2	ca. 55	ca.15	ca. 20	ca. 20

<sup>[a]</sup>  $S_j = \text{mol of products } P_i \text{ formed from 100 mol converted } E_i (= 1i). - ^{[b]}$  Included traces of fluoranthene formed by dehydrocyclization. - <sup>[c]</sup> Preferably decomposition products.

The naphthalenes 2, 3j, and 4j are undoubtedly primary cyclization products of the substrates 1i. Subsequent changes of the naphthalenes formed primarily by radicalcontrolled consecutive reactions, as for instance a partial desubstitution of the substituted naphthalenes to give 2, can be ruled out at temperatures  $\leq$  725 °C. This was shown by independent reference experiments carried out under the conditions used in this work. As expected, the conversion of the substrates and the composition of the liquid pyrolyzates depend on the reaction temperature. Table 2 shows, by way of an example, the temperature dependence of the conversions and the selectivities of the naphthalenes 2, 3a, and 4a and those of the azulene 5a and 1-methylene-1*H*-indene 6a formed from 1a between 625 and 750 °C.

Table 2. Temperature dependence of the selectivities of the formednaphthalenes 2, 3a, 4a, the azulene 5a and 1-methylene-1H-indene6a from 1a in nitrogen

Temperature [°C] Conversion [%]	625 4	650 18	675 32	700 42	725 64	750 82
Products: naphthalene (2) [1-D]naphthalene (3a) [2-D]naphthalene (4a)	14 16 60	13 15 62	11 15 63	9 15 64	9 15 64	8 16 64
azulene <b>5a</b> 1-methylene-1 <i>H</i> -indene <b>6a</b> others	tr. 1 9 tr.	tr. 1 9 tr.	1 8 tr.	1 8 1	3 1 7 1	5 1 7 1

As can be seen, [2-D]naphthalene (4a) is the main product of the cycloisomerization over the whole temperature range studied and its selectivity is almost independent of the conversion. [1-D]naphthalene (3a), a further main product, is also formed independently of the reaction temperature while the  $S_i$  values of undeuterated naphthalene (2) and 1-methylene-1*H*-indene (6a) fall off with increasing temperature. Azulene 5a was also detected, although it is formed in trace amounts only.

#### Thermal Conversion of 2-Ethynylstyrenes 7a-7c

The synthesis of the phenyl- and the trimethylsilyl-substituted 2-ethynylstyrenes (**7b** and **7c**) was carried out by Pdcatalyzed coupling of 2-bromostyrene with phenyl- and trimethylsilylacetylene, respectively, in anhydrous piperidine at 90 °C in analogy to the procedure described in ref.<sup>[16]</sup>. After column-chromatographical purification of the solvent-free crude products, **7b** and **7c** were obtained with GC purities of > 97%. Compound **7c** was used directly as substrate for the synthesis of **7a** by almost complete desilylation followed by deuteration of the unsubstituted 2-ethynylstyrene with NaOD in D<sub>2</sub>O. The D content of **7a** was determined to be  $\geq$  99.5 atom-% by GC/MS and the D atoms were exclusively situated at the terminal C atom of the C-C triple bond (NMR analysis).

The substrates 7i were pyrolyzed and analyzed as described for 1. However, the reaction temperature was set to 650 °C because 7a was already almost completely converted at 700 °C. As shown in Scheme 2, the major products formed in this cases are the naphthalenes 2, 3j and 4j. Minor products, as was expected, are the corresponding 1-methylene-1*H*-indenes 6j. Table 3 lists the selectivities  $(S_i)$  of the cycloisomerization products from 7a-7c. Beside the main products, a number of trace compounds (mainly decomposition products) were detected in the pyrolyzates.

Table 3. Conversion and selectivities  $S_1^{[a]}$  of the reaction products from 7i at 650 °C in nitrogen (N<sub>2</sub>) and nitrogen toluene (N<sub>2</sub>-tol) mixtures

Substrate $E_i$	7a		7b		7c	
Diluent gas Conversion [%]	N <sub>2</sub> 48	N <sub>2</sub> -tol 40	N <sub>2</sub> 45	N <sub>2</sub> -tol 10	N <sub>2</sub> 39	N <sub>2</sub> -tol 7
Products:						
naphthalene (2)	19	14	6	4	19	11
[1-R]naphthalenes 3j	24	35	6	11	10	15
[2-R]naphthalenes 4	28	31	82	80	68	68
1-methylene-1 <i>H</i> -indenes 6i	18	18	<1	1	1	2
others <sup>[b]</sup>	ca. 2	ca. 1	ca. 6	ca. 5	ca. 3	ca. 5

<sup>[a]</sup> See Table 1. – <sup>[b]</sup> Preferably decomposition products.

### Discussion

Tables 1 and 3 summarize the conversions of the studied substrates  $E_i^{[18]}$  and the selectivities  $S_j^{[18]}$  of the products  $P_{i}^{[18]}$  formed from  $E_{i}$  (1a-1c and 7a-7c) in dependence on the nature of two diluent gases at 700 and 650 °C, respectively. Taking the hitherto accumulated knowledge on alternative cyclizations of substrates with a 1,3-hexadien-5yne substructure into consideration, it immediately becomes clear that no single pathway can adequately account for the formation of the cyclization products. From preceding studies<sup>[1][6][9]</sup> on the thermal conversion of unsubstituted 1-phenyl-1-buten-3-yne we know that azulene is formed in a reaction cascade initiated by a 1,2-shift of the H atom of the C-C triple bond and converted to naphthalene in a radical-driven reaction.<sup>[1]</sup> Furthermore, there is no doubt that 1-methylene-1*H*-indene, another  $C_{10}H_8$  isomer, is actually formed but following a multistep radical reaction cascade.<sup>[1]</sup> In contrast, the mechanistic interpretation of the formation of naphthalene (2) (cf. Scheme 3), the main product of the thermal 1-phenyl-1-buten-3-yne conversion,<sup>[1]</sup> has to remain speculative because different mechanisms could be operative for this formation. Starting from 1-phenyl-1buten-3-vne, there are three different precedent reactions which allow a plausible mechanistic interpretation of the formation of 2. These possibilities are: (i) An electrocyclic/ molecule-induced ring closure to the isonaphthalenes 8 (Scheme 3, R = H) and 11 (Scheme 4, R = H), respectively, followed by a 1,5-H shift. (ii) A 1,6-C,H insertion of the initially generated carbenes 9 and 12 (R = H), respectively. (iii) Complex reaction cascades of the vinyl-type radicals 10a/10b and 13a/13b (R = H), respectively, in analogy to the mechanism described in ref.<sup>[5]</sup> for the cycloisomerization of 1,4-diphenyl-1-buten-3-yne (1b) (while the azulene-tonaphthalene rearrangement can be ignored).

Schemes 3 and 4 reveal furthermore that a complete mechanistic analysis of the cyclization events could be carried out if 1-phenyl-1-buten-3-ynes, which are differently substituted at the C–C triple bond, are converted in diluent gases of a different nature (cf. for example ref.<sup>[5][7]</sup>).

Starting from substrates like 1a-1c, and taking wellknown precedent reactions into consideration (Scheme 3), it is easy to derive that [1-R]-substituted naphthalenes 3j are initially formed (i) by electrocyclic/molecule-induced

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Scheme 3



Scheme 4



ring closure from 1i, (ii) by the carbene route from 7i and/ or (iii) via vinyl-type radicals (reversibly generated by addition of chain-carrier radicals, particularly H atoms, to the C-C triple bond of the corresponding substrate molecules) as well.

In contrast, the formation of [2-R]-substituted naphthalenes 4j is based on (i) the electrocyclic or molecule-induced ring closure of 7i, and reaction cascades via (ii) alkenylidene carbenes (from 1i) and/or (iii) vinyl-type radicals. The formation of 2, however, is inevitably put down to C-R bond cleavage of 14 (see Scheme 5) which is thought to control the radical reactions to 2, 3j, and 4j. In this process 14b yields 3j and 14c yields 4j in parallel to  $2^{[5]}$ .

Simultaneously, the experiments in which nitrogen is proportionally repalced by toluene ( $N_2$ -tol) clearly show that the corresponding degree of conversion is significantly lower and the distribution of the naphthalenes changes noticeably as compared to the values obtained in pure nitrogen ( $N_2$ ). This is undoubtedly caused by suppression of the radical-controlled reactions by conversion of reactive radicals into less reactive, resonance-stabilized benzyl radicals

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Scheme 5



(Scheme 6).<sup>[1][5]</sup> Since the reactions (i) and (ii) are exclusively controlled by unimolecular steps, their overall rate constants are independent of the nature of the carrier gas used. Therefore, the essential differences for the conversions and selectivities of the formation of naphthalenes are exclusively caused by higher stationary concentrations of the reactive radicals and hence to a larger extent of radical reactions then in the case of nitrogen.

On the basis of these rationalizations, it is possible to calculate the proportions in which the substrates  $E_i$  (1a-1c and 7a-7c) cyclize electrocyclically, via alkenylidene carbenes and vinyl-type radicals in parallel.

Towards this, the  $S_j$  values of the naphthalenes  $P_j$  formed from the corresponding substrate  $E_i$  (see Tables 1 and 3) are first converted into the molar percentages of the naphthalenes  $P_j$  detected in the corresponding pyrolyzates by using eq. 1, in which  $f_y$  represents the yield factor of the pyrolyzates obtained with referring to the substrate  $E_i$  passing the reactor at reaction temperature, and  $d_{E_i}$  is the conversion factor of the employed  $E_i$ .

$$\frac{P_{\mathbf{j}}}{E_{\mathbf{i}} \cdot f_{\mathbf{y}}} = S_{\mathbf{j}} \cdot d_{E_{\mathbf{i}}} = A_{P_{\mathbf{j}}} \tag{1}$$

The differences in the  $A_{P_i}$  values calculated from the results obtained in N<sub>2</sub> on the one hand and in N<sub>2</sub>-tol on the other (eq. 2), indicate the molar portions of the different naphthalenes  $P_i$  which are additionally formed when nitrogen is used as diluent gas. It represents the relative amounts which are exclusively formed by radical pathways.

$$A_{P_{j,N_2}} - A_{P_{j,N_2}, \text{tol}} = B_{P_j}$$
(2)

The  $B_{P_j}$  values calculated for the different naphthalenes  $P_j$  represent the ratios in which the unsubstituted **2** and the 1- and 2-R-substituted naphthalenes **3j** and **4j** are formed in radical processes. They allow to calculate the molar proportions in which the substituted naphthalenes  $P_j$  are formed in each pyrolysis run by using the rule of three (eq. 3).

$$\frac{A_2}{B_2} \cdot B_{P_j} = C_{rad}(P_j) \tag{3}$$

By subtracting the  $C_{rad}(P_j)$  calculated in each case from the corresponding  $A_{P_j}$  value, the molar proportion in which the corresponding [1-R]-substituted naphthalene are obtained

- by electrocyclic/molecule-induced ring closure (= ec) from  $E_i = 1a-1c$ ,

- by 1,6-C,H insertion of the alkenylidene carbene in question (= carb) from  $E_i = 7a-7c$ ,

and vice versa for the [2-R]-substituted ones (eq. 4).

$$A_{P_{j}} - C_{rad}(P_{j}) = C_{x}(P_{j})$$

$$\tag{4}$$

(with x = ec or carb)

The percentages in which the substrates  $E_i$  cyclize by the different mechanisms are summarized in Figure 1. The percentages for the radical cyclization include naturally the portions of the formed 2, because its generation is caused by two of the three cyclic radical precursors 14 (see Scheme 5).

Figure 1(a) represents the percentages of the naphthalenes 2, 3j, and 4j ( $\Sigma = 100$ ), each formed from the corresponding substrates 1i at 700 °C (0.3 s) following the reaction courses (i), (ii), and (iii) (Scheme 3).

Although one must be careful in interpreting results from experiments with low conversions, the trimethylsilyl group in 1c is obviously able to enter into a 1,2-shift reaction to a certain extent but it is obviously bulky enough to almost prevent the electrocyclization or molecule-induced ring closure in question by steric hindrance. A behavior similar to the trimethylsilyl group shows the phenyl group substituted at the C-C triple bond of 1b: It has a significant lower tendency to undego a 1,2-Ph shift,<sup>[8]</sup> and its space filling is sufficient to disfavor electrocyclization<sup>[5]</sup> or molecule-induced ring closures.<sup>[7b]</sup> Therefore, the conversion of **1b** and **1c** becomes important under conditions which allow the generation of sufficient amounts of reactive radicals by destructive adsorption of substrate molecules at the hot reactor walls.<sup>[1][5][20]</sup> As has been shown,<sup>[5][8][19]</sup> the substituent D in 1a shows a pronounced tendency to rearrange by a 1,2-D shift to give the carbene 9 (Scheme 3, R = D), but it can hardly be considered as a space-filling substituent. From this view, it is not surprising that the carbene (ii) and the radical (iii) routes are able to compete successfully with each other during the cyclization of 1a. However, it is remarkable that the ring closure (i) undergoes only a small change in the complex reaction event. We trace this back to the fact that the formation of the intermediate 8 requires to

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overcome the high resonance stabilization of the phenyl group. While Wentrup et al.<sup>[9]</sup> believed that the cycloisomerization of unsubstituted 1-phenyl-1-buten-3-yne to naphthalene 2 by FVP at approximately 1000 °C (0.001 Torr) occurs exclusively via the corresponding alkenylidene carbene, we found recently that radical pathways operate at temperatures up to 800 °C (13 Torr), and that the participation of competing different mechanisms depends clearly on the reaction temperature.<sup>[1]</sup> To study this effect for 1a, we calculated the percentages of the different mechanisms which compete with each other during the formation of naphthalenes on the basis of the data listed in Table 2 and the corresponding data obtained in N2-tol. The results are depicted in Figure 2. They clearly reveal a significant temperature dependence of the reactions (ii) and (iii), but only a small increase of reaction (i) only in the range between 625 and 750 °C. Therefore, we have every reason to believe that, with increasing temperature the carbene route (ii) is much more favored than both the electrocyclic/moleculeinduced ring closure (i) and the radical cyclization (iii).

At first glance, the statement concerning the radical cyclization (iii) appears to be amazing since the stationary conFigure 2. Temperature dependence of the competing cyclization mechanisms during the thermal conversion of 1a into 2, 3a, and 4a (× radicalic, ■ carbenic, ◆ electrocyclic)



centration of reactive radicals increases, of course, with increasing temperature. But the radical formation is not the rate-determining step. The rate-determining step is the formation of the vinyl-type radicals **11a** and **11b** (Scheme 3) and their decomposition gains importance with increasing temperature by the corresponding back reaction.

Very similar arguments can explain the formation of naphthalenes from the ethynylstyrenes 7i (Scheme 4) considering the essential results which are illustrated in Figure 1b. Two reguliarities are worth mentioning. The different cyclization mechanisms participate in nearly equal percentages when 7a is converted at 650 °C, and the electrocyclic/molecule-induced ring closure (i) remains more influential than the carbene route (ii) during the conversion of 7b and 7c.

The nearly equal contributions of different mechanisms during the conversion of 7a are understandable bearing in mind the following facts:

- At gas-phase temperatures of 650 °C, the reactor-wall temperature is obviously already high enough to generate so-called chain-carrier radicals in the necessary amount.

- The reversible formation of the alkenylidene carbene 12 by 1,2-D shift is known to occur at a level a little below the one known for the 1,2-H shift only (Scheme 5, R = D).<sup>[21]</sup>

- The formation of the transition state of the electrocyclic/molecule-induced ring closure is supposed to be free of significant steric hindrance.

Although the latter statement does not apply to the substituents of 7b and 7c, the electrocyclically formed portions of the corresponding 2-substituted naphthalenes 4j are at least twice as high as the ones of 3j formed by 1,6-C,H insertion of the reversibly generated carbenes 12 (Scheme 4) with R = Ph and TMS, respectively. These results deserve to be mentioned because it is evident that the energetic input necessary for the formation of the corresponding transition state is more important than the steric bulk of the substituent for the participation of mechanism (i) in the total of the cyclization to the naphthalenes. Scheme 6 qualitatively depicts the differences resulting from the electrocyclic/molecule-induced ring closures of the substrates 1i and 7i, respectively. The formation of the radical intermediate 15 requires the annulation of the phenyl resonance stabilization which, however, is not the case for 16. From this, we conclude that the state of hybridization of the C atoms involved in the electrocyclic ring closure seems to be more important than the space demanded from the substituents at the terminal C atom of the C–C triple bond.

#### Conclusions

The experiments presented here are very simple but they lead to new information about the high-temperature cyclizations of substituted 1,3-hexadien-5-ynes. Several mechanistic pathways which are known from corresponding precedent reactions have been discussed hitherto for the cyclization of 1,3-hexadien-5-ynes to naphthalenes (Scheme 3 and 4), but their cyclization remained obscure since the corresponding relative contributions to kinetic data were missing. The data presented in this work, obtained in the presence of diluent gases of different nature, make the calculation of the percentages possible in which electrocyclic ring closure and the alkenylidene carbene as well as the vinyl radical route compete with one other.

Under the conditions employed here, the three processes have a determining influence on the composition of the naphthalene fraction in the liquid pyrolyzates and over and above that on the total of the cycloisomerization products included the corresponding azulenes and 1-methylene-1*H*indenes (c.f. ref.<sup>[1]</sup>). The percentages by which the different mechanisms participate in the naphthalene formation depends on the reaction temperature. At 625 °C, the radical cycloisomerization dominates but it loses importance the higher the temperatures become. At 750 °C, the reaction cascade (ii), initiated by 1,2-D shift and terminated by 1,6-C,H insertion, is the reaction which controls the formation of the naphthalene fraction, while the electrocyclic or molecule-induced ring closure takes place to a lesser extent only despite a moderate increase with increasing temperature.

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### **Experimental Section**

List of Symbols:  $S_i$ : mol of product  $P_j$  formed from 100 mol of converted substrate  $E_i$ .

 $E_i$ : Substrate used as starting compound [mol].

 $P_i$ : Product formed from  $E_i$  (mol per mol of substrate).

 $A_{P_i}$  mol of  $P_i$  in the liquid pyrolyzates.

 $B_{P_i}$ : Molar proportions by which naphthalene (2) as well as the R-substituted naphthalenes are formed by radical cyclization from  $E_i$ .  $C(P_i)$ : Molar proportions by which the substituted naphthalenes in the pyrolyzates are formed from  $E_i$  by radical reactions:  $C_{rad}(P_j)$ ; by electrocyclic ring closure:  $C_{ec}(P_j)$ , and by intermediate alkenylidene carbenes:  $C_{carb}(P_j)$ .

 $f_y$ : Weight percent of the liquid pyrolyzate formed from the each used mass of  $E_i$ .

 $d_{E_i}$ : Conversion factor of the  $E_i$  employed.

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General: NMR: Varian Unity 400, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) or [D<sub>6</sub>]acetone), <sup>2</sup>H NMR (61 MHz, acetone), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> or [D<sub>6</sub>]acetone). - GC: Analytical, total analysis, HP 5890 Series II (FID, H<sub>2</sub>, 25 m  $\times$  0.32 mm  $\times$  1.0  $\mu$ m column, PS 255); GC (cracked gases): HP 5890 Series II (FID,  $H_2$ , 50 m  $\times$  0.32 mm column, Al<sub>2</sub>O<sub>3</sub>/KCl). - GC/MS: HP 5890 Series II/HP 5971 A (He, 12 m  $\times$  0.2 mm  $\times$  0.25  $\mu$ m column, SE-54, 70 eV). – GC/ FT IR: HP 5890 Series II/HP 5965 B (N<sub>2</sub>, 25 m  $\times$  0.32 mm  $\times$  0.25 µm column, SE-54).

cisltrans-[4-D]1-Phenyl-1-buten-3-yne (1a): 2.56 g (20 mmol) of 1-phenyl-1-buten-3-yne, obtained by desilylation of 1c with a 1 N solution of potassium hydroxide in methanol, was dissolved in 5 ml of benzene, 0.8 ml of a 30% solution of NaOD in D<sub>2</sub>O was added and the mixture was stirred for 24 h at room temperature. After neutralization with DCl, the organic layer was separated and the procedure repeated twice. The obtained organic layer was dried with magnesium sulfate and the solvent removed by distillation. The residue (a 7:93 cis/trans mixture of 1a, yield 95%, D content: 99 atom-%) was used as a substrate for the pyrolysis experiments without further purification. - trans-1a: MS; m/z (%): 200 (39)  $[M^+]$ , 186 (18), 185 (100), 169 (14), 155 (9), 141 (7), 129 (7), 115 (8), 43 (14). – IR (FT):  $\tilde{v} = 3080 \text{ cm}^{-1}$ , 3042, 2595, 1961, 1881, 1786, 1598, 1493, 1266, 1023, 954. - cis-1a: MS; m/z (%): 200 (39)  $[M^+]$ , 186 (18), 185 (100), 169 (14), 155 (9), 141 (7), 129 (7), 115 (8), 43 (14). – IR (FT):  $\tilde{v} = 3068 \text{ cm}^{-1}$ , 3043, 2591, 1950, 1882, 1736, 1675, 1601, 1496, 1401, 1221, 947, 778.

cis/trans-1,4-Diphenyl-1-buten-3-yne (1b) was synthesized by catalytic dimerization of ethynylbenzene and separated/purified as described recently.<sup>[5][22]</sup> Yield and purity correspond to the data reported in ref.<sup>[5]</sup>.

cisltrans-1-Phenyl-4-(trimethylsilyl)-1-buten-3-yne (1c): The synthesis was carried out according to the method reported by Gisea and Schulz.<sup>[16]</sup> 9.2 g (0.05 mol) of  $\beta$ -bromostyrene and 5.9 g (0.06 mol) of trimethylsilylacetylene were converted by Pd-catalyzed coupling and gave 8.4 g (0.042 mol) of a 7:93 cis/trans mixture of 1c. The GC/MS and GC/FT-IR data of 1c are identical to those listed in ref.<sup>[1]</sup>.

2-[2-D]Ethynylstyrene (7a): 4 g (0.02 mol) of 7c (see below for preparation) was dissolved in methanol (50 ml), 25 ml of a 1 N solution of potassium hydroxide in water was added, and the mixture stirred at room temp. for 3 h. 100 ml of diethyl ether was added, the organic layer was separated, washed with water , dried with magnesium sulfate, and the crude 2-ethynylstyrene purified by column chromatography (adsorbent: LiChroprep Si 100, yield 50%). - MS; m/z (%): 128 (100) [M<sup>+</sup>], 127 (32), 126 (8), 102 (16), 63 (8), 51 (8). – IR (FT):  $\tilde{v} = 3326 \text{ cm}^{-1}$ , 3075, 3044, 2102, 1919, 1835, 1626, 1478, 1297, 1224, 985, 917. - The undeuterated 2ethynylstyrene served as starting material for preliminary pyrolysis tests and for the synthesis of 1a according to the method described for 1a (yield 99%, GC-purity 99%, D content: 99 atom-%). - MS; m/z(%): 129 (100) [M<sup>+</sup>], 128 (30), 127 (12), 102 (12), 102 (9), 75 (9), 63 (4), 51 (4). – IR (FT):  $\tilde{v} = 3074 \text{ cm}^{-1}$ , 3010, 2596, 1918, 1628, 1478, 1282, 1089, 987, 917.

2-[(2-Phenyl)ethynyl]styrene (7b) was prepared from 6.1 g (0.06 mol) of ethynylbenzene and 9.2 g (0.05 mol) of 2-bromostyrene as described for 7c, with the trimethylsilylacetylene being replaced by ethynylbenzene. The yield of isolated 7b was 72% (GC purity: > 99%). - MS; m/z (%): 204 (87) [M<sup>+</sup>], 203 (100), 202 (96), 201 (14), 200 (14), 176 (69), 126 (6), 101 (30), 89 (9), 88 (10), 76 (9). - IR (FT):  $\tilde{v} = 3070 \text{ cm}^{-1}$ , 3042, 1947, 1884, 1731, 1600, 1492, 1310, 1005, 988, 915.

2-[(2-Trimethylsilyl)ethynyl]styrene (7c): 9.2 g (0.05 mol) of 2bromostyrene was converted with 5.9 g (0.06 mol) of trimethylsilvlacetylene in 100 ml of piperidine as described in ref.<sup>[16]</sup>. 0.18 g of palladium(II) chloride, 0.30 g of triphenylphosphane and 0.05 g of copper(I) iodide were added to the solution and the mixture was stirred at 60 °C for 4 h. The piperidine was removed by distillation (50 Torr) and the residual product extracted three times with benzene. The resulting benzene phase was treated with dilute hydrochloric acid, separated and washed with water, dried with sodium sulfate and the solvent removed by distillation. The crude product was purified by column chromatography with hexane (adsorbent: Al<sub>2</sub>O<sub>3</sub>, type 507 C, yield 42%). - MS; m/z (%): 200 (10) [M<sup>+</sup>] 186 (16), 185 (100), 183 (28), 172 (5), 169 (16), 167 (14), 155 (14), 141 (12), 129 (9), 115 (9), 72 (9), 43 (7). – IR (FT):  $\hat{v} = 3070 \text{ cm}^{-1}$ , 2966, 2907, 2151, 1835, 1628, 1477, 1263, 1094, 987, 872.

Low Partial Pressure Pyrolysis: The pyrolyses were carried out in the presence of oxygen-free diluent gases [nitrogen, and molar mixtures of nitrogen-toluene (ca. 20:1)] using a tubular flow reactor as previously described (quartz, Di: 10 mm, l: 300 mm, electrically heated).<sup>[1]</sup> The amount of carrier gas used was controlled by flow meters in each case. The starting compounds were introduced as 10-% mixtures of benzene by a syringe into a vaporizer controlled by a thermostat and filled with quartz wool at the upper part of the apparatus. The vaporizer brings the carrier gas and the substrate mixture to a temperature, which guarantees that the gas stream contains approximately 2% of the substrate. The reaction temperature was varied between 625 and 750 °C (reaction time 0.3 s). After leaving the reactor, the hot effluent was rapidly cooled down with liquid nitrogen. The liquid products were collected in a trap, and subsequently separated from the cracked gases. All products were analyzed and identified by GC, GC/MS and GC/FT-IR, <sup>13</sup>C-, <sup>2</sup>H- and <sup>1</sup>H-NMR spectroscopy.

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- <sup>[17]</sup> The investigation with 1,4-diphenyl-1-buten-3-yne (already reported in ref.<sup>[5]</sup>) was repeated to ensure a reliable comparison with the data obtained from the other substrates first reported in this work.
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